STRUCTURE AND PROPERTIES OF CONDUCTING POLYMERS INCORPORATED WITH PHTHALOCYANINE

A THESIS SUBMITTED TO
UNIVERSITY OF PUNE (INDIA)

FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)

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APRIL - 2000

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CERTIFIED that the work incorporated in the thesis, **“STRUCTURE AND PROPERTIES OF CONDUCTING POLYMERS INCORPORATED WITH PHTHALOCYANINE”** submitted by **Shri Shripad Dagadopant Deshpande** was carried out by him under my supervision/guidance. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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ACKNOWLEDGEMENTS

I express my deep gratitude's to my research guide **Dr. S. Radhakrishnan**, for it was he who introduced me to the world of Conducting Polymers. I thank him for his constant inspiration and useful suggestions apart from his invaluable guidance. The scientific discussions on the subject were most useful in understanding the subject and were helpful in broadening my outlook. This task would have been a dream, without his constant encouragement and valuable suggestions.

I am grateful to the Director, National Chemical Laboratory, Pune for permitting me to carry out this research work. My sincere thanks to Dr. B.D. Kulkarni, the Head of Chemical Engineering division, N.C.L.

I am thankful to various people in Special Instruments Laboratory, NCL for their kind help in characterization technique. I am also thankful to Mr. G.T.Mane and Mr. P.B.Kulkarni for sketching nice figures for my thesis work.

I wish my sincere thanks to my entire lab colleague and wish to thank specially to Mrs. Swati Panse, Miss C. Saujanya, Mr. P.M. Somani, Mr. Prasad Taranekar, Mr. P.M. Sonar and Mr. M.P. Raut for their outstanding co-operation during entire work period.

I would be doing great injustice if I do not express my heart-felt gratitude to my wife and my other family members, for their constant support and motivation.

S.D.DESHPANDE

DEDICATED TO MY PARENTS

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List of acronyms

APS	Ammonium per sulfate
B.E.	Binding energy
CB	Conduction band
CuPc	Copper phthalocyanine
CPC	Conducting polymer composites
C-V	Cyclic voltammetry
DTA	Differential thermal analysis
EDXS	Energy dispersive x-ray spectroscopy
ESCA	Electron spectroscopy for chemical analysis
FT-IR	Fourier transformed infrared
FWHM	Full width at half maximum
HOMO	Highest occupied molecular orbital
IR	Infrared
ITO	Indium tin oxide
I-V	Current voltage
LED	Light emitting diode
LUMO	Lowest unoccupied molecular orbital
M-I-M	Metal insulator metal
MO	Molecular orbital
NMP	N-methyl pyrrolidone
OD	Optical density
PA	Polyacetylene
PANI	Polyaniline
Pc	Phthalocyanine
PF	Pool-Frankel
PPP	Polyparaphenylene
PPS	Polyphenylene sulfide
PPy	Polypyrrole
P3MT	Poly 3-methyl thiophene

PT	Polythiophene
PVK	Poly (N-vinyl carbazole)
RHE	Reverse hydrogen electrode
SBS	Styrene-butadine-styrene
SCE	Saturated calomel electrode
SCLC	Space charge limited currents
TBAP	Tetrabutyl ammonium perchlorate
$TBABF_4$	Tetrabutyl ammonium tetrafluroborate
$TEABF_4$	Tetraethyl ammonium tetrafluroborate
TGA	Thermo gravimetric analysis
UV	Ultra violet
UV-VIS	Ultra violet visible infrared spectroscopy
VB	Valance band
VRH	Variable range hopping
WAXD	Wide angle x-ray diffraction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

A	Cross section area
A°	Angstrom unit
A_b	Absorbency
β	Pool-Frankel parameter
β	Lattice angle
d	Depth
d_{cal}	Calculated interplanar spacing
d_{obs}	Observed interplanar spacing
d-value	Interplanar spacing
e	Electronic charge
eV	Electron volts
exp	Exponential
ΔE	Activation energy
F	Faraday
I	Current
k	Boltzmann constant
l	Length
ln	Logarithm
M	Molar concentration
nm	Nanometer
$N(E_F)$	Density of localized state
R	Resistance
Ro	Initial resistance
Rv	Resistance after chemical resistance
S	Sensitivity factor
T	Absolute temperature
To	Initial temperature
Tg	Glass transition temperature
V	Applied voltage

Vph	Photon frequency
α	Absorption coefficient
α	Coefficient of exponential decay
λ	Mean free path
μ	Carrier mobility
ρ	Resistivity
σ	Conductivity
σo	Initial conductivity
2θ	X-ray diffraction angle
W	Hopping activation energy

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CHAPTER-I
INTRODUCTION

1.1: INTRODUCTION

The last few decades have been marked by the growing importance of two classes of materials, viz. organic polymers and inorganic semiconductors. The strength to weight, processability, and resistance against corrosion has led to the replacement of metals by polymers. On the other hand, the considerable impact made by inorganic semiconductors can be felt even in everyday life in many fields of modern science and technology. Hence, it is not very surprising that materials capable of simultaneously presenting the properties of organic polymers as well as of semiconductors is rapidly becoming a subject of considerable interest for both academic as well as industrial researchers. In this context conducting polymers are now dominating the research areas of advanced materials.

Conducting polymers are at present extensively studied in view of their multiple potential technological applications extending from bulk antistatic coatings to sophisticated molecular devices such as organic light emitting diodes, modified ion selective electrodes and biosensors. In the past ten to fifteen years' substantial progress has been made in the development and characterization of this important class of materials. The modern era of conducting polymers began at the end of the 1970s when Heeger and MacDiarmid discovered that polyacetylene $[(CH)_x]$ synthesized by Shirakawa's method,[1] could undergo a 12 order of magnitude increase of conductivity upon charge-transfer oxidative doping[2]. The essential structural characteristic of conducting polymers is their conjugated π system extending over a large number of recurrent monomer units. This characteristic feature results in low-dimensional materials with a high anisotropy of conductivity, which is higher along the chain direction.

Commodity as well as specialty polymers are insulators because the atoms in the polymer chain are covalently bonded. Metals are conducting due to the presence of metallic bonds, in which the valance electrons are completely delocalized and form an electron cloud around the metal atoms. In the conjugated molecule of a carbon compound, delocalization of electrons may occur through the interaction of π-bonded electrons, such molecules are conducting. Thus, a long chain conjugated molecule such as the polymer of acetylene, $(\text{--CH=CH--})_n$ is conducting. In fact, it was proposed, that properly substituted polyacetylene molecule would exhibit even superconducting behavior at room temperature[3]. Natta and co-workers[4] first prepared polyacetylene as a dark colored powder completely insoluble in organic solvents. Hatano et.al.[5] reported for the first time the electrical conductivity of the order of 10^{-5} S/cm for the trans-polyacetylene sample. Subsequently, vigorous research activities led to the discovery of polysulphur nitride[6], $(SN)_x$, having metallic conductivity and superconductivity at 0.24 K. This conducting polymer, known as synthetic metal, however, remains an academic curiosity because of its brittleness and explosive nature.

The next significant milestone in conducting polymer research was the observation that polyacetylene, like polycyclic aromatic hydrocarbons[7], on exposure to halogen vapors such as bromine and iodine, showed eight fold increase in conductivity[8]. In the year 1977, Shirakawa et.al.[9] exposed the freestanding polyacetylene film to vapors of chlorine, bromine, iodine, arsenic pentafluoride as well as sodium and reported an increase in conductivity up to 12 orders of magnitude. Increasing the conductivity of polyacetylene by treatment with chemicals was termed as 'doping'. In the late seventies electrochemical synthesis offered a convenient route to obtain conducting polymers that are stable to ambient environments[10]. Since then a large number of polymers have been added to the list of conducting polymers such as polypyrrole[11], polythiophene[12], polyparaphenylene[13], polyphenylene sulfide[14], polyaniline[15], and polyphenylene vinylene[16].

1.2: Types of Conducting Polymers

Electrically conducting polymers are of various types. They are classified into different types on the basis of the conduction process that render electrical conductivity to the polymers. Initially Hermann[17] has classified the conducting polymers into four groups as follows:

1. Polymeric charge transfer complexes.
2. Organometallic polymeric conductors.
3. Conducting polymer composites.
4. Highly conjugated polymers.

1.2.1: Polymeric charge transfer complexes

These are formed by the addition of acceptor like molecules to insulating polymers forming complexes known as conducting charge transfer complexes. Using Mullikan's theory[18-19] for complex formation, the interpretation of the formation of most molecular complexes and understanding a variety of electronic interactions is possible. This theory is based on the electronic interaction between two molecules, one of which are an electron donor (of low ionization potential) and the other an electron acceptor (of high electron affinity). The force corresponding to this stabilization energy is called intermolecular charge-transfer force between the constituent molecules. When a complex is formed between an aromatic compound (donor) and iodine (acceptor) an intense absorption band appears which is not found in the spectrum of the individual molecules. The main principle of Mulliken's theory is to consider the complex as a resonance hybrid between the non-bonded and charge-transfer structures.

An interesting interpretation of molecular complexes in terms of simple molecular orbital (MO) theory was given by Dewar[20] for complexes formed between aromatic hydrocarbons (electron donors) and certain compounds such as chloranil, trinitrobenzene, tetracyanoethylene etc. (electron acceptors). The investigations by Dewar and other seem to confirm theoretical assumptions concerning the structure of charge-transfer complexes. These should be regarded as closely bound polarization complexes, in which the electronic structure of their components is essentially unchanged. Similar model can be adopted for polymeric conductors. However, reasons for high conductivity in polymeric charge-transfer complexes and radical-ion salts are still somewhat obscure. It is likely that in polymeric materials, the donor-acceptor interaction promotes orbital overlap, which contributes to alter molecular arrangements, and enhanced electron delocalization.

There are many charge transfer complexes (CTCs) reported in the literature. To name a few, CTCs of tetrathiafulvalene (TTF) with bromine, chlorine etc. is a good conductor. Also, CTCs of TTF with organic π-acceptors, such as 7,7', 8,8'-tetracyanoquinodimethane (TCNQ) or metal 1,2-dichalocogenolenes, such as $Ni(mnt)_2$ where mnt is malenonitriledithiolate were found to be good room temperature conductors. Since 1990, $(ET)_2Cu[N(CN)_2]Cl$ remains the highest superconducting material based on organic molecules (ET) where ET is bis (ethylenedithio) tetrathiafulvalene.

1.2.2: Organometallic polymeric conductors

These are obtained by adding organometallic groups to polymer molecules[21]. The metal d-orbitals may overlap π-orbitals of the organic structure increasing electron delocalization. The d-orbitals may also bridge adjacent layers in crystalline polymers such as in poly (ferrocenylene) to give conducting property to it (**Fig.1.1**).

Metallophthalocyanines and their polymers are also this class of material. These polymers have extensively conjugated structures. The bridged transition metal complexes.form one of the stable systems exhibiting intrinsic electrical conductivities, without external oxidative doping. They posses a strong potential for future applications such as molecular wires, antistatic foils, fibres and in xerography.

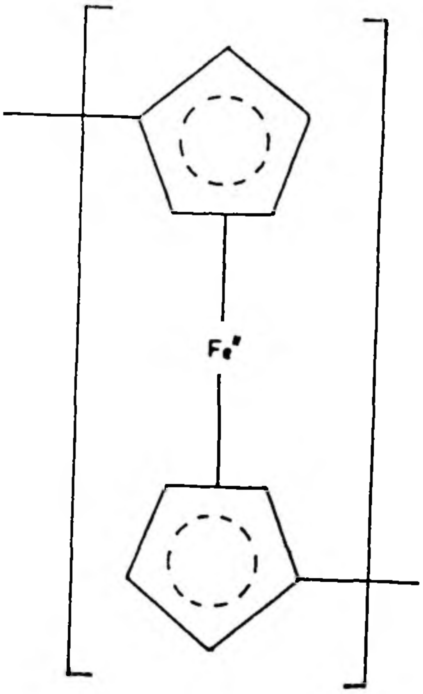


Figure 1.1 : Poly(ferrocenylene)

1.2.3: Conducting polymer composites

Among all the classes of conducting polymers, this type of conducting polymers has been studied most widely. Conducting polymer composites are mixtures/blends of conductive particles and polymers. Various conductors have been used in different forms together with large number of conducting and engineering plastics. These can be injection molded in to desired shapes. Various conductive fillers have been tried such as carbon blacks, graphite flakes, fibers, metal powders etc. The electrical conductivity of the compound is decided by volume fraction of the filler. A transition from insulating to non-insulating behavior is generally observed when volume fraction of conductive filler in the mixture reaches a threshold of about 25%. The various polymers, which have been used as major matrix, are typically ABS, PC, PET, PP, HDPE, Nylon, and PVC etc.

The processes involved in making these composites are different for different polymers. The basic procedure is to take the appropriate volume fraction of polymer and conductor filler and mix them thoroughly so as to form a uniform distribution of the filler particles in the polymer matrix. If both, the polymer and filler are in powder form then they can be dry mixed and then pressed into desired shapes under high pressure and appropriate temperature. In certain cases the polymer is first dissolved in a suitable solvent and the filler is added to it to form a uniform suspension of the filler in a solution. The solvent is then allowed to evaporate to obtain a film. Another method used is melt compounding where the polymer is heated above its melting point in a thin screw extruder and to the free flowing polymer the desired filler is added and mixed thoroughly. This melt can be pressed into dies to get desired shapes. Aluminum flakes, powder, filaments, fibers are commercially available for making conducting polymer composites. ABS/PC with 40% weight load of aluminum flakes is reported to give 40-50 dB attenuations over frequency range of 2.6 to 3.9 GHz.[22].

1.2.4: Highly conjugated polymers

The **Figure 1.2** shows some of the conjugated polymers, which have been studied as electronically conductive polymers. The geometrical structures are also shown in the figure. The unique electronic properties of conjugated polymers are derived from the presence of π-electrons, the wave functions of which are delocalized over long portions of polymer chain when the molecular structure of the backbone is planar (extended π conjugation). It is therefore necessary that there are no large torsion angles at the bonds, which would decrease the delocalization of the π-electron system [23,24].

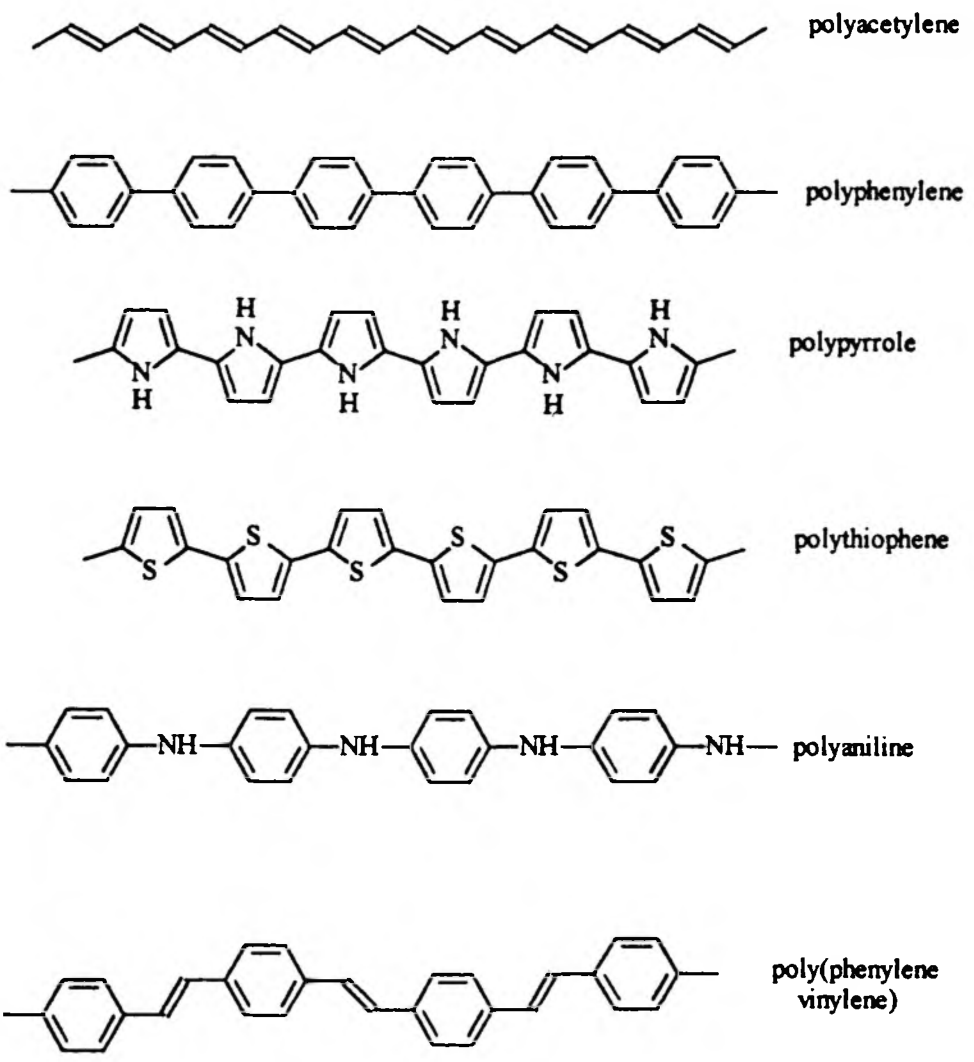


Figure 1.2 : Geometrical structures of conjugated polymers

The essential properties of the delocalized π-electron system, which differentiate a typical conjugated polymer from a conventional polymer with σ-bonds are as follows: (a) the electronic band gap Eg is relatively small (1-3.5 eV) with corresponding low excitations and semiconductor behavior; (b) the polymer molecules can be rather easily oxidized or reduced, usually through charge transfer with dopant species to produce conducting polymers; (c) net charge carrier mobility's in the conducting state are large enough so that electrical conductivity's are realized and (d) quasi-particles, which under certain conditions, may move relatively free through the materials[25]. The electrical and optical properties of these materials depend on the electronic structure and basically on the chemical nature of the repeated unit. The general requirements of the electronic structure in these polymers were recognized and described many years ago. The electronic conductivity is proportional to both the density and the drift mobility of the charge carriers. The carrier drift mobility is defined as the ratio of the drift velocity to the electric field and reflects the ease with which carriers are propagated. Enhancing the electrical conductivity of polymers then requires an increase in the carrier mobility and the density of the charge carriers.

Although many polymers fall under this class of material, we will be dealing with mainly polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT) in these investigations. Hence, a brief survey of these conjugated polymers is given in the following sections.

1.2.4. (A): POLY (ANILINE) [PANI]

Among all conducting polymers, polyaniline has a special representation due to (1) easy synthesis (2) environmental stability and (3) simple doping by protonic acids. Polyaniline is a typical phenylene based polymer having a chemically flexible -NH- group in the polymer chain flanked either side by phenylene ring. The protonation, deprotonation and various other physico-chemical properties of polyaniline are due to the presence of this -NH- group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black[26]. Willstatter and co-workers[27-28] in 1907 and 1909 regarded aniline black as an eight-nucleus chain compound having an indamine structure. However, in 1910 Green and Woodhead[29] were able to report various constitutional aspects of aniline polymerization. These authors carried out oxidative polymerization studies using mineral acids and oxidants such as persulfate, dichromate and chlorate and determined the oxidation states of each constituent by redox titration using $TiCl_3$.

During that period it did not occur to anyone to investigate its electrical and magnetic properties for the obvious reasons that organic compounds are insulators. Almost 50 years later, Surville et.al[30] in 1968 reported proton exchange and redox properties with the influence of water on the conductivity of polyaniline. But interest in polyaniline was generated only after the fundamental discovery in 1977 that iodine doped polyacetylene has a metallic conductivity which triggered research interest in new organic conducting materials. Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization[31]. The chemical oxidative polymerization is of particular importance since this synthesis is the most feasible route for the production of polyaniline on a large scale.

(1) Chemical Synthesis

The most preferred method for synthesis of polyaniline by chemical oxidative route involves the use of either hydrochloric or sulfuric acid with ammonium persulfate as an oxidant in aqueous solution[32-36]. Oxidative polymerization is a two-electron change reaction and hence, the persulfate requirement is one mole per mole of a monomer. However, the smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed. The synthesized polyaniline exists in various oxidation states; they are termed as (1) Leucoemeraldine (2) Emeraldine base (3) Emeraldine salt and (4) Pernigraniline. These various forms of polyaniline are schematically shown in **Figure 1.3**.

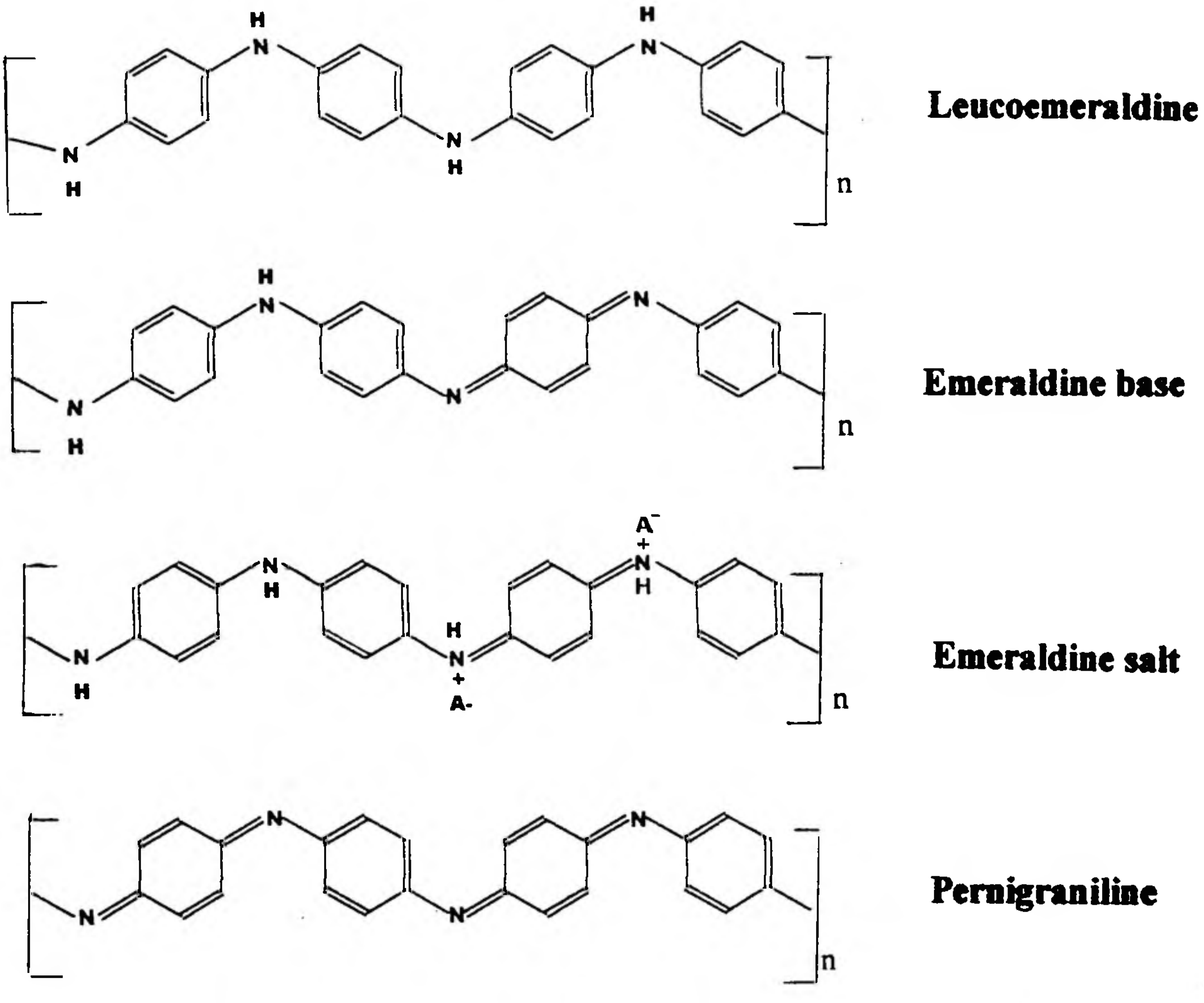


Figure 1.3 : Various oxidation states of Polyaniline

Pron et.al.[37] compared the electrical conductivity and the reaction yield of polyaniline, polymerized with four different oxidizing agents and at different aniline/oxidant ratios. These authors concluded that the redox potential of the oxidizing agent is not a dominant parameter in the chemical polymerization of aniline; most oxidizing agents gave similar results. Armes et.al.[34] studied the polymerization of aniline at 20°C using ammonium persulfate as oxidant. In their study of the effect of the oxidant/monomer initial mole ratio, they concluded that the conductivity, yield, elemental composition and degree of oxidation of the resulting polyaniline are essentially independent of this ratio when its value was below 1.15. On the basis of elemental analysis, the authors concluded that over-oxidation of polyaniline occurs at higher oxidant/monomer mole ratios. Asturias et.al.[35] investigated the influence of the polymerization atmosphere (air or argon) on the degree of oxidation of chemically prepared polyaniline, using $(NH_4)_2S_2O_8$ as an initiator. Cao et.al.[36] established optimum synthesis conditions for the polymerization of aniline by ammonium persulfate with respect to viscosity, electrical conductivity and reaction yield. They found that the reaction yield was not strongly sensitive to most synthesis variables, while the viscosity or molecular weight and electrical conductivity was found to be markedly affected. In addition they reported that the commonly employed procedure for protonation of polyemeraldine salt (long time stirring of as-polymerized polyaniline powder with conc. aq. HCl solution) leads to significant degradation of polyaniline.

(2) Electrochemical Synthesis

Electrochemical polymerization of aniline is generally carried out in protonic acid in distilled water at platinum electrode. This electrochemical synthesis is achieved by using any one of the following methods (1) Galvanostatic: constant current in the range 1-10 mA. (2) Potentiostatic: at constant potentials – 0.7 to 1.1 V versus SCE and (3) Sweeping the potential: between -0.2 to + 1.0 V versus SCE.

Mohilner et.al.[38] have reported mechanistic aspects of aniline oxidation. Buvet et.al.[10] studied the conductivity of polyaniline prepared by this route and the influence of water on conductivity measurements. Major interest in the electrochemistry of polyaniline was generated only after the discovery that aromatic amine, pyrrole, thiophene, furan, indole and benzene can be polymerized anodically to a conducting film[39-41]. The anodic oxidative polymerization of aniline is the preferable method to obtain a clean and better-ordered polymer as a thin film. Diaz et.al.[15] and others[42-43] reported the preparation of polyaniline in an aqueous acid solution using platinum electrode at potentials between -0.2 to 0.8V versus SCE. Toshima et.al.[44] have reported the formation of polyaniline film by decarboxylation of poly (anthranilic acid). The physicochemical properties of polyaniline films cast from organic solvent like NMP are reported by Kang et.al.[45]. The effect of salts on the electrochemical polymerization was reported by Chinese group Shaolin et.al.[46]. These workers reported that the conductivity of PANI films prepared in the presence of NaCl is about 30 times higher than that of PANI films without NaCl. Chen and Lee[47] investigated the structure and doping behavior of PANI freestanding film plasticized with NMP. The preparation of PANI films by using $FeCl_3$ was reported by Yasuda and Shimidzu[48]. They also reported the spectroscopic analysis of these films. Genies et.al.[49] have carried out aniline oxidation in $NH_4F + 2.3\ HF$ at 1.0 V. They proposed an intermediate nitrenium cation as an intermediate in the polymerization reaction. Further from EPR studies they showed that there are two polaron-bipolaron states in the polyaniline.

Various authors[50-55] have reported an X-ray diffraction pattern for acid doped polyaniline. Baughmann et.al.[56] investigated crystals of ClO_4^- and $BF4^-$ salts of "tetramers" and " dimers" of aniline. Pouget et.al[57] have thoroughly carried out x-ray studies on the various oxidation states of polyaniline. They reported that starting from amorphous bases, the crystallinity of polyaniline increases with the doping level. They found the orthorhombic crystal structure with parameters as: a = 7.80 A°, b = 5.75 A° and c = 10.5 A° for the NMP-cast stretched film; a = 7.65

A°, b = 5.75 A° and c = 10.2 A° for the THF/NMP extracted powder. These authors showed that regardless of the type of preparation, almost 50% of the polyaniline base could not be transformed by more doping into "crystalline" salt.

The electrical conductivity of undoped polyaniline is reported to be in the range of 10^{-10} to 10^{-7} S/cm. Upon acid doping it attains higher values in the range 10^{-2} to 100 S/cm. The temperature dependence of the conductivity of PANI shows that most of the currently synthesized PANI grades are somewhat away from the metal-to-insulator transition, i.e. the conduction process is dominated by some sort of hopping conduction. Undoubtedly, the hopping process involves a mechanism having $T^{-1/2}$ temperature dependence. However, the assignment of this temperature dependence of conductivity to the responsible hopping mechanism is not straightforward. Three mechanisms, i.e. the one-dimensional variable range hopping, the three dimensional variable range hopping and Sheng's charge energy limited tunneling effect, could account for the observed temperature behavior.

1.2.4. (B): POLY (PYRROLE) [PPy]

Polypyrrole is an important conducting polymer because of a number of reasons such as high conductivity, stability in the oxidized state and interesting redox properties[58]. The simplicity of the synthetic procedures and availability of the initial monomers are also attractive features of PPy. Of all known conducting polymers, polypyrrole is the most frequently used in commercial applications, due to the long-term stability of its conductivity and the possibility of forming homopolymers or composites with optimal mechanical properties. This is the first polymer for which electrically conducting film was made electrochemically[59]. Conducting polypyrrole has been prepared by various methods such as chemical, electrochemical, vapor phase deposition etc.[11].

(1) Chemical Synthesis

The chemical polymerization of pyrrole was first reported in 1916[60-61] by the oxidation of pyrrole with H_2O_2 to give an amorphous powdery product known as pyrrole black. In general, pyrrole blacks have been prepared in the presence of various oxidizing agents like hydrogen peroxide, lead dioxide, ferric chloride, nitrous acid, quinones or ozone. The materials obtained by this methods have resulted mainly in insulating materials with room temperature conductivity typically of the order of 10^{-10} to 10^{-11} S/cm[62-64], which on doping with halogenic electron acceptors give a conductivity of about 10^{-5} S/cm. In this sense, a lot of efforts have been taken out to get highly conducting polypyrrole. One of the great advantages of polypyrrole from synthetic point of view concerns the low oxidation potential of the pyrrole monomer[65]. Pyrrole is one of the most easily oxidized monomer and hence, a variety of oxidizing agents is available for preparing PPy. Several metallic salts have been employed to polymerize pyrrole such as $FeCl_3$; $Fe(NO_3)_3$, $Fe(ClO_4)_3$, $K_3Fe(CN)_6$, $CuCl_2$, $CuBr_2$ etc. with conductivity's ranging between 10^{-5} to 10^{2} S/cm. Ferric salts are mostly used for this purpose. In case of $FeCl_3$ the polymerization process is summarized below:

$$3m\,Py + n\,FeCl_3 \rightarrow m\,(Py_3Cl) + n\,FeCl_2$$

The polymerization probably follows a mechanism similar to that proposed by Hsing et.al.[66] for the oxidation polymerization of benzene, to yield poly (p-phenylene). Thus the reaction would be initiated by the cationic radical $C_4NH_5^{+}$, which coordinates with other pyrrole units. The transition metal ion, being the electron acceptor, probably forms a donor-acceptor complex with the π system of pyrrole at the chain initiation step, as well as with the polymer intermediate at the final rearomatization step. XPS studies of conducting PPy obtained from chemical polymerization and oxidation of pyrrole by Fe (III) oxidants give a stochiometry that accounts for 25% oxidized pyrrole units being favoured[67].

In general, polymer conductivity is a function of the monomer and oxidant concentration, solvent, time of reaction of the synthesis. Thus, the optimum reactant Fe (III)/monomer ratio for the polymerization of pyrrole by $FeCl_3$ has been suggested to be approximately 2.4[68]. Conductivity of 190 S/cm has been reported for PPy synthesized in solution of $FeCl_3$[69]. An increment in the concentration of the ferric salt yields a drop in the conductivity of the obtained PPy. A similar behaviour is observed by increasing the reaction time. This could be due to the copolymerization of some secondary products, having an oxidation potential of the same order as that of pyrrole and an increasing concentration during the course of reaction. One of the most important reaction gives rises to an undesired presence of saturated bridges between polyconjugated domains. By dissolving ferric chloride, nitrate, perchlorate and sulfate in water, an acidic medium is obtained. If a low amount of urea as buffer is added, the conductivity of PPy obtained is enhanced[70]. Low temperatures (0-5°C) are the most appropriate for obtaining the best conductivities in aqueous solutions of ferric salts[71]. A similar behaviour of the chemical oxidation of pyrrole in organic solvents has been reported[72]. This seems to suggest that lowering the reaction rate results in an increasing conductivity of the polymer. Cyclic voltammetric studies of PPy obtained by using $FeCl_3$, as oxidant showed no evidence of PPy decomposition after repetitive cycling. voltammograms also showed that after the oxidation reaction a high capacitive current remained. A cyclic voltammogram of PPy synthesized by oxidation with $CuCl_2$ showed different and irregular shapes, probably influenced by the presence of copper ion, incorporated into the polymer.

Yoshikawa et.al.[73] have found that highly conductive PPy could be obtained if the oxidation potential of the aqueous solution is controlled to the optimum value during chemical polymerization by adding a suitable amount of $FeCl_2$. In this way PPy having conductivity of more than 200 S/cm was prepared[74]. Apart from the metallic salts, a halogenic electron acceptor, such as bromine or iodine in several solvents, has achieved simultaneous chemical synthesis and doping of PPy. PPy-I_2 and PPy-Br_2 have conductivities around 1 to 30 S/cm[75]. For the mass production of PPy, however, catalytic process is more preferable due to the low cost of extensive post-treatment step. CuCl-$AlCl_3$-O_2 is a typical system applied to synthesize PPy chemically[76]. Another catalytic system using $FeCl_3$ in a form different from an oxidizing agent has been also used. Compared with the relatively high conductivity (1-200 S/cm) of PPy prepared using $FeCl_3$ as oxidizing agent, the conductivity of PPy prepared using $FeCl_3$ as catalyst was around 10^{-2} S/cm.

(2) Electrochemical Synthesis

The electrochemical preparation of polypyrrole has been reported first by Diaz et.al.[10]. According to these workers the electrosynthesis of this film proceeds via the oxidation of pyrrole at the platinum electrode to produce an unstable π-radical cation which then reacts with the neighboring pyrrole species as shown below: **(Fig. 1.4)**

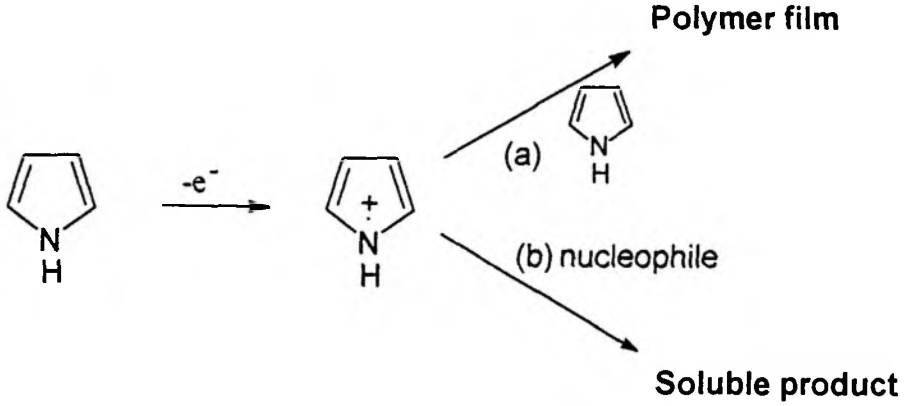


Figure 1.4 : Electro-synthesis of Polypyrrole

Electropolymerization of pyrrole differs from other polymerization reactions, including the radical ones[77]. The anodic oxidation, which results in the formation of conducting polymer, has the stochiometry of 2.07 to 2.6 F per mole of monomer[39, 78.] Of these, only 2 F/ moles are related to the polymerization as such and an extra charge to the oxidation (doping) of the polymer film. Since the oxidation potential of the monomer is always markedly higher than that for the polymer, the two processes, the formation of the polymer and its oxidation proceed in parallel and accompanied by the incorporation of counter ions into the polymer matrix.

Electropolymerization of pyrrole can be performed in both aqueous and non-aqueous media, such as acetonitrile, propylene carbonate, and dichloromethane etc[79-82]. However, with increasing nucleophilicity of solvent, the film growth is inhibited due to the interaction of the solvent with the primary products of monomer oxidation. The film does not form in such nucleophilic aprotic solvents as dimethlyformamide, dimethyl sulfoxide, hexamethylphosphoramide, unless the nucleophilicity of solvent is reduced by addition of a protic acid[83]. Apart from that, the side reactions occurring on the film surface can affect electropolymerization in these solvents. According to the extensively used procedure of Diaz[10], 1% of water is added to acetonitrile solution; this results in improved properties of the film (adhesion to electrode, uniformity). Even better PPy films were obtained with 2% of water in acetonitrile electrolyte[84]. However, a high content of water in the electrolyte (over 20%) results in deterioration of the film properties such as tensile strength and conductivity.

In practice polypyrrole films are prepared by the electro-oxidation of pyrrole in one-compartment cell equipped with platinum working electrode, gold wire counter electrode and a sodium chloride calomel reference electrode (SSCE). In a typical preparation, an acetonitrile solution containing 0.1 M TEATBF$_4$ plus ca.0.02 M pyrrole is employed[10]. The oxygen in the solution is swept out with an inert gas prior to the electrolysis because films prepared in the presence of oxygen have inferior properties [85]. In practice a wide variety of solvents and electrolytes can be used, as the electrical resistance of the solution is not high and the nucleophilicity does not interfere with the polymerization reaction. These conditions can be accomplished by selecting solutions where the electrolyte is highly dissociated and which are slightly acidic. Films of various thicknesses can be prepared by changing current density. Using a current density of 0.22 mA/cm^2 films having thickness of 10-200 μm were prepared by Diaz and Kanazawa that could be physically separated from the electrode.

According to Rodriguez et.al[86] the electrochemical method is most useful since it permits direct grafting of the conducting polymers onto the electrode surface, which can be of special interest for electrochemical applications. As the electrical potential needed for monomeric oxidation is significantly higher than the charging (or doping) of the finally formed polymer, the polymer is obtained in its conducting (doped) state. The film thickness can be easily controlled by the electrical charge employed during polymerization. Also, the electrochemical generation of conducting PPy is a fast, easy and clean method to obtain highly conducting PPy materials. In spite of all these advantages, the electrogeneration of PPy is losing interest as a method of obtaining these materials. This is mainly due to two main problems associated with this method. The first problem is associated to the difficulty in producing large amounts of PPy, due to the limitations introduced by the size of the anode. The second problem associated with the difficulties found in correlating the polymer properties with the conditions of synthesis. According to Rodriguez et.al.[86] these variable conditions can be chemical, such as solvent or reactants (monomers and dopant salt), or physical such as temperature, nature and shape of the electrodes, cell geometry of electrical conditions during synthesis. Another characteristic of electrochemical polymerization of pyrrole arises from the special features of its oxidation process. Electropolymerization of pyrrole and similar monomers differs from the other polymerization reactions. In the common electrochemically induced polymerization process, the electrode triggers chain growth and consequently, the process requires little electricity[87-88]. By contrast, in the anodic oxidation of pyrrole to produce polypyrrole, the charged species of precursor initially formed by the continuous oxidation of the neutral monomer at the anode surface[89]. In consequence, several electrochemical and chemical competitive reactions are possible near the electrode surface.

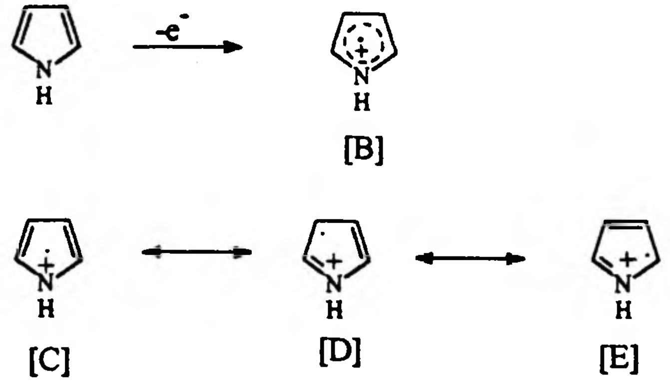
The oxidation of pyrrole to polypyrrole is irreversible. The mechanism of this reaction was extensively studied; yet the problem still remains not fully resolved. Among the mechanisms proposed, two have gained the greatest interest. One of those is the oxidative coupling of monomer molecules (**Fig. 1.5**) [90]. The first stage of the reaction is the electrode oxidation of monomer molecules yielding radical cations with the radical state delocalized over the pyrrole ring (B). The maximum spin density is at the α-position[91]; hence, of the three possible resonance states, (C), (D) and (E), the latter is the most stable. The radical cations dimerise and expel two protons. The dimers, owing to stronger conjugation, are more readily oxidized under the given reaction conditions than the monomer. The chain growth proceeds by addition of a newly formed radical cation to an oligomeric one.

The second most widely discussed mechanism is the free radical reaction. (**Fig.1.6**). This scheme implies that formation of a radical cation on the anode is followed by the loss of proton and attack of the radical on the neutral monomer. After re-oxidation of the dimeric radical and proton loss, the dimeric molecule can experience subsequent oxidation, which results in chain growth.

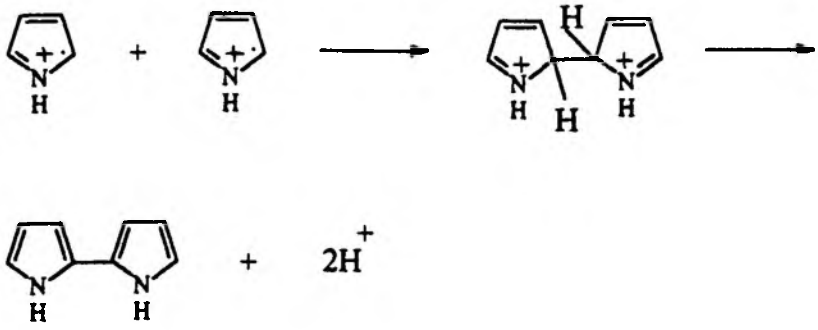
1.2.4. (C): POLY (THIOPHENE) [PT]

Thiophene was found in tar, gas and industrial benzene obtained from coal in the nineteenth century. A large number of thiophene derivatives are described in the literature and their physical properties, nucleophilic substitution and biological activity are still of current interest[92]. Polythiophene (PT) has a molecular structure

1. Monomer oxidation



2. Coupling (Dimerization of cation-radicals)



3. Chain growth

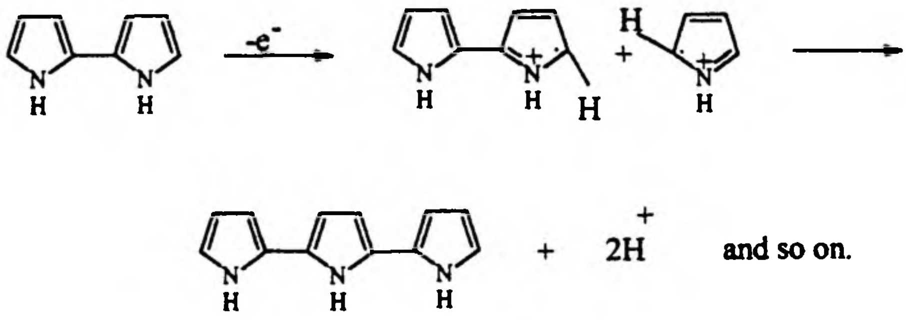


Figure 1.5 : Oxidative coupling mechanism for Polypyrrole

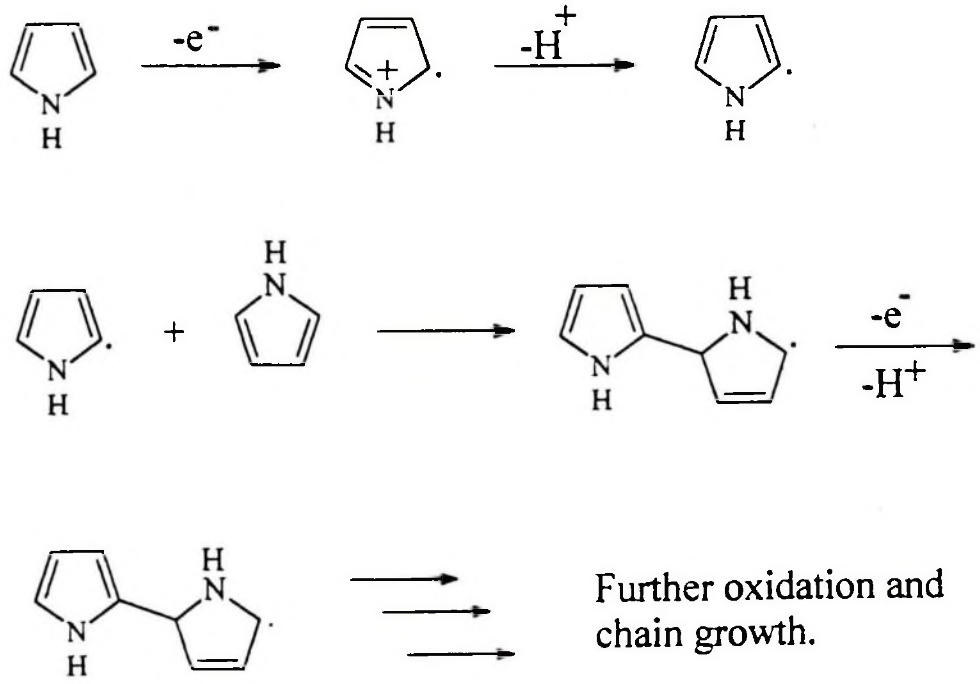


Figure 1.6 : Radical mechanism for Polypyrrole synthesis

consisting of aromatic rings linked at its 2,5-position and is characterized as a conducting polymer, since it becomes highly conductive on doping with electron donors or acceptors[93, 94.] Among the numerous conducting polymers, PT has rapidly become the subject of considerable interest. From the theoretical viewpoint, PT has been often considered as a model for the study of charge transport in conducting polymers with nondegenerate ground state. While on the other hand, the high environmental stability of both its doped and undoped states together with its structural versatility have led to multiple developments aimed at applications such as conductors, electrode materials, and organic semiconductors. Two techniques have been used to synthesize polythiophene: (1) Chemical synthesis and (2) Electrochemical synthesis.

(1) Chemical Synthesis

Chemical synthesis method is quite useful for the simple basic reason that it gives higher yield of the polymer. Elsenbaumer and co-workers[95] first pursued these approaches. Among the oligothiophenes synthesized chemically, the α-α'-linked compounds have reported to have well-developed π-electron delocalization[96]. But the disadvantage with this method lies in the fact that the polymer obtained is in its insulating state. To make it more conducting it is further doped chemically or electrochemically to it's conducting state. Thiophene oligomers have been prepared by several methods and some of them have been proposed as generalizable to the preparation of polymers. Thus, mixtures of several thiophene oligomers have been obtained by the reaction of 2-iodothiophene with copper bronze[97]. Trithiophene has been prepared by cyclization of 1-4-diketones containing one or more thiophene rings[98-99]. Quater- and sexithiophene have been synthesized by coupling the α-lithiated thiophenes in the presence of cupric chloride or organoboranes[100-101].

Thiophene has been polymerized with variety of initiators: sulfuric acid [102], iron (III) chloride, Ziegler catalysts[103] and with AsF_5 complexes[104].

Polythiophene {PT} i.e. [poly (2,5-thienylene)] is usually synthesized from dihalogenated thiophene by utilizing a transition metal catalyzed dehalogenation polymerization[105]. This process leads, however, to a polymer of quite low molecular weight (500-1300) [106]. Diaz et.al.[107] developed a plasma technique to polymerize thiophene. The synthesis of PT by oxidative coupling of bis-lithiated thiophene derivatives has been reported[108]. A conductivity of 14 S/cm has been reported for the PT prepared by nickel-catalyzed Grignard coupling of 2,5-diiodothiophene[109]. Thiophene and 3-methyl thiophene oligomers have been synthesized by $NiCl_2$ (dppp) [dppp=$Ph_2PCH_2CH_2CH_2PPh_2$] coupling of Grignard compounds with the appropriate bromothiophene[110]. Yamamoto et.al.[111] prepared polythiophene by the dehalogenative coupling of 2,5-dibromothiophene with magnesium catalyzed by nickel (II) chloride and bipyridine. Lin and Dudek[112] also prepared polythiophene in a similar way. The conductivity of a PT pellet was 10^{-11} S/cm and was enhanced to 0.1 S/cm after doping with iodine. PT has been prepared by oxidative polymerization of thiophene and bithiophene in the gas phase using AsF_5 under pressure[113]. Oxidative polymerization in liquid phase initially proposed for the preparation of poly (pyrrole) [62], has been extended to PT's [114-116].

Although polythiophenes are essentially amorphous polymers: partial crystallinity has been observed in some cases. Thus crystallinity of 35%, increasing up to 56% after annealing at 380°C has been reported for PT, which was chemically synthesized by Grignard coupling of 2,5-diiodothiophene[117]. These authors have proposed an orthorhombic unit cell with a = 7.83 A°, b = 5.55 A°, and c = 8.03 A°. They also suggest a monoclinic unit cell with a = 7.83 A°, b = 5.55 A° and c = 8.20 A° with $\beta = 96°$ for the crystalline structure of PT. Similar unit cell has been proposed from theoretical studies[118]. It is worth noting that these unit cells imply planar polymer chains with a transoid conformation of thiophene rings. However, there are modifications of structure with temperature giving rise to thermochromism in PT.

The nature of the charged species responsible for conduction in polythiophenes is still a matter of debate. Hence many researchers have carried out identification of the charged species responsible for the conduction mechanism in PT. In polyacetylene, which has a degenerate ground state, solitons have been shown to be the dominant charge carrier species[119]. In contrast PT has a nondegenerate ground state. The two limiting mesomeric structures, i.e. aromatic and quinoidal are not energetically equivalent, the quinoidal form having a higher energy[120]. In this case, the removal of an electron from the conjugated π-system provokes a local distortion of the chain and the appearance of two states in the gap corresponding to a polaron (or radical cation) with spin 1/2. Theoretical calculations have shown that adjacent polarons are unstable and lead to the formation of spinless doubly charges defects e.g. bipolarons (or dications) which have been proposed as the dominant charge carrier species in PT [121-123].

(2) Electrochemical Synthesis

The electro-polymerization of bithiophene was initially mentioned in 1980. PT and its derivatives were developed by Yamamoto et.al.[124] as prototype compounds in the PT family; many researchers have since then synthesized these polymers via electrochemical routes. Tourillon and Garnier[10] first applied the electrochemical technique to synthesis of polythiophene and poly (3-methylthiophene) [P3MT]. They oxidized thiophene in acetonitrile using TBAP as a supporting electrolyte and obtained a thin film of PT on a platinum plate. Which had conductivity in the range of 10-100 S/cm. Tanaka et.al.[125] obtained a high-quality freestanding film by polymerizing thiophene in nitrobenzene in the presence of $TBABF_4$. Hotta et.al.[126] found that electrochemical synthesis in an electrolytic solution composed of nitrobenzene, benzonitrile etc. at low temperatures using a large current density (> 2 mA/cm^2) produces exceedingly dense and flexible PT and P3MT films having conductivities up to 120 S/cm. Sato et.al.[127] reported a conductivity as high as 510 S/cm after optimizing the reaction conditions. Under these conditions the films obtained were, both the free standing and thin. Tourillon and Garnier[128] pointed out that a non-degassed reaction system (electrolyte solution) used for the electrochemical synthesis results in film conductivities lower than those obtained from a carefully degassed system. Taking this into consideration, Hotta[129] further improved his techniques and achieved significant enhancement of conductivity up to 750 S/cm for P3MT film. Roncali et.al.[130] attained a conductivity of about 2000 S/cm for the thin film of P3MT (200-nm thickness) carefully prepared in nitrobenzene. This improved technique was directly applied to the electrochemical syntheses of various polythiophenes. This high quality of the materials is indispensable for various physical measurements and for interpretation of their results.

Despite the large amount of work devoted to electrogenerated PT's, the mechanism of the electropolymerization of thiophene has been only rarely considered. An important aspect of the electropolymerization reaction is that it proceeds with electrochemical stochiometry, with n values in the range of 2.07-2.5 Faradays/ mole. The oxidation of the monomer requires 2 electrons/molecule while the excess of the charge corresponds to the reversible oxidation or doping of the polymer. It is generally accepted that electrochemical polymerization proceeds via radical cationic mechanism. Since it is anodic reaction, this seems reasonable. **Fig.1.7** represent the generally accepted mechanism for electropolymerization of heterocycles[131].

The first electrochemical step consists in the oxidation of the monomer to its radical cation. Since the electron-transfer reaction is much faster than the diffusion of the monomer from the bulk solution, it follows that a high concentration of radicals is continuously maintained near the electrode surface. The second step involves the coupling of two radicals to produce a dihydro dimer dication, which leads to a dimer after loss of two protons and rearomatization. Due to the applied potential, the dimer, which is more easily oxidized than the monomer, occurs in its radical form and undergoes a further coupling with a monomer radical. Electropolymerization proceeds then through successive electrochemical and chemical steps, until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface.

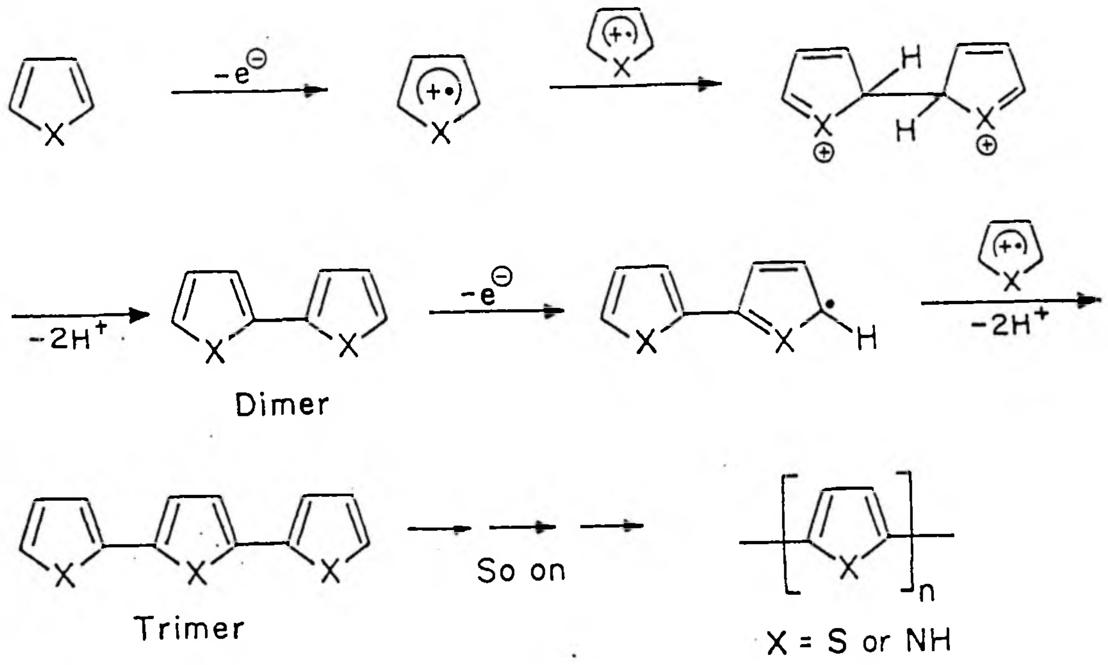


Figure 1.7 : Mechanism for electro-polymerization of heterocycles

The electro-polymerized materials are generally found to be less crystalline than the chemically obtained counterparts. Thus, x-ray diffraction shows invariably that electrochemical polymerization gives more disordered materials. Ito et.al.[132-133] reported x-ray diffraction studies of electro polymerized PT on platinum, in which broad rings could be seen. These developed into diffraction lobes for samples that had been stretched. The lobes were interpreted to be in fair agreement with a 200-reflection (the strongest one) based on the unit cell of Mo et.al[134]. An x-ray diffraction pattern of electropolymerized PT published later by Chen and Ni[135] showed, however, only a broad, amorphous peak between scattering angle of 14° and 28°, which is centered at 21°.

The most conductive PT samples obtained until now have been prepared in rigorously anhydrous aprotic solvents of high dielectric constant and low nucleophilicity such as acetonitrile, benzonitrile, nitrobenzene and propylene carbonate. These solvents also lead to the highest current efficiency for electropolymerization[136]. Acetonitrile generally yields a powdery deposit or to brittle films with conductivities typically comprised between 0.02 and 10 S/cm for PT. As shown by the literature data on electrogenerated PT, benzonitrile, nitrobenzene, or propylene carbonate allows the obtention of compact freestanding films with conductivities exceeding 200 S/cm. A polythiophene film obtained by using Bu_4NPF_6 as an electrolyte in nitrobenzene at room temperature showed highest conductivity of 370 S/cm.

1.3 Charge Transport in Conducting Polymers.

It is well known that polymers with a conjugate bonding system, i.e. an uninterrupted sequence of single and double bonds running through the whole molecule are usually electrically conducting. The electrical properties of conducting polymers depend on the electronic band structure. When the bands are filled or empty, no conduction occurs. If the band gap is small compared with thermal excitation energies, electrons are excited to the conduction band and thus conductivity increases. When the band gap is too wide, thermal excitation is insufficient to excite electrons to the conduction band and the material is an insulator.

The conductive polymers carry current without having partially empty or partially filled bands. The most important characteristic, however, is that when the polymers are highly oxidized the charge carriers are spinless. To explain the conduction phenomena, it is proposed that when an electron is removed from the top of the valance band by oxidation a vacancy (hole or radical cation) is created, but it does not delocalize completely. Partial delocalization occurs over several monomer units, and the units deform structurally. The energy level associated with the radical cation represents a destabilized bonding orbital and thus has a higher energy than that of the valance band i.e. the energy is in the band gap. A radical cation that is partially delocalized over some polymer segment is called a 'polaron'. A dication or 'bipolaron' has two charges associated with the localized polymer segment. Thus, low oxidation levels yield polarons and higher oxidation levels give the bipolarons. Both polarons and bipolarons are mobile and can move along the polymeric chain by the rearrangement of double and single bonds in the conjugated system that occurs in an electric field. Conduction by polarons and bipolarons is the dominant mechanism of charge transport in polymers with non-degenerate ground states.

There are several models for electrical conduction. The most widely used is the one-electron band model. This is based on extending the simple model of a bond between two atoms over whole crystalline solid.

When two identical atoms each having a half filled orbital are brought together closely enough for their orbitals to overlap, the two orbitals interact to produce two new orbitals, one of lower energy and one of higher energy. The magnitude of this energy difference is determined by the extent of orbital overlap. The two electrons go into the lower energy orbital (M.O.Theory). The (now filled) lower-energy orbital is a bonding orbital and the high-energy (empty) orbital is an antibonding orbital (**Fig.1.8**).

The magnitude of the conductivity is determined by the number of charge carriers available for conduction and by the rate at which they move. In order to consider the effect of temperature on the electrical conductivity of the three main

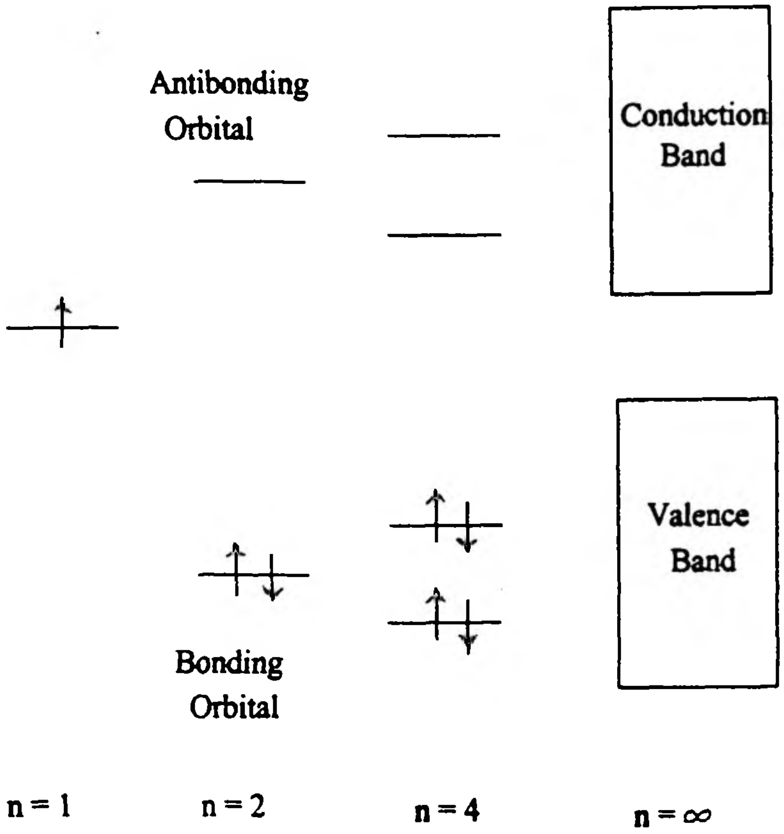


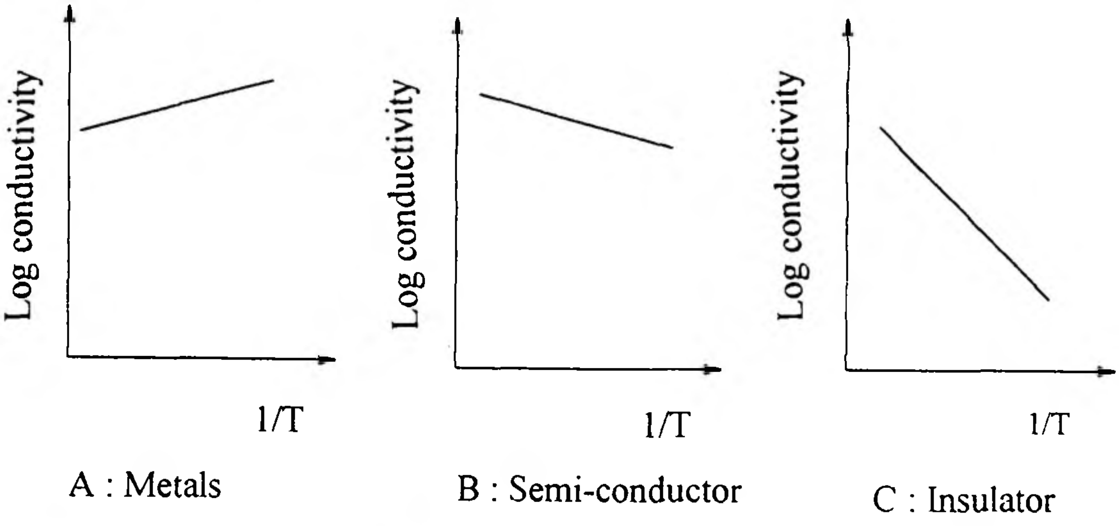
Figure 1.8 : One electron band model for electrical conduction

classes of materials (metals, semiconductors and insulators), it is therefore necessary to consider its effect on both charge carrier concentration and mobility.

In a metal all the electrons are available for conduction, so the conductivity is determined by the mobility. As the temperature of a crystal lattice is increased, the atoms vibrate and interact with the electrons to scatter them. Thus in a metal the conductivity decreases with increasing temperature (**Fig. 1.9 A**).

In a semiconductor the same is true, but also the charge carrier concentration increases with increasing temperature. Since the charge carrier concentration is much more temperature dependent than the mobility, this is the dominant factor and conductivity increases with increasing temperature (**Fig. 1.9 B**).

In an insulator the band gap is so large that it is very difficult to thermally excite electrons across it to provide charge carriers, and thus at reasonable temperatures the conductivity remains low (**Fig.1.9 C**).



A : Metals

B : Semi-conductor

C : Insulator

Figure1.9 : Conductivity behavior of metal, semiconductor and Insulator as a function of reciprocal of temperature

Conducting polymers are amorphous with short conjugation lengths. Therefore, it has been suggested that electrical conduction take place by charge hopping between polymeric chains. A model used to describe the conduction process is the conduction model originally developed for amorphous silicon by Mott and Davis[137]. When applied to conducting polymers, it assumes that electron transport originates from localized or fixed states within the polymer chain. The charge transfer between the chains takes place by hopping, referred to as phonon assisted hopping between two localized states. Lattice vibrations enhance this process of tunneling from one localized state to another. Plot of conductivity versus temperature was parameterized by fitting Mott's Variable Range Hopping (VRH) Conduction Model. Most conducting polymers have shown a temperature dependence of dc conductivity consistent with the VRH conduction process, obeying the following relationship:

$$\sigma = \sigma o \ \exp. [- (To/T)^{1/4}] \ [S / cm] \text{ -----------(1)}$$

Mott's parameters are listed as follows:

$$\sigma o = e^2R^2\nu_{ph}N (E_F) \qquad \text{--------------(2)}$$

$$To = \lambda \alpha^3 / k N (E_F) \qquad \text{--------------(3)}$$

$$R = [9 / 8\pi R^3N(E_F)]^{1/4} \ (cm) \qquad \text{-------------(4)}$$

$$W = [3 / 4\pi R^3N (E_F)] \ (eV) \qquad \text{------------(5)}$$

Where σ is the conductivity of the sample at temperature T (K), σo is the pre-exponential factor (S/cm), To is the characteristic temperature (K), e is the electronic charge (1.602×10^{-19} C), k is the Boltzmann's constant (8.616×10^{-5} eV/K), R is the average hopping distance (cm), ν_{ph} is the phonon frequency (10^{13} Hz), N (E_F) is the density of localized states at the Fermi level (cm^{-3}/eV), λ is the dimensional constant (18.1), α is the coefficient of exponential decay of the localized states (cm^{-1}) and W is the hopping activation energy (eV).

Taking the natural logs on both sides of equation (1), the following relationship is obtained:

$$\ln \sigma = \ln \sigma o - (To) \times (T)^{-1/4} \text{-------------} (6)$$

The linear nature of the ln σ versus $T^{-1/4}$ plots is usually taken as justification for the validity of VRH conduction process represented by equation (1) in conducting polymers.

1.4: Conductivity in Heterogeneous Systems

The electrical conductivity in homogeneous systems can be well explained by quasi-particles such as polaron, bipolaron and solitons. In heterogeneous systems the structure is not uniform but rather a more disordered or branched one. In this type of system the charge transport along the polymer chains takes place by hopping or tunneling process. These processes are already discussed in length in above section.

1.5: Doping of polymers

Doping of polymeric semiconductors is different from that in inorganic or traditional semiconductors[138]. Inorganic semi-conductors, have a three-dimensional crystal lattice and on incorporation of specific dopant, n-type or p-type in ppm levels, the lattice is only slightly distorted. The dopant is distributed along specific crystal orientations in specific sites on a repetitive basis.

Doping of conducting polymers involves random dispersion or aggregation of dopants in molar concentrations in the disordered structure of entangled chains and fibrils. The dopant concentration may be as high as 50%[139]. Also incorporation of the dopant molecules in the quasi one-dimensional polymer systems considerably disturbs the chain order leading to reorganization of the polymer[140]. Doping of inorganic semiconductors generates either holes in the valance band or electrons in the conduction band. On the other hand, doping polymer leads to the formation of conjugation defects, viz. solitons, polarons or bipolarons in the polymer chain[141].

Thus the ultimate conductivity in polymeric semiconductors depends on many factors, viz. nature and concentration of dopants, homogeneity of doping, carrier mobility, crystallinity and morphology of polymers.

1.6: Types of doping agents

Doping agents or dopants are either strong reducing agents or strong oxidizing agents. They may be neutral molecules or inorganic salts, which can be easily, form ions. Thus, dopants may be classified as (a) Neutral dopants (b) Ionic dopants (c) Organic dopants and (d) Polymeric dopants.

Dopants for Polymers

Dopant Active species for doping Polymer

Neutral dopant

I_2	I_2^-	PA, PPS, PPP
Br_2	Br^-	PA (trans)
AsF_2	AsF_6^-	PA, PPS, PPP
Na	Na^+	PA
K	K^+	PPP

H_2SO_4	—	PANI
$FeCl_3$	$FeCl_4^-$	PA
$SnCl_4$	$SnCl_2^-$	PA
Ionic dopants		
$LiClO_4$	ClO_4^-	PPy, PT
Na-naphthalide	Na^+	PA (trans)
$FeClO_4$	ClO_4^-	PA, PPy, P3MT
$LiBF_4$	BF_4^-	PPy, PT
CF_3SO_3Na	$CF_3SO_3^-$	PPy, PT
$(CH)_3NPF_6$	PF_6^-	PPy, PT
	$(CH_3)_4N^+$	PT
Bu_4NClO_4	ClO_4^-	PA (cis)
$LiAsF_6$	AsF_6^-	PA
Organic dopants.		
CF_3COOH	COO^-	PPy
CF_3SO_3Na	SO_3^-	PPy
$p\text{-}CH_3C_6H_4SO_3H$	SO_3^-	PPy
Polymeric dopants.		
PVS	SO_3^-	PPy, PANI
PPS	SO_3^-	PPy, PANI
PS-co-MA	COO^-	PPy

Neutral dopants are converted into negative or positive ions with or without chemical modifications during the process of doping. Ionic dopants are either oxidized or reduced by an electron transfer with the polymer and the counter ion remains with the polymer to make the system neutral. Another types of ionic dopant involve the anion derived from the dissociation of the dopant molecule, which neutralizes the positive charge of the polymer during the electrochemical doping process. Organic dopants are anionic dopants, generally incorporated into polymers from aqueous electrolytes during anodic deposition of the polymer. Polymer dopants are functionalized polymer electrolytes containing amphilic anions.

1.7: Doping Techniques

Doping of polymers may be carried out by the following methods.

(1) Gaseous doping (2) Solution doping (3) Electrochemical doping
(4) Self-doping (5) Radiation induced doping (6) Ion exchange doping.

Of these, the first three methods are widely used because of the convenience in carrying out and low cost. In the gaseous doping process, the polymers are exposed to the vapors of the dopant under vacuum[142]. The level of dopant concentrations in polymers may be easily controlled by temperature, vacuum and time of exposure. Solution doping involves the use of a solvent in which all the products of doping are soluble. Polar solvents such as toluene, acetonitrile, tetrahydrofuran, nitro methane are used as solvents. The polymer is treated with dopant solutions. Simultaneous polymerization and doping generally occurs in the electrochemical doping technique[143]. But sometimes this method is used for doping for polymers obtained by other methods also. In this process only ionic type dopants are used as the electrolyte in polar solvents.

1.8: Effect of Doping on Conductivity

Doping with acceptor or donor molecules causes a partial oxidation (p-doping) or reduction (n-doping) of the polymer molecule. As a result, positively or negatively charged quasi-particles are created presumably polarons in the first step of doping. When doping proceeds, reactions among polarons take place, leading to energetically more favorable quasi-particles, i.e. a pair of charged solitons (bipolarons) in materials with a degenerate ground state. Application of statistical mechanics allows calculation of the density of polarons, bipolarons and solitons and the density of electrons and holes in the band states at any temperature. Thus due to the changes in the environment of the chain, disorders are created from doping.

At low dopant concentrations, the dopant molecules occupy random positions between the chains. They affect the electronic properties by their coulomb potential and by hybridization with the polymer π orbitals. As polarons produced in this state has long lifetime, they are treated as quasi-particles. On this basis Conwell[144] has given an estimate of the density of free electrons at a doping level of about 5% and found a value for the free charge carrier density of about $3 \times 10^{24}/m^3$ or less at 300 K. Thus polarons have significantly lower mobility, which results in obtaining a moderate conductivity at low doping concentration.

As the doping level is increased, the concentration of polarons goes up and they become crowded together, close enough for bipolaron formation to occur. It is at this point in the doping process that the conductivity undergoes a marked increase. Once the radical components of the polarons have combined to form π bonds, the remaining positive charges achieve high mobility along the chain.

1.9: Applications of Conducting Polymers

Recent research and development activities show that conducting polymers exhibit conductivity from the semiconducting range ($\sim 10^{-5}$ S/cm) right up to a metallic conductivity ($\sim 10^{4}$ S/cm). With this range of electrical conductivity and low density coupled with low cost polymeric conductor pose a serious challenge to the established inorganic semiconductor technology.

Application of conducting polymers in the development of a rechargeable battery appears to be feasible and is at the threshold of commercialization. A number of conducting polymers such as polyacetylene, polyaniline and other polyhetrocyclics has been used as electrode materials for rechargeable batteries. In fact, polyaniline-lithium battery has already been marketed. A number of electronic devices such as Schottky diodes, plastic transistors, p-n junction's etc. have been developed using conducting polymers. Plastic field effect transistor (PFET) has been fabricated with polythiophene as the semiconductor and p-toluene sulfonic acid doped polypyrrole as the source drain electrode. Similarly a thin film p-n junction was made by depositing alternate layers of polypyrrole and polythiophene on a platinum substrate with controlled electrochemical doping to make the polypyrrole layer p-type and polythiophene layer n-type. Light-emitting diodes [LED's] can be made by depositing a film of semiconducting polymers on indium-tin-oxide (ITO) coated glass.

Since, the electric conductivity of conducting polymers varies in the presence of different chemical substances; these are widely used as chemical sensors or gas sensors. Conducting polymers have been used to prepare Langmuir-Blodgett (LB) films. If it is possible to cast a multilayered LB film with desired molecular architecture from soluble conducting polymers, the scope for miniaturization of the electronic components such as microcircuits will be remarkably extended.

Some of the new fields for application of conducting polymers include gas separation membrane, photoelectrochemical cell, optical devices, ion gates, memory storage devices, non-linear circuit elements etc. Conducting polymers can be used as biosensors and controlled release devices for pharmaceuticals. The most exciting prospect of conducting polymers has been envisaged in the development of molecular electronics in which individual conducting polymer molecules will act as wires, diodes, transistors and other electronic devices based on phthalocyanine molecules which provides additional attractiveness in their applications.

The emergence of electrically conducting polymers in 1970's opened a new era in the field of material science. These materials were not only found to be useful for static charge dissipation and EMI/RF shielding but also in electronic devices. The positive and negative temperature coefficient of resistance observed in some of the conducting polymers has been used to fabricate thermistors. Such devices for over current protection were reported almost a decade and half back[145]. The conductivity of some conducting polymer changes with applied pressure, which suggested those piezoresistive devices, may be designed using these materials. Electrochromic devices and displays as well as windows are another application area being pursued[146] in which functionalized conducting polymers are being used. Functionalized conducting polymers, which are made by incorporation of functional molecules or by structural control are being investigated for possible applications in the field of photo-chromism, photoelectric conversions etc. Semiconducting polymers are being viewed as future semiconductors and the term semiconducting polymers are being used for obvious reasons. Although these are not viewed as total replacement for the existing electronics technology, the distinct advantages of polymers would be their good performance at lower cost, greater flexibility and probably ease of manufacture. In the last decade the subject of molecular electronics has evolved, as technologists have become aware of the potential applications of conducting polymers in particular and organic materials in general. The molecular devices are seen as distinct possibility in the future generation electronic systems. In future, it is hoped that molecules, either singly or as aggregates of nanometer dimensions, can be utilized to provide the elementary active units of electronic systems with extremely high component density. However, more demanding applications to electronic devices are still some way off as marketable products.

1.9 B: Special Applications of Conducting Polymers

Conducting polymers find various applications in automotive industries, as corrosion protection agents, as electrocatalysts, in display panels, in lithography etc. Apart from these applications, conducting polymers have some special applications in the field of electrochromic devices and chemical sensors. These special applications are described in length for better understanding of the subject.

(1) Electrochromic devices

The phenomenon of electrochromism can be defined as the change of the optical properties of a material due to the action of an electric field. The field reversal allows the return to the original state. An electrochromic material is one that changes color in a persistent but reversible manner by an electrochemical reaction. Accordingly, conjugated polymers that can be repeatedly driven from insulating to conductive state electrochemically with high contrast in color are promising materials for electrochromic device technology.

Conjugated polymers have an electronic band structure. The energy gap (Eg) between the highest occupied π electron band (valence band) and the lowest unoccupied one (conduction band) determines the intrinsic optical properties of the polymers. The color changes elicited by doping are due to the modification of the polymer band electronic structure. The unidimensional character of the polymer system energetically favors the localization on the chain of the charge created by doping and the relaxation of the lattice around this charge. This confinement of the charge then creates the defects that produce the gap in new electronic state, which cause the color changes.

The electrochromic materials first drew interest in large area display panels. The other two main applications are in architecture and automotive industry. In architecture[147] electrochromic devices are used to control the sun energy crossing a window. In United States, smart windows have been used, which allow energy saving by dynamic control of the light transmission. In automotive industry[148] rearview mirrors are a good application for electrochromic systems. With oxidation, polypyrrole turns from yellow to brown-almost black in the case of thick film. Polythiophene turns from red to blue. Thiophene derivatives such as poly (methyl thiophene) in a solution of lithium perchlorate in propylene carbonate were reported to be able to function over long times[149]. Polyaniline was investigated for its electrochromic characteristics in aqueous[150] and non-aqueous[151] solutions.

(2) Chemical Sensors

The conducting polymers are good candidates for the elaboration of chemical or electrochemical sensors in two main ways. (1) As sensitive components: The electronic conductivity related to the redox state (doping level) of a conducting polymer is modulated by the interaction with various substrates. Changes in parameter values, such as resistance, current or electrochemical potential, give a straightforward sensor response of the studied phenomena. (2) As a matrix for specific immobilization: Conducting polymers are often infusible and insoluble. Consequently, immobilization by entrapment of specific molecules that are capable of substrate recognition can be carried out mainly during polymerization process. However, this growing reaction added to the entrance of negatively charge species (sometimes positive ones) makes it possible to entrap various moieties easily in a one-step process, with the further advantages of intrinsic porosity and electronic accessibility.

In its simplest form, a sensor consists of a planar interdigital electrode coated with a conducting polymer thin film. If a particular vapor is absorbed by the film and affects the conductivity, its presence may be detected as a conductivity change. The first evaluation of conducting polymer as sensitive components in chemical sensors are based on their redox interaction with some gases, including a variation of the doping level, resulting in a quite straight forward conductance, monitoring of gas sensor response over orders of magnitude[152]. Interdigited electrodes covered by a PPy layer have been tested by Miasik et.al.[153] for the detection of NH_3, NO_2 and H_2S gases. Yoneyama et.al.[154] have shown that electropolymerized PPy films exhibit noticeable gas sensitivities to electron acceptor gases such as PCl_3, SO_2 and NO_2 at room temperature; especially when PPy is reduced electrochromically before exposure. The same group also investigated the gas sensing properties of polythiophene film[155], but they found a more irreversible behavior in the conductivity change after exposure to NH_3 and H_2S.

The observation that the semiconducting properties of phthalocyanine are modulated by the absorption and desorption of gases has led to significant efforts toward their incorporation in chemical sensors. The phthalocyanine sensors have been reported by early workers[156]. These workers had reported that NO_2 to have large effects (6-8 orders of magnitude) on conductivity of a variety of sublimed phthalocyanine films. It is hoped that making appropriate substitutions of metals in the cavity and organic substituents at the periphery of the phthalocyanine structure may develop the gas specificity.

1.10: Functionalization of Conducting Polymers

During past decade, a work on functionalized phthalocyanine polymers has significantly increased. The use of these materials in electrochromic devices, molecular devices, in chemical sensors and in many catalytic functions has shown promising results. However, very little work has been reported. on the functionalization of well known conducting polymers like polyaniline, polythiophene, polypyrrole etc. by phthalocyanine. Detailed investigation have been carried out in our laboratory on conducting polymers functionalized with phthalocyanine, to focus on mainly its interaction with these polymers, the structural changes during reactions, effect on thermal stability, its chemical sensitivity etc.

A large number of potential applications of conducting polymers are associated with their inherent extended conjugated electronic structure. Further functionalization of such conducting polymers can develop new functions or enhanced properties. The two main strategies for the functionalization of conducting polymers are (1) by incorporation of functional molecules and (2) by structural control. The former has access to a molecular material as a molecular device and the latter approaches an organic quantum material like a super lattice.

There are many functional molecules such as anthraquinones, porphyrins, phthalocyanines, organic dyes, long conjugated alkyl chains and even ions like $PtCl_4^{--}$, $AuCl_4^-$ etc. The functionalization of conducting polymers is easily achieved by incorporation of these functional molecules. The macrocyclic materials such as phthalocyanines, when incorporated into the conducting polymers, give rise to extended conjugated structures. These become available on the polymer matrix to provide an effective pathway for efficient electrochemical activity and better stability. The usual functions of the phthalocyanine such as electrochromism, electrocatalysis etc. can be readily exploited by incorporating them into conducting polymers such as polypyrrole, polyaniline etc.

There are three different methods used to obtain functional molecules incorporating conducting polymers, namely (a) Electrochemical polymerization (b) Chemical polymerization and (c) Photopolymerization. Amongst them, one of the most fascinating methods is electrochemical polymerization to incorporate the functional molecule in the conducting polymer especially as a dopant[157]. The functionalized conducting polymers are prepared by electrolytic polymerization of pyrrole, thiophene, aniline etc. in the presence of negatively charged functional molecules. The incorporation of the functional molecule is driven electrostatically by the positive charges of the partially oxidized conducting matrices through a doping process, as shown in **Fig. 1.10**.

Chemical polymerization methods are also available for preparation of functionalized conducting polymers. The vapor/liquid interface chemical polymerization is used to obtain a thin and highly transparent membrane (film). Bulk chemical polymerization is another way of getting a functional molecule incorporating conducting polymer membrane as well as simple conducting polymer, utilizing an appropriate support. Compared with electrolytic method, chemical polymerization methods, yields materials having lower conductivity.

Photopolymerization is also available in lieu of chemical polymerization, for obtaining the functional molecule incorporated conducting polymer. It is considered that photopolymerization may proceed if the oxidation potential of a photo-excited sensitizer is high enough to polymerize them. A photosensitized polymerization of pyrrole in the presence of ruthenium bipyridine complexes is well known photopolymerization process.

Pioneering works on functional molecules incorporated conducting polymers firstly demonstrated them as modified electrodes for redox catalysis. In these reactions, redox molecules such as ruthenium complexes[158], porphyrins[159] and sulfonated phthalocyanines[160, 161] were incorporated in to insulating polymers. There are few reports[162-163] on the use of tetrasulfonated derivatives of phthalocyanine, which acts as doping agents in polypyrrole and polyaniline. There are no reports available on the direct incorporation of phthalocyanine into the chains of conducting polymers. Hence in the present investigations emphasis was given on the synthesis of conducting polymers incorporated with phthalocyanine.

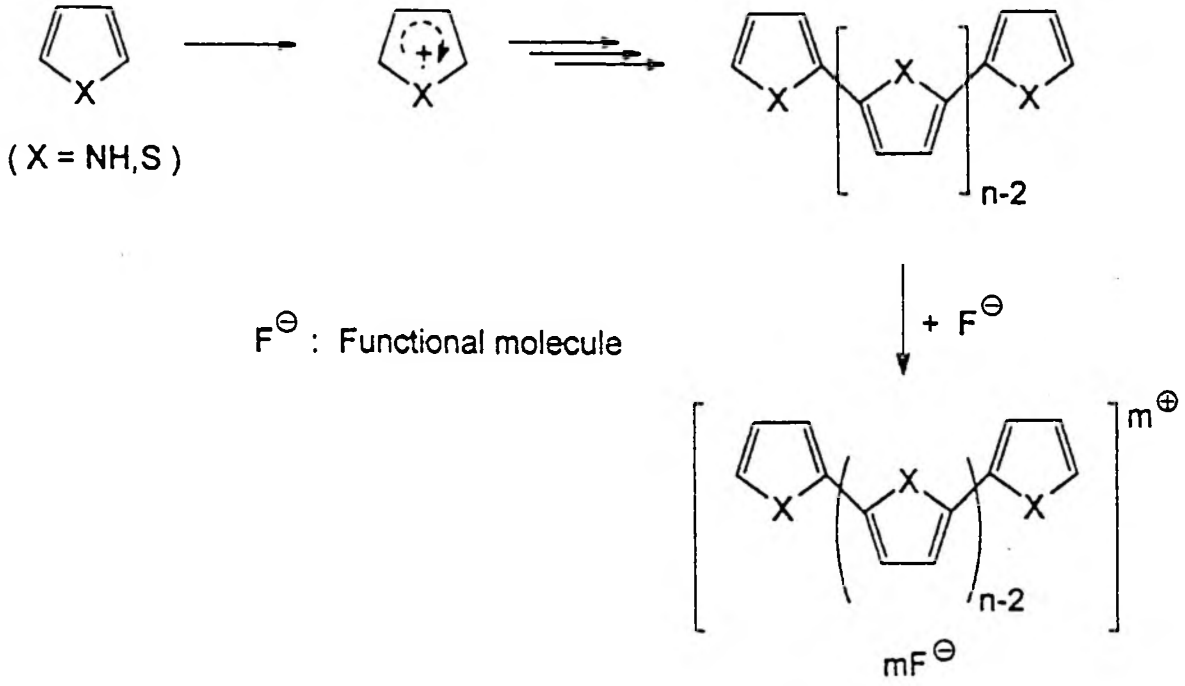


Figure 1.10 : Functionalization of Conducting polymers

1.11: Phthalocyanines and their properties

The phthalocyanines are a class of organic semiconductor with alternate single-double bond structure. Low molecular weight phthalocyanines[164] are synthesized from 1:2-disubstituted benzene derivatives such as phthalonitriles and phthalic anhydrides. The cyclotetramerization reaction takes place with urea, metal salts and catalyst is shown in **Fig.1.11**. The reaction between phthalonitrile and metals is usually very vigorous at 250-300°C and sufficient heat is generated to maintain the reaction temperature. The reactions are normally carried out under pressure. The cyclo-tetramerization of four phthalonitrile molecules into a phthalocyanine macrocycle involves a reduction reaction, which requires two electrons in addition to the 16 π-electrons from the 8-nitrile groups to yield 18 π-electrons, aromatic system. For metallophthalocyanine the two extra electrons are provided by the metal or metal salts.

A phthalocyanine macrocycle has a tendency to organize itself and forms stacks in which there is interaction between the large π-system of the adjacent rings in such a way to give low-dimensional compounds. The phthalocyanine macrocycle although complex in size and structure, is synthetically amenable to many variations and imports novel, unique and useful properties to molecular substances. Phthalocyanines and their polymers are known to have an excellent stability against heat, light, moisture and air. Moreover, they are soluble without decomposing in strong acids. Hence, they have attracted a great deal of attention in the search for environmentally stable electrically conducting materials[165-166]. Phthalocyanine polymers may be divided into two structural groups: (1) Those in which the polymeric linkage is through the axial bonding sites of a complexed metal and (2) Those with the polymeric linkage through the substituted positions at the periphery of phthalocyanine ring. The present study deals with second type of linkages.

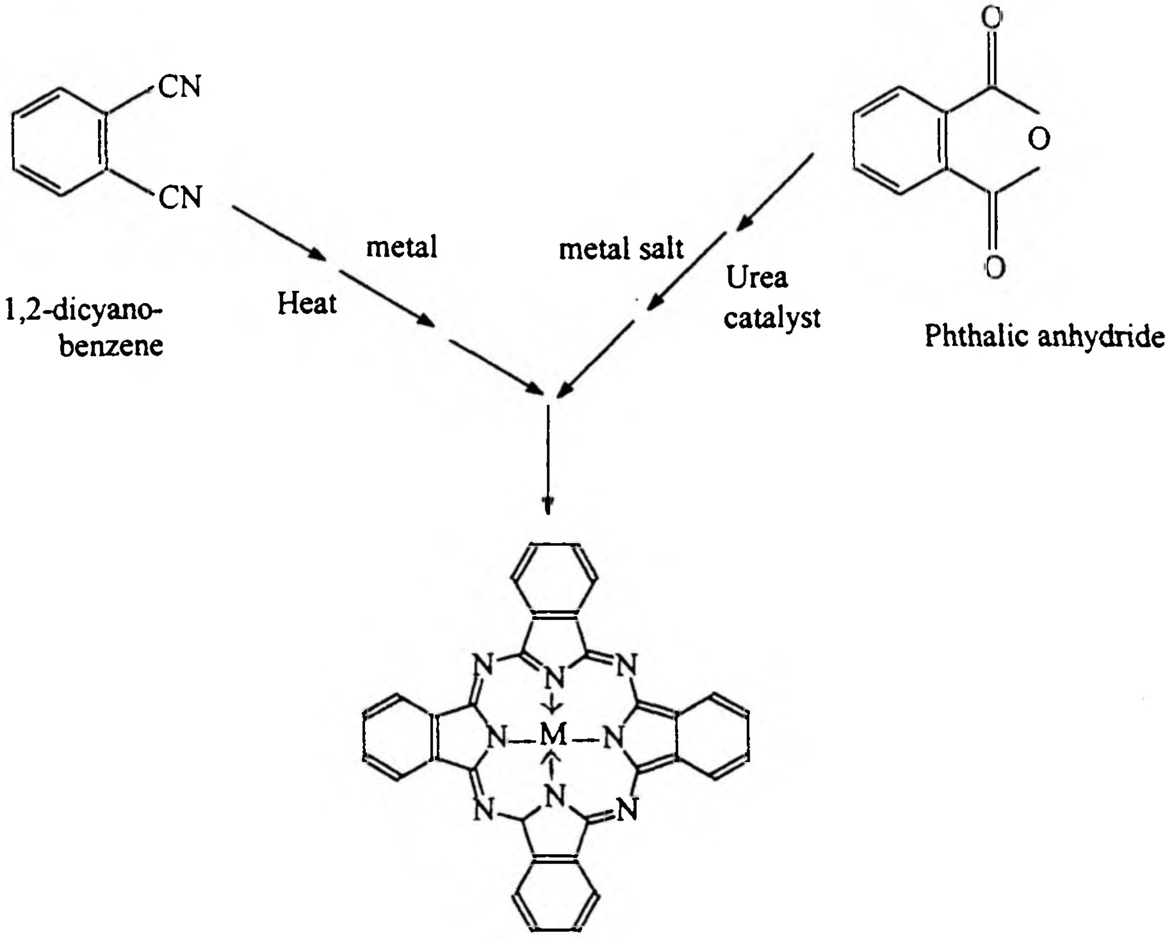


Figure 1.11 : Preparation of Phthalocyanine monomer

Interest in the electropolymerization of phthalocyanines systems in large part from the well-known utility of various metal phthalocyanines as redox catalysts[167]. The high conductivity of many one-dimensional metal phthalocyanine polymers[168] suggests that such systems will be capable of supporting reasonably rapid charge transport across thin films and therefore useful as immobilized electrocatalysts. Electropolymerized films of metallo-phthalocyanine were first reported by Li and Guarr in 1986[169]. These authors extended the work of Murray and coworkers[170-171] on oxidatively electropolymerized metalloporphyrins to various metal complexes of tetraaminophthalocyanine. Later on a novel technique for electrochemical formation of phthalocyanine thin films by disruption of micellar aggregates by cationic surfactants having a ferrocenyl moiety was reported by Saji et.al.[172-173]. The phthalocyanine films find wide range of applications in gas sensors, thin film electrodes, in the field of molecular electronics etc.

1.12: Advantages and Disadvantages of Conducting Polymers

The conducting polymers show many advantages over the other polymers. Particularly, the electrochemically synthesized conducting polymers are obtained in the form of films, which can be directly used in chemical gas sensors and microelectronic devices. The functionalization of conducting polymers with various alkyl chains or other cyclic chains gives better processability to these polymers. The co-polymerization of these polymers reported to give better optical properties by lowering its band gap. Conducting polymers exhibits better electrical conductivity and hence, they are better alternatives to the conventional inorganic semiconductors such as silicon and bismuth arsenate etc. The conducting polymer batteries show better efficiency than the normal lead-sulfuric acid batteries. The other advantage is lying in the fact that former are lightweight and handy as compared to latter. The conducting polymeric films are directly obtained in its doped state, which offers them good scope in electrical coating technology.

The disadvantages with conducting polymers arise from the fact that they are not highly stable compounds even at moderate temperatures (>150° C). The most of the conducting polymers exhibit dark color due to their highly oxidized states. These polymers are insoluble in most of the common organic solvents. Hence, they become practically non-processible. The initial thought by earlier scientist that these materials will be better replacement for metal is so far found to be the dream. Though these are often termed as 'synthetic metals', they have not achieved the higher conductivity, as the metal possesses. To make them processible though many methods are being used, these are adding to the cost of material, which are not economically viable.

1.13: Aim and Scope of work

In the last two decades the field of conducting polymers has shown tremendous growth and it is now an important field of research. The conducting polymers when functionalized with other conjugated systems can be very useful in many applications. As seen in the literature survey, the functionalization with macrocyclic molecules has been mainly used in electrode preparation for reduction of oxygen. The detailed study on functionalization of conducting polymers such as polyaniline, polypyrrole and polythiophene with phthalocyanine is not reported before. In order to have better understanding of the chemistry of this functionalization reaction, the present work was undertaken. The investigations are mainly aimed at looking at the structural changes taking place due to incorporation of phthalocyanine and the effect of phthalocyanine on different properties such as electrical conductivity, thermal stability, photosensitivity etc. of the resulting polymer. It would be quite interesting to investigate the chemical sensitivity of these functionalized conducting polymers to various chemical vapors.

In the present investigations, two methods for synthesizing the functionalized conducting polymers have been employed, namely (a) Chemical polymerization and (b) Electrochemical polymerization. The polymers obtained from former method are expected to be thermally stable due to the presence of phthalocyanine which by itself is stable up to 400 ° C. In the doped state these are expected to give higher conductivity because of enhanced conjugation level. It is also interesting to see the structural modifications imparted in the product because of addition of macrocyclic phthalocyanine. It is expected to impart more structural ordering as a result of stacking of the planar phthalocyanine units. The polymers synthesized by this method if used in surface cell, they are expected to show good chemical sensitivity. The second synthesis method gives polymeric materials in its highly doped states due to the presence of dopant ions in the polymeric films itself. The direct incorporation of phthalocyanine into conducting polymeric films is an innovative idea. The electrochemically prepared films are expected to be highly conducting. These polymeric films are also expected to show good photo effects in the photo-electrochemical mode using different electrolytes. The changes in its structure due to incorporation of phthalocyanine may results in shifting of wavelength to longer absorption in UV-VIS studies giving wider range of electrochromic response.

The present investigations on phthalocyanine incorporated conducting polymers were undertaken based on the above expectations. The development of new materials is a new challenging area in polymers in general and speciality polymers in particular. Although, speciality polymers such as conducting polymers are being studied extensively, their applications would be actually seen only if renewed efforts are made for improving their thermal and chemical stability. On the other hand, it is also desired that useful properties related to their applications in active components such as sensors, switches, diodes, memory devices etc. also be enhanced. Hence, phthalocyanine incorporated conducting polymeric materials would be very important both for fundamental research as well as applications in electronics.

CHAPTER-II
EXPERIMENTAL

EXPERIMENTAL

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 $[CH_3(CH_2)_3]_4NClO_4$ (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 ($CuCl_2.2H_2O$) and sodium sulfide flakes ($Na_2S.xH_2O$) 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 $[(NH_4)_2S_2O_8]$, 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: H_2O (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 stiochiometry 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 × 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: H_2O (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%

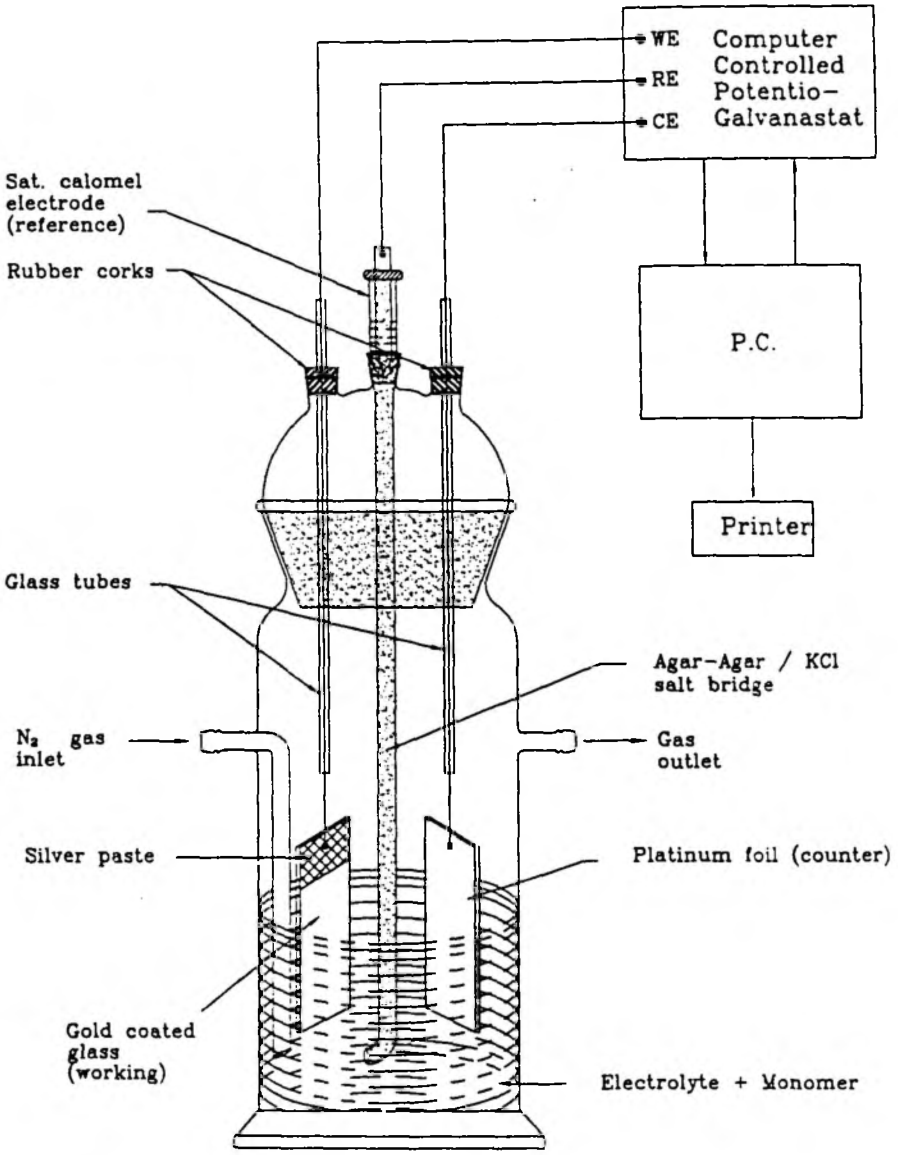

Electrochemical cell

Figure 2.1 : Electrochemical Measurement Apparatus

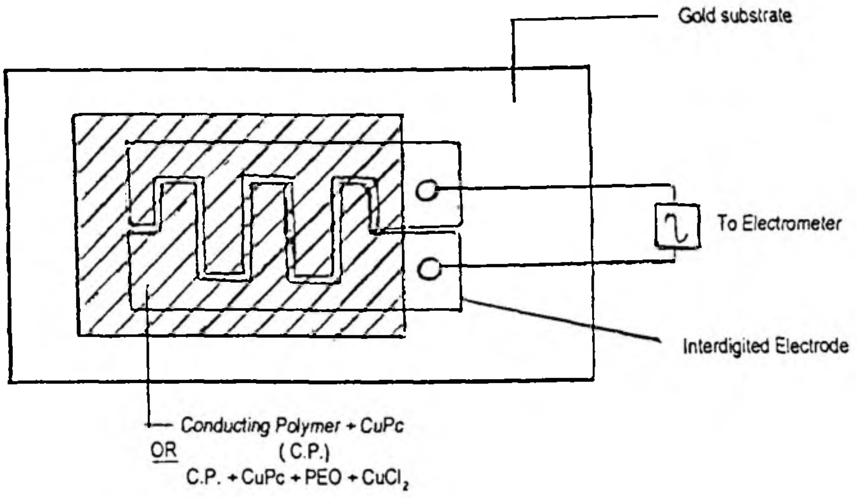
[mole % with respect to monomer] was added to the electrolyte solution and nitrogen gas was bubbled for 10 minutes to form a uniform suspension.

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.

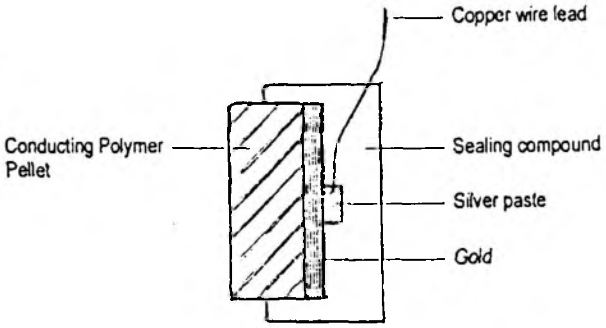
2.4: Samples Preparation for various property Measurements

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.

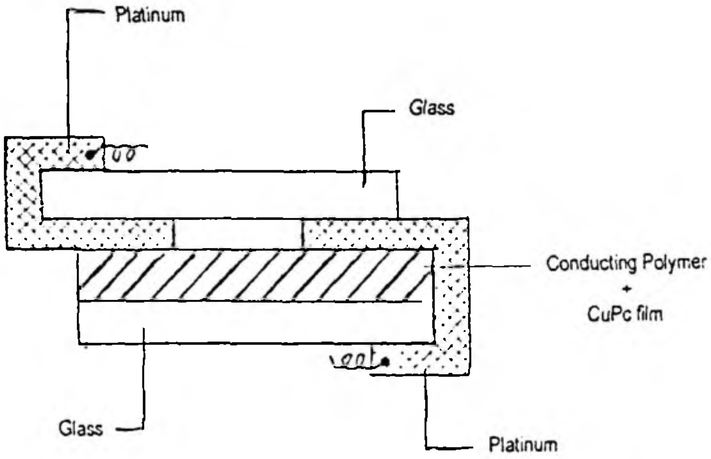
The contacting electrodes on these pellets were then vacuum deposited using pure gold (99.9%). The deposition of gold films was carried out in a vacuum evaporation unit (Hind Hivac Model 12A4D) at 10^{-6} torr by thermal evaporation technique. Thin copper wire leads were connected to these gold film 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 interdigited 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 Tg and Tm, 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 $CuCl_2.2\ H_20$ 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 interdigited 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 $_{Ro}$ are the resistance after the exposure to chemical vapours and initial resistance respectively.

Sensitivity Measurement Apparatus

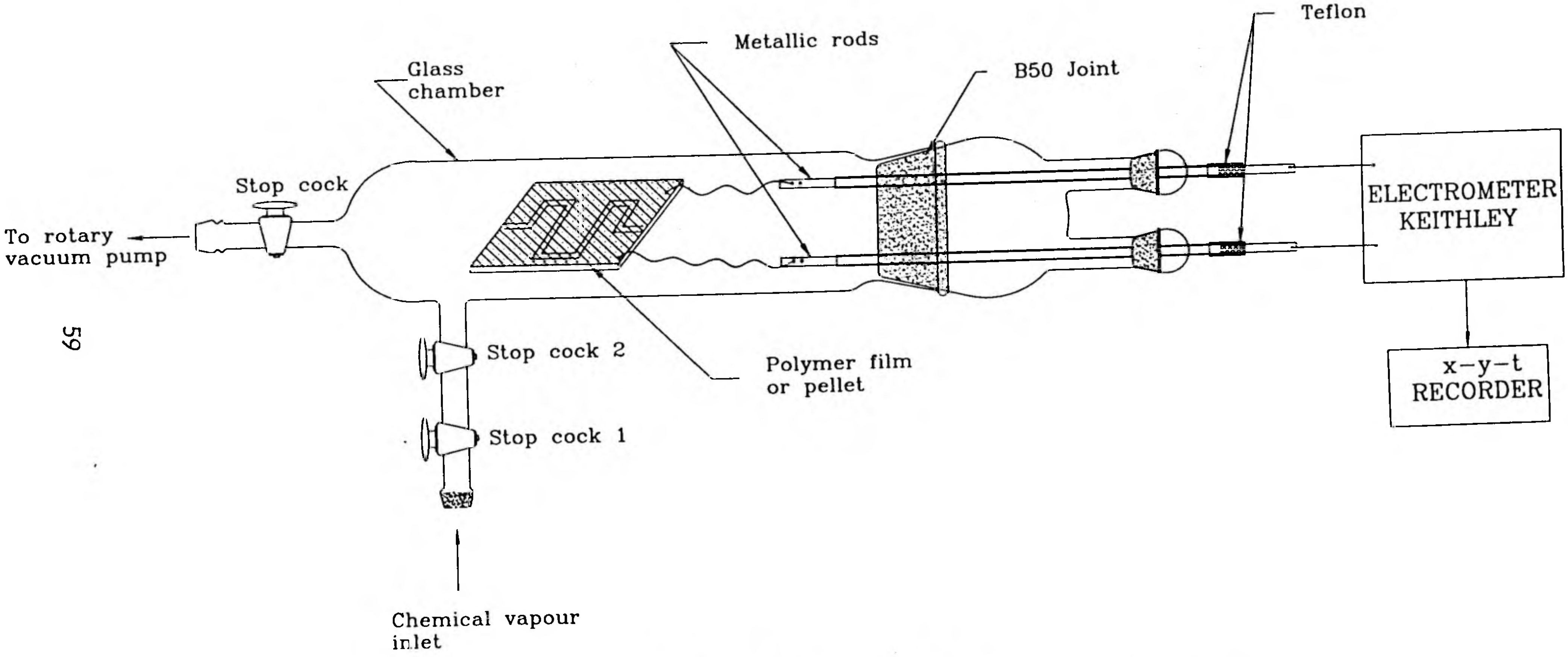


Figure 2.3 : Sensitivity Measurement Apparatus

2.5: CHARACTERIZATION

2.5.1: Infrared (IR) Spectroscopy

Infrared (IR) studies[174] 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 spectroscopy[175]. 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 H_2SO_4 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 technique[176]. 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 CuKα 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 spectroscopy[179] is concerned with a special form of photoemission, namely the ejection of an electron from a core level by x-ray photons of energy hν. 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,

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

Where Io = the intensity from the clean substrate.

λ = Inelastic mean free path (the value is a function of Kinetic energy EK 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-Kα (1486.6 eV) and Mg-Kα (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 analysis[180] 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:

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

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

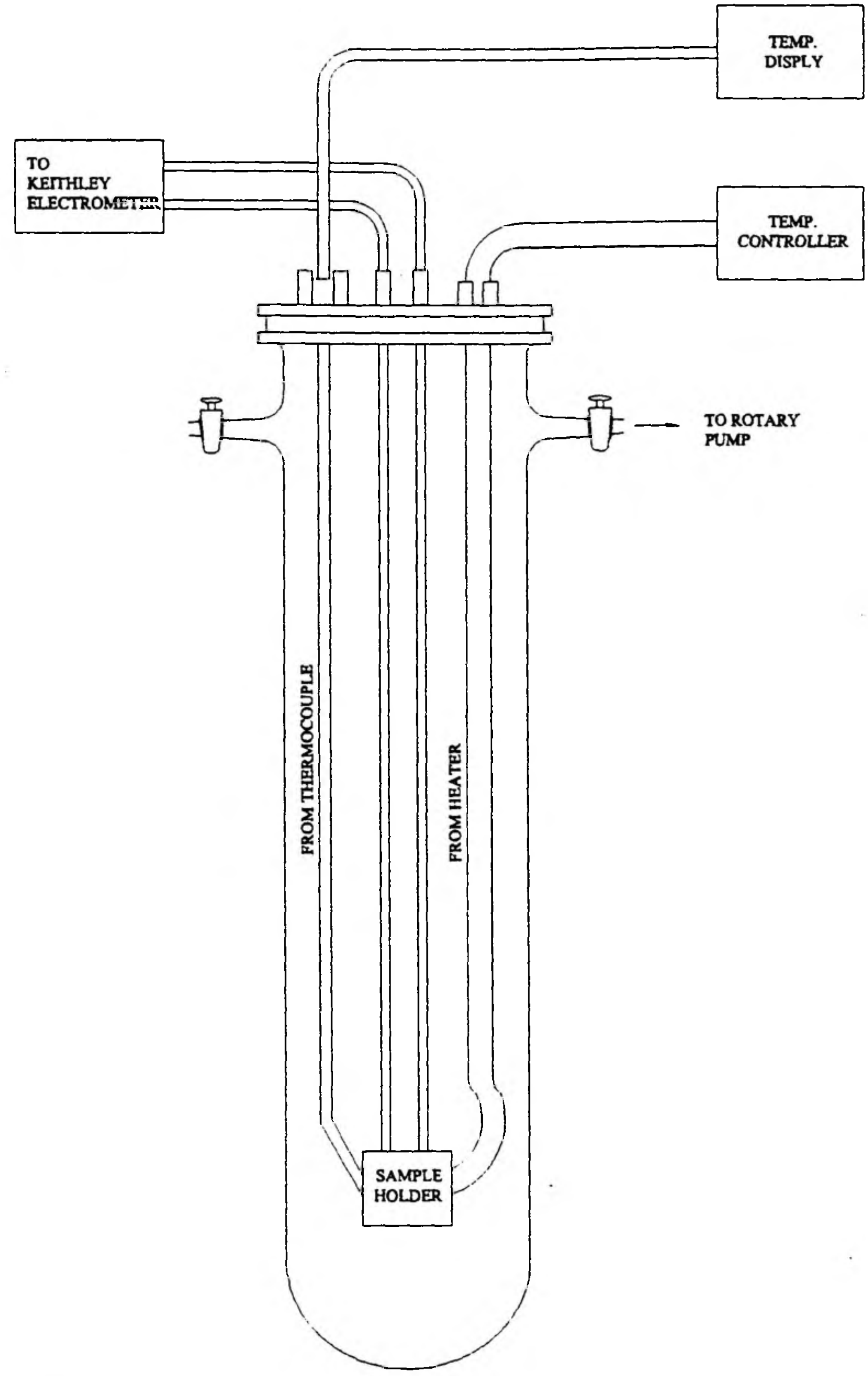


Figure 2.4 : Conductivity Measurement Apparatus

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:

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

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

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 $k = 1.96 \times 10^{-4}$ 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 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, $K_3Fe(CN)_6$ 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.

CHAPTER-III

POLYANILINE FUNCTIONALIZED WITH PHTHALOCYANINE

POLYANILINE FUNCTIONALIZED WITH PHTHALOCYANINE

3.1: INTRODUCTION

Polyaniline is a typical phenylene based polymer having a chemically flexible -NH- group in a polymer chain flanked by phenylene rings. The protonation and deprotonation and various other physico-chemical properties of polyaniline can be said to be due to the presence of –NH- group. Polyaniline is the oxidative polymeric product of an aniline under acidic conditions. The chapter-I describes the literature review of this conducting polymer and the general methods for the synthesis of conducting polymers have been described in chapter II. This chapter describes the specific methods for the synthesis of polyaniline (PANI) functionalized with phthalocyanine. The effects of incorporation of phthalocyanine in PANI on its structure, conductivity, optical properties and chemical-sensing behavior have been described in the following sections.

3.2: EXPERIMENTAL

The general methods of purification of various chemicals used for the synthesis have been described in the earlier chapter. The synthesis of polyaniline and polyaniline containing phthalocyanine co-polymers was carried out by two methods namely, (1) Chemical (2) Electrochemical routes. These are explained in the following sections.

3.2.A: CHEMICAL SYNTHESIS

3.2.A.1: Synthesis of Polyaniline in different mediums

The aim of the present studies is to modify the conducting polymer by macrocyclic compounds such as phthalocyanine. In order to achieve the incorporation of such large molecules in PANI, it is essential to dissolve/disperse the same in a common medium. Hence, a few experiments were carried out on various available solvents to check the solubility of the reactants in them. It was concluded that a mixture of N-methyl pyrrolidone (NMP) with water could be the most appropriate for the present investigations. Since, there are no reports available for synthesis of PANI in such a medium, detailed investigations were carried out on the effect of NMP on synthesis of PANI as well as incorporation of CuPc in the same.

As mentioned above, the incorporation of CuPc in PANI has to be carried out in non-aqueous medium. In order to compare these results with PANI itself, the homopolymer has to be prepared under the same conditions as a co-polymer.

(a) Reaction in aqueous medium

In a 250-ml beaker, containing 80 ml of distilled water 10.2 grams aniline (0.1097 M) and 11-ml conc. HCl (0.11 M) was added. To this reaction mixture, 5.3 grams of ammonium persulfate dissolved in 20ml distilled water was added slowly under constant magnetic stirring. The temperature of the reaction mixture rises up to 55°C and hence it was cooled to room temperature using external ice water cooling. The reaction mixture was kept under constant stirring at room temperature for 18 hours. After the reaction was complete, the reaction mixture was poured into a beaker containing 1000 ml distilled water, with vigorous stirring when green mass of polymer was obtained. The polymeric material obtained was filtered by conventional methods, and washed several times with distilled water and finally with methanol. It was then vacuum dried (10^{-3} Torr) for few hours and finally was dried at 80°C for 4 hours.

(b) Reaction in pure NMP

Exactly similar quantities of aniline, conc. HCl, ammonium persulfate as mentioned above were taken for this set of experiments, except for the reaction medium. Here 100 ml freshly distilled NMP was used as reaction medium. After 18 hours of reaction, the polymer was isolated by the same procedure described above.

3.2.A.2: Synthesis of PANI-CuPc polymers using NMP: H_2O (1:1)

In a 250 ml beaker, containing 10.2 grams of aniline (0.1097 M) in 100 ml NMP: H_2O (1:1) mixture, 11 ml of concentrated Hydrochloric acid (0.11 M) were added carefully. Then the desired amount of phthalocyanine (2 to 20 moles percent) with respect to the aniline monomer was added to the reaction mixture. Finally, 5.3 grams of (0.0214 M) ammonium persulfate solution was added to the same. The temperature of the reaction mixture rises up to 55°C due to exothermic nature of the reaction and hence it was maintained at room temperature by cooling. The reaction was carried out under magnetic stirring for 18 hours at room temperature. As the reaction proceeds, it was observed that the color of the reaction mixture changes from light blue to deep blue and finally to dark green which was an indicative of the propagation of the polymerization reaction.

The polymer product was isolated and recovered from the reaction mixture in the same manner as described above. Pure polyaniline was also synthesized by the same procedure as mentioned above except for the addition of phthalocyanine.

3.2.B: ELECTROCHEMICAL SYNTHESIS

Initially, gold metal film was deposited on either clean glass substrates or on the PET film (100 μm thick) using vacuum deposition method as described in detailed in chapter II. Electrochemical polymerization of aniline was carried out in a single compartment cell using platinum foil as a counter electrode and SCE as reference electrode in the same manner as described in chapter II. The typical electrolyte solution contains 0.2 M aniline (2ml) and 0.4 M HCl (4 ml) in a 100 ml solvent mixture of NMP: H_2O (1:1). To this electrolyte, the desired amount of phthalocyanine blue [1%, 2%, 3%, and 4% (mole) with respect to monomer] was added. The electrochemical cell was purged with dry nitrogen gas to remove dissolved oxygen in the electrolyte. The gold-coated substrates were used as a working electrode. The deposition of polymeric films was carried out at fixed potential of 0.9 V for different deposition time such as 300, 600 and 900 seconds with the help of computer controlled potentio-galvanostat [Vibrant EC 2010 Model].

The electrochemically deposited polymer films were stored for half an hour at room temperature and then washed successively in NMP/H_2O mixture and distilled water several times. Immediate washing caused the pealing property of the films. These films were then dried at room temperature for 24 hours.

3.3: RESULTS AND DISCUSSION

3.3.A: CHEMICALLY SYNTHESIZED PANI-CuPc POLYMERS

The polymerization reaction did not start immediately after the first drop of the ammonium persulfate solution had been added to the reaction flasks, i.e. there is an induction period before the polymerization reaction starts. Other groups have also made similar observations[181-184]. In the reaction of polyaniline in the presence of phthalocyanine, it was observed that as soon as ammonium persulfate was added to the reaction mixture, the colour change was almost instantaneous. This observation indicates that there is a decrease in the induction period due to the addition of phthalocyanine, which may provide large number of reaction sites resulting in faster reaction rate. There was an increase in the temperature after the reaction was started which is indicative of an auto acceleration process. This was even more active for synthesis of polyaniline in the presence of phthalocyanine. The appearance of the co-polymers of polyaniline and phthalocyanine was green to dark green in colour. It was observed that as the phthalocyanine content in the polymer increased, the shade of colour becomes darker. The yields obtained were in the range of 15-30% based on the monomer taken. The various data for chemical synthesis obtained from different experiments are tabulated in **Table-3.1**. The reaction scheme by which chemical synthesis proceeds for PANI-CuPc polymers is presented in **Fig. 3.1**.

(a) Effect of solvent

The most commonly used solvent for the synthesis of polyaniline and its derivatives is the aqueous medium. However, the present investigations involve incorporation of phthalocyanine into conducting polymers and hence the use of

TABLE- 3.1

Chemical Synthesis data of PANI-CuPc polymers

Serial No.	Aniline Grams	Ammonium Persulfate Grams	Hydrochloric Acid ml	Copper Phthalocyanine Grams	% Yield
1	10.2	5.3	11	0.00	15
2	10.2	5.3	11	0.204	20
3	10.2	5.3	11	0.525	24
4	10.2	5.3	11	1.02	27
5	10.2	5.3	11	2.04	30

Solvent: NMP: H_2O (1:1) 100 ml for each experiment.

Reaction temperature: Room temperature (25°C)

Reaction time: 18 hours

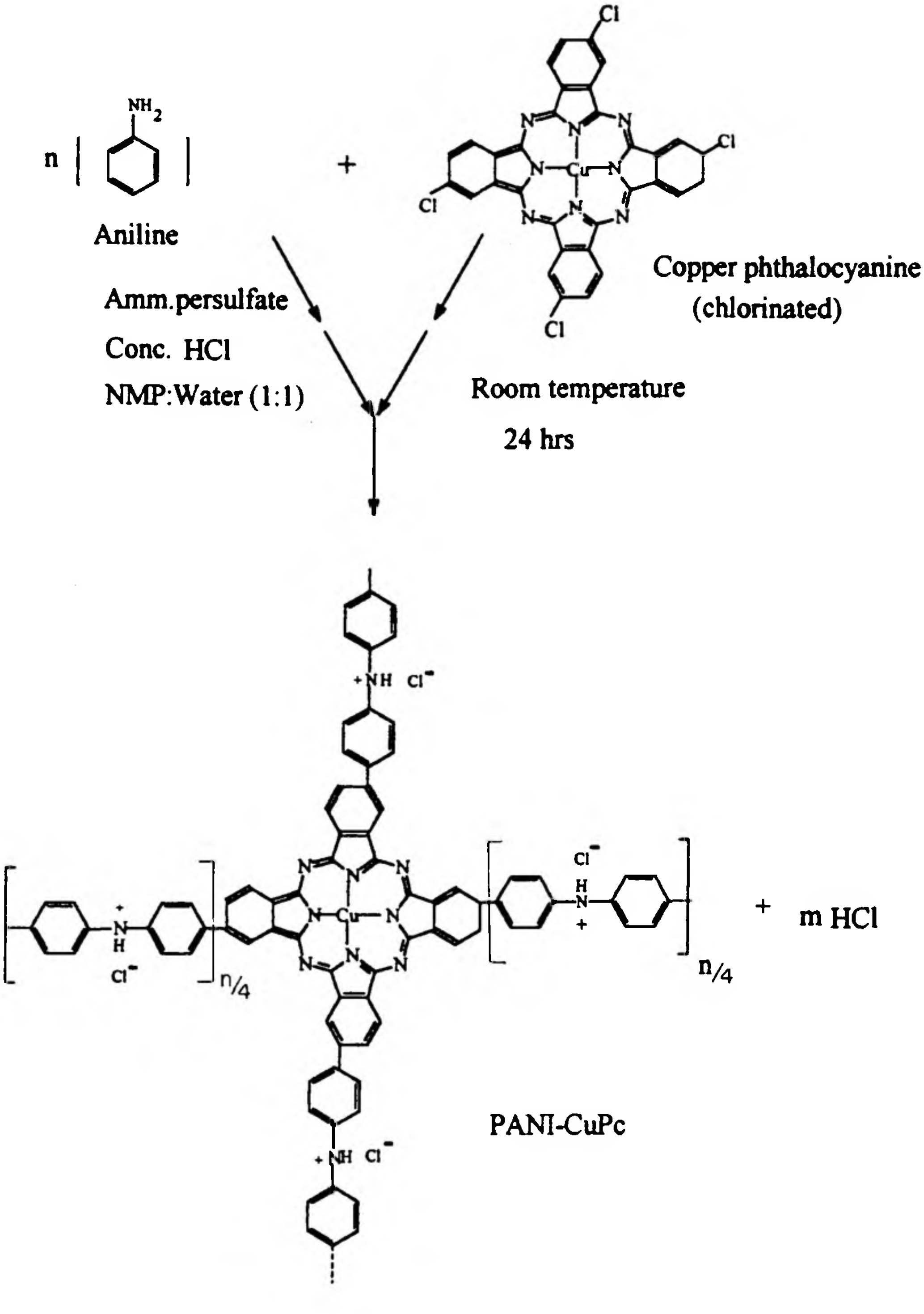


Fig. 3.1 : Diagrammatic sketch for PANI-CuPc chemical synthesis

aqueous system is excluded due to the fact that phthalocyanine is totally insoluble in water. On the other hand, the polymerization of aniline carried out in non-polar solvent such as NMP is found to be sluggish. In this aspect several combinations of NMP/H_2O mixtures were tried and it was found that optimum reaction conditions were obtained at the 1:1 molar concentration of NMP: H_2O. Hence, all further experiments were carried out in NMP: H_2O (1:1) as the reaction medium. This solvent and aniline forms a uniform solution mixture and when the phthalocyanine is added to this mixture, a very fine suspension of phthalocyanine particles was obtained, [confirmed under microscope observation]. The phthalocyanine added has a strong affinity towards NMP, rather than distilled water. In fact, water inhibits the phthalocyanine from dissolving completely in NMP. Thus, the reaction mixture is a heterogeneous system. This suggests that the present reaction may be a suspension type polymerization or more preferentially interfacial polymerization process.

In order to check the effect of solvent NMP on polymerization of aniline, the experiment was carried out using pure NMP as a solvent. The yield obtained in this case was 14%. When the reaction was carried out in the aqueous system alone [pure distilled water] the product obtained was 20%, and under similar experimental conditions, the NMP: H_2O (1:1) gave 17% product, which is intermediate between aqueous and pure NMP. Hence, it can be seen that NMP is retarding the polymerization of aniline to some extent. Then the question would arise why the NMP is used in the reaction. The main reason behind it was that the copper phthalocyanine has better solubility in NMP. Since the present investigation deals with incorporation of phthalocyanine, the solvent system used here was found to be good enough to dissolve or to make a fine suspension of copper phthalocyanine.

(b) Effect of Oxidant

Another factor affecting the polymer yield is the aniline/oxidant ratio. Cao et.al.[185] have studied the polymerization of aniline using various mole ratios of aniline and oxidant. They concluded that this ratio did not affect the degree of oxidation of polyaniline chain but it affected the product yield. The aniline/oxidant ratio of about 1.0 gave high yields of about 75-84%. In another study, Armes and Miller[186] optimized the ratio of monomer/oxidant close to one was best for aniline polymerization in 1.2 M HCl at room temperature. In one set of experiments carried out in our laboratory, when aniline/oxidant ratio of about 1.0 was used there was almost quantitative yield of polyaniline homopolymer even though the reaction medium was NMP: H_2O (1:1). In the present investigations, the monomer/oxidant ratio of 4.75 was used which resulted in a lower yield of polyaniline. It is clear that this was mainly due to the lower concentration of the oxidizing agent. However, this ratio had to be limited to certain levels in order to prevent the possibility of phase segregation / precipitation of phthalocyanine in the reaction mixture.

(c) Effect of Phthalocyanine

The third and important factor is the effect of addition of phthalocyanine on the polymerization of aniline. The present study shows that as the phthalocyanine content in the polymerization increases, the polymer yield also increases. There was also rapid change of colour during polymerization in presence of phthalocyanine with little induction time. This implies that phthalocyanine catalyzes the aniline polymerization. However, if phthalocyanine (CuPc) were a mere catalyst, the final product would be pure PANI with some CuPc as an additive. This was not the case for any of PANI synthesized in present studies, which in fact show complete incorporation of CuPc in main polymer chain. The incorporation of phthalocyanine was clearly evidenced by FT-IR and UV-VIS spectral studies. The polyaniline content in the co-polymers, obtained from thermal decomposition and calculated by actual addition of phthalocyanine shows more prominent differences. The higher values by % T.G. measurements than the calculated value of polyaniline are indicative of less degradation of polyaniline in the co-polymers. These aspects have been discussed in later sections of this chapter.

3.3.A.1: CHARACTERIZATION

(a) INFRARED SPECTROSCOPY

The incorporation of phthalocyanine into the polyaniline chain was confirmed by IR studies. **Fig. 3.2** shows the IR absorption spectrum for PANI-CuPc powder samples. The curve A correspond to the sample of pure polyaniline while curves B and C correspond to the polyaniline containing 5% and 20% CuPc respectively. The frequency data obtained and their probable assignments are presented in **Table- 3.2.** The characteristic IR absorption intensity due to quinoid ring at 1590 cm^{-1} and benzoid ring at 1500 cm^{-1} are clearly indicative of these two states in the polymer chain. The C-N stretching vibrations are appeared at 1380 cm^{-1} and 1305 cm^{-1} in each sample. The benzene ring C-C vibration for stretching is observed at 1463 cm^{-1}. The IR spectra of polyaniline samples, in presence of phthalocyanine exhibit new absorption peaks distinctly at 1210, 1150, 1095, 950, 900, 830, 770, 740 and 510 cm^{-1} which are assignable to phthalocyanine skeletal vibration modes. The absence of peak at 650 cm^{-1} assignable to C-Cl vibrations, in the functionalized polymeric samples clearly shows that polymer (polyaniline) gets attached to the phthalocyanine ring via C-Cl termination. The data represented for these polymers is well matched with the reported literature IR data for polyaniline[187] and phthalocyanine[188]. Thus, IR studies on

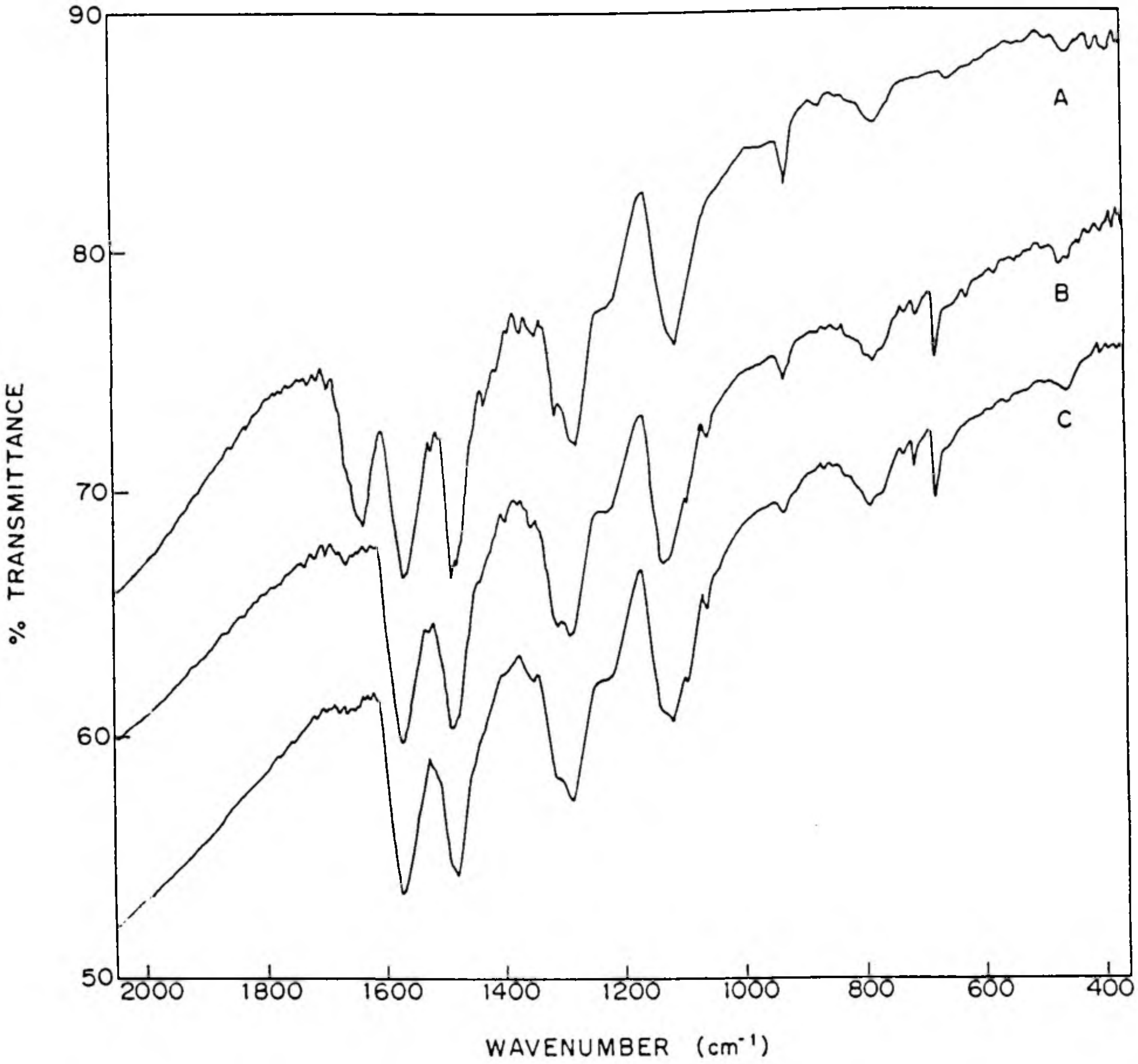


Fig. 3.2 : FT-IR absorption spectrum of PANI-CuPc powder samples (A) Pure PANI (B) PANI + 5% CuPc And (C) PANI + 20% CuPc

TABLE- 3.2

FT-IR DATA OF PANI-CuPc POWDER SAMPLES (IN NUJOL)

Pure PANI Peak cm^{-1}	PANI + 5%CuPc Peak cm^{-1}	PANI + 20%CuPc Peak cm^{-1}	Assignments.
1590.7 (s)	1608.1 (br)	1589.1 (br)	Quinoid N=Q=N str.
1500.0 (m)	1500.0 (m)	1500.0 (m)	Benzoid N-B-N str.
1463.3 (vs)	1463.1 (vs)	1458.3 (br)	Benzene ring str.
1377.2 (vs)	1381.2 (s)	1381.2 (s)	C-N str.
1351.5 (w)	--------	--------	
1304.3 (vs)	1305.6 (s)	1304.9 (s)	C-N str.
--------	1286.2 (m)	1286.2 (m)	
1245.0 (w)	1210.9 (s)	1215.0 (vs)	C=N
1175.5 (s)	1172.2 (m)	1191.2 (w)	Vib. Mode of N=Q=N
--------	1152.3 (m)	1151.7 (m)	Pc skeleton
1131.8 (w)	--------	--------	
--------	1095.0 (s)	1095.0 (s)	Pc skeleton
--------	949.4 (vs)	948.9 (vs)	Pc skeleton
--------	899.0 (m)	887.7 (w)	Pc skeleton
825.6 (s)	833.7 (m)	827.8 (s)	C-H out of plane def.
780.6 (m)	769.7 (s)	769.2 (s)	C-H out of plane bend.
--------	744.7 (m)	738.7 (s)	Pc skeleton
722.0 (s)	715.0 (m)	720.9 (m)	
704.0 (s)	696.2 (s)	697.1 (m)	
498.0 (br)	510.0 (vs)	509.6 (vs)	

functionalized polymer clearly gives an evidence of incorporation of phthalocyanine moieties into the polymer chain.

(b) UV-VIS SPECTROSCOPY

The UV-VIS spectrum of polyaniline depends strongly on its oxidation states. **Fig.3.3** shows the optical absorption spectra (in sulfuric acid solution) of polyaniline and polyaniline functionalized with CuPc samples in the wavelength range 300-900 nm. Curves A to D corresponds to the polyaniline powder samples with CuPc content of 0, 3, 10 and 20 mole percent respectively. It can be seen that there are two new broad absorption bands occurring at 580 nm and 650 nm, which are associated with the chlorinated phthalocyanine (green) moieties[189]. Pure PANI has a broad absorption band centered at 750 nm, which is associated with the oxidation/doping of the polymer, giving rise to polaronic states within the band gap[190]. It is interesting to note that the main absorption band at 320 nm and 420 nm of PANI are also affected by the presence of CuPc in the polymer. This can be due to higher degree of conjugation in PANI-CuPc due to the highly conjugated planar CuPc moieties attached to the main chain as well as high level of dopant present in these polymers as compared to pure PANI.

The UV-VIS spectra of CuPc samples (NMP solution) used in the synthesis are shown in **Fig.3.4.** The curve A correspond to phthalocyanine blue sample while curve B correspond to chlorinated derivative of phthalocyanine i.e. phthalocyanine green. These two samples show quite different nature of absorption peaks. Phthalocyanine blue shows 4 peaks at 380, 580, 620 and 700 nm. These peaks are almost of equal intensity to each other. The chlorinated phthalocyanine sample shows detectable shifts in its peak positions. As can be seen in the spectrum of phthalocyanine green the four peaks appear at 380 nm, 660 nm, 740 nm and 800 nm.

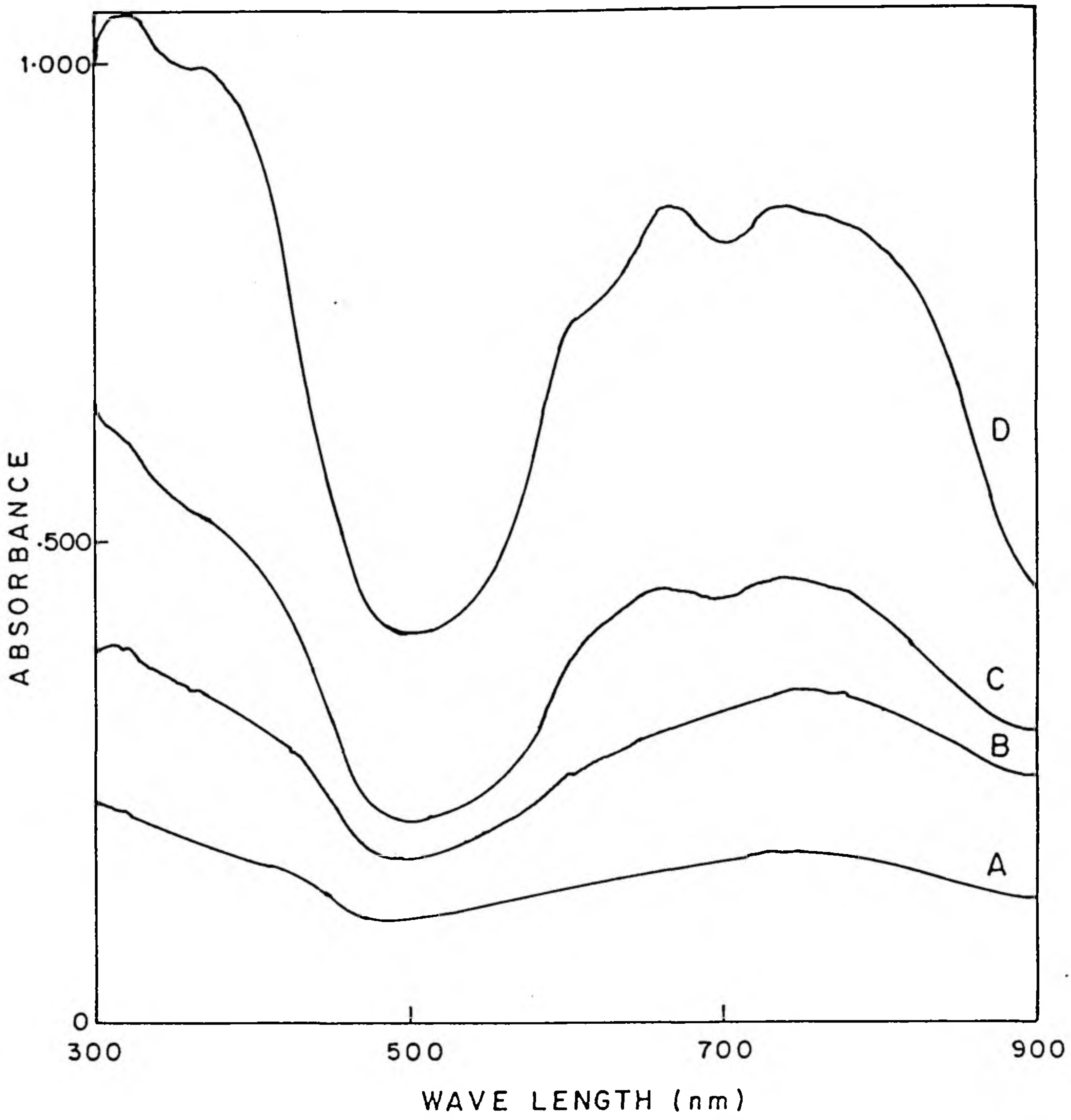


Fig. 3.3 : UV-VIS spectrum of PANI-CuPc powder samples in dil. H_2SO_4 (A) Pure PANI (B) PANI + 3% CuPc (C) PANI + 10% CuPc and (D) PANI + 20% CuPc

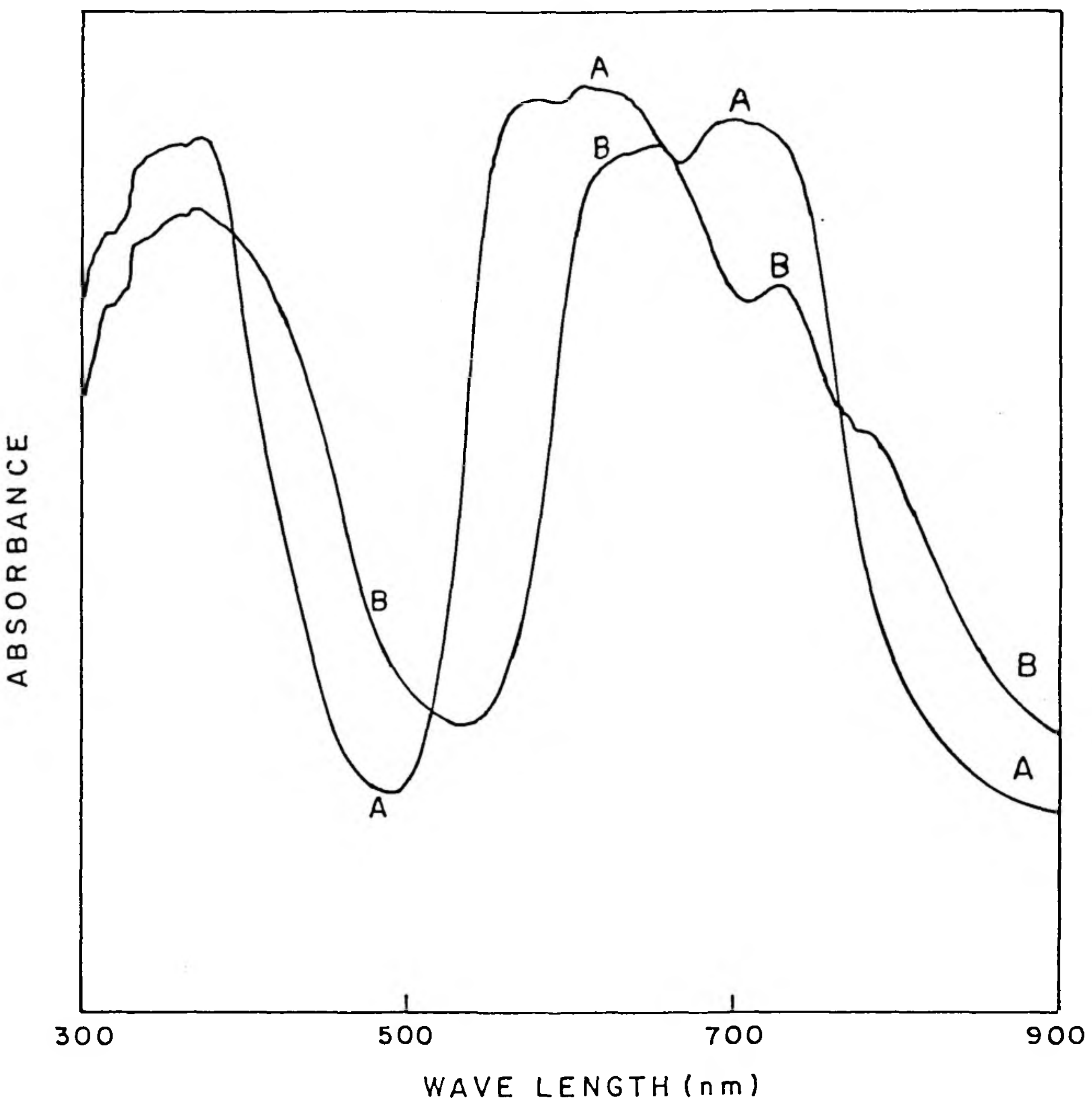


Fig. 3.4 : UV-VIS spectrum of Copper Phthalocyanine in dil. H_2SO_4

(A) Phthalocyanine Blue and (B) Phthalocyanine Green

This sample has maximum peak intensity at 660 nm and peak at 740 nm is small in comparison with the peak at 660 nm. In addition to this, the sample exhibits a shoulder at about 800 nm. The peaks at higher wavelength (above 600 nm) are due to Q band and they showed the splitting. The peak at 380 nm is the Soret band of the phthalocyanine. In the PANI-CuPc polymers, these peaks are slightly shifted from their original positions which can be due to either different crystal structure or the interaction with the dopant ions present in their vicinity.

(c) MICROANALYSIS DATA

Microanalysis of the various functionalized polymers was carried out to investigate the doping levels and also to establish the structural composition of these samples. The calculated and observed values of each element (by weight percent) in various polymers are presented in **Table-3.3**. Assuming an empirical formula $C_{24}H_{18}N_4Cl$, the calculated values for C = 72.45, H = 4.52, N = 14.09 and Cl = 8.90 are well matched with observed values C = 76.55, H = 5.69, N = 15.58 and Cl = 5.17. However, the lower value for Cl content than the calculated value can be explained as follows: The pure polyaniline obtained is high molecular weight fraction due to the fact that NMP–H_2O mixture was used for polymerization and NMP can extract out some of the low molecular weight species. Hence the distribution of available dopant ions over long polymeric chains may reduces the dopant level to great extent. This was also evident from the conductivity measurement data, which is discussed later in this chapter.

The polyaniline containing 10% CuPc sample shows the elemental composition as C = 59.44, H = 3.50, N = 12.64, Cl = 19.80 and Cu = 4.60. The calculated values for the empirical formula $(C_{24}H_{18}N_4)[C_{32}H_{12}N_8Cu]Cl_8$ are well matched with the above obtained values. As can be seen from the **Table-3.3**, chlorine

Table-3.3

Microanalysis data of PANI-CuPc polymers

Elements	Pure PANI		PANI + 5%CuPc		PANI +10%CuPc	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
Carbon	72.45	76.55	66.65	63.24	60.76	59.44
Hydrogen	4.52	5.69	3.73	4.76	3.04	3.50
Nitrogen	14.09	15.58	14.32	14.14	14.18	12.64
Chlorine	8.90	2.17	12.97	14.23	19.97	19.80
Copper	----	----	2.30	3.62	4.02	4.60
Cl/N mole Ratio	0.248	0.055	0.357	0.396	0.555	0.622

Sample	Empirical Formula
Pure PANI	$(C_{24}H_{18}N_4)$ Cl $(PANI)_4 : (Cl)_1$
PANI + 5% CuPc	$(C_{24}H_{18}N_4)_5[C_{32}H_{12}N_8Cu]$ Cl_{10} $(PANI)_{20} : (CuPc)_1 : (Cl)_{10}$
PANI + 10% CuPc	$(C_{24}H_{18}N_4)_2[C_{32}H_{12}N_8Cu]$ Cl_8 $(PANI)_8 : (CuPc)_1 : (Cl)_8$

content (or Cl/N ratio) in the PANI samples containing CuPc goes on increasing as the CuPc content in the polymer increases. As seen in the IR studies, C-Cl peak intensity decreases for higher CuPc containing samples and hence, the rise in Cl/N ratio is indicative of increase of dopant ion concentration. As these polymerization reactions are carried out in strong acidic medium (HCl), due to greater macrocyclic addition (like phthalocyanine) larger space will be available for the dopant ions to diffuse. This result in the increase of the dopant ion concentrations in PANI-CuPc polymers as compared to PANI synthesized under same conditions. The ESCA studies and conductivity measurement of these polymers (discussed in the later part of the chapter) supports this data.

It may be of interest to compare the number of units in the first bracket (corresponding to four aniline units) in the empirical formula derived in each case (see **Table-3.3**). As the phthalocyanine concentration in the reaction mixture is increased, the number of aniline units in the chains attached to CuPc decreases (probably forming oligomers). Such oligomeric chains attached to the four active sites of phthalocyanine forms "dendrimer" as mentioned in the earlier discussions. These observations are very much in agreement with the suggestions made as regards the crystalline structure for these polymers [**section 3.3.A.2 (a)**].

3.3.A.2: CHARACTERIZATION OF STRUCTURE

(a) X-RAY DIFFRACTION STUDIES

Various workers have studied the synthesis and structure of PANI. Controversies have arisen about whether PANI is crystalline or amorphous. According to Wang et.al.[191] crystallinity of PANI decreases with increasing HCl concentration in the range of 0.001- 7 N. That is why the PANI prepared at high HCl concentration was entirely amorphous. The emeraldine base powder was reported to be 50 % crystalline[192-193] (orthorhombic with a=7.65 A°, b=5.75 A° and c=10.20 A°). At the same time, it was reported that emeraldine salt (PANI- hydrochloride) was partly crystalline, while emeraldine base (undoped PANI) was essentially an amorphous polymer. Pouget et.al.[194] reported that when the powdery PANI was doped with HCl, it becomes more crystalline which is reflected in the appearances of several diffraction peaks at 2θ values 9°, 15°, 21° and 26°. XRD studies on HCl doped polyaniline were reported by Chaudhary et.al.[195] who found that the undoped PANI has 45% crystallinity while HCl doped counterpart was more crystalline (74%).

In the present investigation, PANI was functionalized with phthalocyanine in an acidic medium (HCl). Hence it is interesting to note the changes in the crystallinity due to addition of macro cyclic phthalocyanine into polymer matrix. The x-ray diffraction patterns for different polymers are shown in **Fig. 3.5**. The polyaniline homopolymer sample (curve A) showed two prominent reflections at 20.5° and 25° in the 2θ regions. However, the polyaniline samples containing even small amount say 3 or 5 % CuPc (curve B and C) addition suppresses the peak at 20.5° and prominent peak arises at 26.4°. As can be seen from the **Fig. 3.5**, the increase in phthalocyanine content was reflected by the appearance of multiple reflections in the XRD scans (curves D and E). From the XRD patterns indicated in **Fig.3.5**, it appears that the structure of PANI-CuPc polymers gets modified and it neither belongs to pure PANI[194] [orthorhombic with a=7.00 A°, b=8.60 A° and c=10.40 A° for HCl doped PANI] nor to pure CuPc green[196] [a = 26.3 A°, b =3.67 A° and c = 13.9 A°]. Since the d-values of the peaks observed in the present case are not fully matching with those reported for PANI homopolymer or pure CuPc; these had to be analyzed according to new structure. The comparison of the experimentally observed d-value with the calculated values for an orthorhombic structure having lattice parameters of a = 15.3 A°, b =16.5 A° and c = 20.4 A° is given in **Table-3.4.** It may be noted that the XRD pattern at high

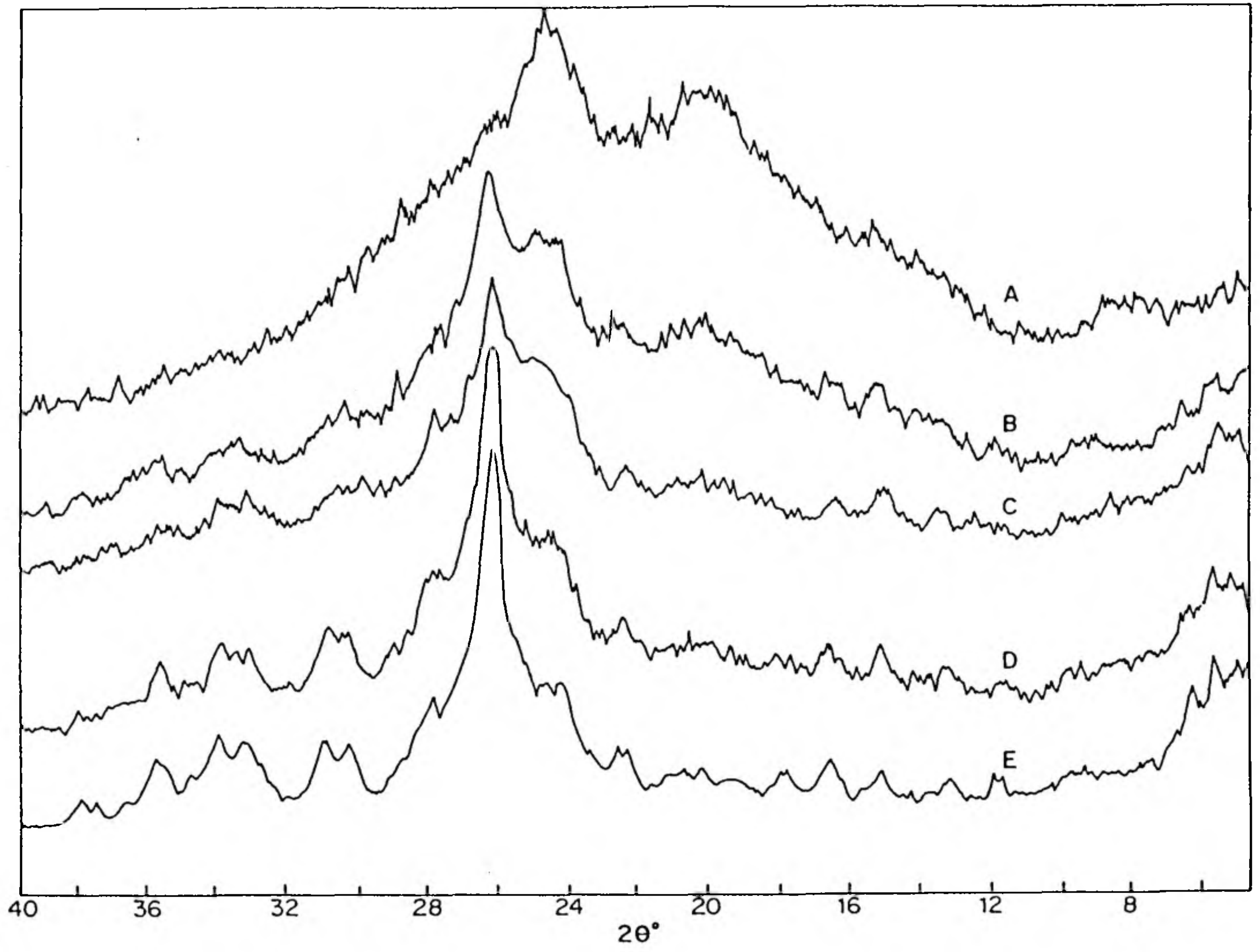


Fig. 3.5 : X-ray diffraction patterns of PANI-CuPc powder samples
(A) Pure PANI (B) PANI + 3% CuPc (C) PANI + 5% CuPc
(D) PANI + 10% CuPc and (E) PANI + 20% CuPc

TABLE –3.4

X-RAY DIFFRACTION DATA OF PANI CuPc POLYMERS.

Polyaniline pure		Polyaniline + 5% CuPc		Assignment		
d Calculated	d Observed	d Calculated	d Observed	h	k	l
-	-	16.5	16.67	0	1	0
15.3	15.24	15.3	15.24	1	0	0
9.87	9.81	9.87	9.83	1	1	1
-	-	8.60	8.51	1	0	2
7.65	7.69	-	-	2	0	0
-	-	7.18	7.14	2	0	1
-	-	6.32	6.33	1	0	3
6.16	6.11	-	-	2	0	2
-	-	5.77	5.72	2	1	2
5.62	5.64	-	-	2	2	0
-	-	5.32	5.28	0	3	1
4.34	4.33	4.30	4.31	2	0	4
4.23	4.21	-	-	1	2	4
-	-	4.16	4.15	2	1	4
4.01	4.02	-	-	1	0	5
-	-	3.90	3.90	1	1	3
3.55	3.55	3.55	3.53	3	1	4
3.35	3.36	3.35	3.36	4	0	3
-	-	3.16	3.16	2	0	6
2.88	2.92	2.88	2.88	1	3	6
2.71	2.72	2.70	2.67	3	2	6
-	-	2.61	2.62	1	4	6
-	-	2.51	2.49	2	4	6
-	-	2.45	2.41	4	2	6

As per orthorhombic structure a = 15.3 A°, b = 16.5 A° and c = 20.8A°

TABLE- 3.5

X-RAY DATA OF PANI-CuPc POLYMERS

CuPc content Wt. %	**% Crystallinity**
0.0	37.0
3.0	43.5
5.0	50.0
10.0	62.5
20.0	75.0

concentration of CuPc has some similarity with that observed / reported for CuPc (green). However, there are number of differences in the d-values for PANI-CuPc and pure CuPc (green). Since, the PANI chains are linked to CuPc through C-Cl substituted groups in all four possible directions, at low concentrations of CuPc, more linearity in the chains is retained. On the other hand, at higher concentration of CuPc, there are many sites available for aniline polymerization (as discussed in earlier sections) which takes at the interface. Considering the fact that the PANI-CuPc product obtained at these concentrations of CuPc has similarity of XRD pattern to that of CuPc (green), it may be containing large number of CuPc moieties with substitutions of PANI oligomers at the four sites. Such "dendrimer" forms of CuPc can crystallize by stacking of molecules on top of each other[197].

The change in the crystallinity due to addition of phthalocyanine was calculated using x-ray diffraction pattern and the results are summarized in **Table-3.5**. As such pure PANI sample shows % crystallinity value of 37, whereas PANI containing CuPc sample exhibits this value as 75. This is in agreement of above suggestion of formation of low molecular weight aggregates at higher concentration of CuPc.

(b) ESCA (XPS) Studies

A number of recent X-ray photoelectron spectroscopic (XPS) studies on chemically[198-199] and electrochemically[200-201] synthesized PANI have demonstrated that the quinoid imine (=N-), benzenoid amine (-NH-) and positively charged nitrogen to any particular intrinsic redox state and protonation level of PANI can be quantitatively differentiated from the properly curve fitted N_{1s} core-level spectrum. The XPS studies also can reveal presence of co-monomer, dopant ions etc.

The **Fig. 3.6** shows the N_{1s} and C_{1s} core levels spectrum of PANI and CuPc (green) samples. The spectrum A and B corresponds to the sample of PANI and CuPc (green) samples respectively. The peak components with binding energy (B.E) at about 399.0 eV, 400.6 eV and 402.6 eV are the quinonoid imine (=N- structure), benzenoid amine (-NH- structure) and positively charged nitrogen in the sample of pure polyaniline. The N1s spectrum for CuPc (green) can be resolved into 4 peaks after deconvolution. These appear at the binding energy values of 398.7 eV, 399.8 eV, 401.3 eV and 405.0 eV respectively. The core level N_{1s} and C_{1s} for the samples containing 5% and 20% CuPc are depicted in **Fig 3.7**, in which curve C correspond to PANI + 5% CuPc and curve D represents the PANI + 20% CuPc sample. If one compares the curves A, B, C and D, it is observed that multiple peaks are present in N_{1s} core level for the samples containing phthalocyanine. The presence of multiple peaks in N_{1s} core level for PANI-CuPc samples implies the chemical interaction between the polymeric chains and the phthalocyanine moieties. Also, the broadening of the peak indicates that structural changes have taken place. The contribution from neutral species (which appeared at low binding energies), is very high as compared to charged species (which appeared at higher binding energy) which indicates lower electrical conductivity to these samples. Conductivity measurements supported this argument well. The data obtained for N_{1s} core level has been tabulated in **Table-3.6**. In the C_{1s} core levels there are four peaks obtained in these samples. The contribution from the neutral carbon species appeared at lower binding energy (about 285 eV). This is the major contribution in each sample. As the phthalocyanine content in the PANI increases the contribution from charged carbon species increases. These observations can be easily verified from the data presented in **Table 3.7.**

Chlorine Cl_{2p} core level spectrum of PANI-CuPc samples are shown in **Fig 3.8**. The curve B and D represents the CuPc (Green) and PANI containing 20% CuPc sample respectively. The major peak at 203.3 eV in CuPc sample can easily be assigned to the covalently bonded Cl groups to the phenyl rings. This is totally absent

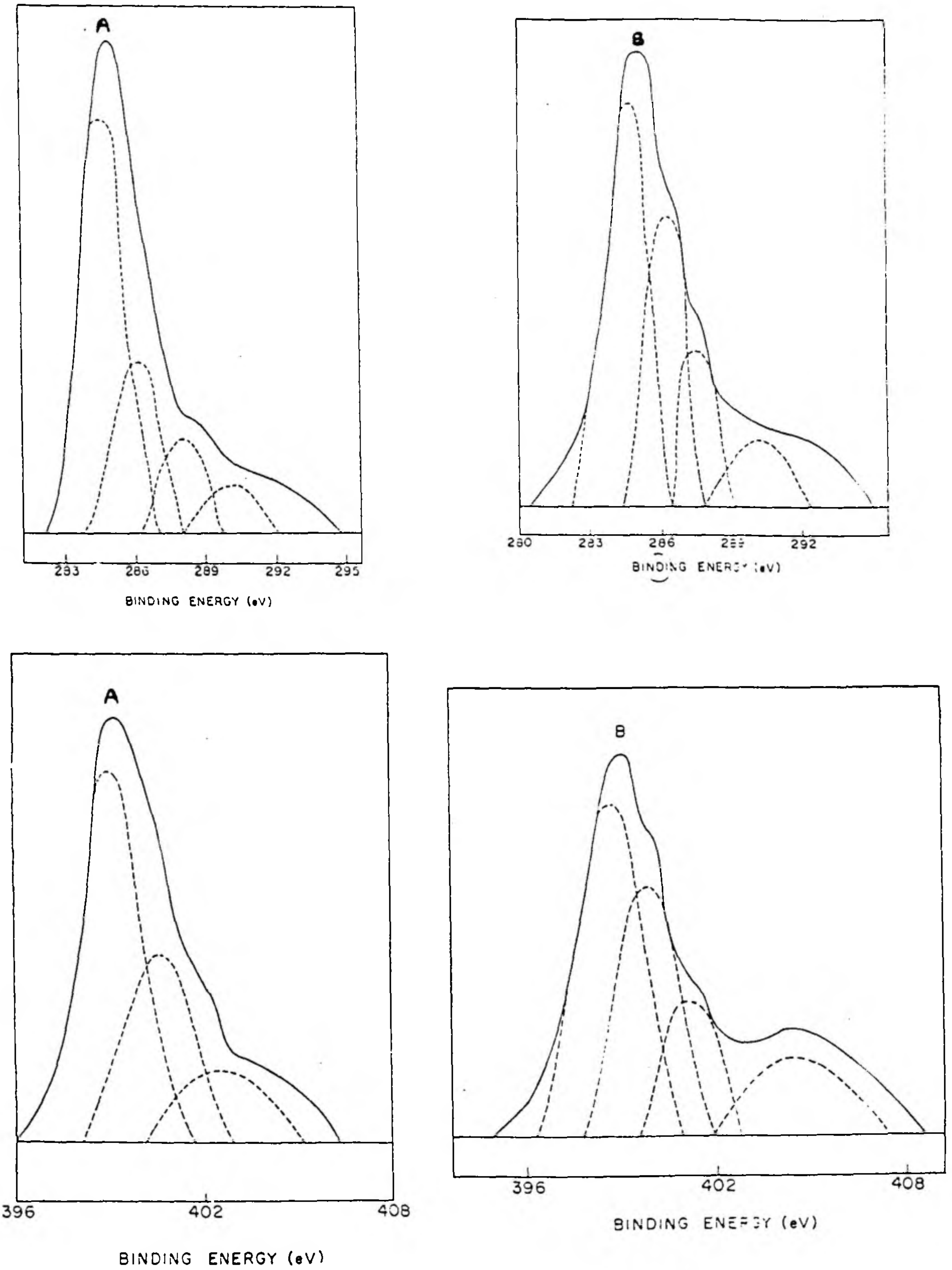


Fig.3.6 : N_{1s} and C_{1s} core-level spectrum of (A) PANI and (B) CuPc Green powders

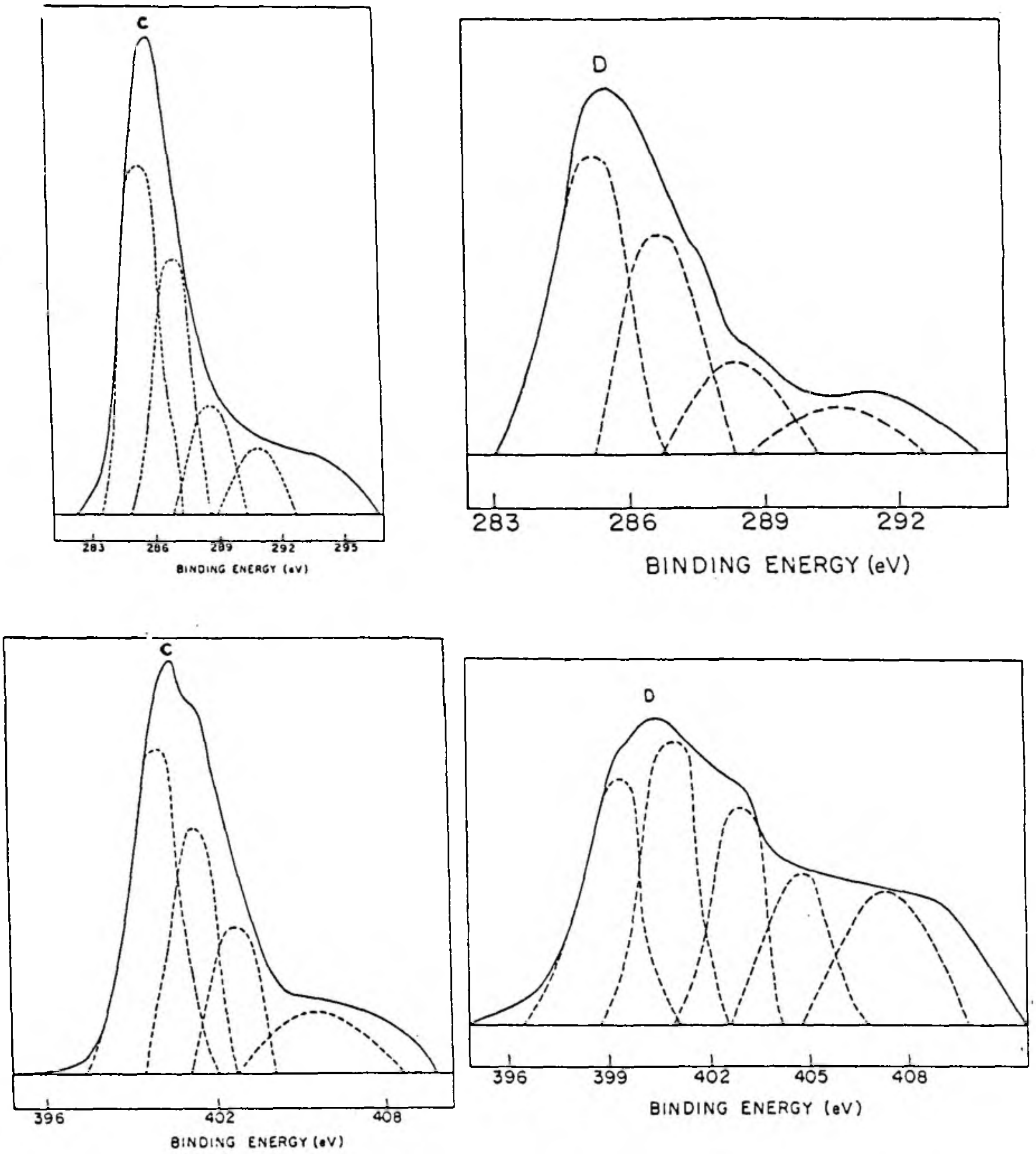


Fig. 3.7 : N_{1s} and C_{1s} core-level spectrum of (C) PANI + 5% CuPc And (D) PANI + 20% CuPc samples

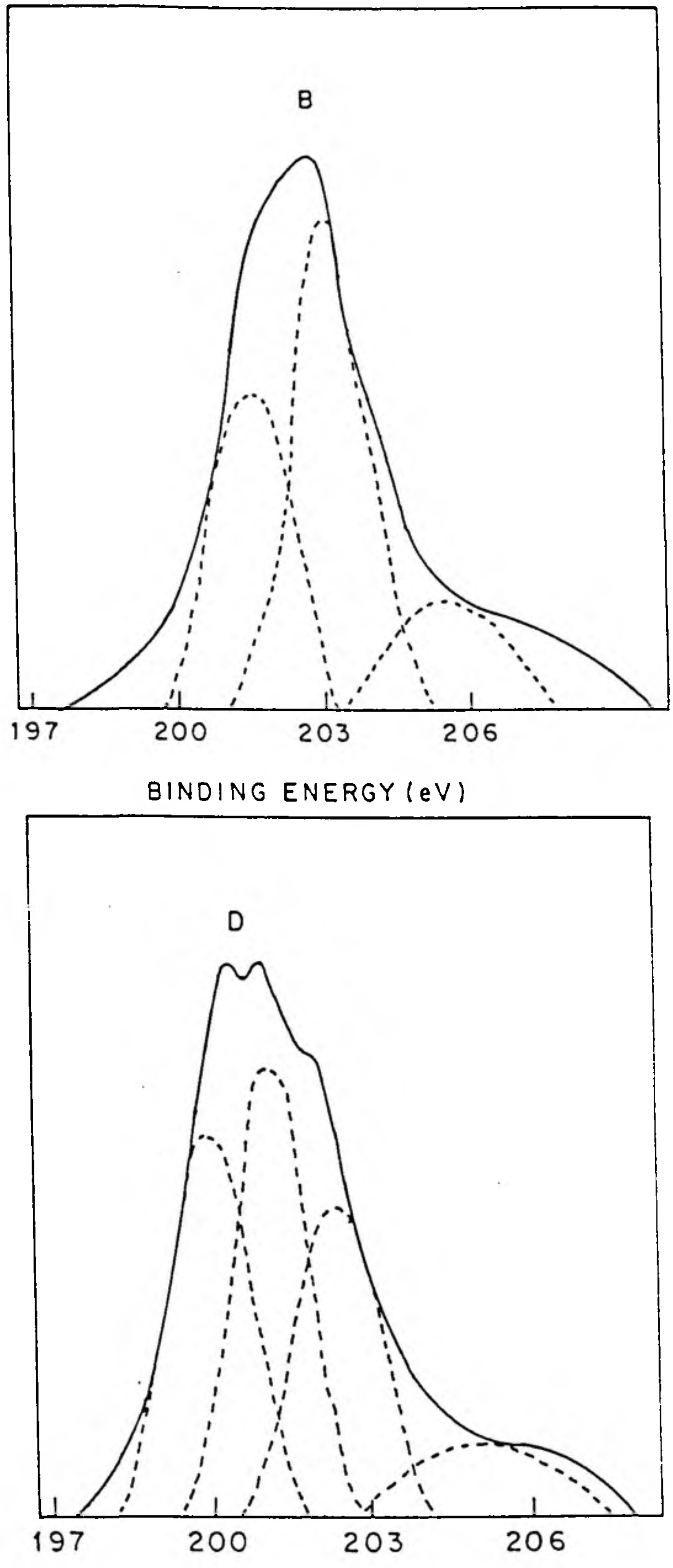


Fig. 3.8 : Cl $_{2p}$ core-level spectrum of CuPc Green (B) and (D) PANI + 20% CuPc samples

TABLE- 3.6

ESCA RESULTS OF N_{1s} LEVEL FOR PANI-CuPc POWDERS

Sample	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
PANI (A)	N_I = 399.0 N_{II} = 400.6 N_{III}= 402.6	2.00 2.50 2.62	54.1 31.4 14.5
CuPc (green) (B)	N_I = 398.7 N_{II} = 399.8 N_{III} = 401.3 N_{IV} = 405.0	2.62 2.25 2.12 4.00	45.6 25.4 16.8 12.2
PANI + 5 % CuPc (C)	N_I = 399.9 N_{II} = 401.0 N_{III} = 402.7 N_{IV} = 405.6	2.00 1.87 2.12 4.00	43.0 26.2 17.2 13.6
PANI + 20 % CuPc (D)	N_I = 399.2 N_{II} = 400.8 N_{III} = 403.0 N_{IV} = 404.6 N_V = 406.8	2.00 2.00 2.12 2.75 3.00	32.0 17.0 16.3 15.7 19.0

TABLE- 3.7

ESCA RESULTS OF C_{1s} LEVEL FOR PANI-CuPc POWDERS

Sample	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
PANI (A)	C_I = 284.6 C_{II} = 286.0 C_{III} = 288.0 C_{IV} = 290.0	2.12 2.25 2.50 2.75	57.70 23.00 12.10 7.20
CuPc Green (B)	C_I = 284.6 C_{II} = 286.2 C_{III} = 287.8 C_{IV} = 290.2	2.12 2.00 1.87 2.87	46.50 30.40 13.55 9.55
PANI + 5 % CuPc (C)	C_I = 285.4 C_{II} = 286.8 C_{III} = 288.6 C_{IV} = 290.6	2.00 1.87 2.25 2.37	46.30 30.30 14.10 9.30
PANI + 20 % CuPc (D)	C_I = 285.2 C_{II} = 286.8 C_{III} = 288.4 C_{IV} = 290.6	1.87 1.87 2.12 2.75	45.10 31.50 15.25 8.15

in the PANI sample containing 20% CuPc. This implies that CuPc gets attached to polyaniline chain through these sites. The broadening of the peak in the PANI sample containing 20% CuPc shows that more number of Cl species are present in this sample. This is quite obvious due to the incorporation of macrocyclic molecule, which will provide more conjugation for the dopant ions to sit. The obtained data for Cl_{2p} core level is shown in **Table 3.8**. The higher binding energy values for CuPc sample can be explained on the basis of length of conjugation. The chlorine attached to the phenyl ring is reported[202] to appear at about 201 eV. The chlorine-doped sample of polyvinyl carbazole (PVK) [203] shows the Cl_{2p} core level at 202.5 eV. In CuPc the conjugation length is still more i.e. chlorine is attached to the phenyl ring which in turn is attached to another heterocyclic ring. Hence, in general, we can say that as the length of conjugation increases, the Cl_{2p} core level shifts to higher binding energy.

From these figures it is clear that the polyaniline and PANI-CuPc exists as a mixture of quinonoid and benzenoid type of structure. The protonation has occurred at the heteroatom. The higher Cl/N ratios are observed at the top surface of polyaniline containing phthalocyanine. The increase in Cl/N ratio for the samples containing phthalocyanine obtained has also been confirmed from the results of microanalysis data.

3.3.A.3: MEASUREMENT OF PROPERTIES

(a) ELECTRICAL CONDUCTIVITY

The electrical conductivity of polyaniline is expected to be high, since the polymerization reactions were carried out in highly acidic (1-2 pH) conditions. Another interesting part in the conductivity measurements is to observe the effect of phthalocyanine on the overall conductivity behaviour in these samples. The results

TABLE- 3.8

ESCA RESULTS OF Cl $_{2p}$ LEVEL OF PANI-CuPc POWDERS

Sample	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
CuPc Green (B)	Cl_{I} = 201.6 Cl_{II} = 203.3 Cl_{III} = 205.6	2.00 1.75 2.75	29.3 60.0 10.7
PANI + 20% CuPc (D)	Cl_{I} = 199.8 Cl_{II} = 201.0 Cl_{III} = 202.4 Cl_{IV} = 205.0	1.75 1.62 1.87 3.50	30.0 37.0 25.0 8.0

obtained for the conductivity as a function of CuPc concentration are depicted in **Fig. 3.9.** The conductivity for pure polyaniline sample obtained was 4.2×10^{-5} S/cm while it increases to a value of 4.6×10^{-3} S/cm in the sample of PANI containing 10% CuPc. This effect can be explained as follows,

A phthalocyanine macrocycle has a tendency to organize itself and forms stacks in which there is an interaction between the large π-system of the adjacent rings in such a way to give low dimensional compounds. Molecular stacking of phthalocyanine macrocycle allows intermediate interactions necessary for electrical conductivity. Two energetically equal structures at a point where they couple gives a surface effect known as 'soliton'. The soliton excitations present in the phthalocyanine polymers probably interact with each other or with neighboring chains leading to free or delocalized electron or hole states, depending upon the coulombic forces between the interacting moieties. Soliton type excitations within these polymers are possible because they possess degenerate ground states. When there is a transition from one phase to another, the system has to pass through soliton bound states and therefore, the electronic transport in both heated and unheated polymers containing phthalocyanine could be explained via hopping of charge carriers from one chain to another[204-205].

The variation of conductivity with respect to temperature for PANI-CuPc polymer is shown in **Fig.3.10**. From the curves, it can be observed that the conductivity increases as the phthalocyanine content increases. The conductivity obtained for the co-polymers is lower (10^{-3} S/cm) as compared to that reported for pure polyaniline samples of about 200 S/cm. In order to check the conductivity of fully oxidized (i.e. 50% max.) polymeric samples, the synthesized samples were further doped in 2 N HCl (aqueous) for about 24 hours. These doped samples exhibit conductivity values one order of magnitude higher than the as synthesized polymers. In the present studies we have carried out polymerization of aniline in NMP: H_2O (1:1)

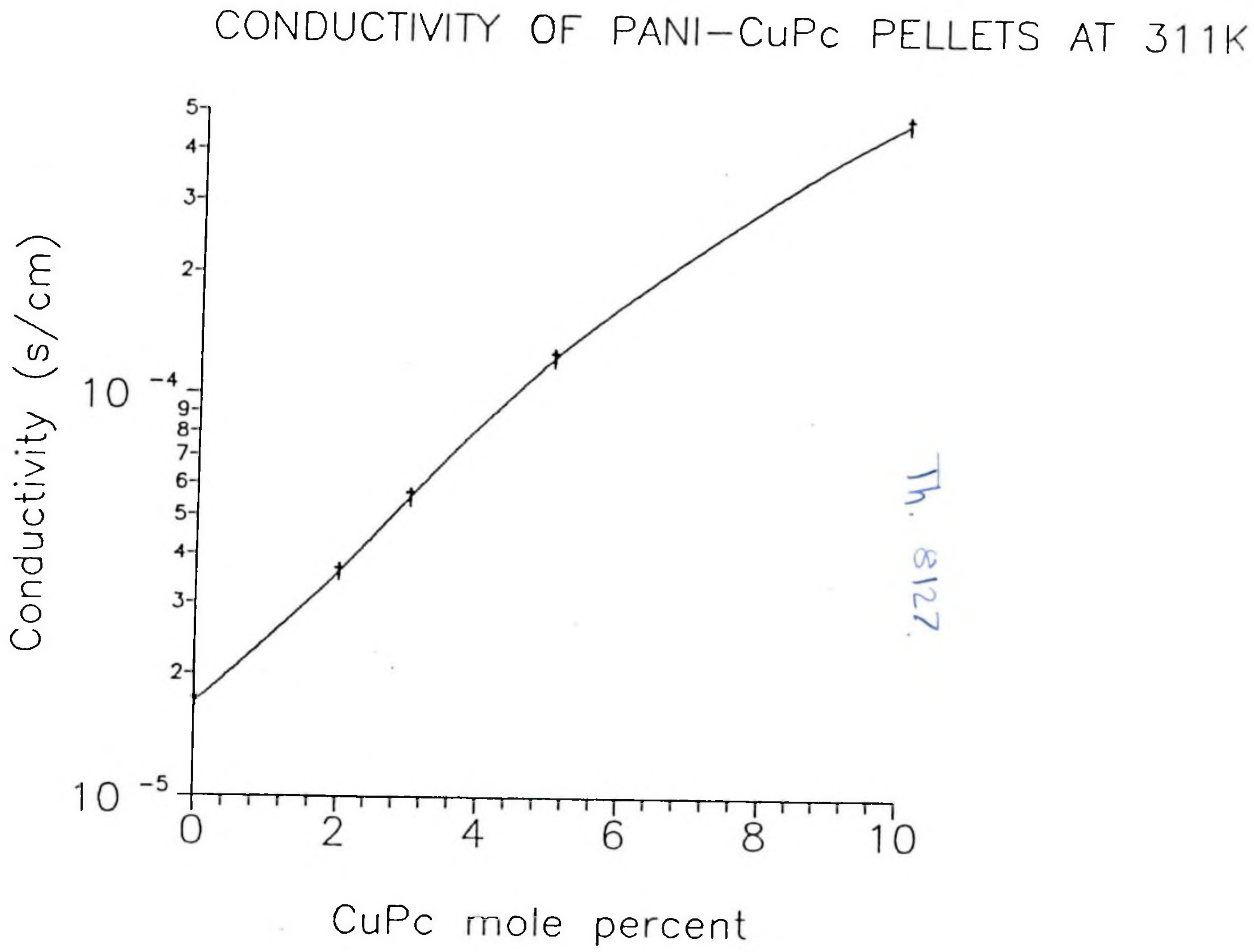


Fig. 3.9 : Plot of conductivity versus CuPc concentration for PANI-CuPc powder samples

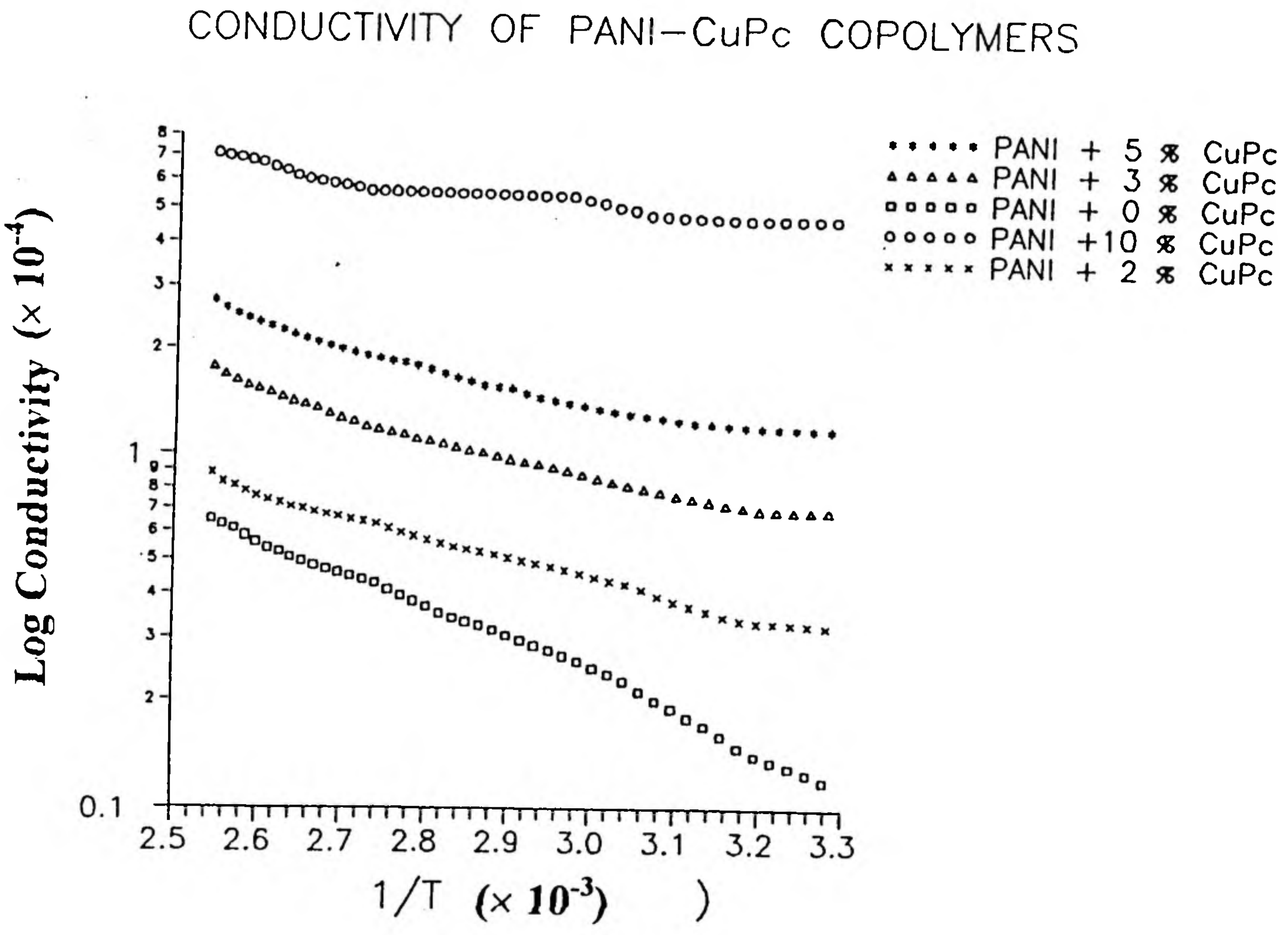


Fig. 3.10 : Plots of log conductivity versus reciprocal of temperature

For PANI-CuPc powder samples

solvent mixture. The C=O group in NMP would favor hydrogen bonding interactions with the NH group in polyaniline as well as with acid dopant. The comparable extents of the hydrogen bonding interactions of NMP with polyaniline and with acid dopant implies that acid doping of polyaniline in the presence of NMP would be difficult. This is due to the fact that protons are hindered from doping the polyaniline, resulting from their interaction with NMP. These effects lead to the low conductivity of polyaniline as well as its co-polymers synthesized in NMP: H_2O mixture. Chen and Lee[206] obtained a similar type of results, in the study of polyaniline films synthesized in NMP: H_2O mixture.

The electrical conductivity in these functionalized materials is associated with thermal excitation of the mobile π-electrons from the valance band containing the highest occupied molecular orbital to the conduction band containing the lowest unoccupied molecular orbital and the charge hopping between polymer chains[207]. To explain the conduction phenomenon, it is proposed that when an electron is removed from the top of the valance band by oxidation (of polyaniline) a vacancy (hole or radical cation) is created. A radical cation that is partially delocalized over some polymer segment is called a polaron. A dication or bipolaron has two charges associated with the localized polymer segment. Thus low oxidation level yields polarons and at higher oxidation levels bipolarons are produced. Both polarons and bipolarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds in the conjugated system. Conduction by polarons and bipolarons is the dominant mechanism of charge transport in polymers with non-degenerate ground states. The final magnitude of conductivity depends both on the number of charge carriers as well as their mobility. The number of charge carriers is essentially dependent on the dopant level while the mobility is associated with the distance / barrier between the two defect sites in which the charge carrier hops. It was seen that the incorporation of CuPc moities not only increases the net dopant concentration, but also creates an additional band gaps. This can lead to higher conductivity in PANI-CuPc than the homopolymer.

In co-polymers electron transfer is always faster than in pure polymer, which may be due to the difference in charge density on substituted and unsubstituted constituents of the polymer chain as a result of the electronic effect of substituents which may facilitate faster electron transfer. Trivedi[208] reports similar type of observations.

The dependence of conductivity on the temperature is given by the equation,

$$\sigma = \sigma o \ \exp. (-\Delta E/K_B T)$$

Where σo is the constant, ΔE is the activation energy and K_B is the Boltzman constant. The activation energy can be defined by the equation,

$$\Delta E = - K_B \, \partial (\ln \sigma) / \partial (1/T)$$

Hence, from the slopes of the curves of log σ Vs 1/T, one can calculate the activation energy.

The plot of activation energy (ΔE) versus phthalocyanine concentration is shown in **Fig. 3.11**. The gradual drop in activation energy was seen with increase in phthalocyanine concentration. The pure polyaniline sample has ΔE value of 0.25 eV while polymer sample containing 10% phthalocyanine has a value as low as 0.08 eV. These results indicate that by incorporation of phthalocyanine, the thermal excitation of the carriers is easier which can arise from either reduction in the band gap (due to higher conjugation) or introduction of additional defect / impurity states within in the

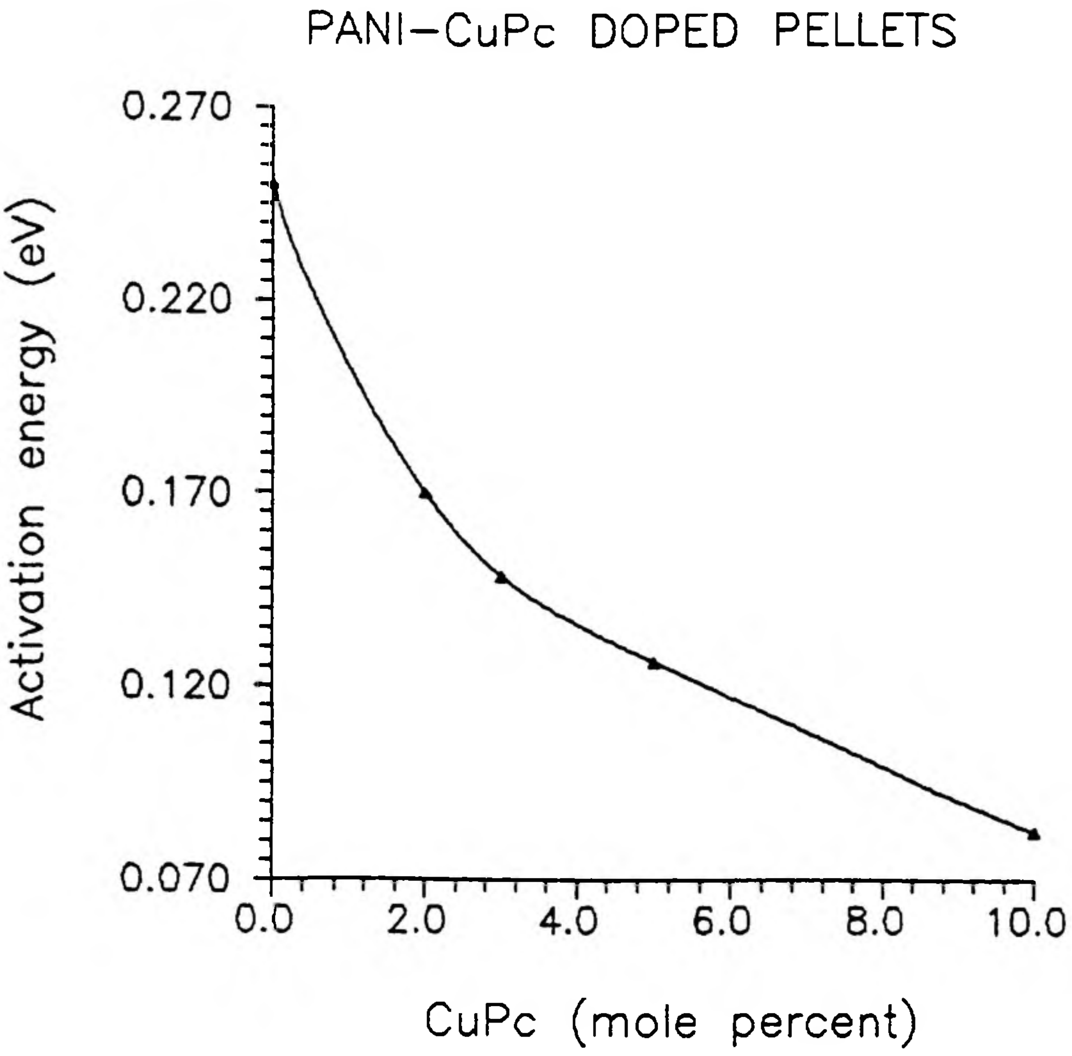


Fig. 3.11 : Plot of activation energy versus CuPc concentration for PANI-CuPc powder samples

band gap. Also, at higher doping levels bipolaronic states will give two additional levels resulting in lowering of ΔE. Further, the movement of charge carriers will be facilitated across the chains due to coupling between the CuPc groups, resulting in greater conductivity and less activation energy value.

(b) CYCLIC VOLTAMMETRIC MEASUREMENTS

The electrochemical response of PANI-CuPc polymer was determined in aqueous 0.1M hydrochloric acid. **Figures 3.12, 3.13 and 3.14** show the cyclic voltammograms of polyaniline powder samples containing different amount of CuPc such as 0%, 2% and 5% respectively. The curves designated as D and L correspond to the C-V recorded in dark and under white light illumination (5 mW/cm^2). The C-V of PANI exhibits typically two oxidation peaks with corresponding reduction peaks in the negative voltage cycle. The exact positions of the oxidation peaks depend on the electrolyte as well as pH used. Many authors[209-213] have reported similar observations regarding the C-V of PANI. The peak occurring at about 0.2 V (SCE) is usually attributed to the doping or insertion of the dopant ions in the polymer and this does not shift much with pH. On the other hand, the second peak occurring at higher voltage is very sensitive to the nature of the electrolyte, pH and the substituted groups on PANI chain. Some authors have attributed the second peak to over-oxidation, degradation, inter-polymer chain reaction and even cross-linking. It is interesting to note that with the incorporation of CuPc the first oxidation peak does not get affected much while the height of second peak decreases and in fact, it is totally suppressed at higher CuPc content (compare **Fig.3.12 D** with **Fig. 3.14 D**). It can also be noted that pure PANI does not have much sensitivity to illumination in both anodic or cathodic regions while PANI-CuPc exhibits considerable photosensitivity especially in the cathodic region (compare **Fig.3.12 L** with **Fig.3.14 L**). Thus, incorporation of CuPc in PANI clearly induces sensitization of photocurrent and samples show sharp C-V in the

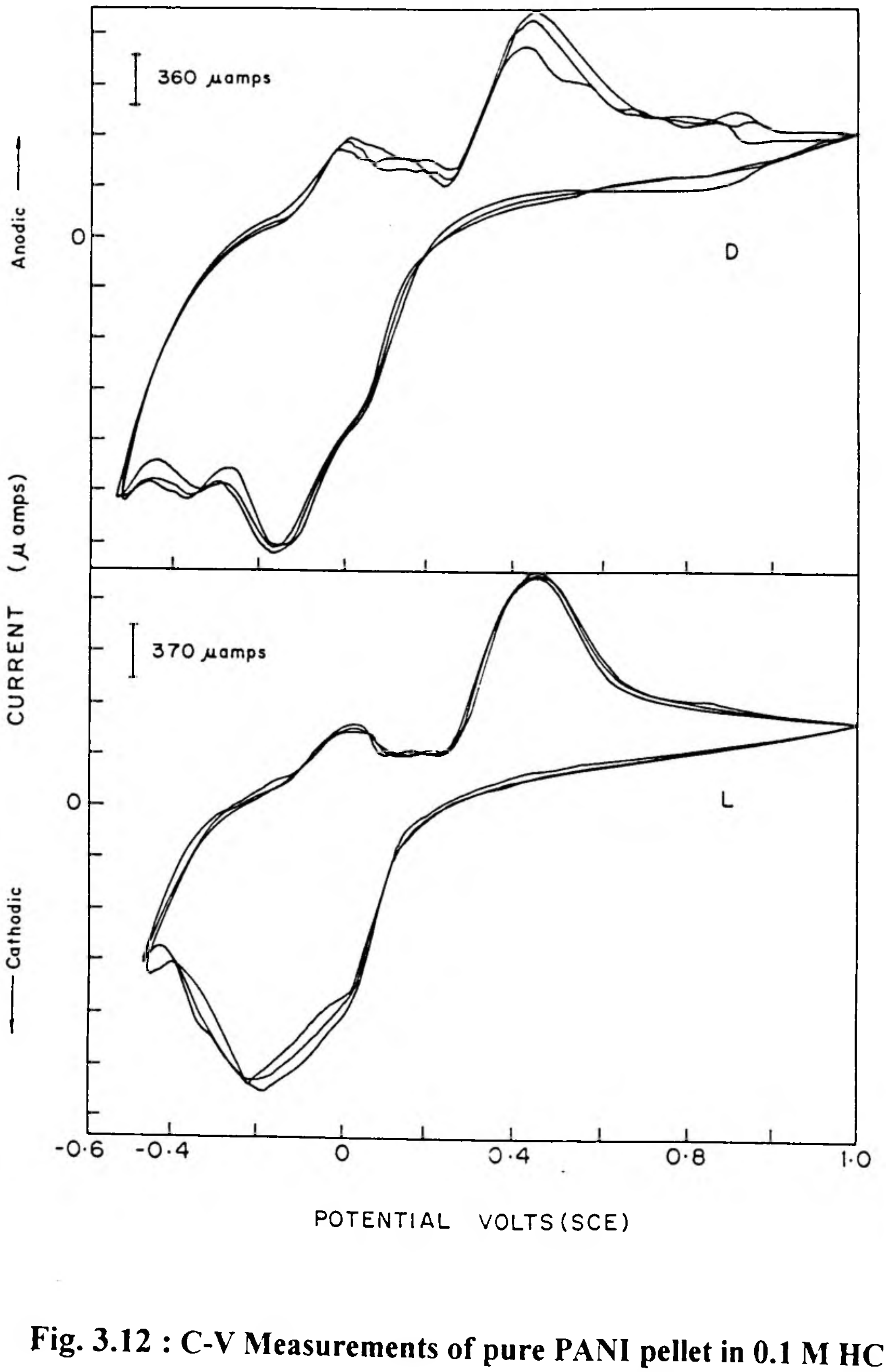


Fig. 3.12 : C-V Measurements of pure PANI pellet in 0.1 M HCl (D) in dark and (L) under illumination

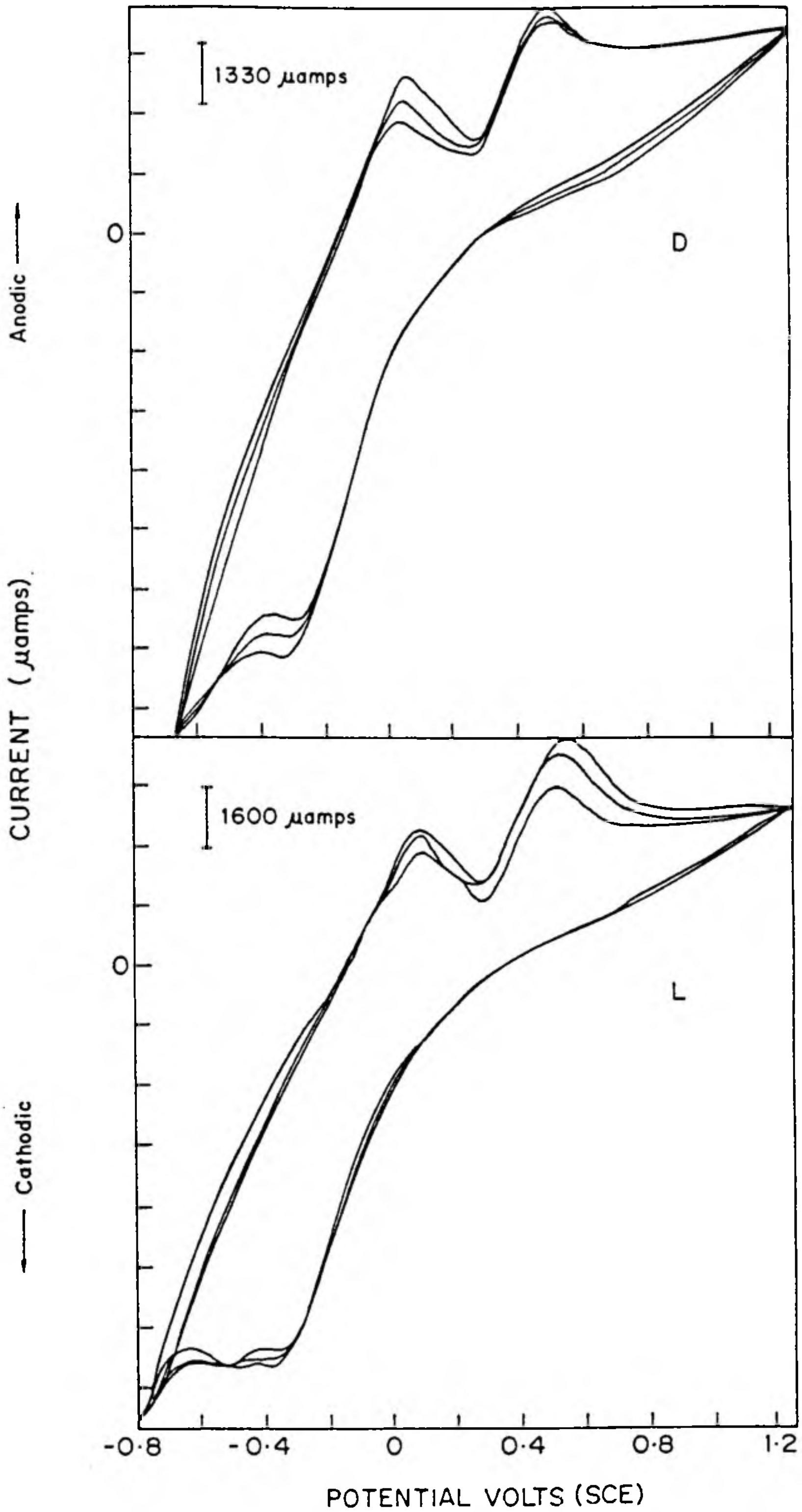


Fig. 3.13 : C-V Measurements of PANI + 2% CuPc pellet in 0.1 M HCl (D) in dark and (L) under illumination

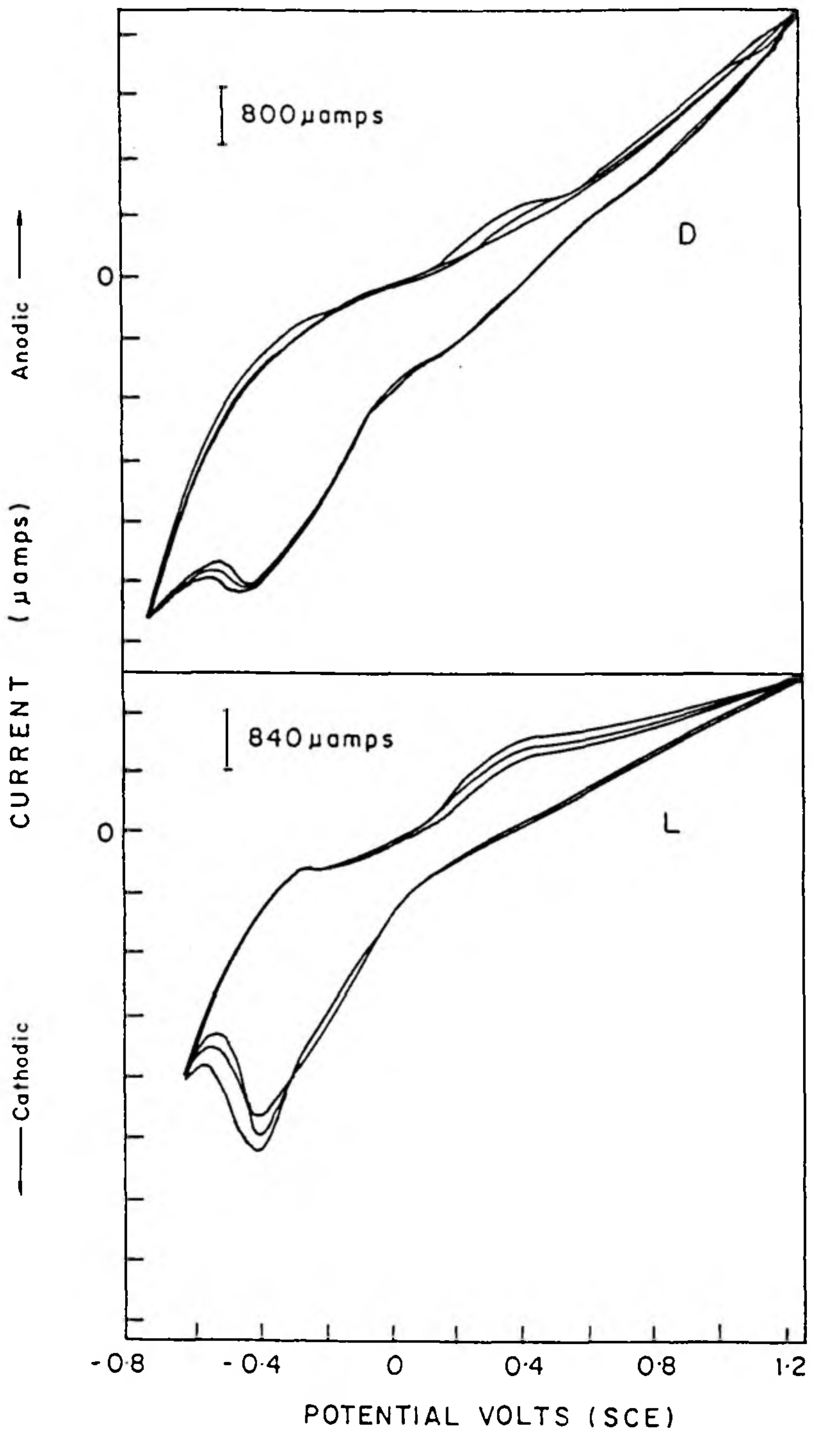


Fig. 3.14 : C-V Measurements of PANI + 5% CuPc pellet in 0.1 M HCl (D) in dark and (L) under illumination

cathodic regions. This can be attributed to the increase in the number of photons absorbed due to additional bands associated with the CuPc groups as well as generation and efficient transfer of charge carriers from CuPc groups to PANI.

(c) THERMAL STABILITY

The PANI-CuPc polymers were subjected for thermal analysis in nitrogen atmosphere. The results obtained from these studies are shown in **Table 3.9**. The table shows the percent weight loss with respect to temperature for various polymeric compositions. The thermal degradation was actually carried out from room temperature to 500°C. The degradation occurred to have in two stages. The first stage was from room temperature to 200°C, which involves mostly moisture, solvent vapour and dopant ions. The second stage is the polymer degradation, which starts from 200°C to 500°C. Hence, the **Table-3.9 (A)** shows the degradation data only in the second stage. The corresponding thermograms are depicted in **Fig. 3.15**. From these results it is evident that the thermal stability of polyaniline increases with the addition of phthalocyanine. The thermal analysis in static air has been carried out. The **Table-3.9 (B)** shows the results obtained in static air. The results also show that after the phthalocyanine incorporation into PANI the thermal stability of co-polymers increases. This is quite remarkable point to note that not only in nitrogen atmosphere but also in air atmosphere the thermal stability of PANI-CuPc polymers increases. These presumably because the phthalocyanine is much stable in air up to 250°C. Incorporation of phthalocyanine macrocyclic moiety renders more stability to the polymeric chain.

The thermal analysis data was exploited for checking the chemical incorporation of phthalocyanine into polymeric matrix [**Table-3.9(c)**]. The polyaniline content in each composition can be calculated from data on weight loss at

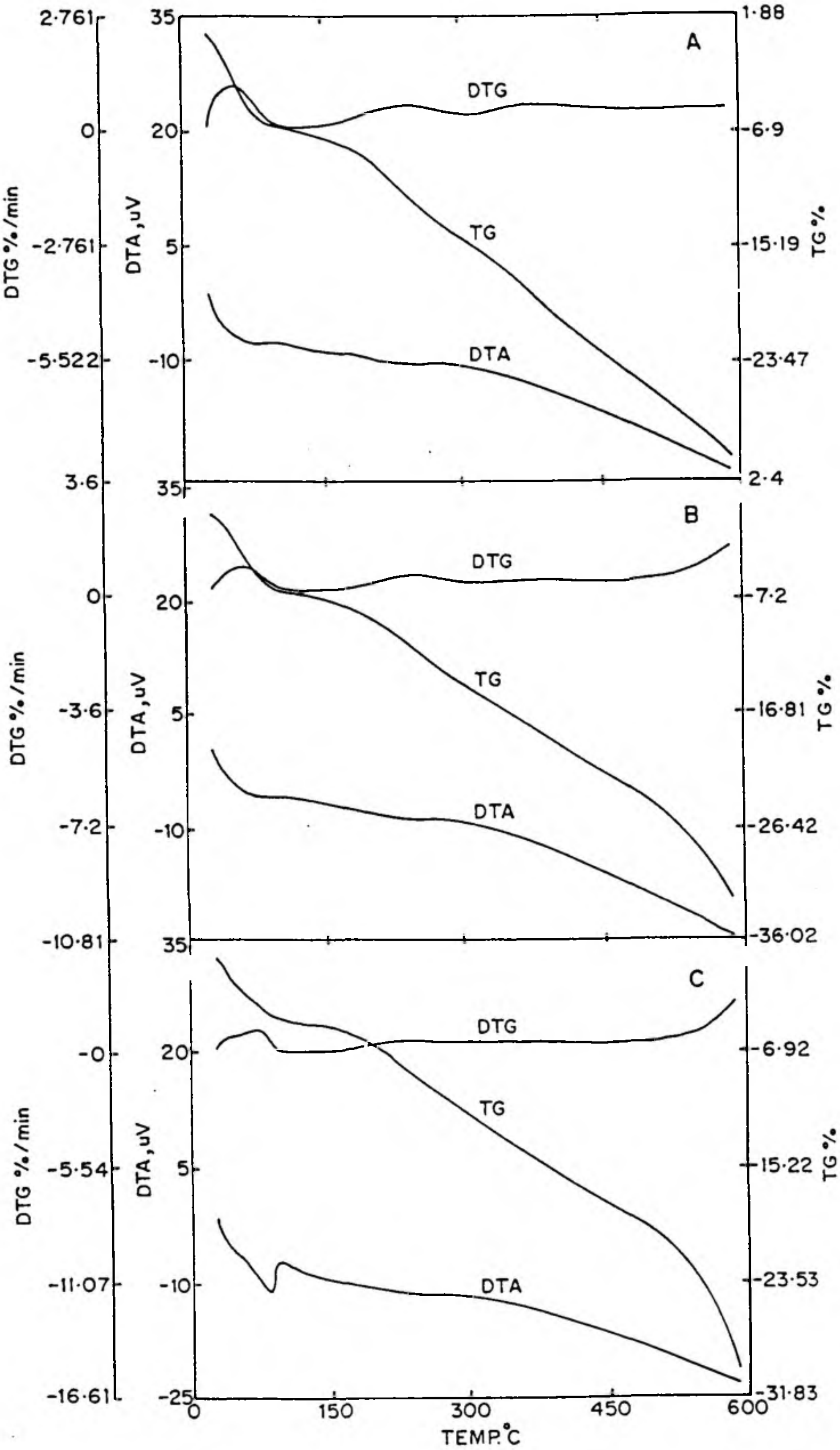


Fig. 3.15 : TGA/DTA thermograms of PANI-CuPc powder samples In nitrogen atmosphere (A) Pure PANI, (B) PANI + 5% And (C) PANI + 10% CuPc

TABLE- 3.9

(A) THERMAL DATA OF PANI-CuPc POLYMERS (In Nitrogen)

Temperature ^0C	Pure PANI	PANI + 3% CuPc	PANI + 5% CuPc	PANI + 10% CuPc
200	8.90	8.60	8.30	6.30
250	11.80	11.10	10.70	8.70
300	14.40	13.50	12.40	11.0
350	16.60	15.40	15.00	13.40
400	20.10	18.30	17.30	15.60
450	22.85	21.10	20.85	18.00
500	25.20	24.70	23.70	19.80

(B) THERMAL DATA OF PANI-CuPc POLYMERS (In Air)

Temp. °C	Pure PANI Wt. loss %	PANI + 10% CuPc Wt. loss %
200	8.20	7.14
250	9.60	8.20
300	12.85	11.20
350	15.50	14.10
400	25.70	21.80
450	44.30	36.00

(C) THERMAL DATA OF PANI-CuPc POLYMERS

CuPc Content Wt. %	Wt. loss from 200-500°C	% PT observed from % T.G.	% PT expected from actual CuPc Wt. addition
0.0	16.30	100.00	100.00
3.0	16.10	98.77	85.07
5.0	15.40	94.50	77.37
10.0	13.50	82.80	63.10

temperatures higher than the degradation temperature. The weight loss for pure aniline at 500 °C was taken as standard and then taking ratio of wt. loss in each composition to the wt. loss in polyaniline one can get actual polyaniline content in each composition. The amount of phthalocyanine added originally to each of the reactions is known. The yield of polyaniline homopolymer is also known. The ratio of total wt. of reactants in the reaction mixture to the yield of pure polyaniline gives the PANI content in each composition. Thus, from the comparison of the values obtained from T.G.A. and those from actual addition, it can be observed that the former values are higher than the latter ones. This confirms that phthalocyanine is incorporated into the polyaniline matrix, which was confirmed earlier by the techniques such as FT-IR and UV-VIS. These observations also imply that the degradation of polyaniline was restricted by the addition of phthalocyanine.

(d) CHEMICAL SENSITIVITY

The gas sensing ability of pure polyaniline as well as polyaniline functionalized with phthalocyanine was checked. For this study the samples were prepared as described in detail in Chapter-II (**section 2.3.A**). The pure polyaniline was not found to be much sensitive to chemical vapours and it does not dissolve in solvents from which it can be cast as a film. Hence, it was mixed with polyethylene oxide-$CuCl_2$ complex for making surface cells by applying a thin paste of polyaniline dispersed in PEO-$CuCl_2$ complex on interdigited PCB[214]. Such surface cell type sensors were prepared for different compositions of PANI-CuPc. These samples were then exposed to various chemical vapours such as methanol, nitrogen dioxide and ammonia gas in a specially designed pre-evacuated glass chamber (**Fig.2.2, Chapter II**). The sensitivity factor (S) calculated for different phthalocyanine concentration are shown in **Fig.3.16**. The curves A, B and C correspond to sensitivity on exposure to the vapors

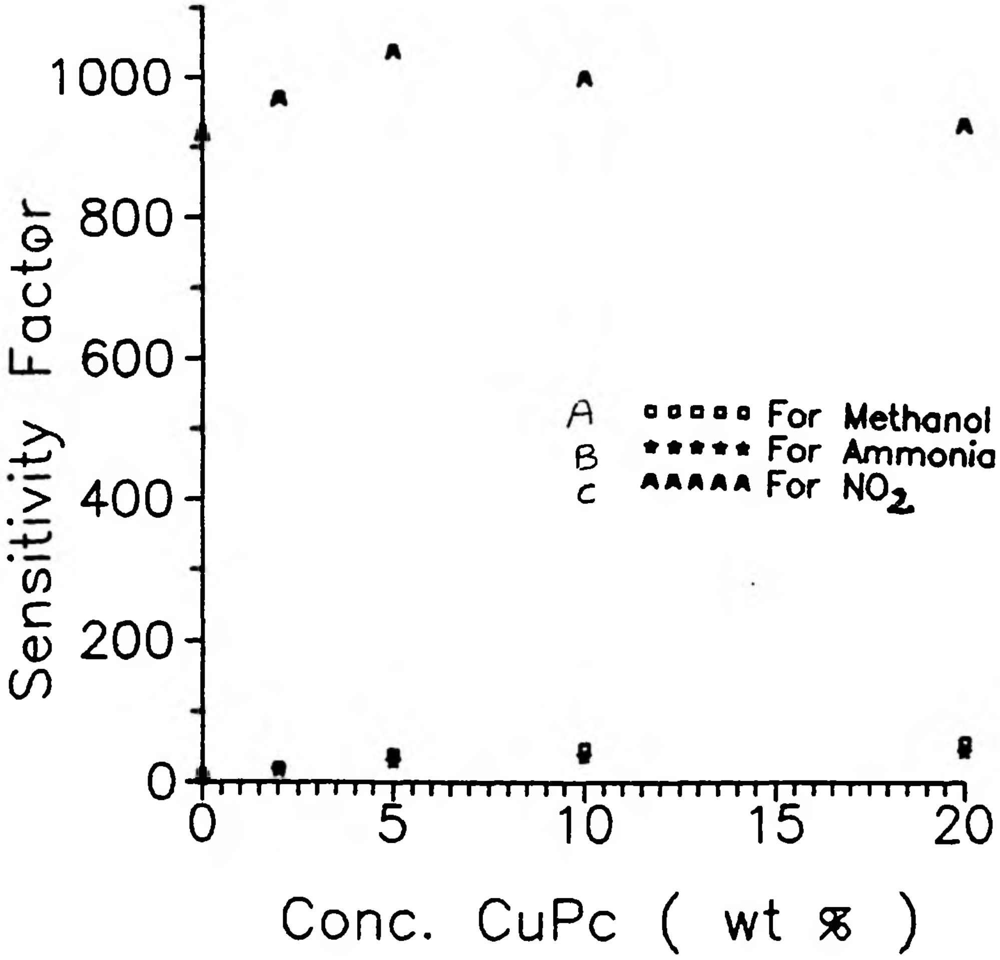


Fig. 3.16: Plots of sensitivity factor versus CuPc concentration for (A) Methanol (B) ammonia and (C) nitrogen dioxide vapors with PANI-CuPc/ PEO/ $CuCl_2$ interdigited electrodes

of methanol, NH_3 and NO_2 respectively. The sensitivity factor S can be calculated using the expression,

$$S = Rv / Ro,$$

Where Rv is the resistance after the exposure to chemical vapour and Ro is the initial resistance.

The sensitivity to methanol vapours was comparatively low (S in the range of 10 to 20) for pure polyaniline sample but almost twice (S = 55 to 65) for the PANI-CuPc samples. The exposure of these samples to ammonia vapour showed slightly higher sensitivity as compared to methanol. However, it is quite interesting to note the tremendous sensitivity of these samples to the vapours of nitrogen dioxide. In this case, the sensitivity factor of about 900 to 1100 was obtained depending upon the phthalocyanine concentration in the polymeric sample. The results obtained from these investigations are compiled in **Table-3.10**.

The action of chemical vapours on such sensor system would proceed as follows. Firstly the PEO-$CuCl_2$ matrix, which is the major component, absorbs the vapour which then has to diffuse through the inter-domain spaces and reach the conducting polymer (polyaniline) moieties. It then interacts with the impurity states in PANI and transfer electronic charge. The transfer of electrons leads to a lowering of the potential barrier at the interface, giving rise to an increase in conductivity (or decrease in resistivity). The enhancement of sensitivity of PANI – CuPc to NO_2 is mainly due to the CuPc groups and there seems to be an optimum concentration required for maximum sensitivity.

TABLE- 3.10

Sensitivity of PANI-CuPc polymers with chemical vapours

Sr. No.	CuPc content Wt. %	Sensitivity Factor (S)		
		Methanol	Ammonia	Nitrogen dioxide
1	0.0	11.0	6.0	100.0
2	2.0	20.0	18.0	970.0
3	5.0	40.0	30.0	1040.0
4	10.0	49.0	37.0	1000.0
5	20.0	57.0	44.0	930.0

3.3.B: PANI-CuPc POLYMERS SYNTHESIZED BY ELECRTOCHEMICAL TECHNIQUE

The electrochemical polymerization of aniline in the presence of phthalocyanine was carried out using 0.2 M aniline in 0.4 M hydrochloric acid in 100 ml of NMP: H_2O (1:1) solvent mixture in a single electrochemical cell. **Section 3.2.B** (this chapter) describes the details of experimental procedures. These films were mainly deposited on two substrates namely gold deposited glass substrates with SBS (styrene-butadiene-styrene) backing material and ITO (Indium-Tin-Oxide) glass substrates. The appearance of dark green colour of polyaniline samples changes to dark bluish green as the phthalocyanine content in the polymer increases.

3.3.B.1: CHARACTERIZATION

(a) FT-IR STUDIES (ECP FILMS)

The incorporation of phthalocyanine in the polymeric backbone was confirmed by the appearance of additional peaks in the co-polymeric sample (**Fig.3.17**) as compared to original PANI. The curves A, B and C correspond to pure PANI, PANI containing 2% and 4% CuPc respectively. The peaks appearing at 1157, 1092, 966, 823.5 and 706 cm^{-1} are assignable to the phthalocyanine skeletal vibrations. The sharp peaks at 1582 and 1498 cm^{-1} are due to quinoid and benzoid rings respectively. The vibrations due to C-N stretching mode are seen at 1313 cm^{-1}. The absence of peak at 1680 cm^{-1} of the C=O vibrations of NMP indicates that the films are free from the solvent used in the synthesis. The peaks obtained for various polymeric samples and their possible assignment were tabulated in **Table-3.11**. These peak positions are in good agreement with the reported values in the literature[215-216]. Thus,

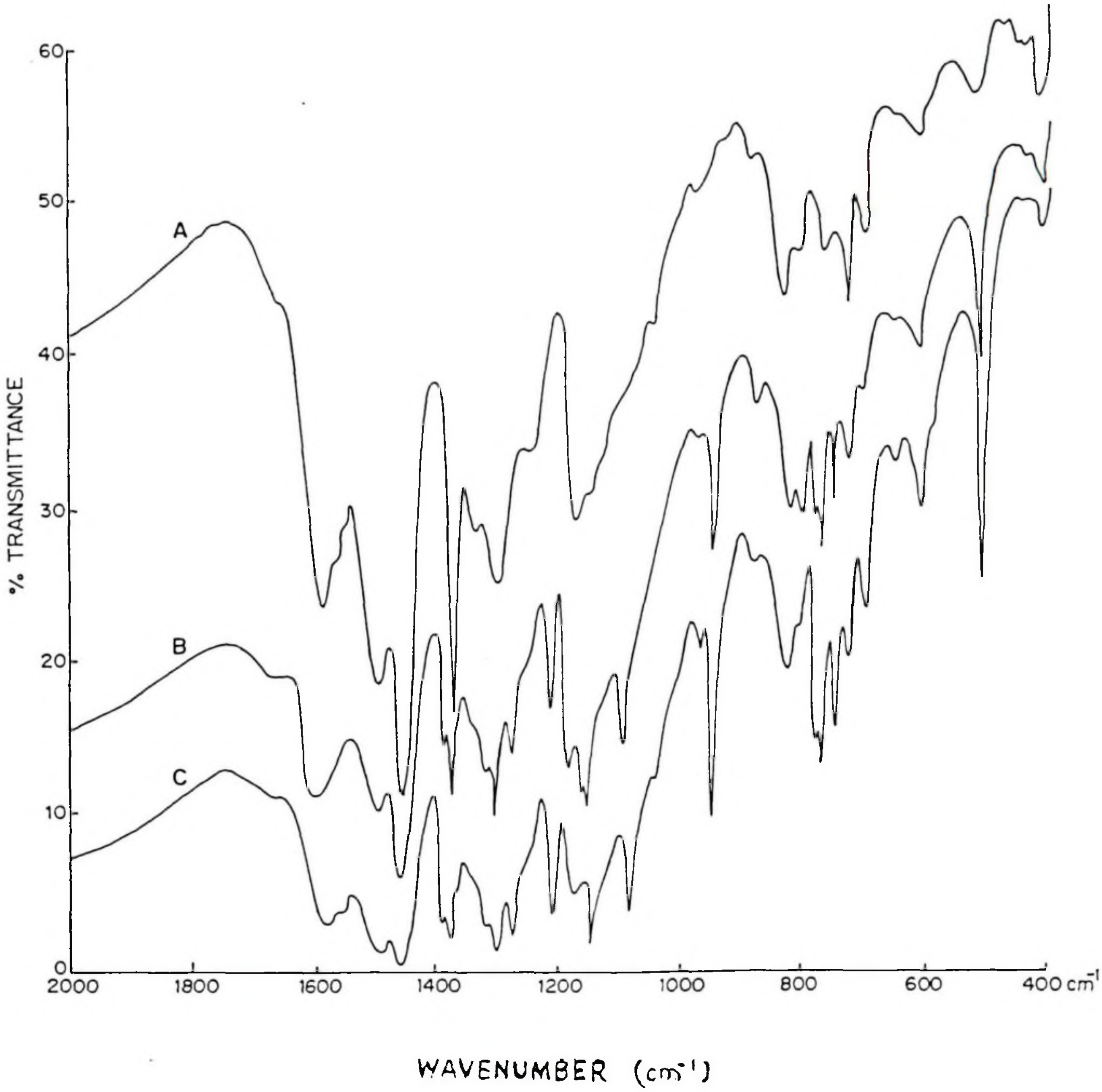


Fig. 3.17 : FT-IR absorption spectrum of PANI-CuPc films

(A) Pure PANI (B) PANI + 2% CuPc

And (C) PANI + 4% CuPc

TABLE- 3.11

FT-IR DATA OF PANI-CuPc FILMS.

Pure PANI Peak cm^{-1}	PANI +2% CuPc Peak cm^{-1}	PANI + 4% CuPc Peak cm^{-1}	Assignment
1654.8	--------	--------	
1585.4	1583.4	1583.4	Quinoid N=Q=N str.
1498.6	1496.7	1494.7	Benzoid N-B-N str.
1456.2	--------	--------	
1307.6	1311.5	1305.7	C-N str.
--------	1259.4	1249.8	Pc skeleton
1145.6	1145.6	1143.7	
--------	1120.6	1120.6	Pc skeleton
--------	1091.6	1089.7	Pc skeleton
966.3	966.3	966.3	
821.6	821.6	821.6	C-H out of plane def.
--------	754.1	754.1	Pc skeleton
--------	719.4	719.4	Pc skeleton

these investigations show that phthalocyanine was incorporated into the polyaniline backbone.

The morphology of these films was checked under optical polarizing microscope, which indicated that all of the polymeric films made by ECP were mainly amorphous in nature. There was a slight change in the shape of X-ray diffraction scans of the PANI-CuPc films but the crystallinity was much less than 5%.

(b) UV-VIS STUDIES (FILMS)

The UV-VIS spectra of polyaniline and PANI-CuPc films deposited on ITO coated glass plates are shown in **Fig. 3.18**. The curves A, B, C and D correspond to samples of pure PANI and PANI polymeric films containing 4%, 6% and 10% CuPc respectively. Polyaniline pure sample shows three absorption peaks: a major absorption peak around 320 nm and two weak ones at 450 and 670 nm respectively. The first one is assignable to π- π^* transitions of the benzenoid ring, while 670-nm absorption is from exciton absorption of the quinoid rings. The phthalocyanine containing co-polymeric samples exhibits rather a broad absorption pattern. They showed absorption bands at 350 nm, 400 nm, 700 nm and 850 nm. These shifts in the absorption spectra can be due to the extended conjugation of electrons in phthalocyanine with polyaniline. The appearance of new absorption peaks at 700 and 850 nm may be due to splitting of Q band structure of phthalocyanine. Thus, UV-VIS spectral analysis indicates that phthalocyanine is indeed coupled with polyaniline backbone in these samples.

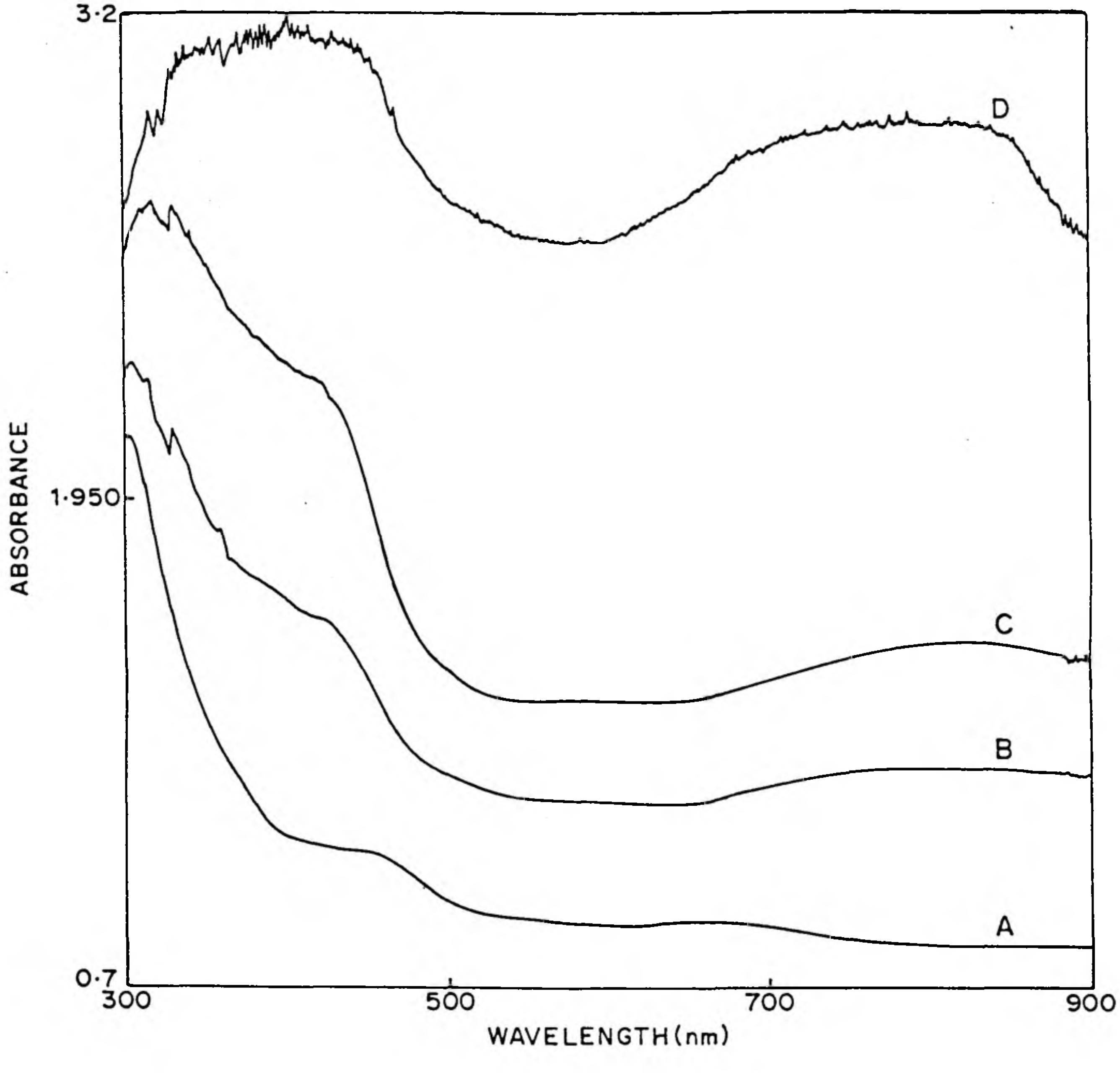


Fig. 3.18 : UV-VIS spectrum of PANI-CuPc films deposited on ITO (A) Pure PANI (B) PANI + 4% CuPc (C) PANI + 6% CuPc And (D) PANI + 10% CuPc

3.3.B.2: CHARACTERIZATION OF STRUCTURE

(a) XPS (ESCA) Studies

The N_{1s} and C_{1s} core level spectra for the films of polyaniline, polyaniline containing 3% CuPc and CuPc (Blue) powder are shown in **Fig.3.19**, which have been designated as FILM-1, FILM-2 and E respectively. The polyaniline film containing phthalocyanine shows the presence of more number of components in the nitrogen spectra than the film of pure polyaniline. The much broader nature of N_{1s} spectra in the films containing CuPc indicates that the phthalocyanine has been incorporated with polyaniline chains. The results for C_{1s} core level deconvoluted peaks and their relative areas are shown in **Table-3.12,** whereas those corresponding to N_{1s} core level spectra with their relative areas are presented in **Table- 3.13.**

The comparison of the N_{1s} core levels of chemically (**Fig.3.6**) and electrochemically (**Fig. 3.19**) synthesized samples shows that the π-π^* contribution in electrochemically prepared PANI is much more than that with chemically synthesized PANI. This suggests that there are many more charged nitrogen species available in the electrochemically synthesized polymeric films than chemically synthesized PANI. Hence, it is expected that the conductivity of these samples should be high. The electrical conductivity data supports these predictions. Further it can be seen that in order to exhibit high conductivity, the chemically synthesized polyaniline requires more amount of phthalocyanine (>10%) than the electrochemically synthesized PANI (3% CuPc). The contribution from the neutral species in chemically synthesized polymer is quite higher than the electrochemically prepared films. The broadening of the peak on the low B.E. side in chemically synthesized materials is associated with the presence of higher number of neutral species, which results in lower conductivity

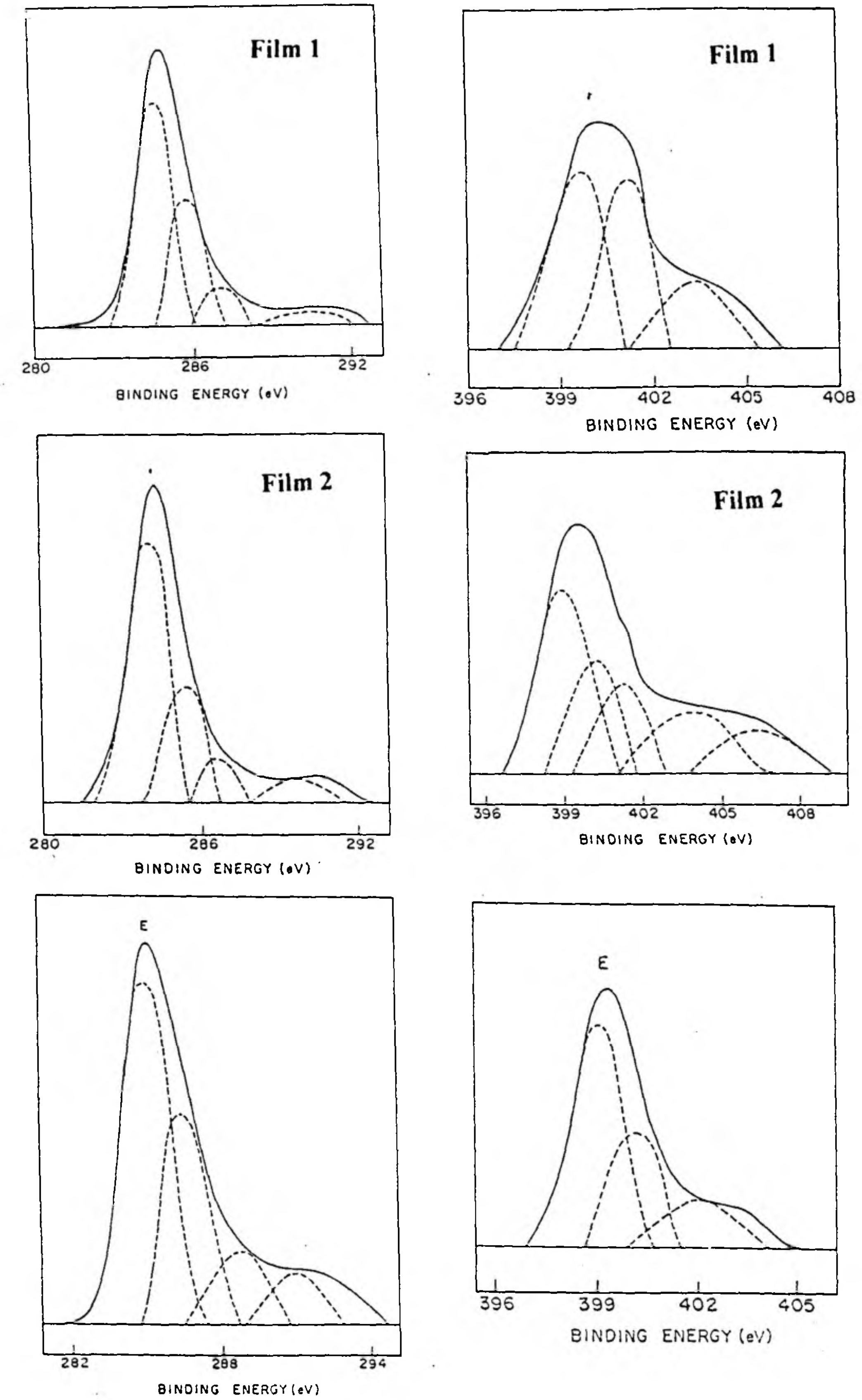


Fig. 3.19 : N$_{1s}$ and C$_{1s}$ core-level spectrum of PANI-CuPc films
(Film 1) Pure PANI (Film 2) PANI + 3% CuPc
And (E) CuPc blue film

TABLE- 3.12

ESCA RESULTS OF C_{1s} LEVEL FOR PANI-CuPc FILMS

Sample Film	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
PANI (**F$_1$**)	C_I = 284.6	1.3	57.55
	C_{II} = 286.0	1.2	29.80
	C_{III} = 287.2	1.3	8.55
	C_{IV} = 290.2	2.0	4.10
CuPc Blue (**E**)	C_I = 284.8	1.8	51.00
	C_{II} = 286.8	2.1	29.70
	C_{III} = 288.8	2.1	11.45
	C_{IV} = 291.0	2.1	7.85
PANI + 3 % CuPc (**F$_2$**)	C_I = 284.7	1.3	61.30
	C_{II} = 286.0	1.9	25.80
	C_{III} = 287.3	1.2	7.50
	C_{IV} = 290.3	2.0	5.40

TABLE- 3.13

ESCA RESULTS OF N_{1s} LEVEL FOR PANI-CuPc FILMS

Sample Film	**Binding energy (in eV)**	**FWHM (in eV)**	**% Area (Relative)**
PANI (F_1)	N_I = 399.7 N_{II} = 401.2 N_{III} = 402.8 N_{IV} = 406.2	2.25 2.12 2.12 3.00	43.3 35.8 12.1 8.8
CuPc (Blue) (E)	N_I = 399.0 N_{II} = 400.2 N_{III} = 402.0	1.75 1.87 2.75	55.0 31.1 13.9
PANI + 3 % CuPc (F_2)	N_I = 399.0 N_{II} = 400.2 N_{III} = 401.2 N_{IV} = 403.8 N_V = 406.2	2.50 2.37 2.37 3.50 2.50	37.2 20.2 15.2 16.7 10.7

of those samples. On the other hand, ECP made films exhibit higher contributions from charged species at higher B.E. regions than the neutral one.

3.3.B.3: MEASUREMENT OF PROPERTIES (ECP FILMS)

(a) ELECTRICAL CONDUCTIVITY

The variation in conductivity of PANI films at room temperature with respect to concentration of phthalocyanine added in the electrolyte is plotted in **Fig. 3.20**. As expected, the conductivity increases as the phthalocyanine content in the electrolyte increases. This effect can be explained on the basis of extended conjugation available due to the addition of macrocyclic moieties such as phthalocyanine in PANI. The doping level increases because of the larger space available for the dopant ions (Cl^- ions in this case) to enter the polymer network which results in higher conductivity for the films containing phthalocyanine as compared to films of pure PANI.

The conductivity measured as a function of temperature for the films containing different amounts of phthalocyanine is depicted in **Fig. 3.21**. The conductivity values obtained are in the range of 10^{-4}-10^{-3} S/cm. These values are lower by 2 orders of magnitudes reported for the PANI films prepared in aqueous protonic acid medium. The source of lower conductivity values observed in the present case has already been explained in the earlier sections. The activation energy (ΔE) was calculated from the slope of the plot of log conductivity versus 1/T, in the same manner as described in **section 3.3.A**. The concentration dependence of the activation energy with respect to CuPc content is shown in **Fig.3.22**. The pure PANI film has activation value as 0.22 eV while the film of PANI containing 4% CuPc shows this value as 0.05 eV. As discussed earlier, these results indicate that the incorporation of CuPc reduces the band gap and /or the activation energy required for charge transport

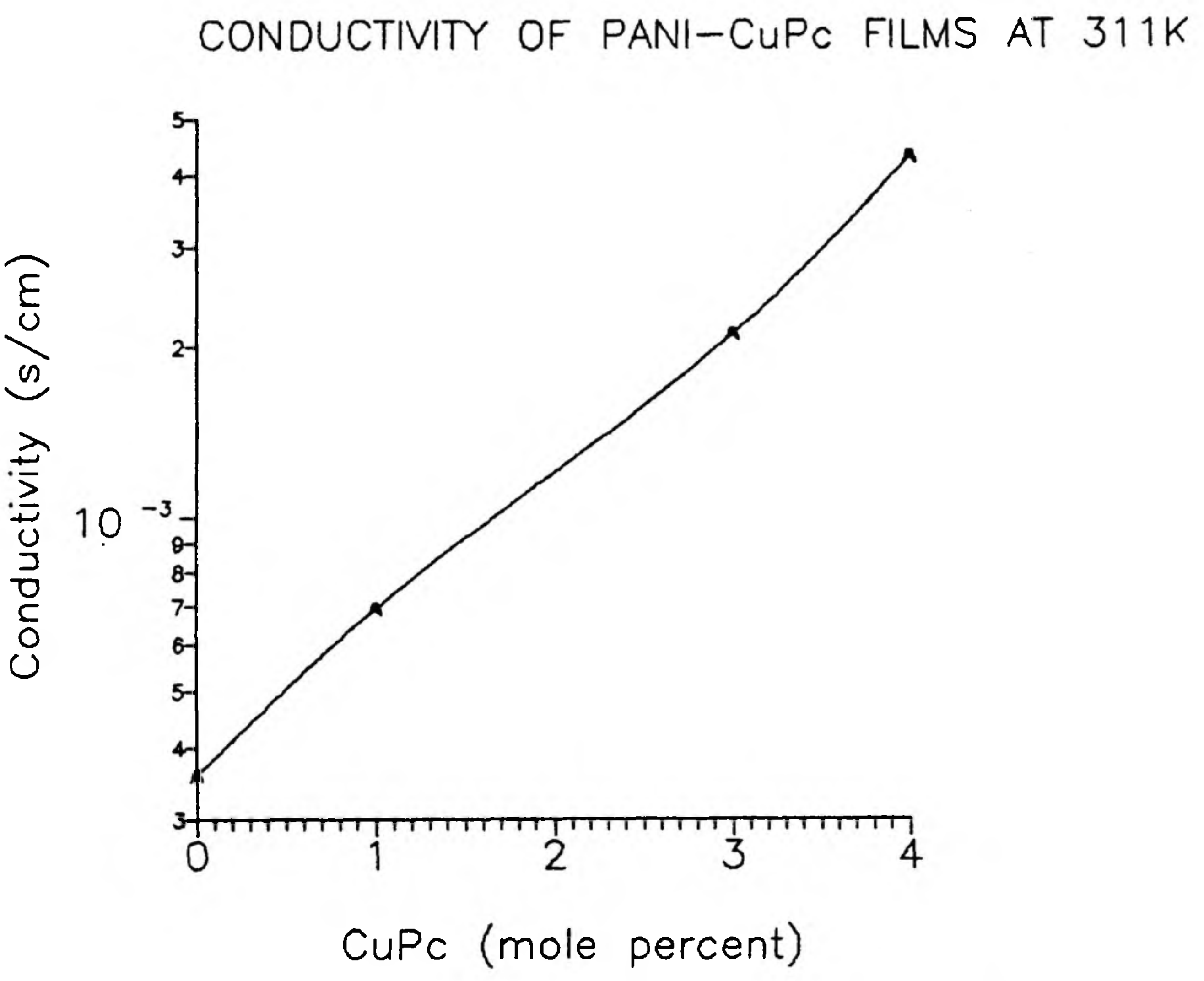


Fig. 3.20 : Plot of conductivity versus CuPc concentration for PANI-CuPc films

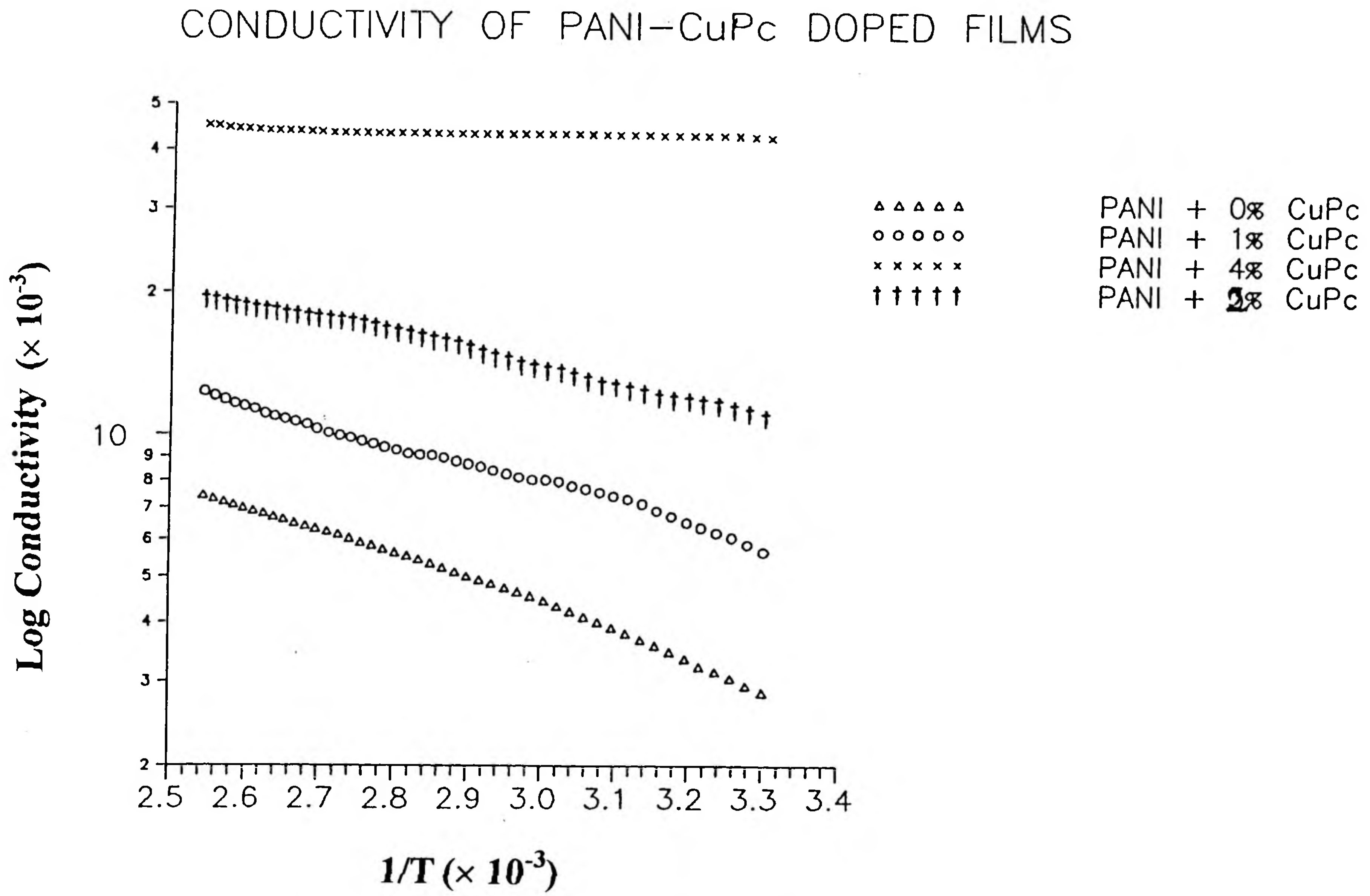


Fig. 3.21 : Plots of log conductivity versus reciprocal of temperature For PANI-CuPc films.

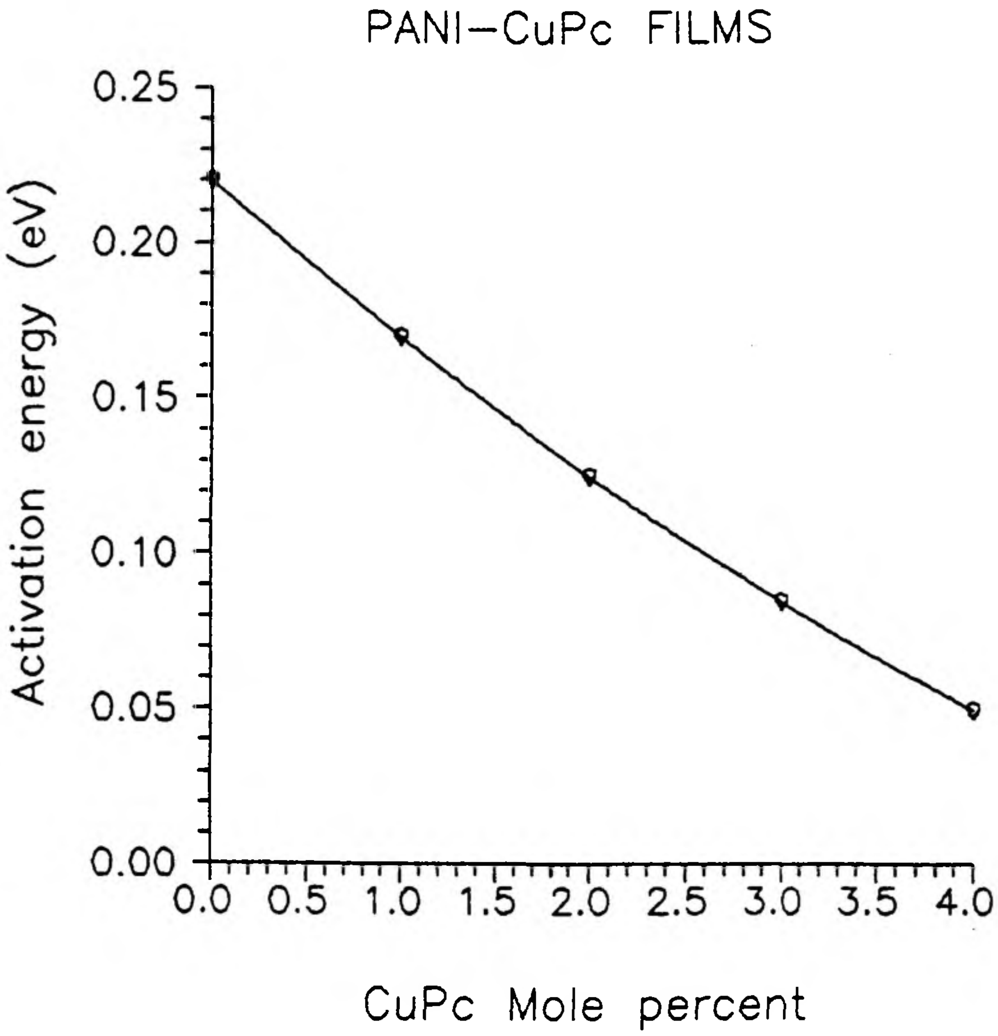


Fig. 3.22 : Plot of activation energy versus CuPc concentration for PANI-CuPc films

in the defect states. This effect has been explained in detailed in **section 3.3.A.5** of this chapter.

(b) CYCLIC VOLTAMMETRIC MEASUREMENTS (FILMS)

Cyclic voltammograms of PANI and PANI-CuPc films obtained in an aqueous solution of 0.1 M HCl are shown in **Fig. 3.23**. The curves A corresponds to pure PANI film and curve B corresponds to PANI containing 3% CuPc. From these curves it can be observed that with the phthalocyanine addition the electrochemical activity of PANI is increased much above the original. The repeated cycles do not show any shifts in the peak positions, which means that the doping and de-doping processes are reversible. The incorporation of macromolecule such as phthalocyanine allows the dopant ions to penetrate through the large conjugated system and electron migration becomes much faster, resulting into the increase in the currents tremendously. The increase in peak height is more profound in CuPc containing PANI films, which indicates that these films contain more charged species. The XPS analysis of these samples showed that the CuPc containing PANI films have more charged species.

Cyclic voltammograms of PANI and PANI-CuPc films obtained in propylene carbonate containing 0.1 M $LiClO_4$ are depicted in **Fig.3.24**. Curve A represent pure PANI film while curve B represents PANI containing 3% CuPc film. From these curves it can be seen that the cathodic currents are much higher in the films containing CuPc. This observation is typical for the phthalocyanine compounds, which also exhibit electrochromism [217].

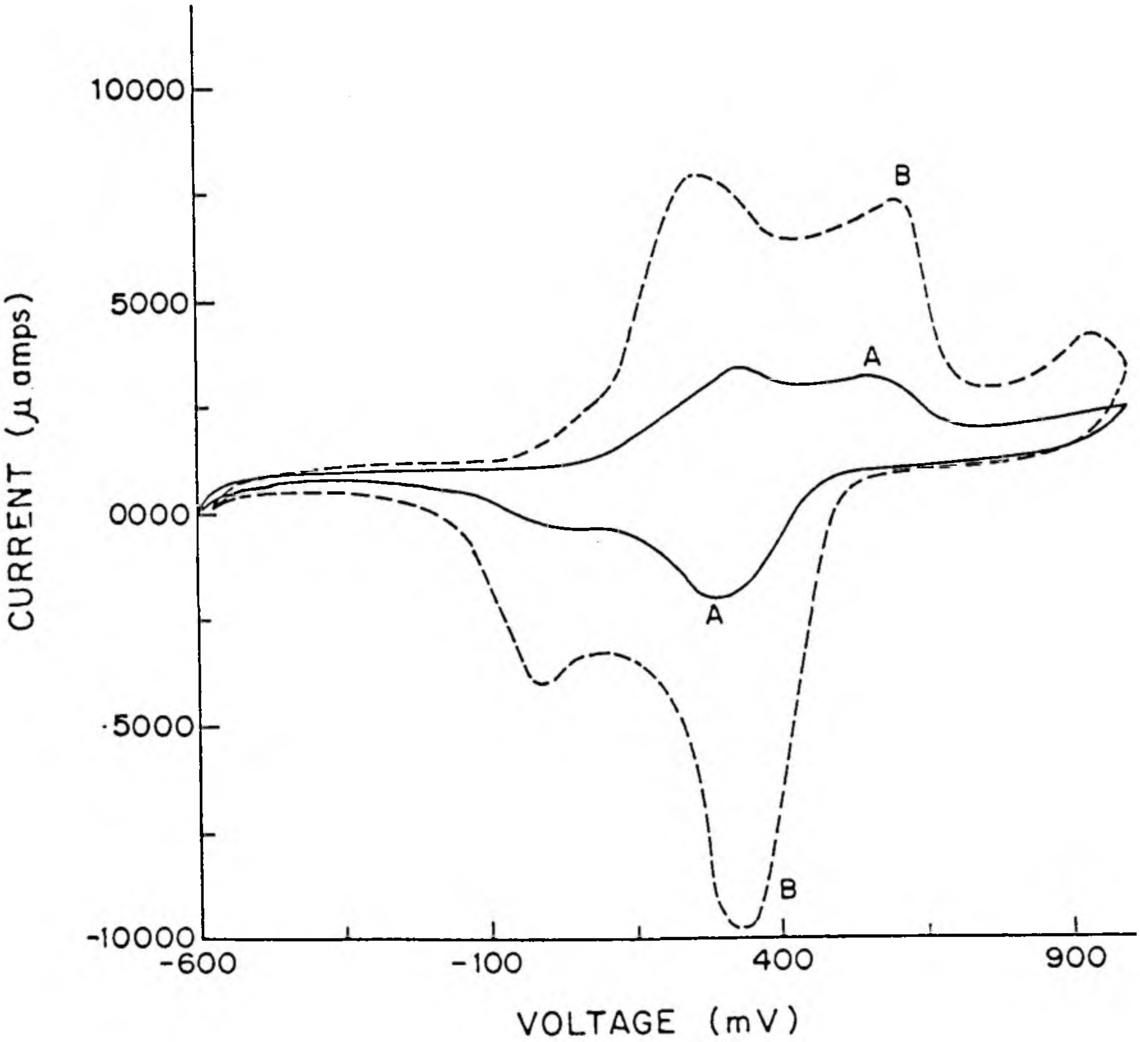


Fig. 3.23 : C-V Measurements of PANI-CuPc films in 0.1 M HCl

(A) Pure PANI and (B) PANI + 5% CuPc

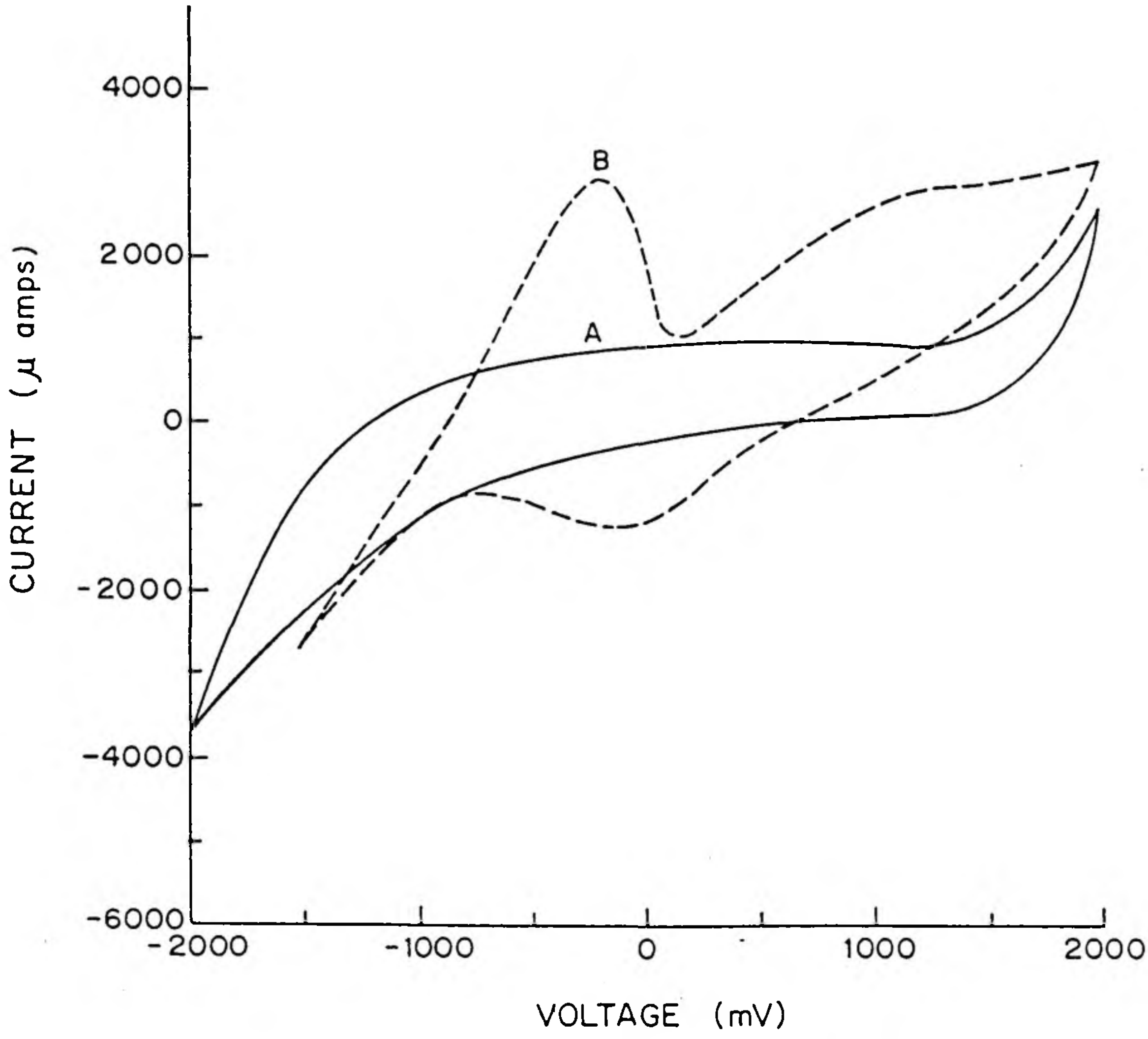


Fig. 3.24 : C-V Measurements of PANI-CuPc films in 0.1 M $LiClO_4$

(A) Pure PANI and (B) PANI + 5% CuPc

(1) Effect of Light

In order to study the effect of light on the electrochemical characteristics of these films, their C-V's were recorded in aqueous 0.1 M HCl with and without illumination. The **Fig. 3.25**, **Fig. 3.26** and **Fig. 3.27** represents the cyclic voltammograms for the films of PANI, PANI + 2% CuPc and PANI + 3% CuPc respectively. The terms D and L designate the C-V in the dark and under illumination respectively. From these voltammograms it can be seen that, as such pure PANI film does not show much photosensitivity. On the other hand, the incorporation of phthalocyanine into these films even to a small extent (2%) gives a noticeable increase in the currents under illumination. As the concentration of phthalocyanine is increased, the photo-generated current was almost four times higher than that obtained for pure PANI film. The increase of photo-generated current as compared to the dark current for the PANI, PANI – CuPc containing 2% and 4% CuPc was 7%, 10% and 16.6 % respectively. Thus, from these studies it can be concluded that the presence of phthalocyanine into PANI polymeric chains makes it photo-electrochemically active.

3.4 CONCLUSION

The chapter describes the incorporation of phthalocyanine into polyaniline matrix by chemical and electrochemical methods. Their physical appearances were studied. The powder samples were green in colour and as the phthalocyanine content increases they becomes darker and darker. The electrochemically synthesized PANI films were dark green in colour. As these were functionalized with phthalocyanine, their colour changes to dark bluish green. FT-IR and UV-VIS analysis confirmed the incorporation of phthalocyanine into the polymer matrix. The polymers were characterized using wide angle X-ray diffraction technique. It was found that the crystallinity increases with the increase of CuPc concentration. The new modified

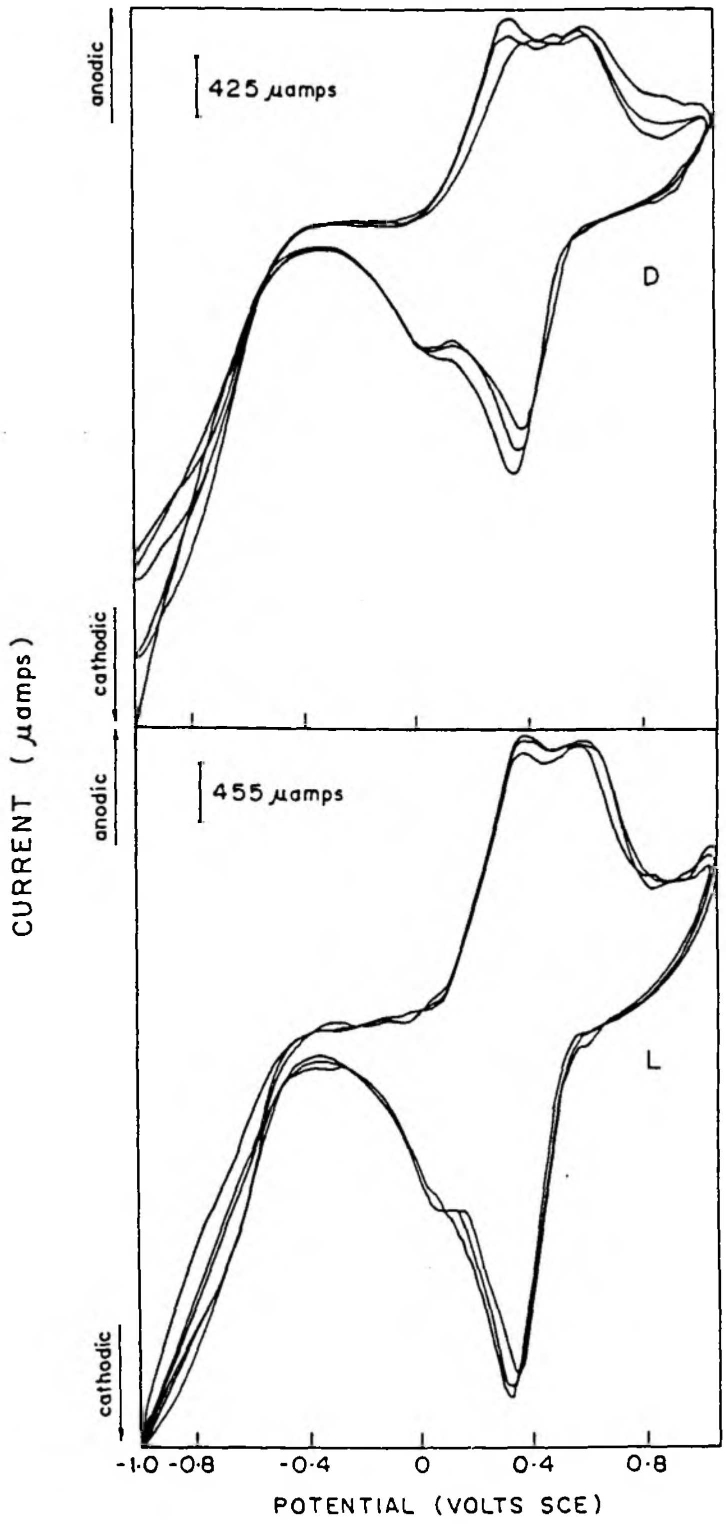


Fig. 3.25 : C-V Measurements of pure PANI film in 0.1 M HCl (D) in dark and (L) under illumination

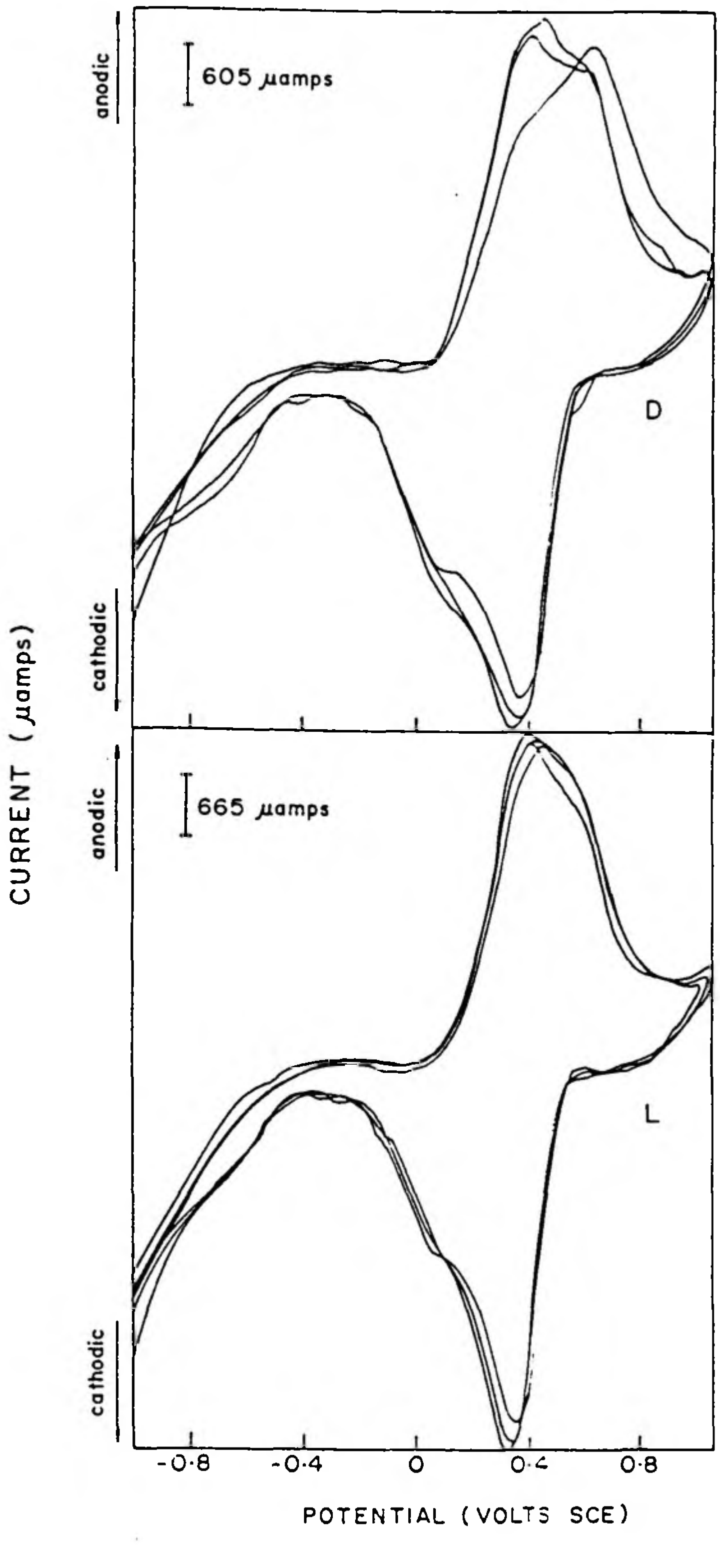


Fig. 3.26 : C-V Measurements of PANI + 2% CuPc film in 0.1 M HCl (D) in dark and (L) under illumination

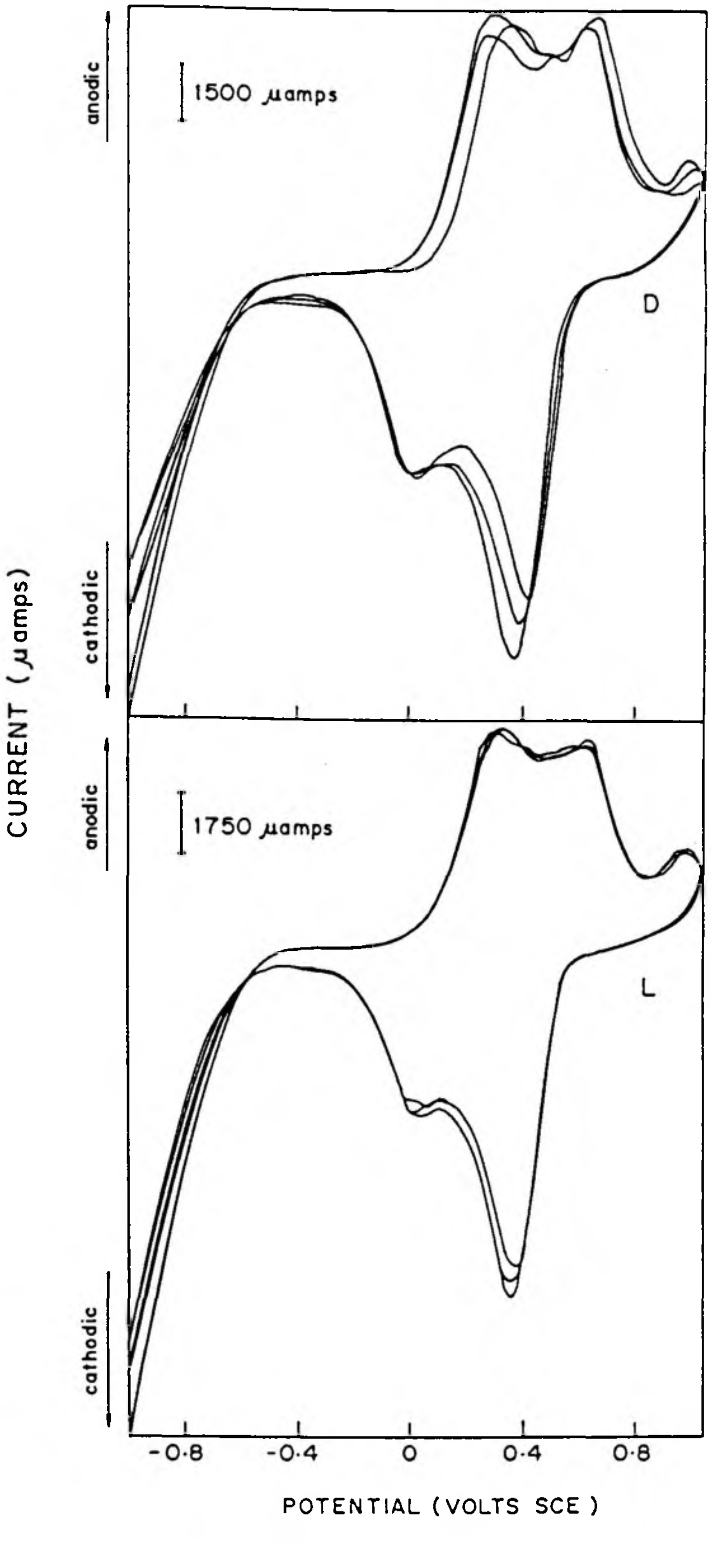


Fig. 3.27 : C-V Measurements of PANI + 3% CuPc film in 0.1 M HCl (D) in dark and (L) under illumination

orthorhombic crystal structure has been assigned with lattice parameter as a = 15.3, b = 16.5 and c = 20.8 A°. XPS (ESCA) studies were carried out to evaluate the various chemical constituents in these polymers as well as polymeric films. It was found that the various species of C_{1s}, N_{1s}, Cl_{2p} and Cu_{2p} were present in these polymeric compounds. XPS studies also showed that, with the increase in CuPc content in the PANI results in more doping i.e. more charged species were seen.

Thermal analysis of the synthesized polymers showed that the thermal stability of PANI in nitrogen atmosphere increases as the CuPc content increases. The peculiarity lies in the fact that even in the static air medium, the thermal stability increases as the CuPc content increases in PANI chains. The change in the electrical conductivity as a function of temperature was thoroughly studied for this system. It was found that the electrical conductivity increases as temperature increases. This is a characteristic behaviour of a semi-conducting material. The effect of CuPc addition on the conductivity behaviour was studied. It was found that the electrical conductivity increases as CuPc content in the polymeric chain increases. This increase was about 2-3 orders of magnitudes (10^{-5} to 10^{-2} S/cm). The overall conductivity obtained is still lower than the conductivity reported for the PANI synthesized in aq. HCl systems. The lower conductivity obtained in our system was discussed in terms of the solvent used. The solvent used in our system is NMP: H_2O (1:1). It was reported that NMP has a tendency to form hydrogen bonding with the water present in the system. This will cause a steric hindrance for the doping process in acidic medium, resulting in getting slightly lower conductivity values. A similar type of behaviour was seen in the electrochemically-synthesized films. When we compare the electrical conductivity of powder samples and the films, it was found that the electrical conductivity in case of films were higher than that of powder samples by about two orders of magnitudes. The studies on the temperature dependence of conductivity show that it has a complex conduction mechanism. The probable mechanism thought to be a polaron and bipolaron effect at lower temperatures and it shows variable range hopping (VRH) effect at higher temperatures.

Cyclic voltammetric measurements showed that these materials are photosensitive in presence of CuPc. These studies also showed that the doping and dedoping processes in this type of polymers are reversible. Repetitive cycles in various electrolytes do not change the peak positions, which is indicative of the electrical stability of these polymers. The possibility of use of these polymers into gas sensors has been exploited by checking its sensitivity towards various chemical vapours such as ammonia, alcohol and nitrogen dioxide. It was observed that among all these chemical vapors, nitrogen dioxide shows maximum gas sensitivity, with a sensitivity factor of about 1000-1100. The microanalysis studies showed that as the CuPc concentration increases the doping level of the parent conducting polymer i.e. PANI increases. It also provides an idea about structural arrangements in the polymeric chains.

Thus, incorporation of phthalocyanine into PANI gave interesting polymeric compounds, which has a better conductivity and thermal stability. Direct incorporation of macromolecules (such as phthalocyanine) into polymeric backbone by electrochemical means is probably reported first time in this study.

CHAPTER-IV

POLYPYRROLE FUNCTIONALIZED WITH PHTHALOCYANINE

POLYPYRROLE FUNCTIONALIZED WITH PHTHALOCYANINE

4.1: INTRODUCTION

Amongst the known conducting polymers, polypyrrole (PPy) is the most frequently studied material for a variety of applications, due to the long-term stability of its conductivity and the possibility of forming copolymers or composites with optimal mechanical properties. One of the great advantages of PPy (polypyrrole), from a synthetic point of view, concerns the low oxidation potential of the pyrrole monomer.[218] Pyrrole is one of the easily oxidised monomers and hence a variety of oxidising agents are available for preparing PPy. In addition, polypyrroles are obtained directly in a conducting state, because the polymer oxidation occurs during synthesis with the polymerisation initiator compounds acting as doping agents. There are several reports in the literature, which mention the use of transition metal ions as oxidising agents for pyrrole polymerization[219-223]. Ferric salts are most commonly used for this purpose.

Not much work has been reported in the field of co-polymerisation of PPy. A slight improvement in the mechanical properties of PPy has been achieved by the co-polymerisation of pyrrole with styrene[224]. Random co-polymers have been reported by electropolymerization of a mixture of terthienyl derivatives and pyrrole[225]. The thiophene-pyrrole block co-polymers showing electrical and electrochemial properties intermediate between those of PPy and PT (polythiophene) has been reported by electropolymerization of 2-2' thienylpyrrole [226].

Recently, a great deal of attention has been given to the electrochemical preparation of a number of polypyrroles, utilising a variety of ionic complexes and polyelectrolytes as the electrolytes which serve as charge - balancing dopant anions during electropolymerization. This has led to a new class of multicomponent materials with controllable electrical, mechanical, electrochemical, catalytic ion-binding and ion-releasing properties. These approaches include the preparation of PPy containing Ru-bipyridine complexes[227], naphthoquinone and benzoquinone groups[228], complexes with metallotetraphenyl-porphyrin[229] and phthalocyanine complexes[230] etc.

Metal phthalocyanine complexes have been widely studied for their electrochemical[231-232], electrocatalytic[233-234], photocatalytic[235], non-linear optical[236] and photo electrochemical properties[237]. Polypyrrole, containing metal phthalocyanine complexes, is thus a potential electro switchable, multifunctional material for modified electrodes. Various research groups have focused their interest on the stability of such polymers[238]. All these reports on metallophthalocyanine complexes mainly concern with the complexes soluble in aqueous media due to carboxyl groups being attached at the sides. In the present study emphasis was given on incorporation of phthalocyanine in conducting polypyrrole in an organic solvent medium. This study was focused mainly on the effect of incorporation of phthalocyanine into polypyrrole on its electrical conductivity, thermal stability, photosensitivity and chemical gas sensitivity.

The present chapter describes the preparation of polypyrrole (PPy) and polypyrrole incorporated with phthalocyanine (PPy-CuPc) materials. There are two methods used to synthesize these materials namely: (1) Chemical and (2) Electrochemical polymerisation. The chemical synthesis method using various oxidising agents and their characterisation was discussed in Section A. The various property measurements such as structure characterisation by X-ray, surface modification by ESCA along with its application as chemical sensor were also discussed in this section. The electrochemical method employed for the PPy-CuPc film deposition was described in detail in Section B. The section B also deals with the characterisation of the films using FT-IR, UV-VIS studies. The property measurements such electrical conductivity, cyclic voltammetry and chemical sensitivity for these films were discussed in length in the same section. The conclusions drawn from the present study on incorporation of phthalocyanine into polypyrrole matrix has been presented at the end of the chapter.

4.2: EXPERIMENTAL

4.2.A: CHEMICAL METHOD

Preparation of polypyrrole functionalized with CuPc

(A) Reactions using $FeCl_3$ as oxidising agent

In a 250-ml beaker, 100-ml NMP: H_2O (1:1) mixture was taken in which 4.875 grams (0.3 M) $FeCl_3$ anhydrous powder was dissolved carefully [exothermic]. Reaction mixture was cooled to room temperature. With the help of addition funnel, 0.67 grams (0.01 M) pyrrole monomer was added drop wise in to the reaction mixture with constant stirring. As soon as addition of pyrrole progresses, the initial yellow colour of the solution becomes progressively dark. After about an hour the solution becomes dark green or black. The reaction mixture was kept at room temperature for about 24 hours to ensure complete oxidation of pyrrole monomer into polymer.

In a similar set of experiments, varying amounts of phthalocyanine [CuPc green] were added to the reaction mixture ranging from 1.0 to 4.0 mole percent with respect to pyrrole monomer, the other conditions being same as above. The reaction mixture was poured into 500-ml distilled water and stirred well. It was filtered by conventional method and the product was washed several times with distilled water till the filtrate obtained was colourless. The solids were suspended in 250-ml methanol, filtered and washed with additional 50-ml methanol. The polymers were dried at room temperature for 48 hr. and then they were preserved in the desiccator. The yields obtained were 40 to 70 % based on the initial monomer taken. The chemical synthesis data obtained from various experiments are tabulated in **Table-4.1**.

(B) Reactions using $K_2S_2O_8$ as oxidizing agent

In a 250-ml beaker, 100-ml NMP: H_2O (1:1) mixture was taken in which, 5.4 grams $K_2S_2O_8$ [0.02 M] was dissolved completely (slight warming is necessary). The reaction mixture was cooled to room temperature (28°C). To this solution, then 0.67 grams pyrrole monomer [0.01 M] was added drop wise in 15 minutes. As the time progresses the colour of the reaction mixture becomes dark. The reaction mixture was kept under stirring at room temperature for 18 hours.

Reaction mixture was diluted with 100-ml distilled water and the precipitated Polymer was filtered using vacuum filtration method. The polymer was washed with distilled water till the filtrate obtained was colourless. Finally the polymer was washed with 100-ml methanol and dried at room temperature for 48 hours. The yields obtained were 80-100 %. The chemical synthesis data using $K_2S_2O_8$ is presented in **Table-4.2.**

4.2.B: ELECROCHEMICAL METHOD

Preparation of PPy-CuPc films

Initially, glass slides or PET transparencies were gold deposited by thermal evaporation deposition technique (in vacuum) as described in detailed in chapter II. These substrates were used as working electrodes in deposition of PPy-CuPc films.

TABLE- 4.1

Chemical Synthesis Data of PPy-CuPc Polymers

A: Reactions Using $FeCl_3$ As Oxidizing Agent

Serial Number	Pyrrole Taken Grams	$FeCl_3$ Taken Grams	CuPc Taken Grams	$FeCl_3$/Pyrrole Mole ratio	% Yield
1	0.67	1.625	-----	1:1	25.3
2	0.67	1.625	0.072	1:1	30.8
3	0.67	1.625	0.143	1:1	35.0
4	0.67	1.625	0.214	1:1	47.2
5	0.67	4.875	-----	3:1	40.8
6	0.67	4.875	0.143	3:1	55.0
7	0.67	4.875	0.285	3:1	70.5

Solvent: NMP: H_2O (1:1), 100 ml for each experiment.

Reaction temperature: Room temperature (27°C)

Reaction Time: 4 Hours

TABLE- 4.2

Chemical Synthesis Data of PPy-CuPc Polymers

B: Reactions Using $K_2S_2O_8$ As Oxidizing Agent

Serial no.	Pyrrole Taken Grams	$K_2S_2O_8$ Taken Grams	CuPc Taken Grams	$K_2S_2O_8$/Pyrrole Mole ratio	% Yield
1	0.67	5.4	-----	2:1	77.23
2	0.67	5.4	0.143	2:1	90.00
3	0.67	5.4	0.214	2:1	100.00
4*	0.67	5.4	-----	2:1	100.00

Solvent: NMP: H_2O (1:1), 100 ml for each experiment.

Reaction temperature: Room temperature (27°C)

Reaction Time: 4 Hours

*** Reaction in distilled water**

The electrolytic bath containing 2.15-ml (0.4 M) conc. H_2SO_4 in 100 ml NMP: H_2O (1:1) mixture was prepared to which pyrrole monomer (2.8 grams or 0.4 ml) was added with stirring. The desired amounts of CuPc say 1, 2, 3 and 4 % (mole percent per monomer) phthalocyanine blue, was added to the electrolyte with constant stirring. The electrolytic cell comprised of a single compartment cell containing SCE (Saturated Calomel electrode), platinum foil as a counter electrode and gold coated PET film or glass plate substrates as a working electrode. The deposition of polymeric films was carried out at the constant potential of + 700 mV for a fixed time such as 120, 180, 240 or 300 seconds with the help of computer controlled potentio-galvanostat [Vibrant EC 2010 model] so as to obtain films of different thickness.

The deposited films were then rinsed successively in NMP: H_2O mixture and distilled water a number of times. The films were allowed to dry at room temperature for 24 hours. These films were then characterised by UV-VIS and FT-IR spectroscopy. The cyclic voltammetric measurements were recorded in the electrolytes such as 0.1 N KCl, 0.1 N $LiClO_4$ and 0.1 N KI/I_2 solutions. The conductivity of the deposited films was measured as a function of temperature and CuPc concentration using Keithley electrometer.

4.3: RESULTS AND DISCUSSION

4.3.A: PPy-CuPc Polymers by Chemical Method

The polymerisation of pyrrole monomer was carried out using $FeCl_3$ as oxidizing agent in the NMP: H_2O solvent mixture, as described in detail in **section 4.2 A**. The polymers obtained after purification were dark green/black in colour. The yields of polymers were 25-30% based on the monomer taken. The monomer to oxidant mole ratio has an effect on the product yield. When monomer/oxidant ratio equal to 1.0 was used, moderate yields were obtained in the range of 25% to 50%. If this ratio was maintained as 1:3 then significant increase in the product was observed. With this reactant ratio, the yields obtained were between 40 to 70 %. The reaction carried out in distilled water alone gave a product yield of 50%. Sak-Bosnar et.al.[239] have reported chemical polymerisation of PPy using $FeCl_3$ and $CuCl_2$ as oxidizing agents in aqueous medium. These authors obtained the yield of 49.7% and 95.0% for the $FeCl_3$/monomer ratios of 1:1 and 3:1 respectively.

The reaction carried out with ferric nitrate [$Fe(NO_3)_3$] as an oxidizing agent gave same yield as obtained with ferric chloride. When pyrrole oxidation was carried out in the presence of potassium per sulphate ($K_2S_2O_8$) as oxidizing agent in the 1:2 mole ratio of monomer/oxidant in the same solvent (NMP: H_2O 1:1), almost quantitative yield was obtained. Thus, oxidation of pyrrole is greatly affected by the oxidizing agent, it's mole ratio with monomer and solvent used. The reaction using $K_2S_2O_8$ was carried out to compare the yields using this oxidizing agent with the reaction using $FeCl_3$. In PANI, similar oxidizing agent i.e. $(NH_4)_2S_2O_8$ was used for polymerisation. Although $K_2S_2O_8$ gave better yields, it was preferred to carry out further studies using $FeCl_3$, since this oxidizing agent is report to impart the highest conductivity in PPy. It is interesting to study the polymerisation of these two chemically different entities i.e. pyrrole and aniline with the same oxidizing agent. In aniline –NH group is on the side chain of aromatic rings whereas in pyrrole it is in the hetero atomic ring itself. In the case of aniline, the –NH groups are flanked in between aromatic rings which will have some steric hindrance in the polymerisation, whereas in the case of pyrrole there will be less hindrance and in fact more reactive sites are available for polymerisation to occur. Another fact in choosing $FeCl_3$, as oxidizing agent is that the oxidised product is Cl doped one. The incorporated macromolecule such as phthalocyanine is reported to have better interaction with this dopant ion. Hence, it is expected to give polymer with better conductivity.

Another interesting factor lies with the effect of addition of phthalocyanine into the polymerisation reaction on its yield, electrical conductivity etc. It was observed that as the phthalocyanine content increases from 1 to 4 mole percent, the polymer yield also increases. The polymeric chains of polypyrrole when functionalized with macrocyclic molecules such as phthalocyanine at the end groups have much higher electron withdrawing capacity/reactivity than homopolymer. This can result in high yields with the increase of CuPc concentration. Similar type of effect was observed in the polymerisation of aniline as discussed in chapter-III of the present thesis.

4.3.A.1: CHARACTERIZATION

(a) FT-IR STUDIES

The functionalization of pyrrole with phthalocyanine was confirmed with FT-IR analysis of these polymers. The FT-IR spectrum for the solid samples of polypyrrole containing phthalocyanine in KBr is shown in **Fig. 4.1**. The absorption peaks observed and their possible assignments are tabulated in **Table 4.3.** The values obtained for the PPy and CuPc skeletal modes are well matched with the reported values of PPy[240] and CuPc[241] respectively. The polymers exhibit IR bands at 1151, 1095, 770 and 509 cm^{-1}, which are assignable to the phthalocyanine skeletal motions. Additionally, the 1556, 1464, 1305, 1211, 1047, 968, 931.6, 800, 721, 682 and 617 cm^{-1} bands are also seen which are characteristic bands of polypyrrole. The absence of C-Cl band at 650 cm^{-1} in the PPy-CuPc samples indicates that the incorporation of phthalocyanine occurs via the Cl groups attached to CuPc green. However, the spectrum of the polymer is characterised by the loss of fine structures and lowering of the intensities of the bands as compared to those for parent polypyrrole. It may be

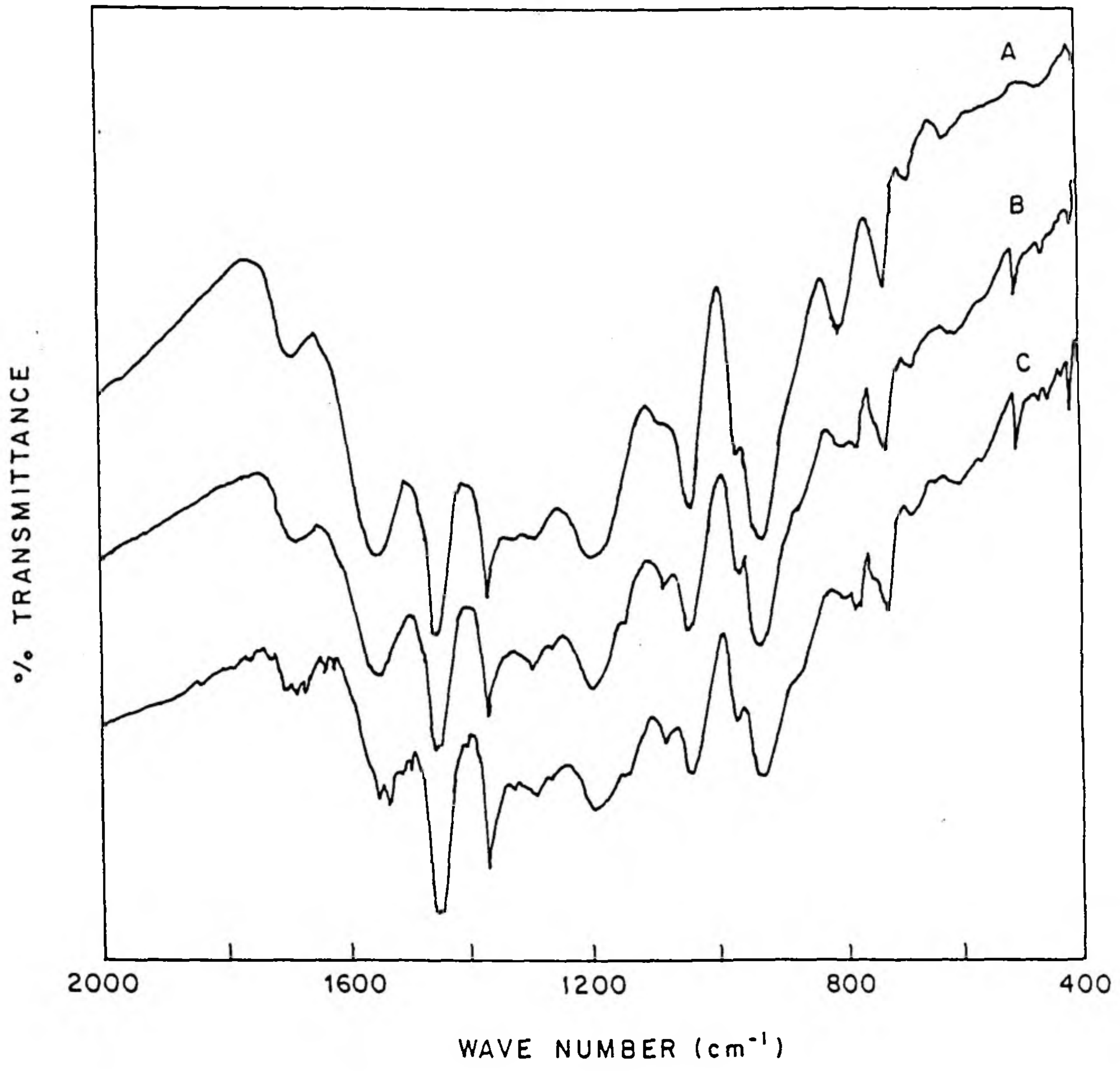


Fig. 4.1 : FT-IR absorption spectrum of PPy-CuPc powder samples
(A) Pure PPy (B) PPy + 2% CuPc
and (C) PPy + 4% CuPc

TABLE- 4.3

FT-IR Absorption Data of PPy-CuPc Polymers.

PPy Pure Peak cm $^{-1}$	**PPy + 2% CuPc Peak cm $^{-1}$**	**PPy + 4% CuPc Peak cm $^{-1}$**	**CuPc Green Peak cm $^{-1}$**	**Assignment**
1682.0 (s)	1697.0 (m)	1697.0 (m)	-	C = O 0f NMP
1556.4 (s)	1556.4 (s)	1548.0 (m)	1556.0 (w)	-
1464.0 (s)	1464.0 (s)	1456.2 (s)	1470-45 (br)	C-C Vib.
-	-	-	1392-85 (br)	C-C Vib.
1377.1 (s)	1377.1 (s)	1377.1 (s)	1378.0 (br)	C-C Vib.
1304.0 (w)	1302.0 (w)	1300.0 (w)	1305.0 (m)	C-N str.
-	-	-	1277.0 (m)	-
1211.0 (br)	1209.3 (br)	1207.4 (br)	1215.0 (s)	C = N str.
-	1151.4 (w)	1151.4 (w)	1151-80 (br)	Pc skeleton
-	1095.0 (m)	1095.0 (m)	1095.0 (s)	C-H bend.
1047.3 (s)	1047.3 (s)	1045.3 (s)	-	-
966.0 (m)	968.0 (m)	968.0 (m)	968.0 (w)	C-H Vib.
-	-	-	949.0 (s)	C-H str.
931.6 (s)	931.6 (s)	931.6 (s)	-	-
796.5 (s)	800.0 (w)	800.0 (w)	-	-
-	777.3 (w)	777.3 (w)	770.0 (s)	C-H Vib.
721.3 (s)	723.3 (s)	721.3 (s)	721.0 (m)	C-H Vib.
682.8 (w)	682.0 (w)	682.8 (w)	690.0 (w)	N-H Vib.
617.2 (w)	603.0 (w)	603.7 (w)	605.0 (m)	-
-	509.2 (s)	509.2 (s)	-	-

mentioned here that although the dopant is Cl^- in the present case, it is not bonded chemically and therefore, it will not contribute to C-Cl band in IR.

(b) UV-VIS STUDIES

The **Fig. 4.2** shows the UV absorption peaks of the PPy-CuPc samples in dilute sulfuric acid. The pure polypyrrole sample (D) shows two broad absorption peaks at 360 and 840 nm. The curves A, B and C correspond to PPy containing 4%, 2% and 1% of phthalocyanine powder samples respectively. However, the phthalocyanine containing polypyrrole samples (A, B and C) exhibits multiple strong absorption peaks at 380, 620, 650, 720 and 850 nm. The appearance of these multiple peaks and their increase in intensity is indicative of coupling of the phthalocyanine with the parent polymer polypyrrole. Thus, both the FT-IR and UV-VIS studies reveals that phthalocyanine has been incorporated into PPy polymeric chains.

(c) MICROANALYSIS

In order to confirm the chemical compositions of various polymers synthesised, their microanalysis was carried out. The atomic percentage ratios of the elements present in various polymers along with their expected values for typical empirical formulae are shown in **Table-4.4**. From these results, it can be seen that pure polypyrrole sample show the elemental composition as $(C_4H_3N)_3(Cl)$ with calculated values as C = 62.47, H = 3.90, N = 18.22 and Cl = 15.40 which are well matched with observed values as C = 70.62, H = 5.35, N = 18.22 and Cl = 5.81. The Cl content is much lower than the calculated value as this is a high molecular weight fraction of the polymer. The distribution of available dopant ions over this large polymer results in getting lower value for the Cl. The elemental analysis of the PPy sample containing

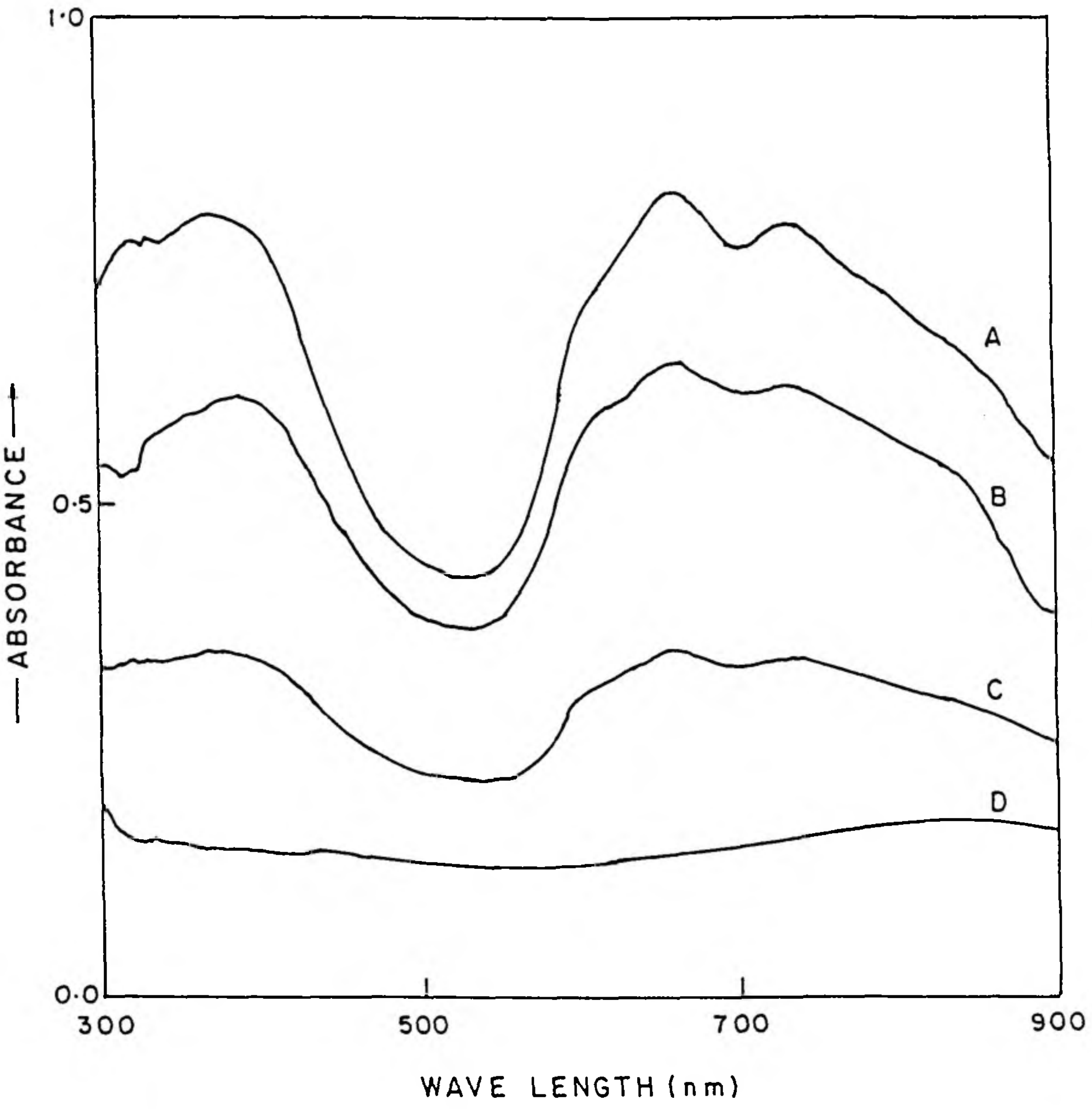


Fig. 4.2 : UV-VIS absorption spectrum of PPy-CuPc powder samples in dil. H_2SO_4. (A) PPy + 4% CuPc (B) PPy + 2% CuPc (C) PPy + 1% CuPc and (D) Pure PPy

Table-4.4

Microanalysis data of PPy-CuPc polymers

Elements	Pure PPy		PPy+2%CuPc		PPy+3%CuPc		PPy + 4%CuPc	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
Carbon	62.47	70.62	54.34	54.19	51.78	50.87	51.47	46.73
Hydrogen	3.90	5.35	3.16	2.66	2.91	2.74	2.80	2.55
Nitrogen	18.22	18.22	15.85	14.11	12.94	13.01	11.00	12.75
Chlorine	15.40	5.81	25.38	28.00	30.64	31.95	32.55	35.67
Copper	----	----	1.26	1.00	1.70	1.40	2.00	2.31
Cl/N mole Ratio	0.333	0.126	0.632	0.781	0.934	0.968	1.166	1.100

Sample	Empirical Formula
Pure PPy	$(C_4H_3N)_3\,Cl$ $(PPy)_3 : (Cl)_1$
PPy + 2% CuPc	$(C_4H_3N)_{49}[C_{32}H_{12}N_8Cu]\,Cl_{36}$ $(PPy)_{49} : (CuPc)_1 : (Cl)_{36}$
PPy + 3% CuPc	$(C_4H_3N)_{33}[C_{32}H_{12}N_8Cu]\,Cl_{33}$ $(PPy)_{33} : (CuPc)_1 : (Cl)_{33}$
PPy + 4% CuPc	$(C_4H_3N)_{16}[C_{32}H_{12}N_8Cu]_2\,Cl_{16}$ $(PPy)_{16} : (CuPc)_2 : (Cl)_{16}$

4% (mole) CuPc show the composition as $(C_4H_3N)_{24}$ $[C_{32}H_{12}N_8Cu]Cl_{24}$. The calculated values for various elements in this composition are C = 51.47, H = 2.80, N = 11.00 and Cl = 32.55, whereas the observed values are C = 46.73, H = 2.55, N = 12.75 and Cl = 35.67. As can be seen from the **Table-4.4**, the Cl/N ratio is increasing as the phthalocyanine concentration increases in the reaction mixture. These results suggest that the dopant ion concentration for CuPc containing PPy samples is higher than that of pure PPy this is because the more space is available for the dopant ions to sit due to phthalocyanine. This effect is discussed in length in the later section of this chapter. These results are quite consistent with the electrical conductivity data obtained for these samples.

4.3.A.2: CHARACTERIZATION OF STRUCTURE

(a) X-RAY DIFFRACTION STUDIES

The X-ray diffraction studies show that pure polypyrrole sample has mainly amorphous nature. Interestingly, the X-ray diffraction patterns for the PPy-CuPc sample exhibits small but distinct new reflections, which have similarity with those from phthalocyanine structure. The X-ray diffraction patterns obtained for various PPy polymers containing CuPc are shown in **Fig.4.3**. The curves A, B and C corresponds to pure PPy, PPy + 2% CuPc and PPy + 4% CuPc respectively. The X-ray diffraction data such as d-value and its h, k, l assignments are presented in **Table-4.5**. The d-value calculations for these samples show that they have an orthorhombic crystal structure with lattice parameters as a = 6.8 A°, b = 5.33 A° and c = 12.62 A°.

The strong oxidizing agent $FeCl_3$ used in the synthesis has a great effect on the rate of reaction. Probably, oxidation of pyrrole monomer proceeds at a much faster rate than that required for the product to form an ordered structure. This was reflected

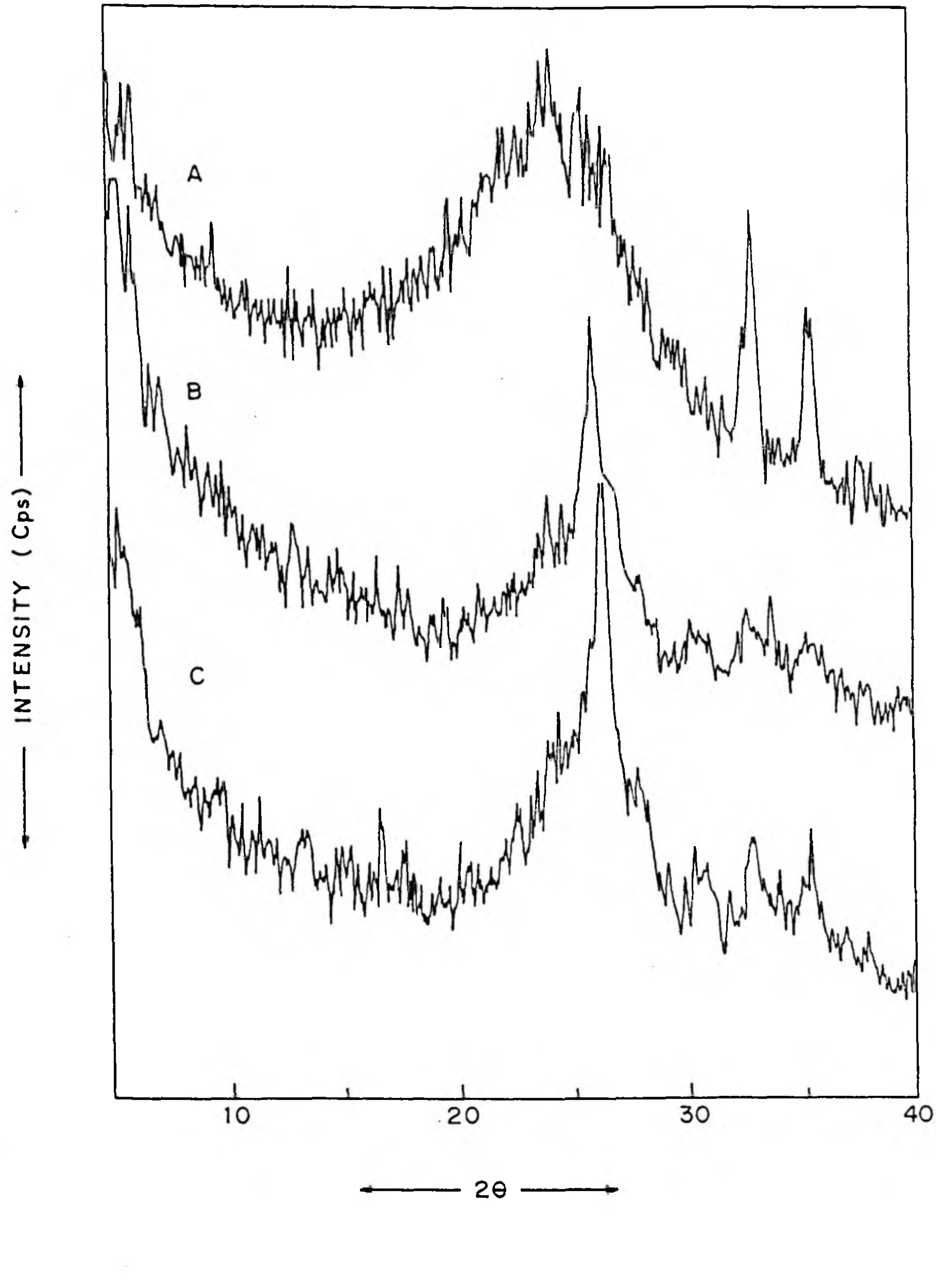


Fig. 4.3 : X-ray diffraction patterns of PPy-CuPc powder samples.
(A) Pure PPy (B) PPy + 2% CuPc
and (C) PPy + 4% CuPc

TABLE- 4.5

Analysis of WAXD patterns of PPy-CuPc polymers.

d observed (A°)	d calculated (A°)	h k l
12.62	12.62	0 0 1
6.80	6.80	1 0 0
5.33	5.33	0 1 0
5.03	4.98	0 1 1
4.03	4.02	1 1 1
3.63	3.60	1 1 2
3.38	3.40	2 0 0
3.24	3.30	2 0 1
2.93	2.87	2 1 0
2.75	2.75	2 0 3
2.55	2.49	0 2 2

Orthrombic, a = 6.8 A°, b = 5.33 A°, c = 12.62 A°

in the amorphous polypyrrole obtained in chemical synthesis as seen from X-ray studies. The addition of phthalocyanine results in stiffening of the polymer chain and possibility of stacking of the same increases. A few reports have appeared in literature regarding the crystalline structure of PPy. Electron diffraction studies of pure PPy suggest a monoclinic type crystalline structure with a = 8.2 A°, b = 7.35 A° and c = 6.82 A° [242]. When PPy is vapour phase polymerised on crystalline substrates, it assumes an orthorhombic type structure with a = 6.11 A°, b = 7.19 A° and c = 16.31 A° [243]. It is interesting to note that the c axis (chain axis) has increased considerably in the present case, which suggests the incorporation of the large CuPc unit in the main chain. It is also likely, as in the case of PANI, that these polymers have dendrimer type of molecular configuration, which can give better order at higher CuPc contents in the reaction mixture.

(b) ESCA (XPS) STUDIES

Fig. 4.4 shows typical core level spectra corresponding to C_{1s}, N_{1s} and Cl_{2p} levels of pure PPy powder sample recorded at standard settings (MgKα radiation, incident angle θ = 30°). It is seen that both C_{1s} and N_{1s} peaks have complex shapes that can be deconvoluted into three components. In case of C_{1s} these are C (I) 285.0 eV, C (II) 286.6 eV and C (III) 288.2 eV, while for N_{1s} they are at N (I) 399.6 eV, N (II) 401.0 eV and N (III) 403.2 eV respectively. The Cl_{2p} peak can also be resolved into three components, Cl (I) 198.2 eV, Cl (II) 200.2 eV and Cl (III) 202.6 eV respectively. The peaks obtained and their relative area (contribution to total) for different species C, N and Cl core-levels are shown in **Table-4.6**, **Table-4.7** and **Table-4.8** respectively.

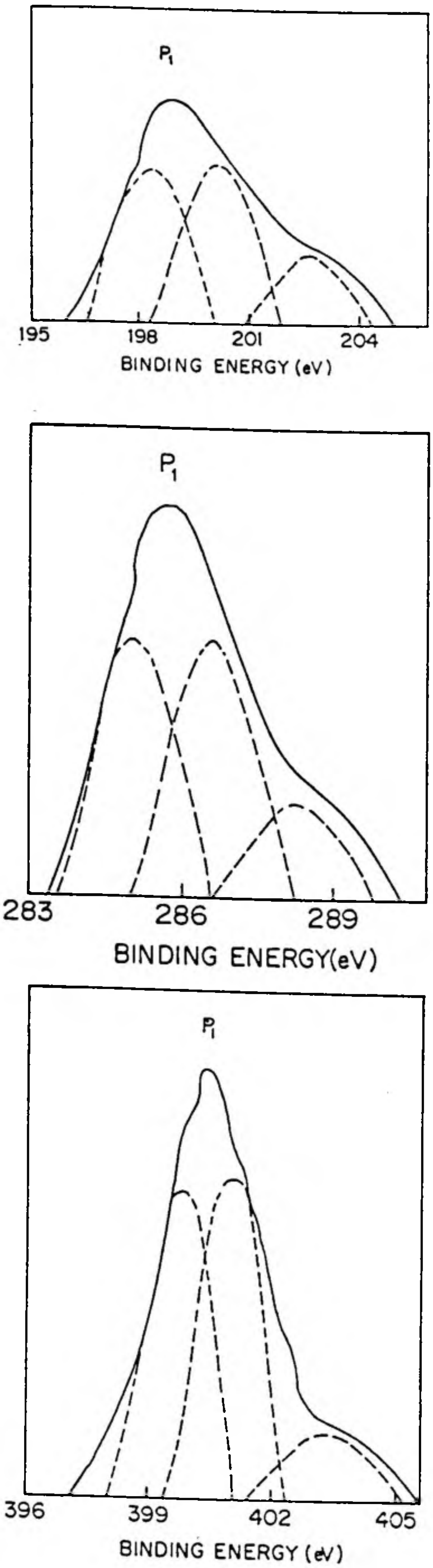


Fig. 4.4 : Cl_{2p}, C_{1s} and N_{1s} core-level spectrum of pure PPy (P_1) powder

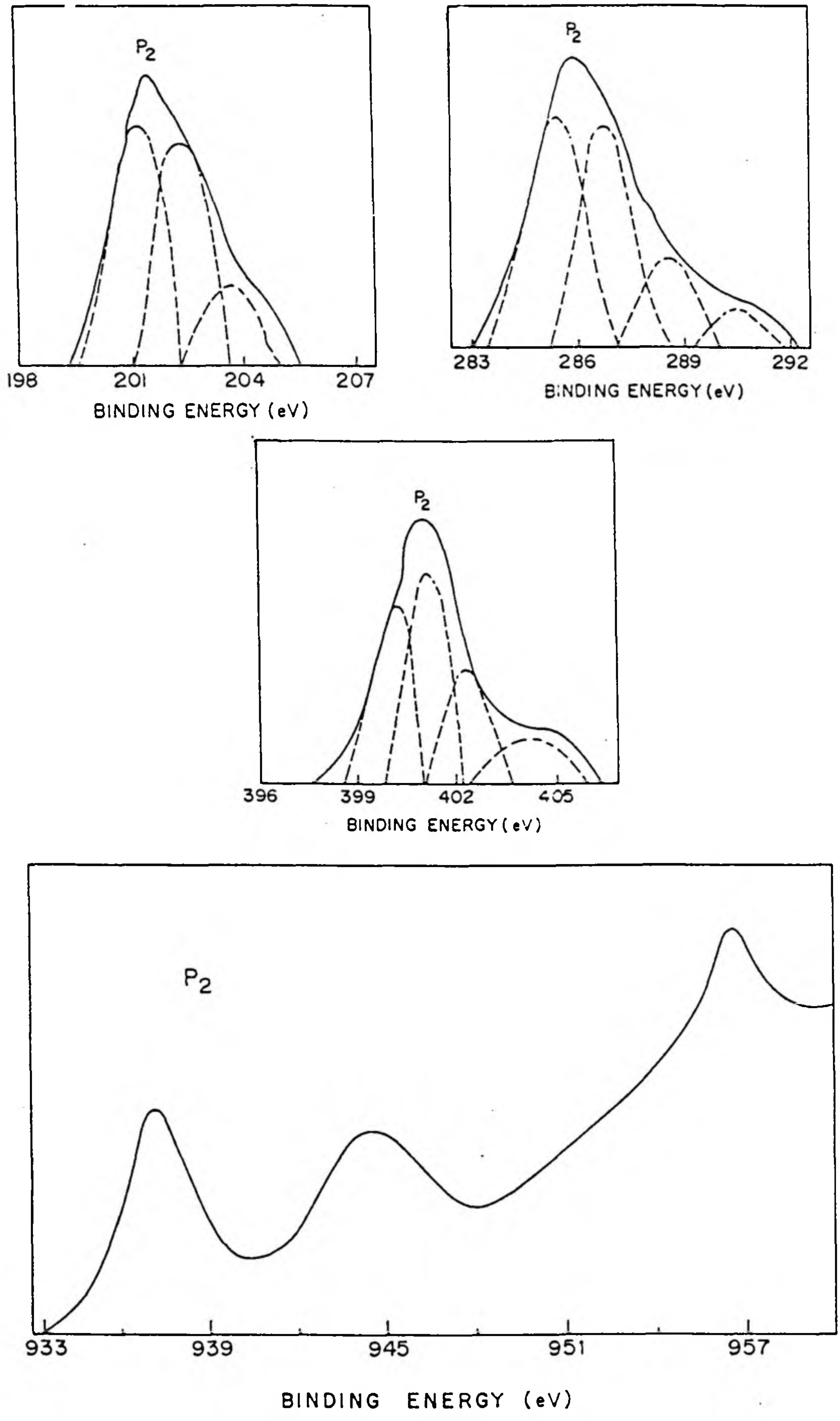


Fig. 4.5 : Cl_{2p}, Cu_{2p},C_{1s} and N_{1s} core-level spectrum of PPy + 4% CuPc (P_2) powder

TABLE- 4.6

ESCA RESULTS OF C_{1s} CORE-LEVEL FOR PPy-CuPc POWDERS

Sample name	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
Pure PPy (**P_1**)	$C_I = 285.0$ $C_{II} = 286.6$ $C_{III} = 288.2$	1.75 2.00 2.12	41.85 41.85 16.30
PPy + 4% CuPc (**P_2**)	$C_I = 285.0$ $C_{II} = 287.0$ $C_{III} = 288.6$ $C_{IV} = 290.6$	2.00 1.62 2.00 1.87	39.30 37.85 15.00 7.85

TABLE- 4.7

ESCA RESULTS OF N_{1s} CORE-LEVEL FOR PPy-CuPc POWDERS

Sample name	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
Pure PPy (P_1)	$N_I = 399.6$	1.75	43.50
	$N_{II} = 401.0$	1.87	45.65
	$N_{III} = 403.2$	2.25	10.85
PPy + 4% CuPc (P_2)	$N_I = 399.8$	1.37	32.60
	$N_{II} = 401.0$	1.62	38.00
	$N_{III} = 402.4$	1.75	20.30
	$N_{IV} = 404.2$	2.50	8.70

TABLE- 4.8

ESCA RESULTS OF Cl_{2p} CORE-LEVEL FOR PPy-CuPc POWDER SAMPLES.

Sample name	**Binding energy (in eV)**	**FWHM (in eV)**	**% Area (Relative)**
Pure PPy **(P_1)**	$Cl_{I} = 198.2$	2.37	40.00
	$Cl_{II} = 200.2$	2.50	42.35
	$Cl_{III} = 202.6$	2.25	21.15
PPy + 4% CuPc **(P_2)**	$Cl_{I} = 201.2$	1.75	44.15
	$Cl_{II} = 202.5$	1.75	40.85
	$Cl_{III} = 203.8$	1.87	15.00

There have been several reports in the past on the XPS studies of doped and undoped PPy[244-248]. To name a few important ones, Plfuger and Street[245] studied the effect of doping on the XPS of PPy and showed that the core levels for C_{1s} and N_{1s} can be resolved into three components. In case of C_{1s} they assigned these to α,β carbon atoms of the main chain and 'disordered' structure of the polymer. In the N_{1s} spectra they ascribed the occurrence of the three components to neutral and charged nitrogen species due to presence of the dopant ion at every third/fourth nitrogen site of PPy. Kang and co-workers[246] also reported multicomponent C_{1s} and N_{1s} core level spectra in halogen doped PPy.

The spectra corresponding to C_{1s}, N_{1s}, Cl_{2p} and Cu_{2p} core level for the sample PPy containing 4% CuPc are shown in **Fig. 4.5.** It is seen that C_{1s} and N_{1s} peaks can be deconvoluted into four components each. The C_{1s} peaks appeared at C (I) 285.0 eV, C (II) 287.0 eV, C (III) 288.6 eV and C (IV) 290.6 eV. When these results are compared with the pure PPy sample, the neutral carbon species are at 285.0 eV in both the samples, whereas the charged carbon species are shifted towards higher BE side. There is an additional peak at 290.6 eV, which may be assigned to carbon atom in the close proximity of dopant ions i.e. more charged carbon atom appearing at higher BE.

The appearance of the Cu_{2p} peaks at 937.2 eV, 944.4 eV and 957.0 eV for the PPy samples, functionalized with phthalocyanine is clearly evident. These peaks were totally absent in the pure PPy sample. The peak at 937.2 eV can be assigned to the core level Cu ($2p_{3/2}$) and peak at 944.4 eV appeared as its satellite. The peak at higher B.E. (957.0 eV) is due to Cu ($2p_{1/2}$)-core level. These results clearly show the presence of CuPc in PPy chains.

The PPy sample containing 4% CuPc shows a broad chlorine peak which can be easily deconvoluted into three components. They appeared at Cl (I) 201.2 eV, Cl

(II) 202.5 eV and Cl (III) 203.8 eV respectively. The chlorine peak data are presented in **Table-4.8**. The appearance of three components in Cl suggests that CuPc moieties also got doped or form charge transfer complex with Cl. Thus highly charged Cl species (II) and (III) may be due to different sites on the polymer at which Cl dopant is interacting. From this table it can be seen that the B.E. values for chlorine in the PPy-CuPc samples are higher than the sample of pure PPy sample. The conductivity measurements of these samples also showed the same results.

4.3.A.3: MEASUREMENT OF PROPERTIES

(a) ELECTRICAL CONDUCTIVITY

The effect on electrical conductivity with the addition of phthalocyanine was studied and results obtained are shown in **Fig. 4.6**. As can be seen from the figure the conductivity increases with the addition of the phthalocyanine. Here, the increase in conductivity may be associated with reduction in the band gap due to the addition of phthalocyanine. This effect has been described in detail in the following section.

The increase in the conductivity of polypyrrole was observed, when the phthalocyanine was added to it. As seen in the case of polyaniline, phthalocyanine moieties get incorporated in the polymeric backbone. A similar type of attachment results in polypyrrole to get PPy-CuPc polymers. Due to the addition of phthalocyanine, the extent of the conjugation increases giving higher number of delocalized electrons. The electrical conductivity in these materials is associated with thermal excitation of mobile π electrons. The soliton type excitations could be possible in phthalocyanine type of compounds, as they possess degenerate ground states. These soliton excitations probably interact with each other or with neighbouring chains leading to free or delocalized electron or hole. Thus increase in the conductivity of

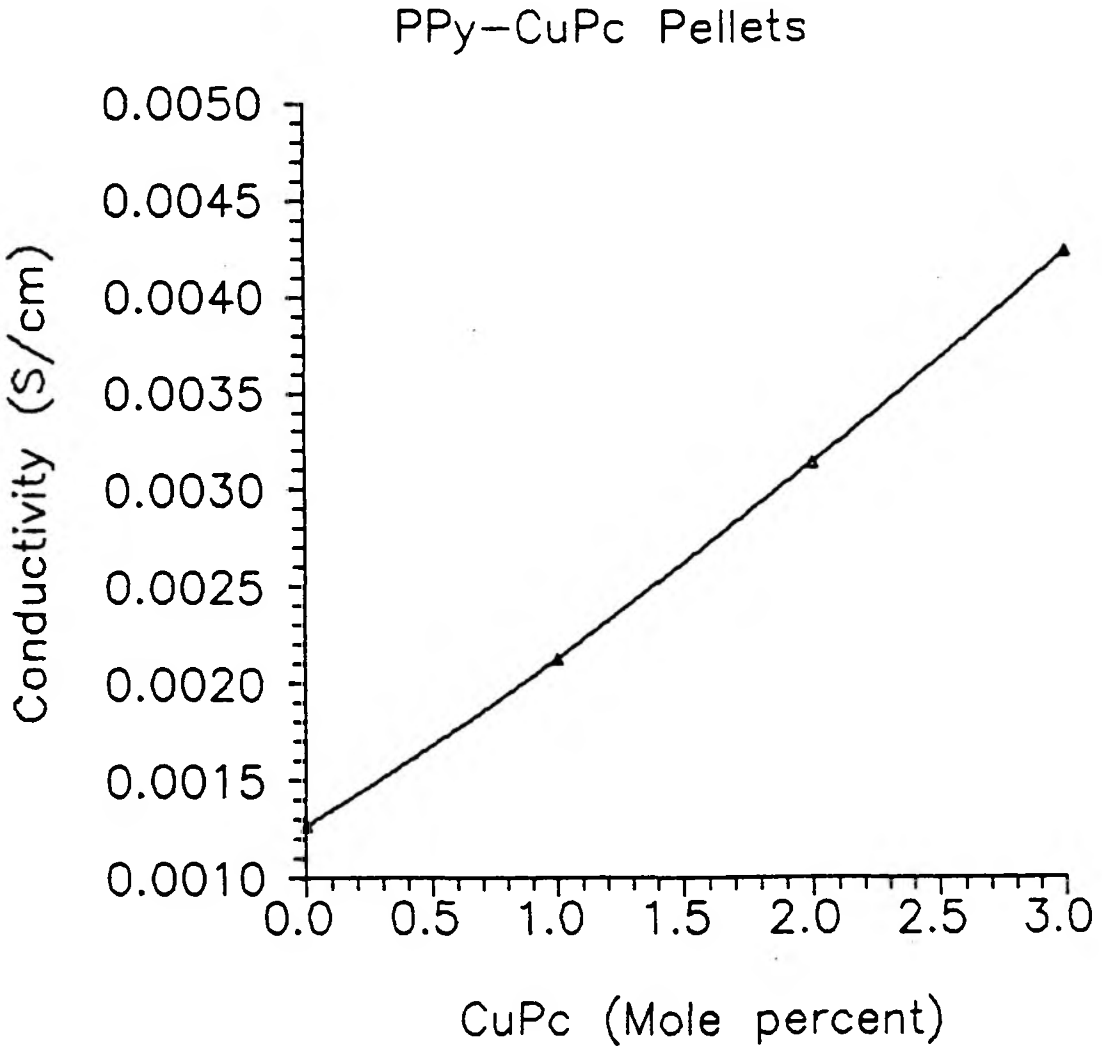


Fig. 4.6 : Plot of conductivity versus CuPc concentration for PPy-CuPc powder samples

polypyrrole by incorporation of phthalocyanine could be explained via hopping of soliton bound states from one chain to another. The chemical synthesis of PPy-CuPc is presented in **Fig. 4.7**.

The electrical conductivity (σ), of PPy-CuPc polymers was measured in it's pellet form. The results of the variation in electrical conductivity as a function of temperature are shown in **Fig.4.8**. The conductivity of the order of 10^{-3} S/cm was obtained. The slightly lower conductivity values than the reported ones, can be explained on the basis of the different conditions used in the synthesis step viz. solvent used was NMP: H_2O (1:1) mixture and oxidizing agent was ferric chloride. The solvent NMP shows hydrogen-bonding interactions with the water molecules present in the reaction. This prevents the doping of the polymer to great extent, which results in getting the low conductivity for these polymers.

The activation energy (ΔE) for the polypyrrole and PPy-CuPc polymers was calculated using the curves of log conductivity versus 1/T. The results obtained for activation energy are plotted in **Fig. 4.9** as a function of phthalocyanine concentration. The activation energy for pure polypyrrole sample was 0.18 eV whereas, polypyrrole containing 3% phthalocyanine sample showed this value as 0.04 eV. The lowering of activation energy with increase in phthalocyanine is associated with lowering the band gap in these polymers. Thus, lowering the band gap results in requirement of fewer amounts of energy for excitation. The decrease in the activation energy is associated with increase in electrical conductivity. A similar type of results was obtained for polyaniline functionalized with phthalocyanine in the studies reported in Chapter III.

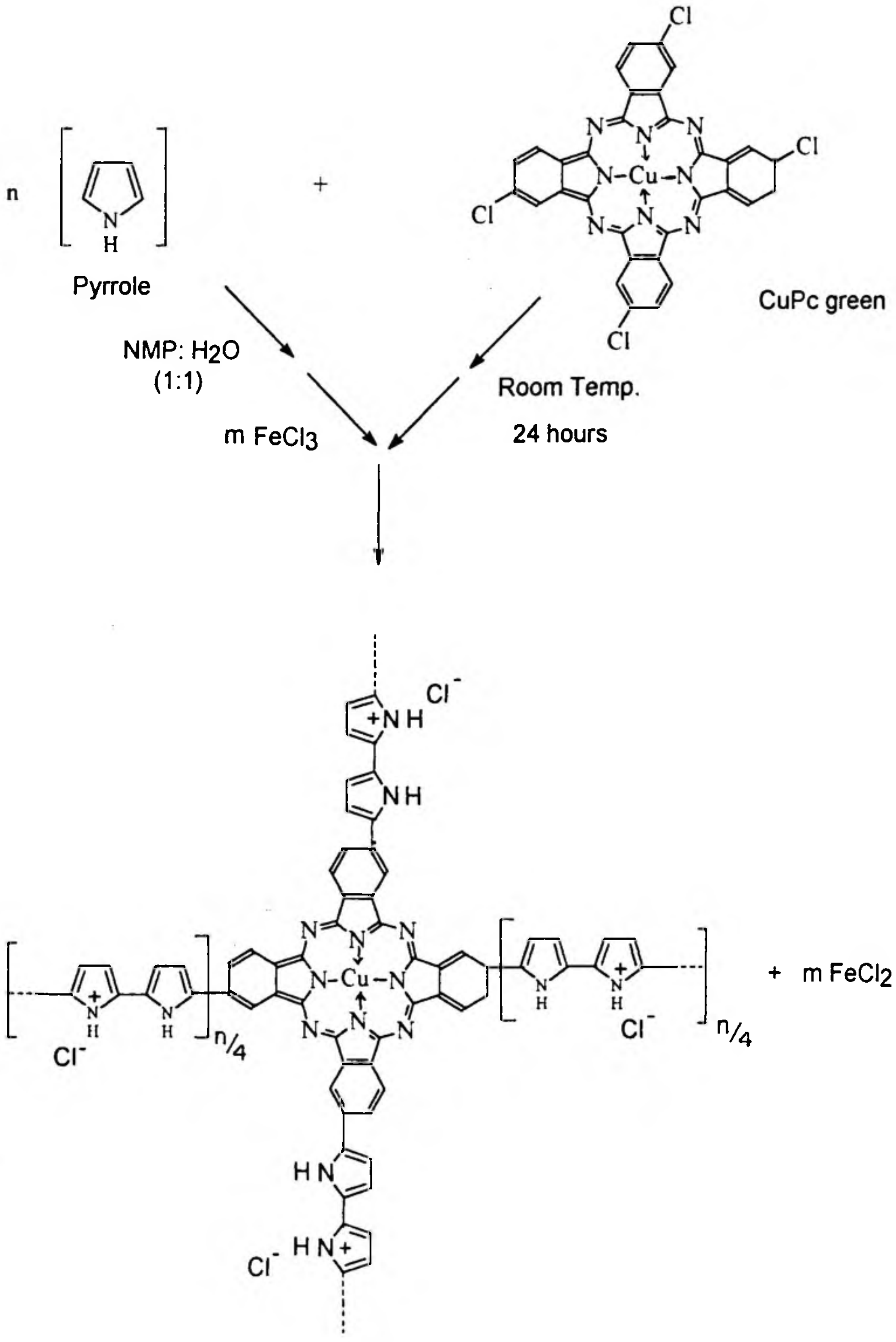


Fig. 4.7 : Reaction scheme for chemical synthesis of PPy-CuPc polymer

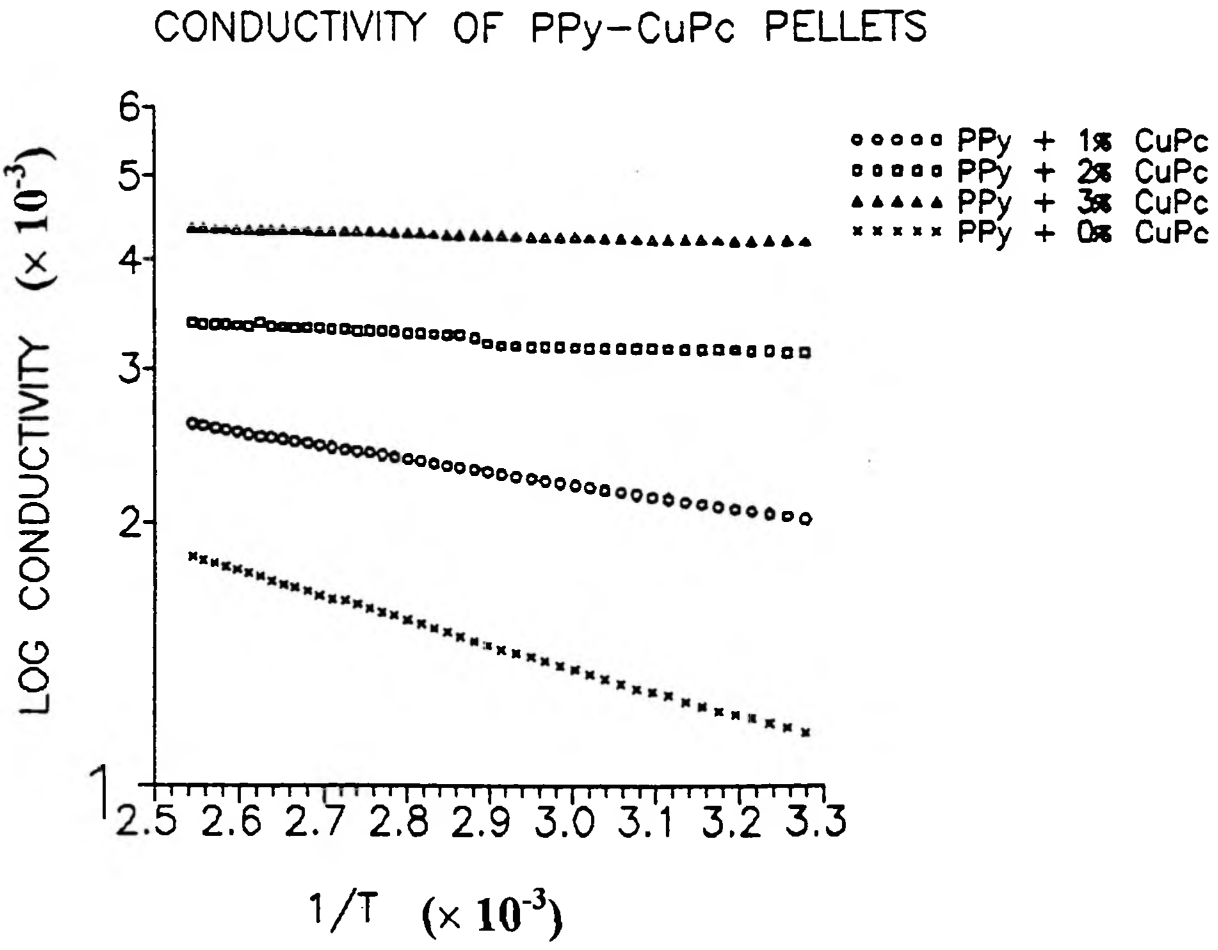


Fig. 4.8 : Plots of log conductivity versus reciprocal of temperature for PPy-CuPc powder samples

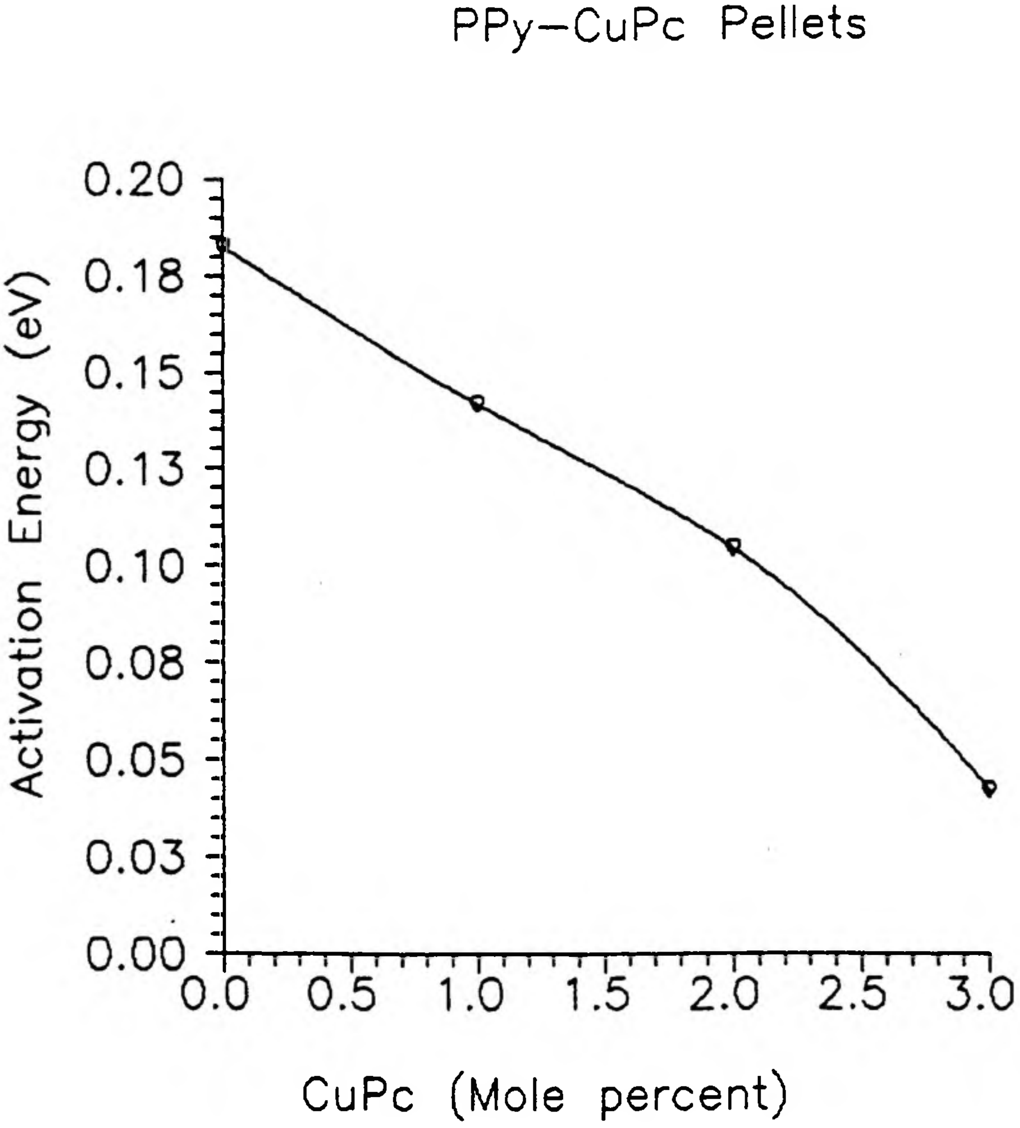


Fig. 4.9 : Plot of activation energy versus CuPc concentration for PPy-CuPc powder samples

(b) CYCLIC VOLTAMMETRIC MEASUREMENTS

The cyclic voltammograms obtained from the 0.1M KCl aqueous solution under illumination are shown in **Fig. 4.10**. The sample preparation for these measurements is described in **chapter-II.** The curves A, B and C corresponds to samples of PPy, PPy + 2% CuPc and PPy + 3% CuPc respectively. The voltammograms were recorded for three cycles between the potentials –1.0 V to +1.0 V. Each sample exhibits two peaks, one at about 0.3-0.47 V corresponding to oxidation of PPy (doping) and the other is at -0.7 to - 0.8 V corresponding to reduction of polymer (undoping). As can be seen from the curves the anodic peak shifts more to the positive side, while cathodic peak shifts more towards negative side with the addition of phthalocyanine. The increase in electrochemical activity is more pronounced when these voltammograms are recorded under illumination. The current obtained vary from 650 μamps for pure PPy sample to 4530 μamps for the PPy sample containing 3% CuPc [compare **Fig.4.10 A and C**]. These results suggest that the PPy containing phthalocyanine materials can be used as photoelectrochemical cell electrode.

(c) THERMAL STABILITY

The PPy-CuPc polymeric samples were tested for it's thermal degradation behaviour by using thermal analysis technique. The curves shown in **Fig. 4.11** are TG, DTG and DTA of the PPy-CuPc samples. The curve A correspond to pure polypyrrole sample and curves B and C correspond to PPy containing 2% and 4% phthalocyanine respectively. The results of the thermal degradation for various polymers at different temperatures are tabulated in **Table 4.9**. From this data it can be clearly seen that up to 450°C, the thermal stability of the polypyrrole increases as the phthalocyanine content in the polymer increases. Thus, similar to polyaniline, the polypyrrole also showed

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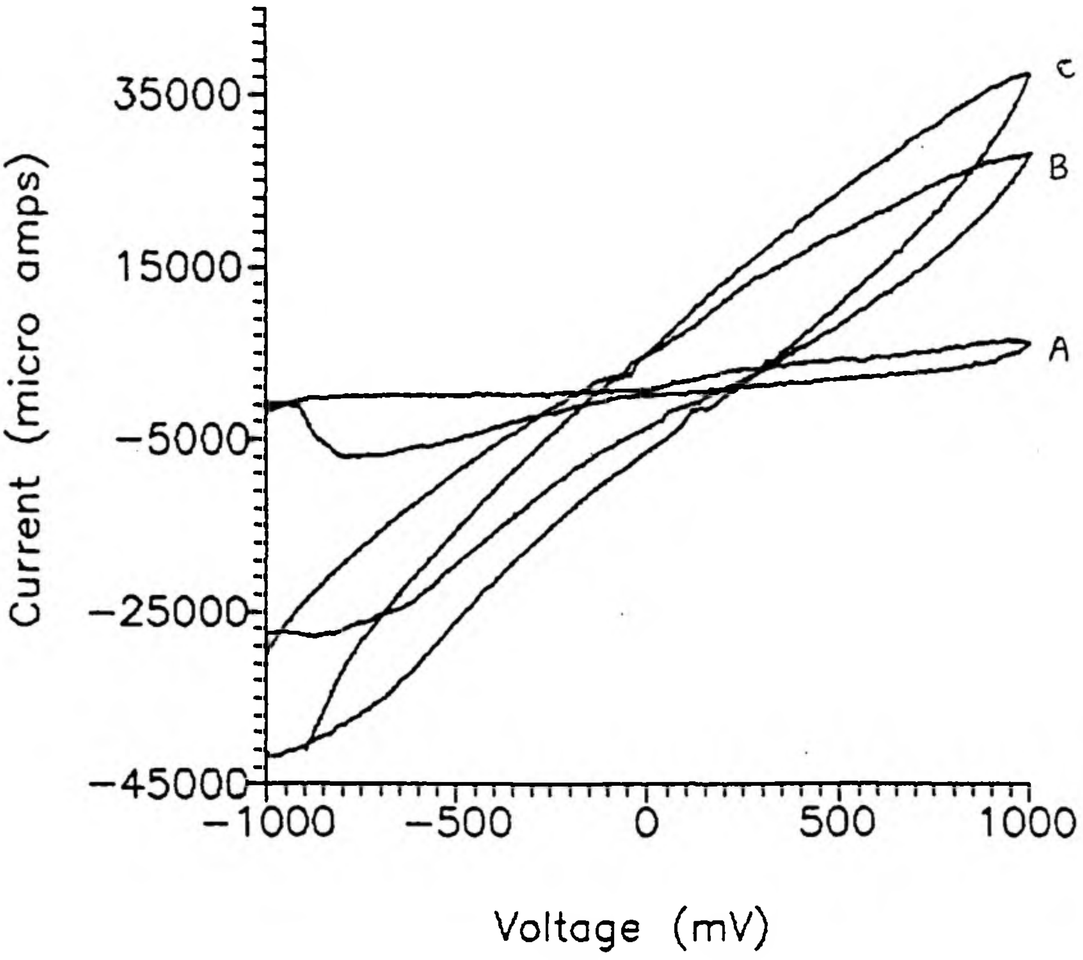


Fig. 4.10 : C-V Measurements of PPy-CuPc pellet in 0.1 M KCl electrolyte

(A) Pure PPy (B) PPy +2 % CuPc

And (C) PPy +3 % CuPc

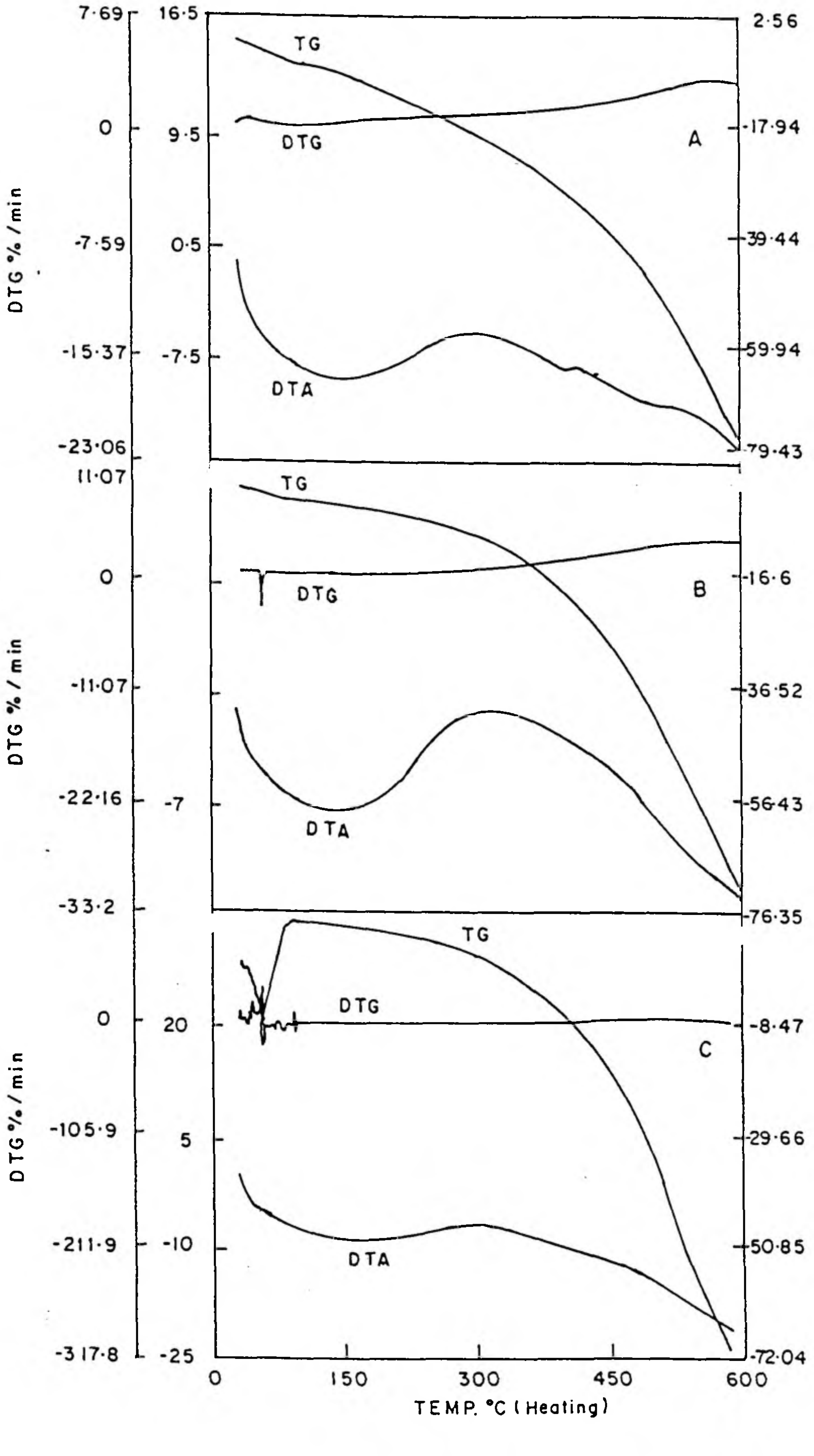


Fig. 4.11 : TGA/DTA thermograms of PPy-CuPc powder samples In nitrogen atmosphere. (A) Pure PPy (B) PPy + 2% CuPc and (C) PPy + 3% CuPc

TABLE-4.9

(A) THERMAL DEGRADATION DATA OF PPy-CuPc POLYMERS

Temperature °C	Percent Weight Loss		
	Pure PPy	PPy + 2% CuPc	PPy + 3% CuPc
200	10.1	5.7	0.0
250	13.0	8.0	0.0
300	18.0	9.5	0.0
350	21.8	12.3	0.0
400	28.7	18.5	5.5
450	36.5	26.1	16.5
500	45.3	39.3	29.6

(B) THERMAL DEGRADATION DATA OF PPy-CuPc POLYMERS

CuPc content Mole %	Wt. loss From 200-500°C	% PPy observed from % T.G	% PPy expected from actual CuPc Wt. addition
0.0	35.2	100.00	100.00
2.0	33.6	95.45	54.60
3.0	29.6	84.10	44.56
4.0	29.0	82.10	37.72

more thermal stability with the increase of phthalocyanine content in the polymer backbone. The thermal analysis data was used for calculating the actual polypyrrole content in the polymeric sample. The loss up to 500°C for homopolymer PPy was determined and compared with the loss up to same temperature for PPy-CuPc samples. Also the polypyrrole content in the polymeric mixture can be easily calculated by knowing the yield of PPy reaction and the actual amount of CuPc added. When we compare the polypyrrole content by thermal analysis we got more values than the actual weight addition samples. In other words, the thermal stability of polypyrrole was enhanced by the addition of copper phthalocyanine into it.

4.3.B: ELECTROCHEMICAL METHOD

The polymeric films of polypyrrole and those containing phthalocyanine were obtained on gold substrates, as described in **section 4.2.B**. The pure polypyrrole film exhibits a dark brown colour. The colour of the film changes to blue, as the phthalocyanine content in the electrolyte was increased. The thickness of the deposited films depends upon the time of deposition, which was maintained same in all cases. These films were characterised by FT-IR and UV-VIS techniques. The films from the same set were used for measurement of properties.

4.3.B.1: CHARACTERIZATION

(a) FT-IR ANALYSIS

The FT-IR spectra (recorded in reflection mode) for the ECP deposited pyrrole containing varying amounts of phthalocyanine are shown in **Fig.4.12**. Curves A, B and C correspond to CuPc concentration of 0, 1 and 2% (mole) respectively in PPy films. The peak position and the probable assignments for these spectrums were

Fig. 4.12 : FT-IR absorption spectrum of PPy-CuPc films. (A) Pure PPy (B) PPy + 1% CuPc And (C) PPy + 2% CuPc

TABLE- 4.10

FT-IR DATA OF PPy-CuPc FILMS.

Pure PPy Peak cm^{-1}	PPy + 1% CuPc Peak cm^{-1}	PPy + 2% CuPc Peak cm^{-1}	Possible Assignment
1700.0 (s)	1694.4 (m)	1697.2 (s)	
1562.0 (vs)	1571.9 (vs)	1552.6 (vs)	Vib. C=C
1480.0 (m)	1485.1 (s)	1481.2 (m)	Vib. C-N
1370.0 (m)	1350.0 (w)	1360.0 (w)	
1320.0 (w)	1322.0 (w)	1317.3 (w)	
1290.0 (w)	1300.0 (w)	--------	Pyr. Skeleton
1210.0 (s)	1213.1 (s)	1203.5 (s)	C=N
1105.0 (m)	1100.0 (m)	1100.0 (m)	β (C-H) Pyr. Ring
1050.0 (m)	1051.0 (s)	1049.2 (s)	β (C-H)
--------	960.0 (w)	960.0 (w)	Pc skeleton
935.0 (s)	931.6 (s)	918.1 (s)	
805.0 (s)	810.0 (s)	810.0 (br)	
750.0 (w)	750.0 (w)	750.0 (w)	δ (C-H)
720.0 (m)	720.0 (w)	--------	
690.0 (m)	--------	--------	
670.0(w)	--------	--------	

tabulated in **Table-4.10**. From the spectrum of pure PPy sample peaks at 1700, 1562, 1480, 1320, 1105, 935, 805, 750 and 690 cm^{-1} can be easily assigned to polypyrrole moiety. These values for PPy are well matched with the reported[249] values for PPy. The polymeric films functionalized with phthalocyanine exhibit peaks at 1440, 1350, 1210, 1100, 1050 and 960 cm^{-1} which are assigned to phthalocyanine bands. The peak at 1700 cm^{-1} is associated with C = O carboxyl group as a result of hydrogen bonding of NMP with water as a nucleophile. The decrease in intensity of this peak with increasing phthalocyanine indicates that the NMP has more affinity towards the added phthalocyanine rather than water. Thus, phthalocyanine helps to prevent hydrogen bonding between NMP and water. The peak intensity at 1562 cm^{-1}, was associated with the C = C / C - C stretching modes of PPy. These results clearly show an evidence for the incorporation of phthalocyanine into polypyrrole chains.

(b) UV-VIS STUDIES

The UV-VIS spectra of PPy and PPy-CuPc polymeric films on gold deposited glass are depicted in **Fig. 4.13** (gold coated semitransparent glass was taken as standard). The pure PPy film shows a broad absorption spectrum centred at 350 nm and 600 nm. Similar type of results were obtained by Hourch et.al.[250] in their investigation of phthalocyanine modified PPy electrodes by UV-VIS studies. As can be observed from the absorption curves the samples incorporated with phthalocyanine exhibits additional absorption peaks at longer wavelength region. The new absorption at 680 nm and 770 nm are characteristic of the phthalocyanine excitonic transitions. The phthalocyanine groups chemically coupled with PPy give rise to modified structure, which affect the extent of conjugation and hence the energy level/band structure. This results in additional optical transitions giving rise to new absorption peak. Here, again it is seen that the phthalocyanine is not merely an inert additive but highly interactive with PPy.

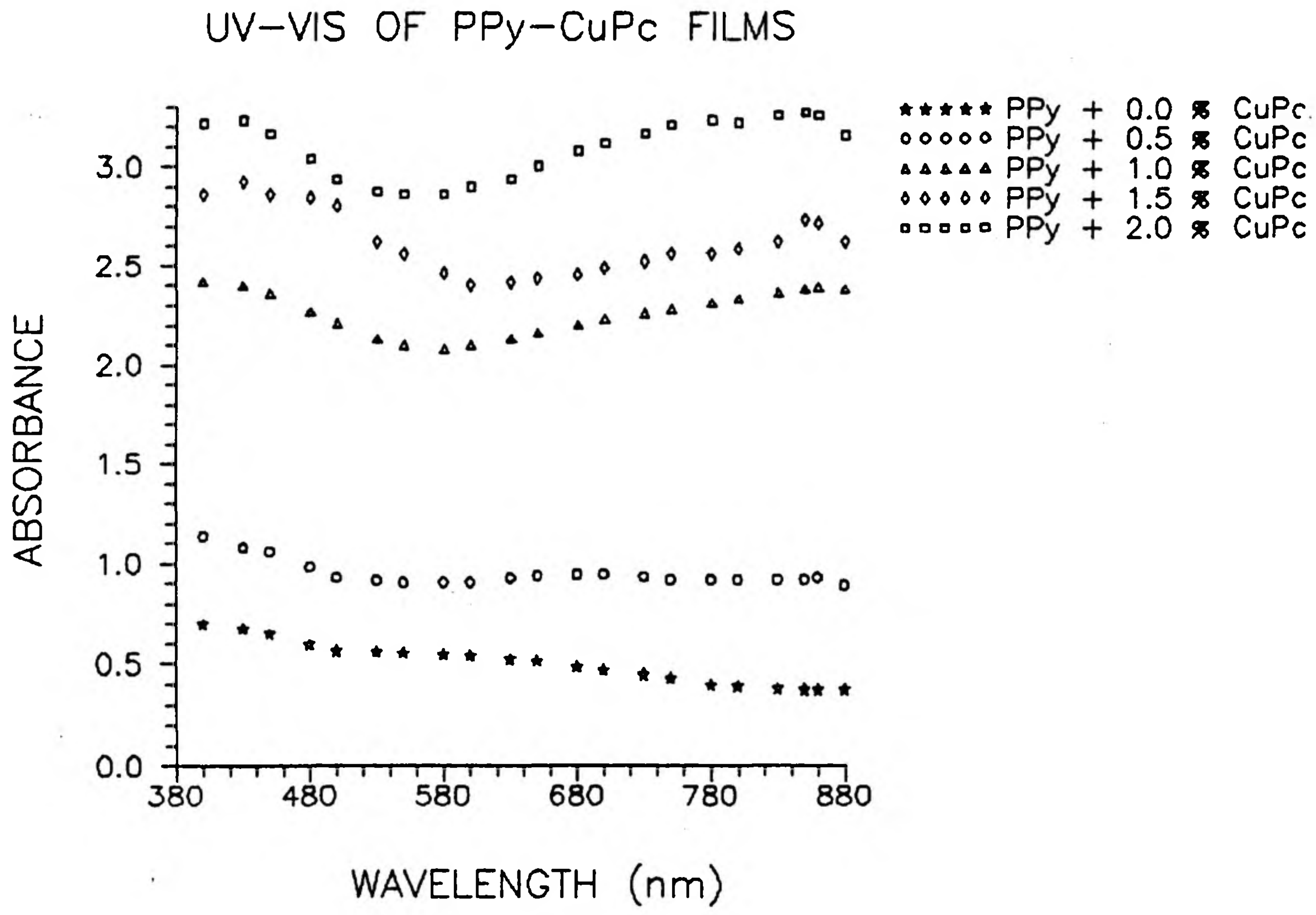


Fig. 4.13 : UV-VIS spectrum of PPy-CuPc films deposited on gold glass

4.3.B.2: CHARACTERIZATION OF STRUCTURE

(a) X-ray Diffraction Studies

The various films of PPy and PPy-CuPc were checked under microscope, but all of these samples were found to be amorphous. This was then confirmed by scanning it using X-ray diffraction. The X-ray studies also show the amorphous nature for these films. This is rather surprising but considering the fact that electrochemical deposition takes place at very rapid rate that there is no sufficient time given for crystallisation to occur before next layer of polymer is formed.

(b) ESCA (XPS) STUDIES

The N_{1s} and C_{1s} core level spectra obtained for PPy-CuPc polymeric films are shown in **Fig.4.14**. The spectra A, B and C correspond to the samples of pure PPy, PPy + 1% CuPc and PPy + 2% CuPc films respectively. All these spectra show four components in each of its C_{1s} and N_{1s} core levels. The varying components obtained after deconvolution and their relative contributions to total area under the peak for C_{1s} and N_{1s} core-level spectra are presented in **Table-4.11** and **Table-4.12** respectively. From these data it is clear that N_{1s} peaks in the PPy-CuPc samples are obtained at higher B.E. as compared to pure PPy sample. The increase in the peak intensity is clearly evidenced in the polymeric films which, contains more phthalocyanine. The charged nitrogen species increases as CuPc content in the polymeric film increases. The broadening of the peak at higher B.E. is indicative of this fact.

Eaves et.al.[251] reported the XPS spectra of electrochemically prepared PPy at various stages of oxidation, which revealed two additional components to the main

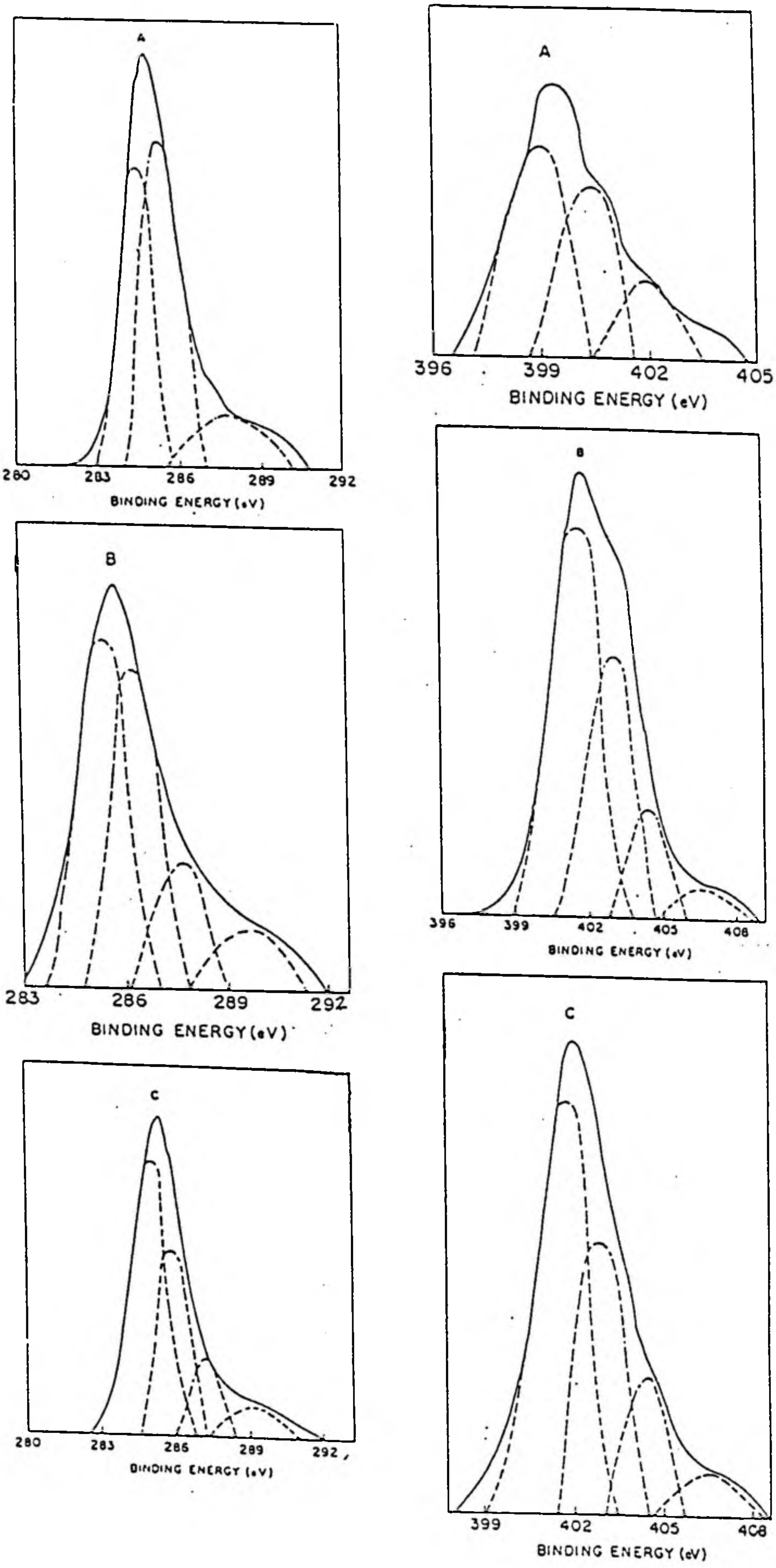


Fig. 4.14 : N_{1s} and C_{1s} core-level spectrum of PPy-CuPc films.

(A) Pure PPy (B) PPy + 2% CuPc

And (C) PPy + 3% CuPc

TABLE- 4.11

ESCA RESULTS OF C_{1s} LEVEL OF PPy-CuPc FILMS.

Sample	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
Pure Polypyrrole (A)	C_I = 284.6 C_{II} = 285.8 C_{III} = 287.0 C_{IV} = 288.6	1.50 1.50 1.62 2.50	43.2 39.6 12.8 4.4
PPy + 1% CuPc (B)	C_I = 285.4 C_{II} = 286.4 C_{III} = 287.6 C_{IV} =289.6	1.75 1.62 1.75 2.62	41.0 37.0 15.0 7.0
PPy + 2% CuPc (C)	C_I = 285.0 C_{II} = 286.0 C_{III} = 287.2 C_{IV} = 289.0	1.62 1.62 1.50 2.75	44.1 34.8 13.1 8.0

TABLE- 4.12

ESCA RESULTS OF N_{1s} LEVEL OF PPy-CuPc FILMS

Sample	**Binding energy (in eV)**	**FWHM (in eV)**	**% Area (Relative)**
Pure Polypyrrole (A)	N_I = 398.8 N_{II} = 400.4 N_{III} = 401.5 N_{IV} = 403.2	1.87 1.87 1.50 1.75	42.10 35.00 17.50 5.40
PPy + 1% CuPc (B)	N_I = 401.5 N_{II} = 403.2 N_{III} = 404.4 N_{IV} = 406.8	2.37 2.50 2.00 3.37	45.0 33.0 15.0 7.0
PPy + 2% CuPc (C)	N_I = 401.4 N_{II} = 403.0 N_{III} = 404.4 N_{IV} = 406.2	2.00 2.12 2.00 2.50	46.0 30.5 15.3 8.2

peak (400 eV) for N_{1s} spectra with the increase of oxidation / doping. Kang et.al.[252] have carried out extensive studies on electrochemically prepared doped PPy films. Their study of N_{1s} core-level spectra indicates the presence of the main pyrrolium nitrogen (-NH- structure) peak at about 398.8 eV. They also indicate the presence of a charged species at slightly above 400.5 eV. The presence of peak at above 402.0 eV is due to delocalized positive charges or positively charged nitrogen atoms.

4.3.B.3: MEASUREMENTS OF PROPERTIES

(a) ELECTRICAL CONDUCTIVITY

The effect on electrical conductivity due to incorporation of phthalocyanine into PPy films has shown in **Fig.4.15**. As seen from the figure, the conductivity increases moderately as the CuPc concentration goes on increasing. This effect can be explained as follows:

The phthalocyanine has more conjugated structure due to large number of hetero cyclic/aromatic groups present in it. The incorporation of this macrocycle into polymeric chains of PPy results in the increase in the conjugation length. Moreover, due to the large molecular dimensions of CuPc, the amorphous films produced have more inter chain separation in which dopant ions get incorporated. This will increase the doping level of these polymeric materials and consequently exhibit higher conductivity than pure PPy.

The electrical conductivity of the as synthesised polymeric film w.r.t. changes in temperature were measured using Keithley electrometer. **Fig. 4.16** shows the graph of conductivity as a function of temperature for PPy-CuPc films. The conductivity obtained for these samples were in the range of 10^{-2} S/cm. It can be seen that

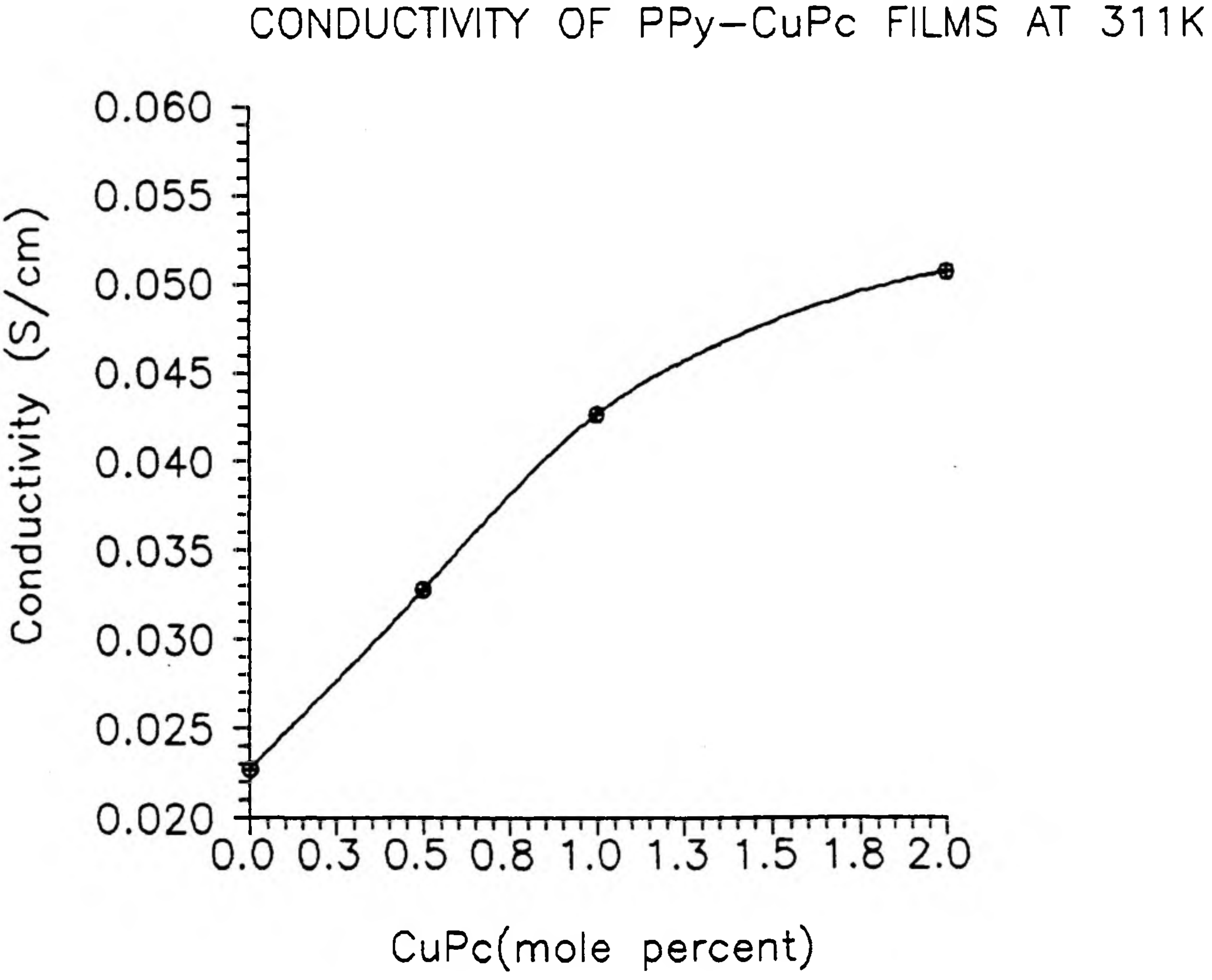


Fig. 4.15 : Plot of conductivity versus CuPc concentration for PPy-CuPc films

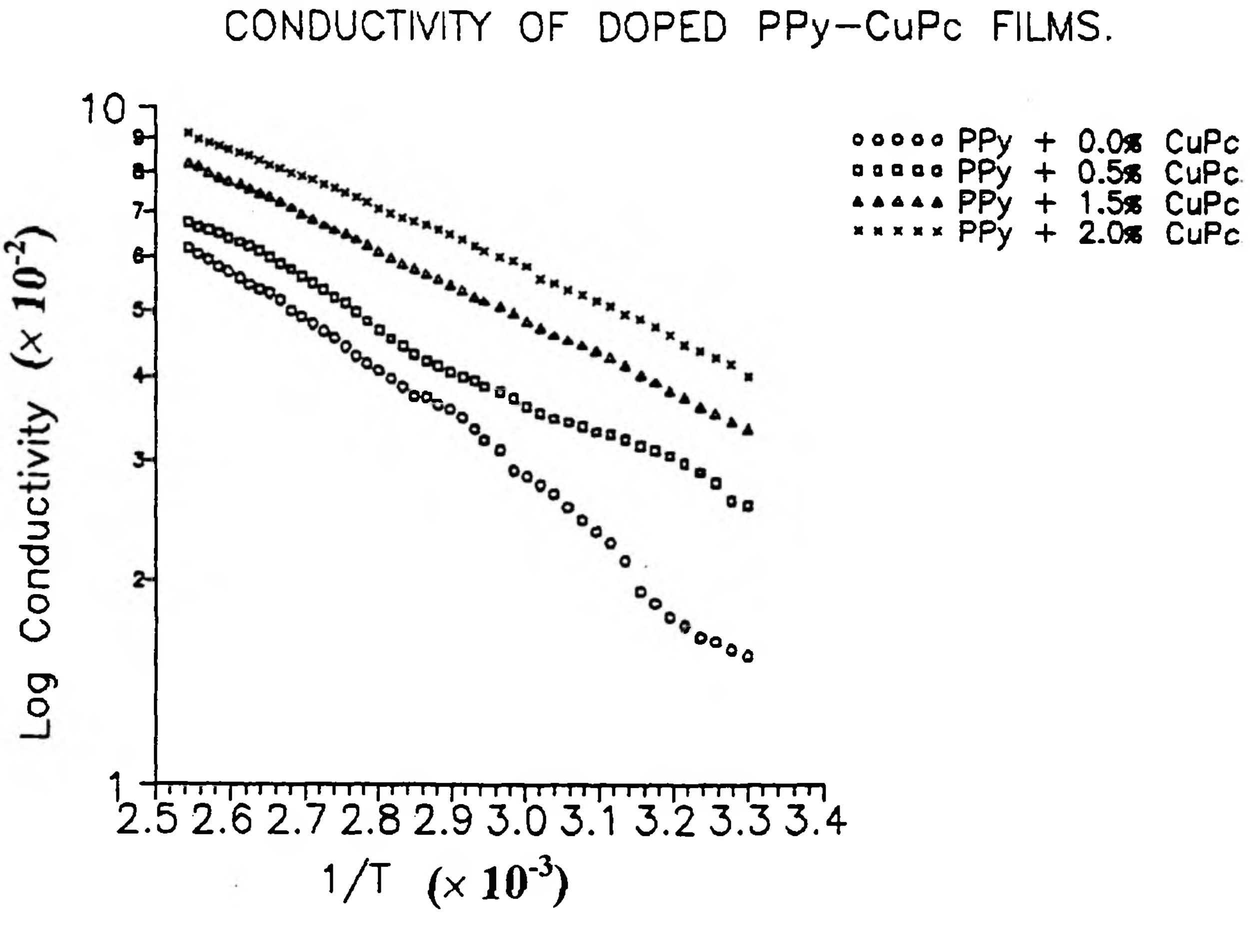


Fig. 4.16 : Plots of log conductivity versus reciprocal of temperature For PPy-CuPc films

conductivity increases as the phthalocyanine concentration in the PPy film increases. There is a threefold increase in the conductivity of PPy even for small incorporation of CuPc (2-mole%). The PPy films obtained in the present study were SO_4^{-2} doped films in their highly conductive nature. The phthalocyanine used in this study has shown its conductivity in the range 10^{-9} to 10^{-10} S/cm. Hence one can expect marginal rise in conductivity of PPy after the incorporation of this phthalocyanine moiety. The results obtained shows similar type of observations.

The results of activation energy obtained as a function of phthalocyanine concentration are shown in **Fig. 4.17**. The increase in conductivity is associated with decrease in activation energy of the polymer. It is seen that as the phthalocyanine content increases even to the level of 1 to 2% in the PPy films, there is a drop in activation energy from 0.133 eV to 0.08 eV. The phthalocyanine added to PPy reduces the band gap and hence less energy is required for thermal excitations of charge carriers. This is well supported by the optical absorption data wherein it was seen that additional transitions due to mid gap levels were present for PPy-CuPc doped polymers.

(b) CYCLIC VOLTAMMETRIC MEASUREMENTS

The typical cyclic voltammograms or essentially current voltage curves obtained for PPy-CuPc films in an aqueous electrolyte containing KCl are depicted in **Fig. 4.18**. It is seen that, in case of aqueous KCl electrolyte, there are two distinct peaks in the C-Vs at –0.5 V and -0.1 V corresponding to reduction and oxidation of PPy accompanying undoping and doping of the film. Similarly, the C-Vs recorded in the aqueous electrolyte containing lithium per chlorate ($LiClO_4$) is shown in **Fig. 4.19**.

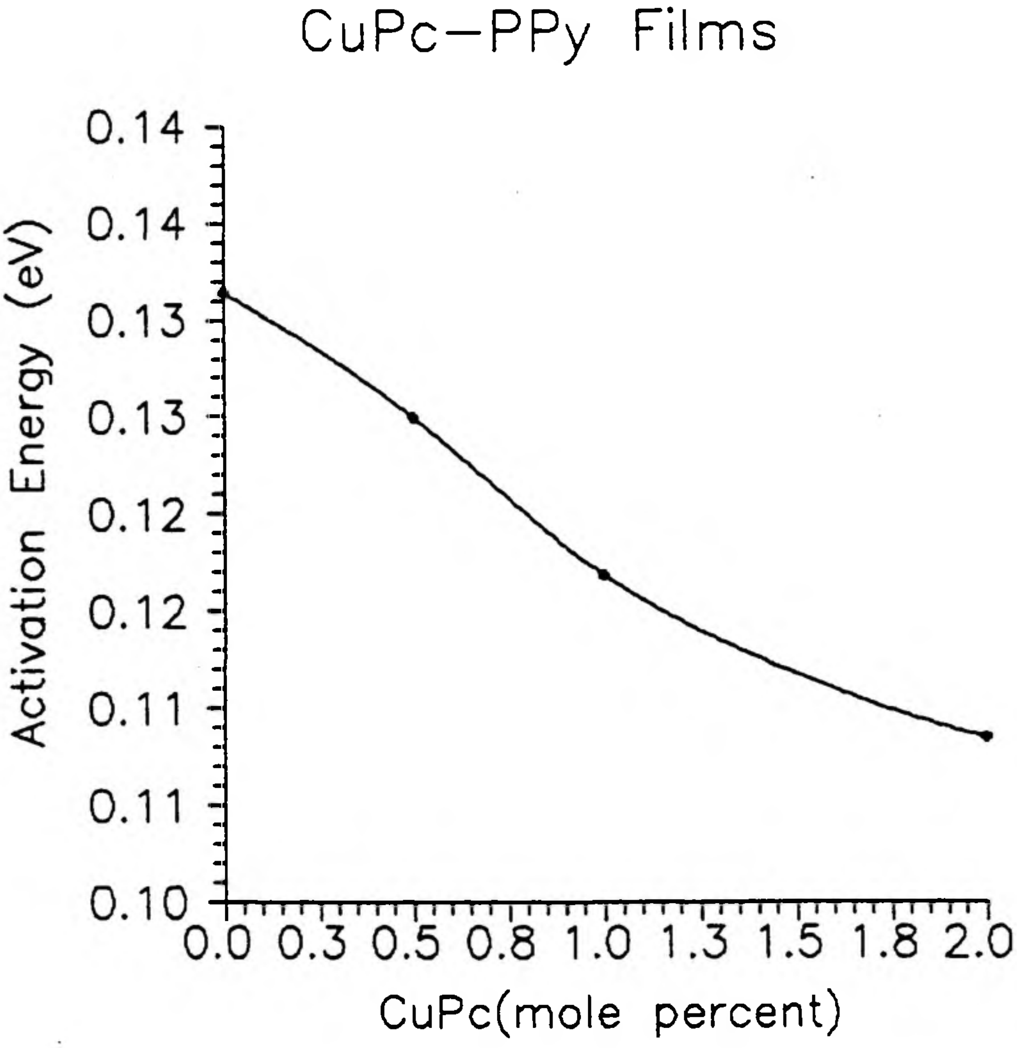


Fig. 4.17 : Plot of activation energy versus CuPc concentration for PPy-CuPc films

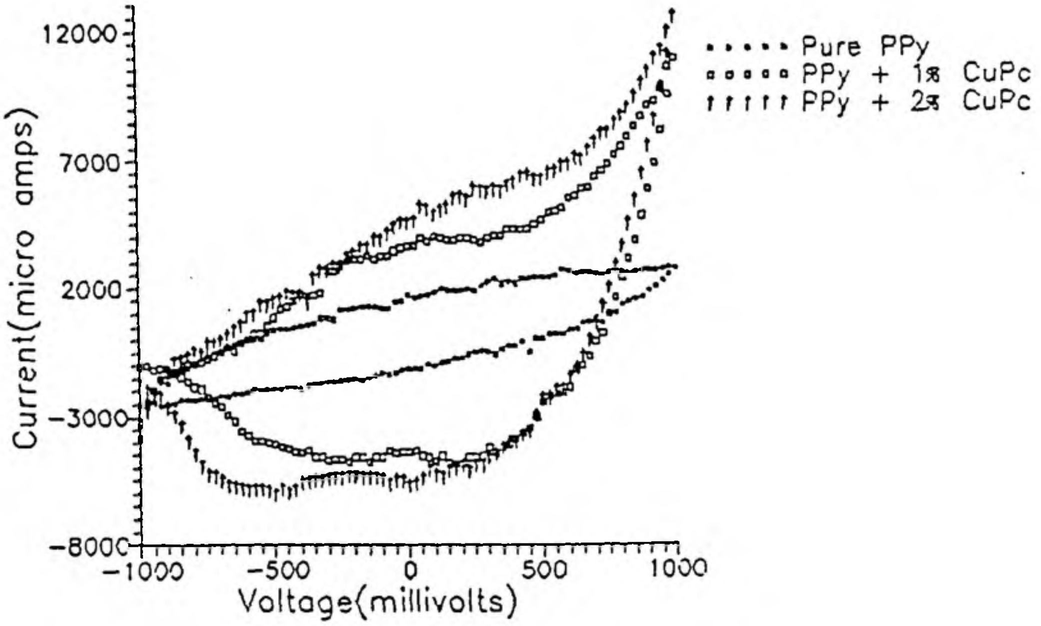


Fig. 4.18 : C-V Measurements of PPy-CuPc films under illumination.

in 0.1 M aq. KCl electrolyte

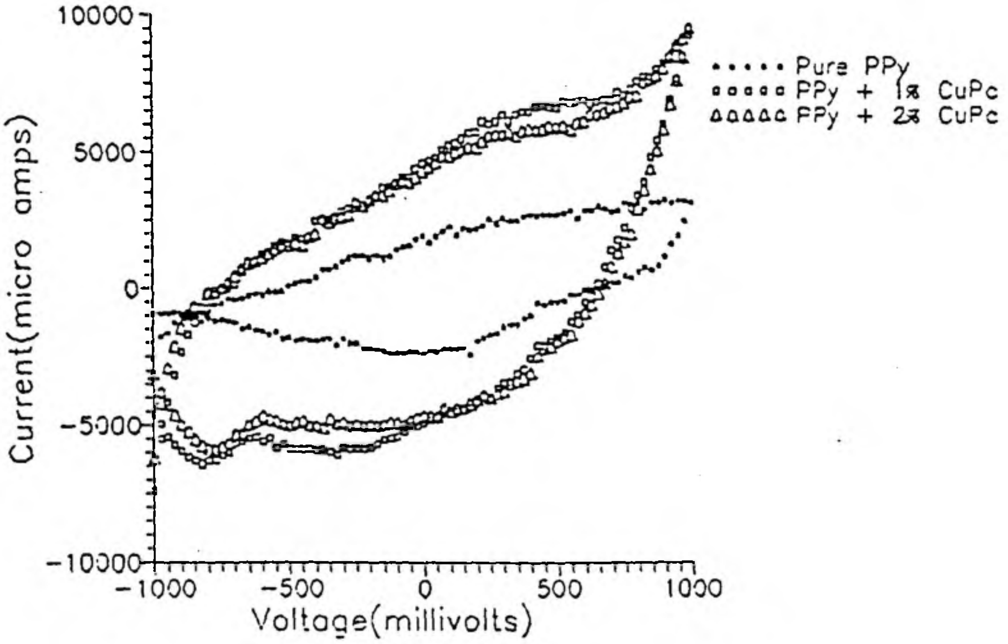


Fig. 4.19 : C-V Measurements of PPy-CuPc films under illumination.

in 0.1 M aq. $LiClO_4$ electrolyte

Several authors have studied the cyclic voltammetry of PPy films in liquid electrolytes, and these are well documented in the literature[253-256]. Although there are some changes in the actual potential values from one report to another, the overall features in the C-Vs are the same (viz. two peaks are observed in the C-Vs that correspond to the reduction and oxidation of the PPy films). This process of reduction and oxidation of the PPy is understood in terms of the transport of ions / charge carriers in and out of the polymer. The peak position and its sharpness depend on the nature of the dopant ion present in the electrolyte. The pure PPy by itself does not exhibit much photosensitivity as such. However, after CuPc incorporation, the films respond to illumination. This is clearly evident from the **Figs. 4.18 and 4.19.** There is a large increase in current under illumination, which is dependent on concentration of phthalocyanine molecules.

The PPy film containing CuPc exhibits two oxidation peaks at –0.15 V and +0.2 V. The first oxidation peak correspond to oxidation of PPy and the second oxidation peak is due to the incorporated phthalocyanine. This peak was absent in pure PPy film. It seems that this oxidation peak arises from doping process of the macrocycle. Similar type of peak has been reported for the phthalocyanine film[257]. It may be noted that the peak currents in both the anodic as well as cathodic regions are increasing as the phthalocyanine concentration in these films is increasing. This suggests that transport of both types photo generated carriers is facilitated due to the presence of mid gap levels. This may be contrasted with the results in the case of polythiophene containing CuPc discussed later in the thesis.

(c) CHEMICAL SENSITIVITY

The PPy and PPy-CuPc films obtained in its highly conducting form were exposed to the various chemical vapours such as methanol, ammonia and nitrogen dioxide in an apparatus already described in **Chapter-II (Fig. 2.3)**. The results obtained from this study are shown in **Fig. 4.20**. The curve A represents the sensitivity towards nitrogen dioxide gas, whereas curve B shows the sensitivity towards the ammonia and methanol vapours. The term sensitivity factor is already described in Chapter-II. From these curves it can be seen that PPy-CuPc films shows moderate sensitivity towards the methanol and ammonia vapours. To mention here, the ammonia vapour sensitivity is higher than that of methanol vapour. It is quite interesting to note that PPy-CuPc polymers show tremendous sensitivity towards nitrogen dioxide vapours. This very high response to nitrogen dioxide vapours can be explained as follows,

The PPy films are functionalized with CuPc to obtain PPy-CuPc films. Nitrogen dioxide was reported [258-259] to have large effects (6 to 8 orders of magnitude) on the conductivity of phthalocyanine films. Chadwick et.al.[260] interpreted that a charge transfer complex is formed between a phthalocyanine donor and nitrogen dioxide acceptor, and the charge carriers are the holes produced in the phthalocyanine matrix. Nitrogen dioxide is π-electron acceptor, and accepted electron would delocalize over the nitrogen dioxide planar structure. Since the hole is also delocalized over the phthalocyanine structure the coulombic force between the opposite charges is weakened and charge carrier movement is facilitated. Ammonia is a competing electron donor and can displace phthalocyanine in the interaction. Thus, we can observe the less response towards the ammonia and on the other hand, tremendous response for nitrogen dioxide vapours in case of PPy films containing CuPc.

4.4: CONCLUSION

The incorporation of phthalocyanine into polypyrrole backbone has been successfully carried out, using both chemical as well as electrochemical method. The

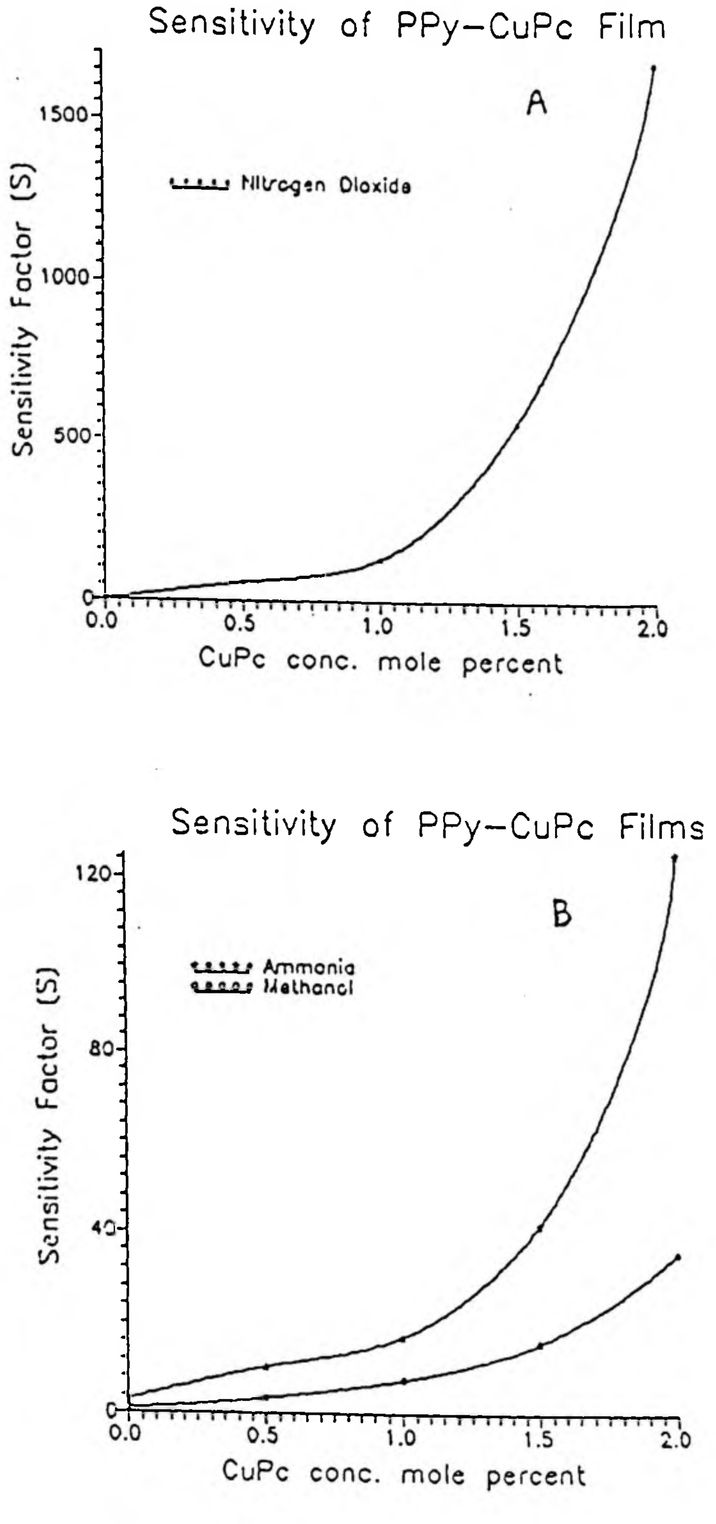


Fig. 4.20 : Plots of sensitivity factor versus CuPc concentration For PPy-CuPc films

TABLE- 4.13

Sensitivity of PPy-CuPc polymers with chemical vapours

Sr. No.	CuPc content mole %	Sensitivity Factor (S)		
		Methanol	Ammonia	Nitrogen dioxide
1	0.0	1.00	3.00	5.00
2	0.5	3.25	10.00	55.00
3	1.0	7.25	16.75	125.00
4	1.5	15.50	41.50	555.00
5	2.0	35.00	125.00	1665.00

polymers obtained by chemical synthesis are black in colour. The electrochemically-synthesised polypyrrole is dark brown in colour and it changes its colour to blue as the phthalocyanine concentration increases in the electrolyte. The FT-IR and UV-VIS techniques were used to confirm the incorporation of phthalocyanine in the synthesized polymers. The chemically synthesized PPy shows mainly amorphous nature, but by incorporating phthalocyanine into its backbone some crystallinity is seen in the resulting polymer. The detailed analysis of XRD shows that PPy-CuPc polymers have an orthorhombic crystal structure with lattice parameters as a = 6.8 A°, b = 5.33 A° and c = 12.62 A°. The ESCA studies show the presence of many components in the C_{1s}, and N_{1s} core-level peaks in these polymers, which could be associated with corresponding charged atoms formed due to polymer/dopant interaction. The Cu_{2p} core-level peaks were present in the PPy samples containing phthalocyanine, whereas this peak was totally absent in pure PPy sample. These results indicate that the phthalocyanine moieties have been incorporated in to the PPy chains, The net effect of addition of phthalocyanine in the PPy polymeric chain is the enhancement in the thermal stability and moderate increase in electrical conductivity. The polymers obtained have shown fairly higher conductivity values (10^{-2} to 10^{-1} S/cm) as compared to PPy synthesized under same conditions.

The pure polypyrrole film obtained by electrochemical route was dark brown in colour, but those containing phthalocyanine became increasingly blue. The polymeric films containing phthalocyanine exhibit higher conductivity than the pure PPy films. The electrochemical activity of the PPy is enhanced by the incorporation of phthalocyanine into the PPy polymeric chain. Further, the photo response in PEC mode increases in PPy by CuPc incorporation. Quite interesting results were obtained in case of exposure of this material towards nitrogen dioxide gas. The films containing phthalocyanine shows tremendous response for this gas. These results show that PPy-CuPc materials can be used in sensor devices.

CHAPTER-V
POLYTHIOPHENE FUNCTIONALIZED WITH PHTHALOCYANINE

POLYTHIOPHENE FUNCTIONALIZED WITH PHTHALOCYANINE

5.1: INTRODUCTION

The conducting polymers that have aromatic rings as repeated constituent units show excellent thermal and air stability. Poly (p-phenylene) [PPP], polypyrrole (PPy), polythiophene (PT) and their derivatives are included in this group[261-265]. Amongst these numerous conducting polymers, PT has rapidly become the subject of considerable interest. From the theoretical point of view, PT has been often considered as model for the study of charge transport in conducting polymers with nondegenerate ground state, while on the other hand, the high environmental stability of both it's doped and undoped states together with it's structural versatility have led to multiple developments aimed at applications such as conductors, electrode materials, and organic semiconductors.

A large number of thiophene derivatives have been described in the literature and their physical properties, nucleophilic substitution and biological activity are of great current interest.[266] Polythiophene has a molecular structure consisting of thiophene rings linked at its 2,5-position and is characterized as a conducting polymer, since it becomes highly conductive on doping with electron donors or acceptors.[267-268] Modern studies on polythiophene[269], aiming at the preparation of electrically conductive polymers began in the 1980's. The extraordinary properties exhibited by PT and its oligomers (hexi-thiophene) such as thermochromism, electrochromism, diode like characteristics etc. have drawn considerable interest in this polymer. A general literature survey of PT has been given in chapter I.

In the present chapter, the synthesis, characterization and properties of polythiophene functionalized with phthalocyanine (PT-CuPc) using chemical as well as electrochemical methods are described. The chapter is mainly divided into two sections. Section A describes the chemical method of synthesis. This section also contains the characterization and measurements of properties of PT-CuPc polymers. The electrochemical method used for synthesis and the measurements of properties of polythiophene containing phthalocyanine (PT-CuPc) are described in section B.

5.2 EXPERIMENTAL

5.2.A: CHEMICAL SYNTHESIS OF PT – CuPc POLYMERS

(1) Synthesis using $FeCl_3$ as oxidizing agent

In a 100ml dry nitrobenzene, 9.75 grams (0.06 M) of ferric chloride ($FeCl_3$) was added quickly taking precaution that no moisture was absorbed during the process of weighing and mixing. To this mixture, desired amount of copper phthalocyanine chloride (CuPc green) was added. Nitrogen gas was bubbled for about half an hour through the solution so as to remove any dissolved oxygen. Then 1.68gram (0.02 M) of thiophene monomer was added to the above mixture drop wise within a duration of 15 minutes. It was then cooled by keeping it in an ice bath or at room temperature water bath under continuous flow of nitrogen gas.

After the reaction period of 6 hrs, the reaction mixture was directly poured into 500-ml methanol solution and stirred well for half an hour to precipitate the polymer. The polymer obtained was filtered then washed successively with methanol till the filtrate obtained was colorless. Finally, the polymer was dried at about 80°C for 4 hours. Polythiophene having different concentrations of CuPc ranging from 0 to 5 mole percent per monomer unit was synthesized by this method. The polymer samples obtained were additionally doped with 1N iodine solution as described in chapter II.

(2) Synthesis using $CuCl_2$-$AlCl_3$ mixture as oxidizing agent

In a 100ml beaker containing 50ml dry nitrobenzene, 1.34 grams [0.01 M] anhydrous $CuCl_2$ and 1.33 grams [0.01 M] anhydrous $AlCl_3$ powder were added and the contents stirred for 10 minutes. $AlCl_3$ dissolved completely while few suspended particles of $CuCl_2$ were seen in the solvent. Then the desired amount of phthalocyanine ranging from 3, 5 and 10 mole % was added into the reaction mixture. The contents of the beaker were heated up to 75°C and then 1.68 grams [0.02 M] thiophene monomer was added drop wise within 10-15 minutes of time under constant stirring of the reaction mixture. The original pale brown color of the mixture suddenly changed to dark brown/black. The temperature was further increased to 85°C. The reaction mixture was kept at this temperature for about 6 hours. For the synthesis of pure polythiophene same conditions as described above were used except for the addition of CuPc green.

After the desired time, the reaction mixture was cooled to room temperature. The reaction mixture was then poured into the beaker containing 250ml methanol, which was stirred for about half an hour. The polymer thus precipitated was filtered, thoroughly washed using additional 500ml methanol and dried at 80°C for 4 hours.

5.2.B: ELECTROCHEMICAL METHOD

The direct incorporation of phthalocyanine into polythiophene was carried out in a single compartment cell having a gold film coated glass substrate as working electrode, platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode which were connected to computer controlled potentio-galvanostat (Vibrant EC 2010 Model) as described in chapter II.

Typically the electrolyte contains 3.42 grams tetra butyl ammonium perchlorate (TBAP) [0.1 M] dissolved in 100ml dry nitrobenzene. The desired amount of CuPc (blue) ranging from 0.5 to 4 mole percent of monomer (thiophene unit) was thoroughly dispersed in the electrolyte by nitrogen purging for about half an hour. Further, 3.36 grams of thiophene monomer [0.4 M] was added to the electrolyte and the electrolytic cell was kept saturated with nitrogen atmosphere. The electrochemical polymerization was performed potentiostatically with an applied potential of 1.8-2.0 V for the stipulated time intervals of 300, 450, 600 and 900 seconds respectively so as to obtain polymeric films of different thickness values. The films were thoroughly rinsed in distilled water several times and dried at room temperature and later preserved in a desiccator.

5.3: RESULTS AND DISCUSSION

The synthesis of polythiophene containing phthalocyanine was carried out using $FeCl_3$ at two different temperatures namely 0°C and room temperature. The reaction carried out at room temperature was almost instantaneous and gave small quantity of precipitated polymer immediately along with the color change from light yellow to dark black with the addition of thiophene monomer into the reaction mixture. This implies that the reaction rate is very fast at room temperature. In order to slow down the reaction, the polymerization was carried out at low temperature (0°C). Even at this temperature, the reaction rate was observed to be equally fast. In this case also the polymer precipitated immediately after the addition of thiophene monomer into the reaction mixture. Since no advantage was seen in lowering the reaction temperature, further experiments were carried out at room temperature itself. The data for chemical synthesis of PT-CuPc polymers using $FeCl_3$ and $CuCl_2$-$AlCl_3$ as an oxidizing agent are presented in **Table-5.1** and **5.2** respectively.

The reactions carried out using $CuCl_2$-$AlCl_3$ mixture as an oxidizing agent, was successful in synthesizing pure polythiophene only. The functionalization with phthalocyanine in this oxidizing mixture was unsuccessful, which was confirmed by the fact that the added phthalocyanine was precipitated back. This may be due to the weak acidic character of the $CuCl_2$-$AlCl_3$ oxidizing mixture as compared to $FeCl_3$. Another factor, which has influence on the reaction, may be quite large size of the phthalocyanine molecule. Initially it was thought that the substituted chlorine atoms in the CuPc (green)

TABLE- 5.1

CHEMICAL SYNTHESIS DATA FOR PT-CuPc POLYMERS USING $FeCl_3$ AS OXIDIZING AGENT.

Serial Number	Thiophene Taken Grams	$FeCl_3$ Taken Grams	CuPc Taken Grams	$FeCl_3$ to Thiophene Mole ratio	% Yield
1	1.7*	9.75	-----	3:1	78.3
2	1.7	9.75	-----	3:1	90.4
3	1.7	9.75	0.143	3:1	93.0
4	1.7*	9.75	0.285	3:1	87.9
5	1.7	9.75	0.285	3:1	100.0
6	1.7	9.75	0.428	3:1	100.0
7	1.7	9.75	0.713	3:1	100.0

Solvent: Nitrobenzene, 100 ml for each experiment.

Reaction temperature: Room temperature (27°C)

Reaction Time: 1 Hour

*** Reactions at 0°C**

TABLE-5.2

CHEMICAL SYNTHESIS DATA FOR PT-CuPc POLYMERS USING $AlCl_3$-$CuCl_2$ AS OXIDIZING AGENT.

Serial Number	Thiophene Taken Grams	$AlCl_3$ Taken Grams	$CuCl_2$ Taken Grams	CuPc Taken Grams	% Yield
1	1.7	1.33	1.34	0.0	85.37
2	1.7	1.33	1.34	0.238 G	No polymer
3	1.7	1.33	1.34	0.713 G	No polymer
4	1.7	1.33	1.34	0.571 B	No polymer
5	1.7	1.33	1.34	1.140 B	No polymer

G = CuPc green and B = CuPc blue.

Solvent: Nitrobenzene, 100 ml for each experiment.

Reaction temperature: 85 + 2°C

Reaction Time: 6 Hours

molecule might be hindering the coupling reaction, but the reaction with unsubstituted CuPc (blue) also precipitated the CuPc back. The FT-IR spectrum reported for this polymer showed the peaks which are characteristic of polythiophene but no distinct peaks for phthalocyanine peaks were observed in this case. Hence, it can be said that the incorporation of phthalocyanine into polythiophene is not possible with $CuCl_2$-$AlCl_3$ oxidizing mixture under present conditions.

The appearance of pure polythiophene (PT) synthesized with $FeCl_3$ was red in color. The addition of phthalocyanine into PT changes its color from red to pale brown. As the content of phthalocyanine was increased above 5%, the polymer turns dark brown. The changes in the color of PT with the addition of phthalocyanine are depicted in the photographs (see **Fig. 5.1**)

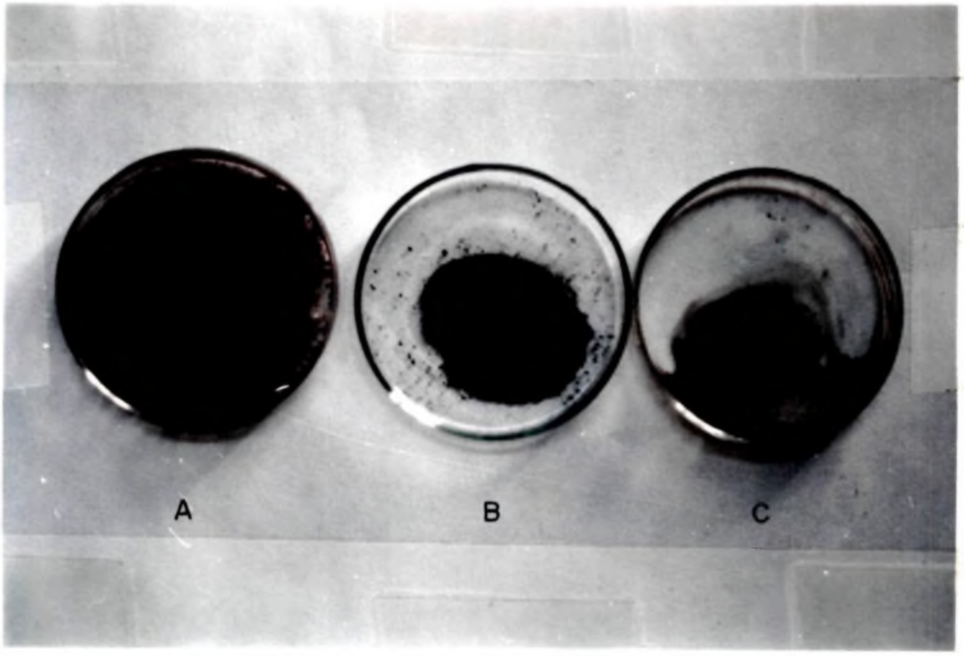


Figure 5.1 : Colour changes in PT powder samples with CuPc (A) Pure PT (B) PT + 2% CuPc and (C) PT + 5% CuPc.

5.3.A. CHEMICALLY SYNTHESIZED PT-CuPc POLYMERS

5.3.A.1: CHARACTERIZATION

(a) FT-IR STUDIES

The functionalization of polythiophene with CuPc was confirmed by the FT-IR spectral studies. The spectra obtained for the different polymers are shown in **Fig. 5.2**. The absorption peaks of the corresponding polymers along with their assignment are given in **Table-5.3**. The characteristic bands of polythiophene were observed at 2921, 2343, 1625,1440, 1028, 784, 701, 690 and 440 cm^{-1} respectively. These observed values match very well with the reported data.[270] The absorption bands at 1387, 1270, 1207, 1153,1028, 944, and 506 cm^{-1} which are assignable to the phthalocyanine skeleton, were found to be present in the spectra of polymer sample functionalized with phthalocyanine together with the above mentioned polythiophene peaks. The characteristic band of C-Cl vibrations are totally absent in the spectra of polythiophene functionalized samples, which clearly indicate that polythiophene gets attached to the phthalocyanine ring via C-Cl termination. Thus, IR spectral data clearly gives an evidence of presence of CuPc in the backbone of polythiophene.

(b) UV-VIS STUDIES

The UV-VIS spectra of the solid polymeric samples were recorded in its diffuse reflection mode. These data were converted in terms of absorption with respect to wavelength using computer-controlled program. The spectra so obtained are depicted in **Fig. 5.3**. The spectrum of pure polythiophene undoped sample shows a single broad absorption peak centered at 400 nm (curve A). The spectrum of polythiophene containing phthalocyanine exhibits two additional absorption peaks at 660 nm and 730 nm along

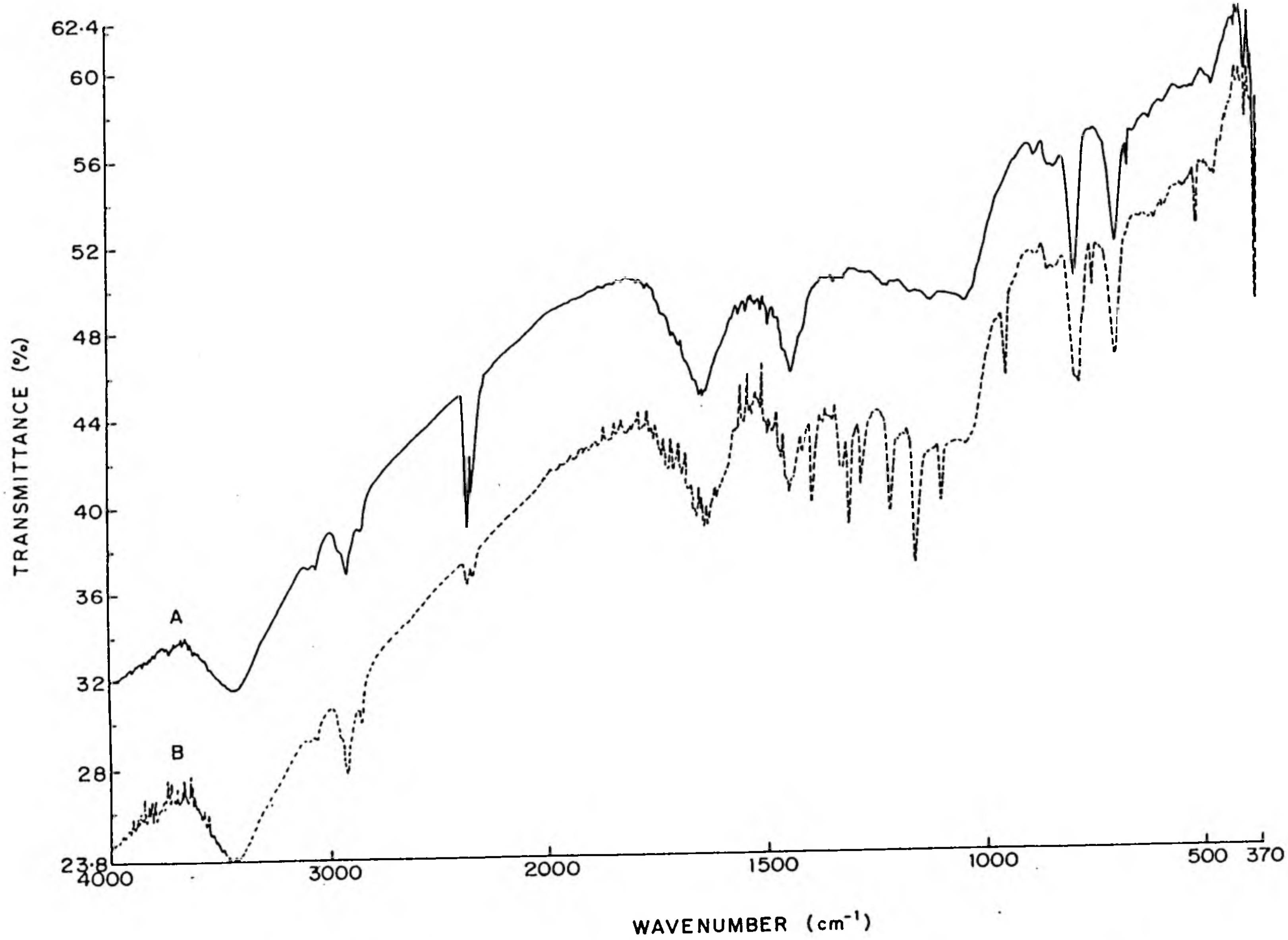


Figure 5.2 : FT-IR absorption spectrum of PT-CuPc powder samples.

In KBr (A) Pure PT and (B) PT + 5% CuPc

TABLE- 5.3

FT-IR ABSORPTION DATA FOR PT-CuPc POWDER SAMPLES (KBr pellet).

Pure PT	PT + 5% CuPc	Possible Assignments.
3446.60 (br.)	3436.89 (br.)	
2912.62 (S)	2922.33 (S)	C-H stretching
2359.22 (S)	2359.22 (w)	
1637.24 (br.)	1627.56 (br.)	
1434.09 (br.)	1434.09 (S)	C = C symmetric stretching
-------	1385.72 (S)	C – C Vibrations
-------	1300.00 (S)	(B)-C-N stretching
-------	1274.48 (m)	C = N stretching
-------	1206.76 (S)	CuPc skeleton
-------	1152.80 (VS)	C-H In Plane Deformation
-------	1090.68 (m)	C-H Bending Vibration
1018.10 (w)	1018.13 (w)	C-H In Plane Bending
-------	945.57 (S)	CuPc skeleton
785.96 (S)	785.96 (S)	2,5 Disubstituted Thiophene
694.06 (S)	698.90 (S)	C-H Out Of Plane Vibration
-------	505.43 (m)	Aromatic Ring Deformation

S = strong **w = weak** **m = medium**
VS = very strong **B = benzene** **br. = broad .**

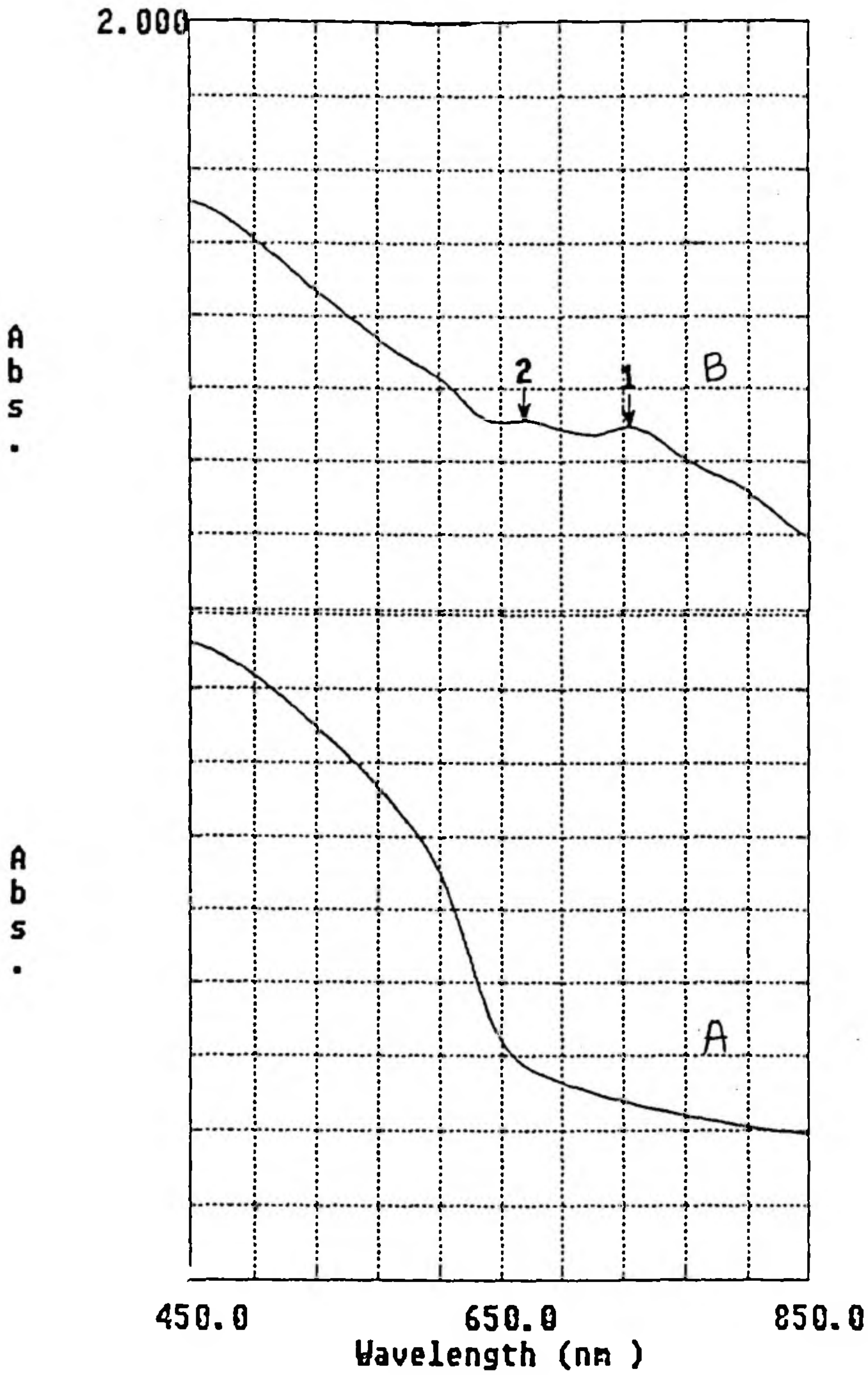


Figure 5.3 : UV-VIS spectrum of PT-CuPc powder samples In its reflection mode (A) Pure PT (B) PT + 5% CuPc

with the very broad absorption centered at 400 nm (curve B). The absorption bands at higher wave length (λmax) values i.e. at 660 and 730 nm are characteristic of the phthalocyanine molecule. The incorporation of phthalocyanine increases the conjugation length of the polymer. The phthalocyanine acts as doping agent and creates defects in the polymer chain. The structural changes that occur in the polymer exhibits additional peak in the spectra of functionalized polythiophene polymer. These results indicate the incorporation of phthalocyanine molecule into polymeric chains. The absorption values for CuPc match well with the reported values given by Dudek et.al.[271]

The UV-VIS spectrums for PT-CuPc samples recorded in dilute H_2SO_4 are shown in **Fig.5.4**. The spectrum A corresponds to pure PT sample, whereas spectrums B and C correspond to PT with 2 and 5% CuPc respectively. The pure PT sample shows a broad spectrum. The two broad peaks centered at about 480 nm and 850 nm are clearly seen in this sample. The PT samples containing phthalocyanine shows much stronger absorption peaks compared to pure PT sample. The new absorption peaks observed at 380, 670 and 730 nm can be easily assigned to phthalocyanine moiety. The peaks at higher absorption wavelength i.e. 670 and 730 nm are due to splitting of the Q-band of the phthalocyanine. As the phthalocyanine content increases, the intensity of these peaks also increases. The acid doping of polythiophene creates defects in the form of polaron/bipolaron. The charge transport occurs through these polarons and bipolarons over the extended conjugation of phthalocyanine. So, the changes in the peak position as well as change in the intensity implies that the structural changes have taken place in the PT due to the addition of CuPc.

(c) MICROANALYSIS

The calculated and observed values for various PT-CuPc polymers are presented in **Table-5.4**. As can been seen from this table, the chlorine content increases with an increase in the phthalocyanine content in the polymeric samples. In the synthesized form, these samples are chlorine doped because the synthesis was carried out in $FeCl_3$. From the values of chlorine content, it can be easily pointed out that the doping level is very low.

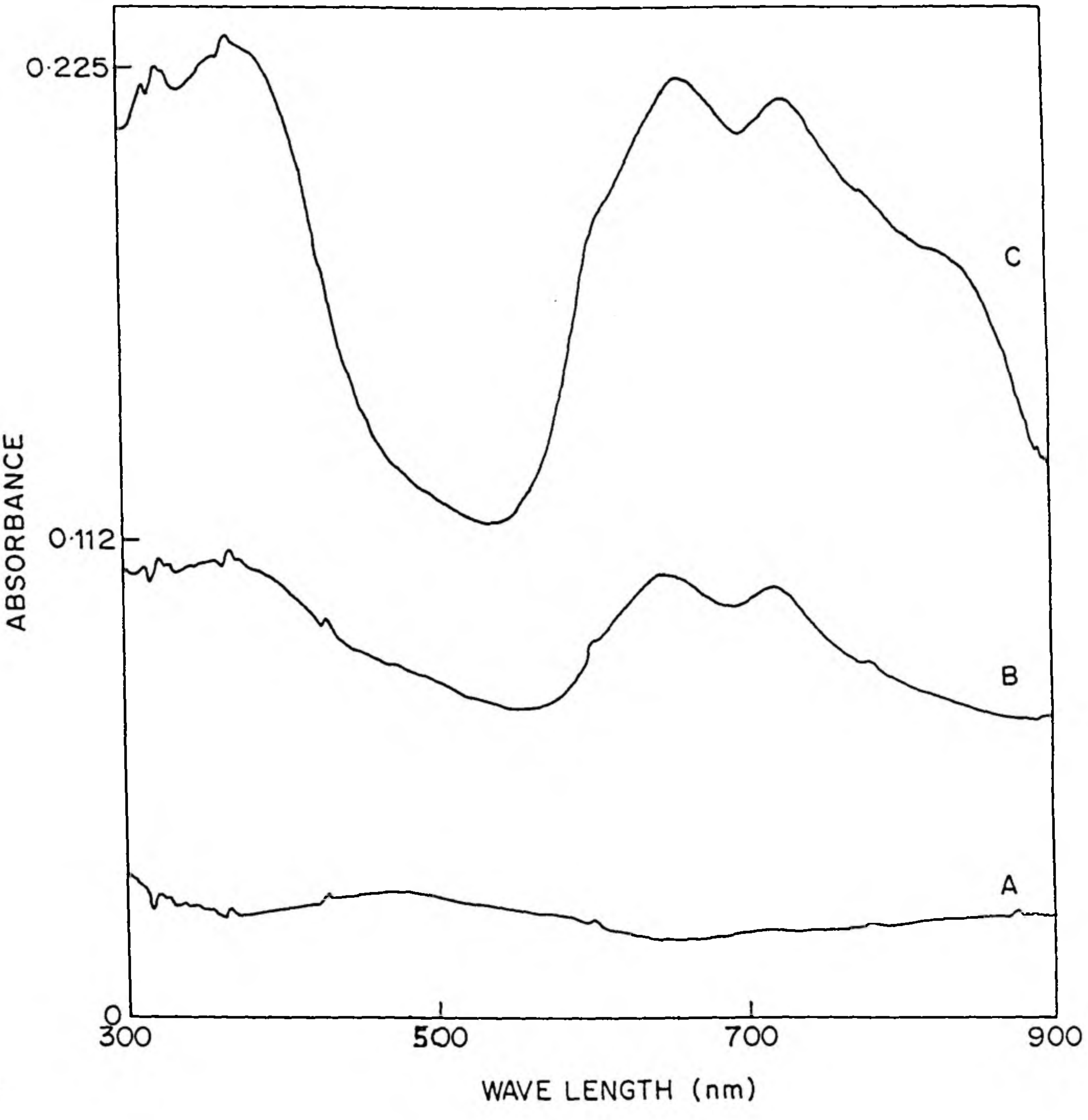


Figure 5.4 : UV-VIS spectrum of PT-CuPc powder samples in dil. H_2SO_4 (A) pure PT (B) PT + 3% CuPc and (C) PT + 5% CuPc

TABLE- 5.4

Microanalysis data of PT-CuPc polymers

Elements	Pure PT		PT + 3%CuPc		PT +5%CuPc	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
Carbon	54.59	56.16	55.17	54.36	51.15	51.91
Hydrogen	2.27	2.31	2.18	2.94	2.02	2.11
Sulfur	36.40	36.02	29.42	32.98	27.28	27.44
Chlorine	6.72	5.38	8.27	7.73	14.13	13.40
Nitrogen	----	----	3.22	0.70	2.98	2.98
Copper	----	----	1.70	1.21	2.44	2.15
Cl/S mole Ratio	0.166	0.133	0.253	0.211	0.466	0.440

Sample	**Empirical Formula**
Pure PT	$(C_4H_2S)_6$ Cl $(PT)_6$: $(Cl)_1$
PT + 3% CuPc	$(C_4H_2S)_{32}[C_{32}H_{12}N_8Cu]$ Cl_8 $(PT)_{32}$: $(CuPc)_1$: $(Cl)_8$
PT + 5% CuPc	$(C_4H_2S)_{16}[C_{32}H_{12}N_8Cu]$ Cl_8 $(PT)_{16}$: $(CuPc)_1$: $(Cl)_8$

In other words, these samples are not highly conductive. The conductivity measurements data carried out on these samples show the similar type of observation. The calculated values for the various elements present in pure PT samples are C = 54.59, H = 2.27, S = 36.40 and Cl = 6.72 are well matched with observed values for this sample of C = 56.16, H = 2.31, S = 36.02 and Cl = 5.38. These values show the molecular composition of $(C_4H_2S)_6$ (Cl). The chlorine content is very low i.e. 5%, which also suggests that the substitution/grafting take place mainly at these moieties of CuPc green.

Interestingly, the PT samples containing 5% phthalocyanine shows that for about 16 repeat units of monomer, there exists one molecule of phthalocyanine. In these phthalocyanine-containing samples, the chlorine content is higher than that of pure PT. Thus, the doping level increases as the phthalocyanine content increases ($FeCl_3$ was used for synthesis). This was reflected in getting higher conductivity in these samples as compared to pure PT sample. The calculated values of C = 51.15, H = 2.02, S = 27.28, N = 2.98, Cl = 14.13 and Cu = 2.44 for the molecular composition of $(C_4H_2S)_{16}$ $[C_{32}H_{12}N_8Cu]$ $(Cl)_8$ are well matched with the calculated values of C = 51.91, H = 2.11, S = 27.44, N = 2.98, Cl = 13.40 and Cu = 2.15. From these results it can be concluded that four thiophene units replace the four chlorine atoms present on each of the phthalocyanine ring. Thus, microanalysis studies clearly suggest that PT-CuPc polymers contain central CuPc molecules linked with PT short chains.

5.3.A.2: CHARACTERIZATION OF STRUCTURE

(a) X-RAY DIFFRACTION STUDIES

The X-ray diffraction patterns obtained for the PT-CuPc powder samples are shown in **Fig.5.5.** In this figure curve A belongs to pure PT sample and curves B and C correspond to PT with 2 and 5% CuPc samples respectively. From the diffraction patterns, it is very clear that the polymers obtained are largely amorphous in nature. Pure PT sample exhibits a broad amorphous peak which is centered at about 19° in the 2θ

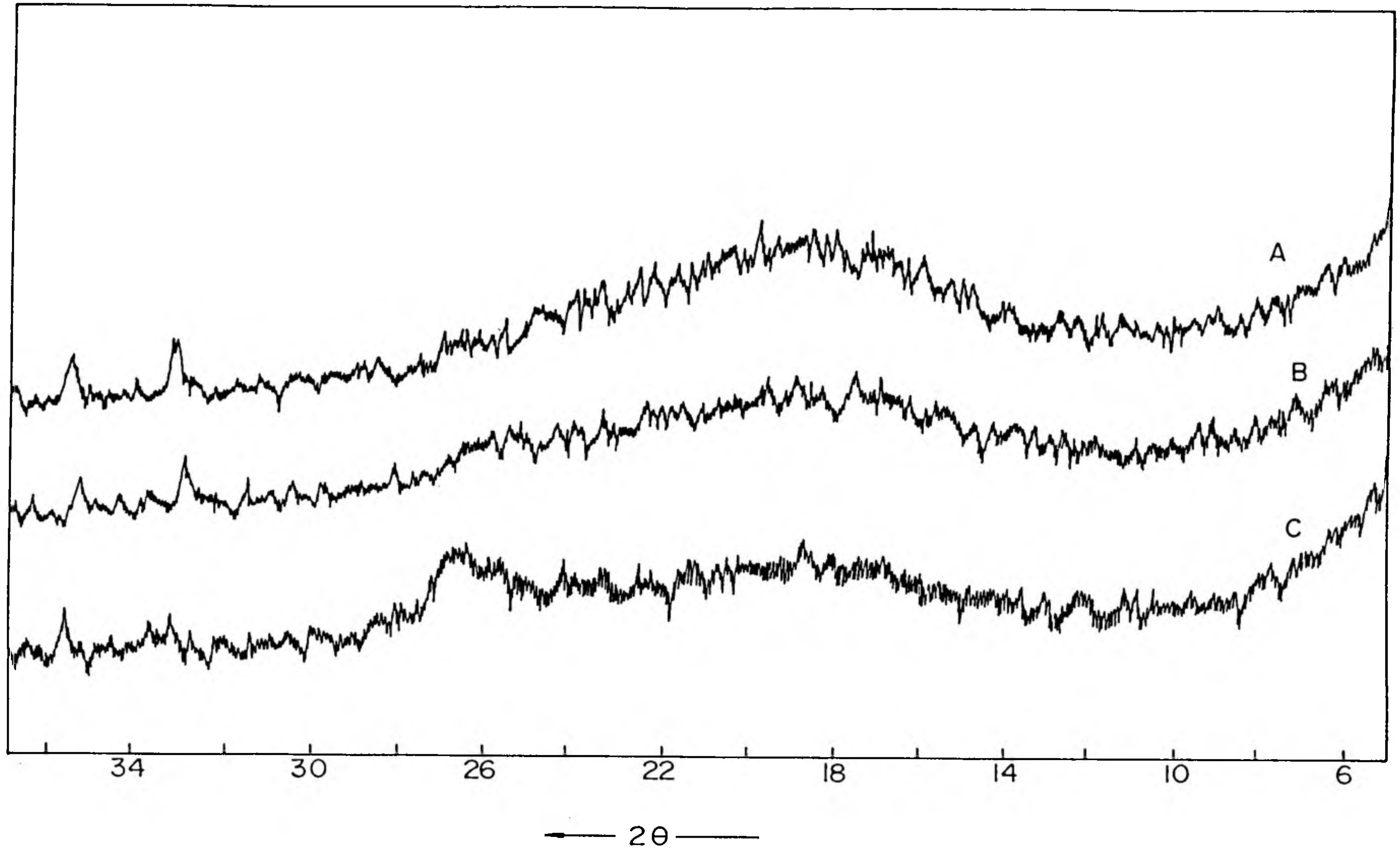


Figure 5.5 : X-ray diffraction patterns of PT-CuPc powder samples.
(A) Pure PT (B) PT + 3% CuPc and (C) PANI + 5% CuPc

region. The polymeric samples containing phthalocyanine shows the crystalline peaks in the 2θ region of 24-30°. These reflections are characteristic for the phthalocyanine moieties which have layered stacked structure.

Although PTs are essentially amorphous polymers, partial crystallinity has been reported in some cases especially for the PT chemically synthesized by Grignard coupling reactions[272]. These authors proposed two models of crystalline structure for PT, one is the orthorhombic structure with unit cell parameters as a = 7.80 A°, b = 5.55 A°, and c = 8.03 A° and the other a monoclinic unit cell with a = 7.83 A°, b = 5.55 A°, and c = 8.20 A° and β = 96°. The results obtained in the present studies somewhat contradict the earlier observations regarding its crystallinity. This can be explained as follows: As $FeCl_3$ (strong oxidising agent) has been used in the present studies, the reaction proceeds at a much faster rate, which may not allow to form a well ordered structure. Also, while carrying out experiments, it was observed that as soon as the thiophene monomer was added to the reaction mixture containing $FeCl_3$ and nitrobenzene, a dark black colored precipitate was immediately seen. In order to control the reaction rate, experiments were carried out at low temperatures such as 0°C and with slow addition rate of thiophene monomer. However, these experiments also resulted in amorphous PTs.

In another set of reactions, the synthesis of PT homopolymer was carried out using $AlCl_3$-$CuCl_2$. In this case also a good yield was obtained as that in $FeCl_3$ system. If one compares the oxidizing power of $FeCl_3$ with $AlCl_3$-$CuCl_2$ mixture then obviously latter is a weak oxidizing mixture compared to former. The reaction time to obtain quantitative yield with $FeCl_3$ was just about 1 hour, whereas for the same yield using $AlCl_3$-$CuCl_2$, the time required was about 6-8 hrs. Hence, the fact that PT synthesized by $FeCl_3$ route, which is much faster than the $AlCl_3$-$CuCl_2$ gives an amorphous PT is quite explainable. The earlier reports[272] on crystalline PT are based on mainly the Grignard coupling reactions, which are known to be very slow reactions.

(b) ESCA (XPS) STUDIES

The C_{1s} and S_{2p} core-level spectrum of pure polythiophene in its undoped and doped state are shown in **Fig.5.6.** The C_{1s} peak was deconvoluted in to three components: at 284.8 eV (α and β carbon of the thiophene units), 286.2 eV (charged carbon atoms) and 288.0 eV ($\pi \rightarrow \pi^*$ shake up satellite) for pure PT sample. There is an additional peak for the PT sample containing CuPc, which appeared at higher B.E. (291.2 eV). This peak is due to charged carbon species arising from phthalocyanine skeleton. When PT is functionalized with CuPc, more conjugated carbon species are available for delocalization of charge, which resulted into appearance of higher B.E. peaks. The S_{2p} core-level spectrum was best fitted into two major spin-orbit split doublets ($S2p_{3/2}$ and $S2p_{1/2}$) with the B.E. for $S2p_{3/2}$ at 164.2 eV and 165.6 eV. The former is characteristic of the neutral thiophene unit. The peak at 165.6 eV has been associated with the positively polarized or partially charged sulfur species, resulting from charge extraction of some thiophene units by the dopant. The high B.E. tail in the S_{2p} at 167.8 eV core-level spectra is due to the satellite structure.

Figures 5.7 (C) and **(D)** represents the C_{1s} and S_{2p} core-level spectrums for the undoped and doped states of PT sample containing 5% CuPc. In the doped state, both the C_{1s} and S_{2p} core-level peaks were obtained at higher B.E. as compared with its undoped state. The observed data for C_{1s} and S_{2p} peaks are presented in **Table-5.5** and **5.6** respectively. The area of data peaks clearly indicate that after doping, the higher number of charged species are present in the sample, which is quite expected.

The ESCA or XPS of C_{1s} and S_{2p} core-level spectra for the thiophene oligomers, thiophene polymers and alkyl substituted thiophene polymers are well documented in the literature[273-276]. A number of studies[277-278] have suggested charge withdrawal to occur only from the ring carbon atoms, on the basis of the observed positive B.E. shift in the C_{1s} core-level spectrum and essentially no chemical shift in the S_{2p} core-level spectrum for the doped PT. A similar type of results were seen in the present investigation [see **Table-5.5 and 5.6**]. On the other hand, PT sample containing 5% CuPc in its doped state show

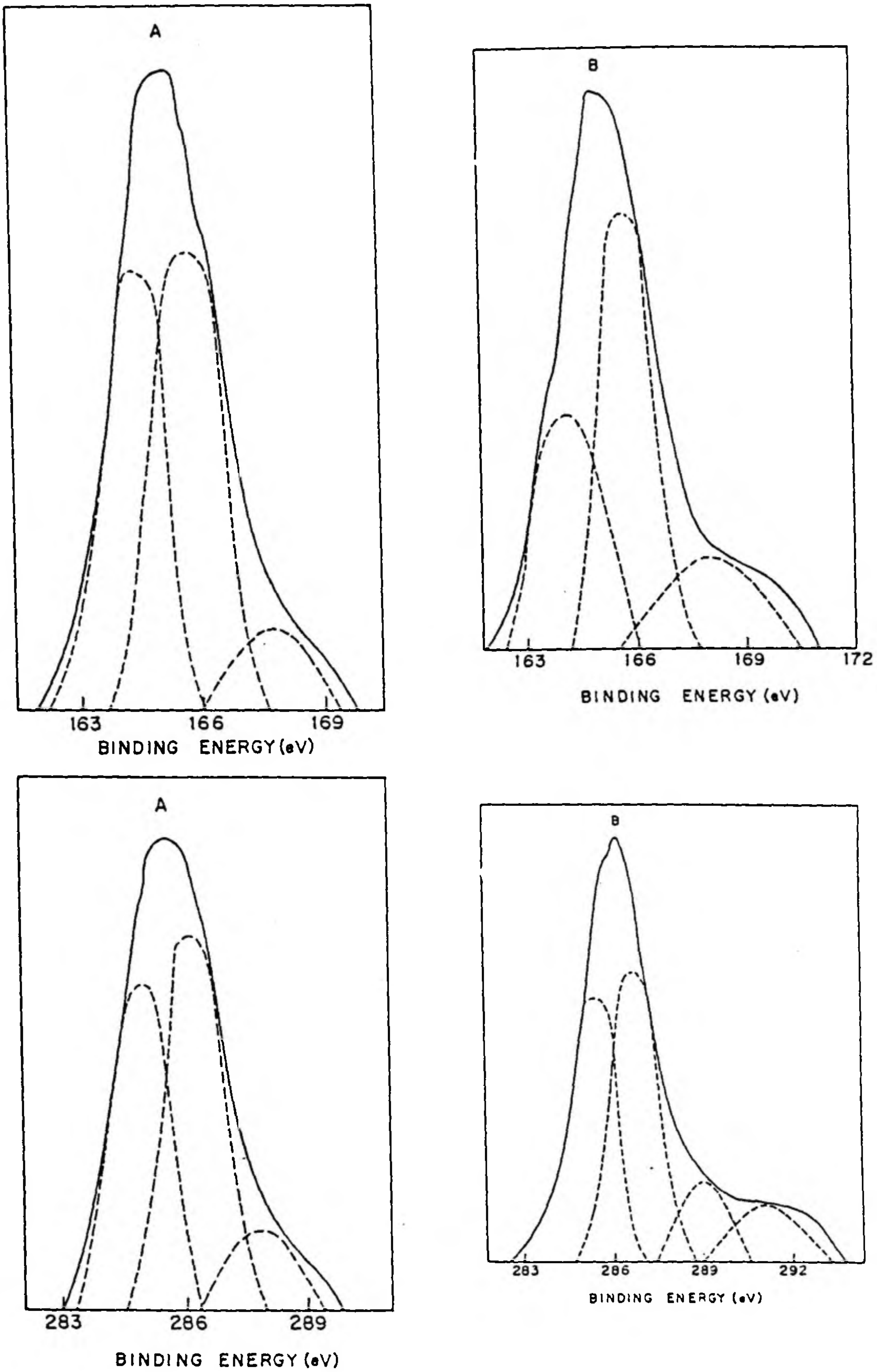


Figure 5.6 : S_{2p} and C_{1s} core-level spectrum of pure PT powder (A) undoped and (B) iodine doped samples

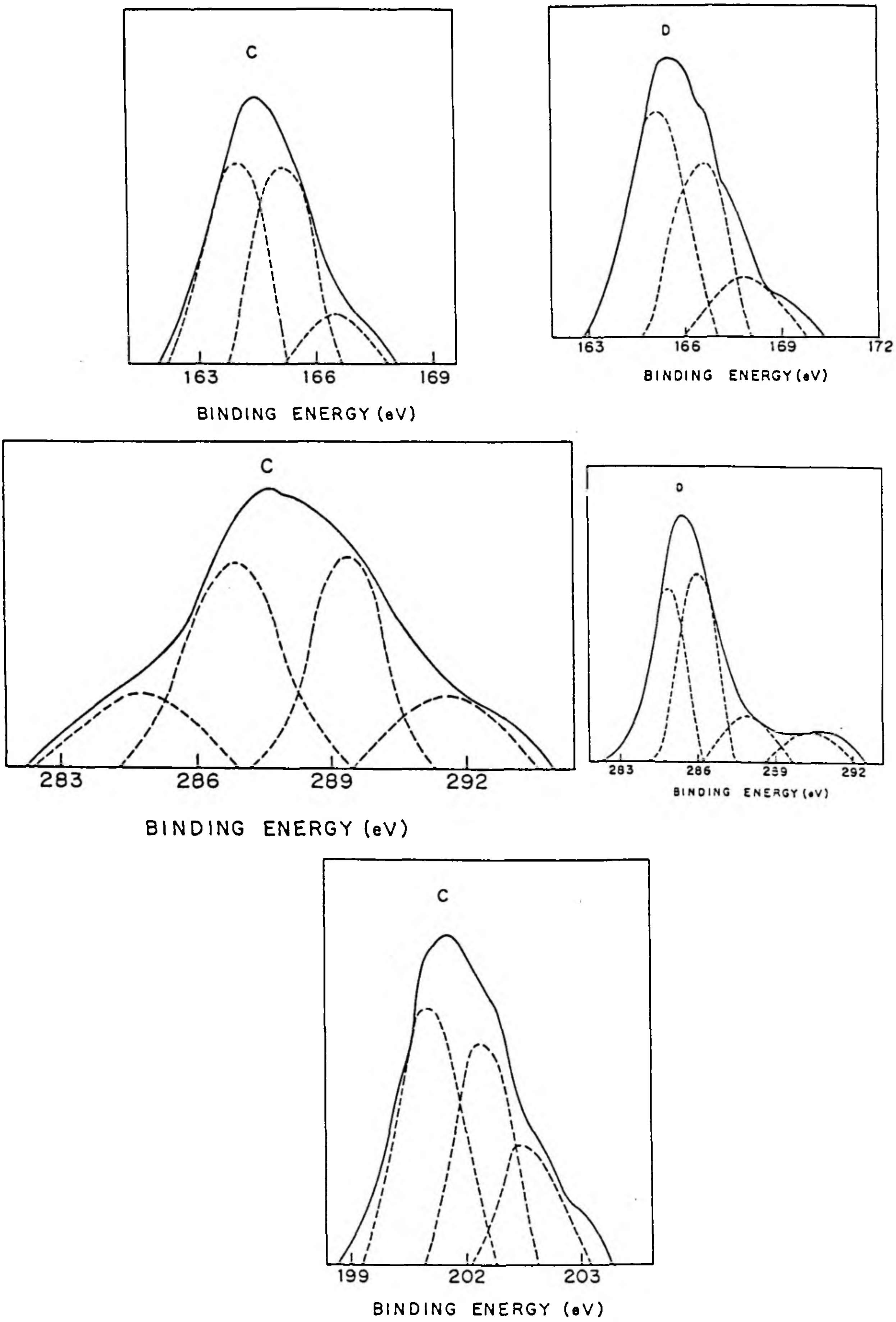


Figure 5.7 : S_{2p}, C_{1s} and Cl_{2p} core-level spectrum of PT + 5% CuPc (C) undoped and (D) iodine doped powder samples

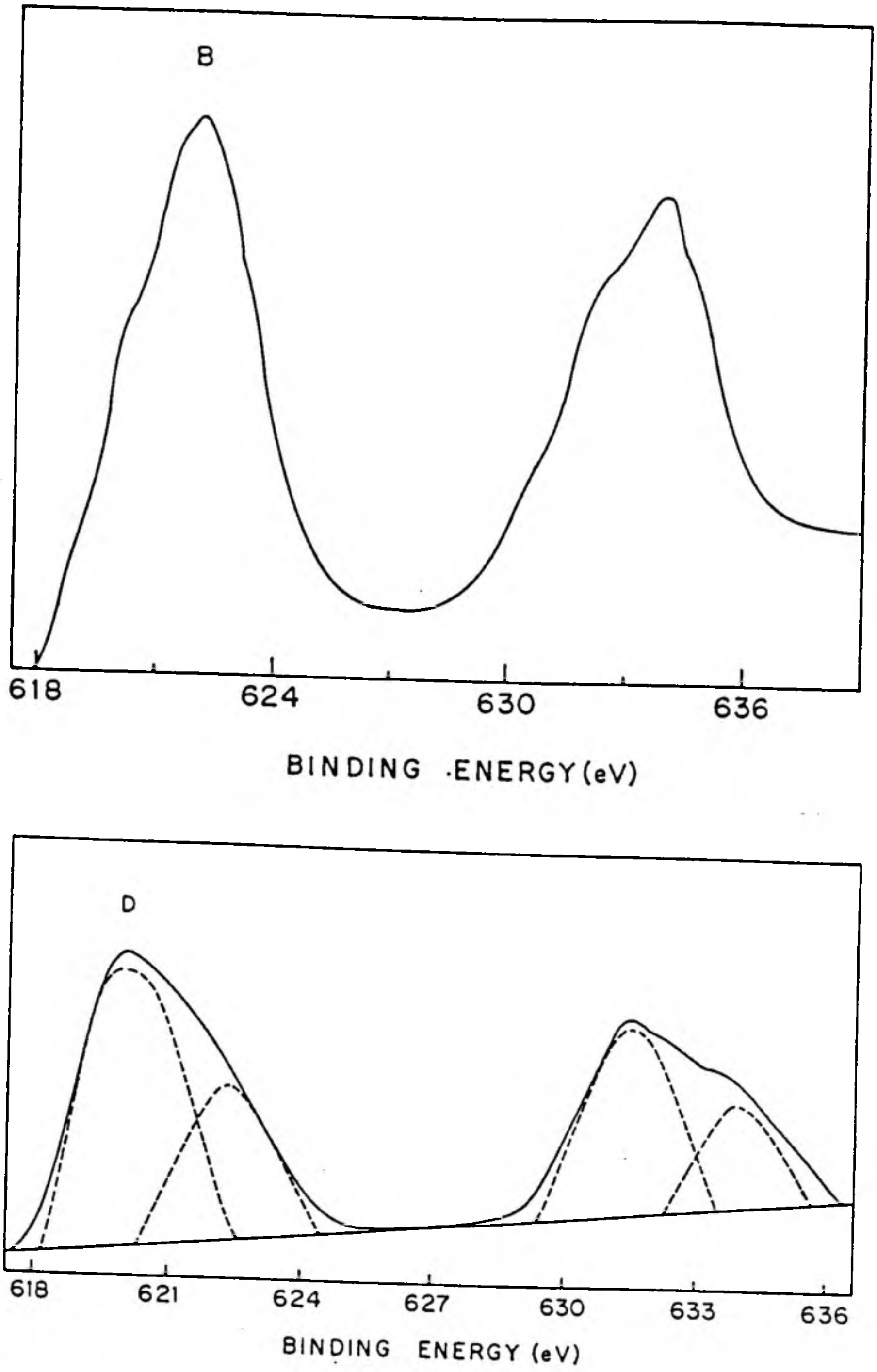


Figure 5.8 : I $_{3p}$ core-level spectrum of PT-CuPc powder samples (B) pure PT and (D) PT + 5% CuPc

that both the carbon and sulfur atoms are positively polarized, with C_{1s} and S_{2p} core-level spectra showing an overall +1.2 eV shift in BE.

The effect of doping on these samples shows interesting spectrum of iodine core-level, which is shown in **Fig. 5.8 (B)** and **(D)**. It is well reported that PT and CuPc both have great affinity towards the iodine molecules. Hence, in iodine doped PT-CuPc samples, there is a competition between the PT and CuPc molecules to react with iodine dopant ions. Due to this competitive reaction, the dopant ions get distributed among PT and CuPc skeletons. The net result shows splitting of the iodine core-level spectrum into two doublets. The first doublet appearing at 620.3 eV and 622.4 eV can be easily assigned to I ($3d_{5/2}$) core-level, whereas the second doublet appearing at 631.4 eV and 633.8 eV can be due to I ($3d_{1/2}$) core-level. In comparison to this, the iodine doped PT homopolymer sample exhibits iodine core spectrum having two sharp well-defined peaks at 621.8 eV and 633.6 eV respectively. These results are tabulated in **Table-5.7**

Thus, ESCA studies clearly give an evidence of incorporation of phthalocyanine in PT chains. The functionalization of PT with phthalocyanine results in more number of charged species both in C_{1s} as well as the dopant I ($3p_{5/2}$) which suggests that these polymers have more delocalization of charges and hence, would be expected to have higher conductivity.

5.3.A.3: MEASUREMENT OF PROPERTIES

(a) ELECTRICAL CONDUCTIVITY

The effect on electrical conductivity as a function of phthalocyanine concentration was studied and the results obtained are shown in **Fig.5.9**. The undoped samples show the rise in conductivity from 10^{-12} to 10^{-8} S/cm with the increase of concentration of phthalocyanine from 0 to 5 mole percent. While the doped sample show the conductivity rise from 3×10^{-4} to 1.3×10^{-3} S/cm for the same concentration of CuPc

TABLE- 5.5

ESCA RESULTS OF C_{1s} LEVEL FOR PT-CuPc POWDERS

Sample	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
PT pure Undoped (A)	C_I = 284.8 C_{II} = 286.2 C_{III} = 288.0	1.75 1.75 2.25	41.90 47.80 10.30
PT pure I_2 doped (B)	C_I = 285.4 C_{II} = 286.6 C_{III} = 288.5 C_{IV} = 291.2	1.62 1.87 2.12 2.25	38.20 41.90 11.50 8.40
PT + 5 % CuPc Undoped (C)	C_I = 284.8 C_{II} = 286.2 C_{III} = 287.6 C_{IV} = 290.2	3.12 2.50 1.87 3.00	13.30 36.20 38.10 12.40
PT + 5 % CuPc I_2 doped (D)	C_I = 285.0 C_{II} = 287.0 C_{III} = 289.4 C_{IV} = 291.5	1.75 1.87 2.50 2.75	39.60 43.00 10.50 6.90

TABLE- 5.6

ESCA RESULTS OF S_{2p} CORE-LEVEL FOR PT-CuPc POWDERS

Sample	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
PT pure Undoped (A)	S_I = 164.2 S_{II} = 165.6 S_{III} = 167.7	2.37 2.25 2.50	45.60 46.70 8.70
PT pure I_2 doped (B)	S_I = 164.2 S_{II} = 165.6 S_{III} = 167.8	2.37 1.75 3.37	30.00 57.30 12.70
PT + 5 % CuPc Undoped (C)	S_I = 163.8 S_{II} = 165.3 S_{III} = 166.6	1.87 1.87 1.75	45.20 44.20 10.60
PT + 5 % CuPc I_2 doped (D)	S_I = 165.0 S_{II} = 166.6 S_{III} = 167.8	2.12 2.12 2.62	47.00 38.10 13.90

TABLE- 5.7

ESCA RESULTS OF I_{3p} LEVEL FOR PT-CuPc POWDERS

Sample	Binding energy (in eV)	FWHM (in eV)	% Area (Relative)
PT pure I_2 doped (B)	$I_{2\,I}$ = 621.8 $I_{2\,II}$ = 633.6	2.62 3.12	53.5 46.5
PT + 5% CuPc I_2 doped (D)	$I_{2\,I}$ = 620.3 $I_{2\,II}$ = 622.4 $I_{2\,III}$ = 631.4 $I_{2\,IV}$ = 633.8	2.75 2.50 2.50 2.12	38.0 21.9 25.5 14.6

mentioned above. The electrical conductivity for the PT-CuPc polymers showed a sharp increase of about 7 to 8 orders of magnitudes, after doping with iodine. This rise in conductivity due to incorporation of phthalocyanine as well as after iodine doping has been explained in detail in the later part of the section.

The change in the electrical conductivity as a function of temperature was measured and the results are shown in **Fig. 5.10**. It may be noted that these plots are for the synthesized polymers as such and not in fully doped states. The conductivity for the PT-CuPc samples was found to be at least three to four orders of magnitude higher than that of pure PT sample. It is interesting to note that as the phthalocyanine content in the PT increases, the electrical conductivity increases considerably. The nature of the graph of log conductivity (σ) versus 1/ T becomes more flat as the CuPc concentration goes on increasing.

The changes in the electrical conductivity as a function of temperature in iodine doped powder samples are shown in **Fig. 5.11**. This very high conductivity upon iodine doping can be explained as follows. The doping of conducting polymers involves random dispersion or aggregation of dopant in molar concentrations in the disordered structure of entangled chains and fibrils. In doped samples, the iodine atoms are mainly associated with the phthalocyanine moieties due to strong charge transfer interaction between them. Thus, the resulting formation of phthalocyanine-iodine complex may also be responsible for high conductivity domains. Also, incorporation of the dopant molecules into the polymer systems disturbs the chain order considerably leading to reorganization of the polymer[279]. Thus, polymer doping leads to the formation of conjugated defects viz. soliton, polaron or bipolaron in the polymer chain ultimately results in sharp increase in the conductivity[280].

The activation energy (ΔE) was calculated from the slopes of the plots of log conductivity versus 1/T as described in Chapter-III. These values were plotted as a function of phthalocyanine concentration and are shown in **Fig. 5.12.** The activation energy for the doped PT sample containing 5% CuPc was as low as 0.05 eV. Whereas for

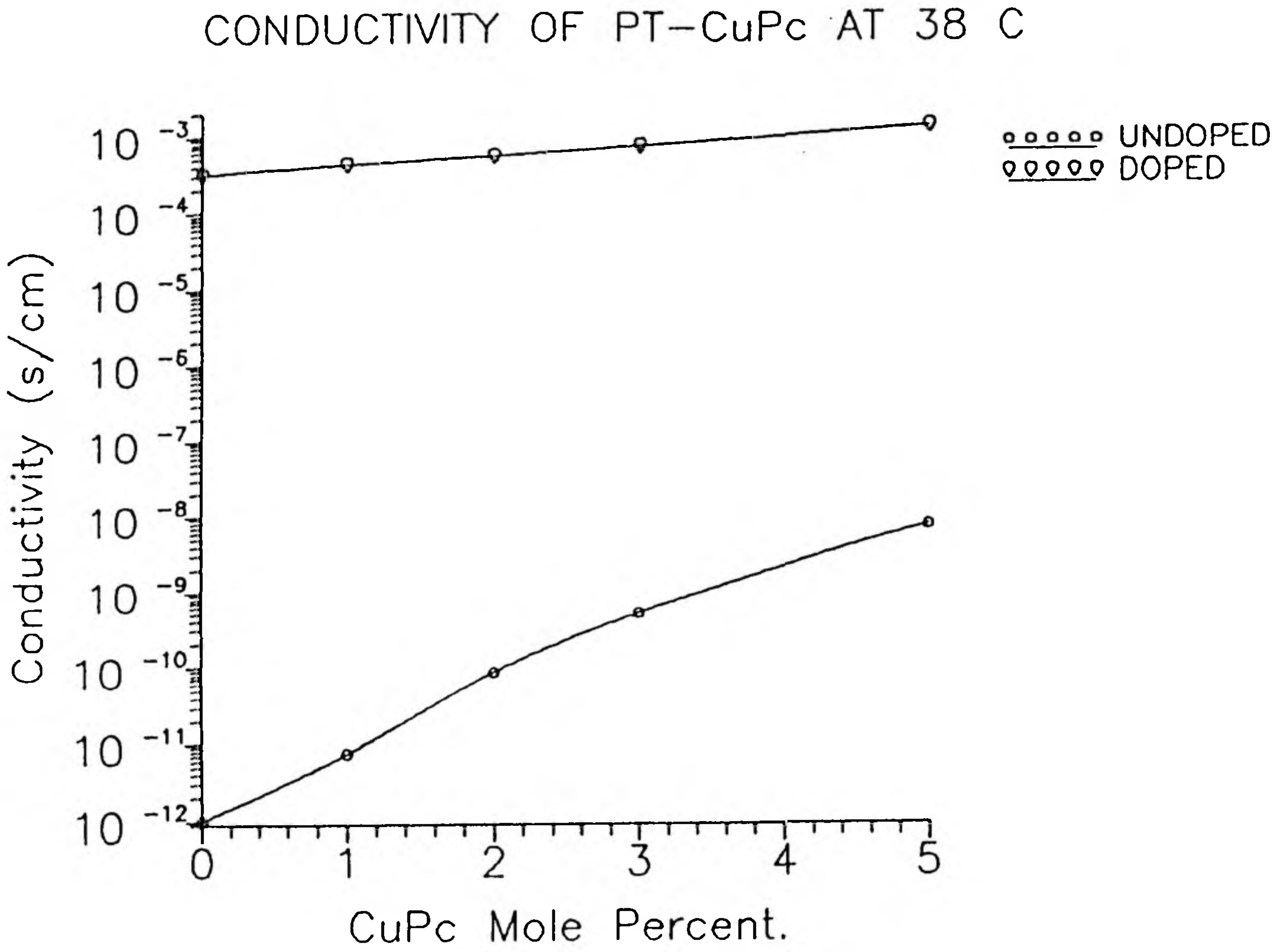


Figure 5.9 : Plots of conductivity versus CuPc concentration for Doped and undoped PT-CuPc powder samples.

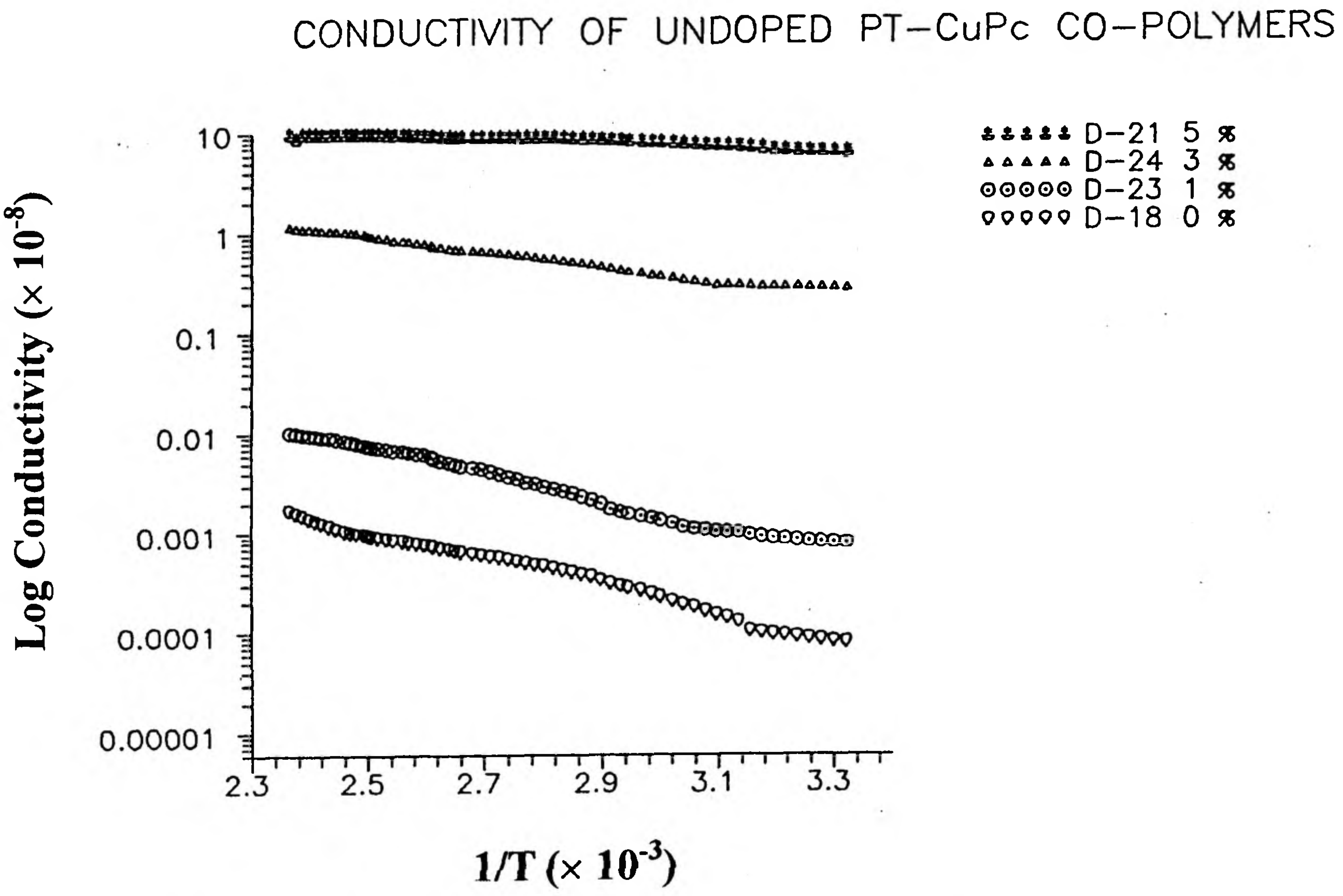


Figure 5.10 : Plots of log conductivity versus reciprocal of temperature For PT-CuPc undoped powder samples

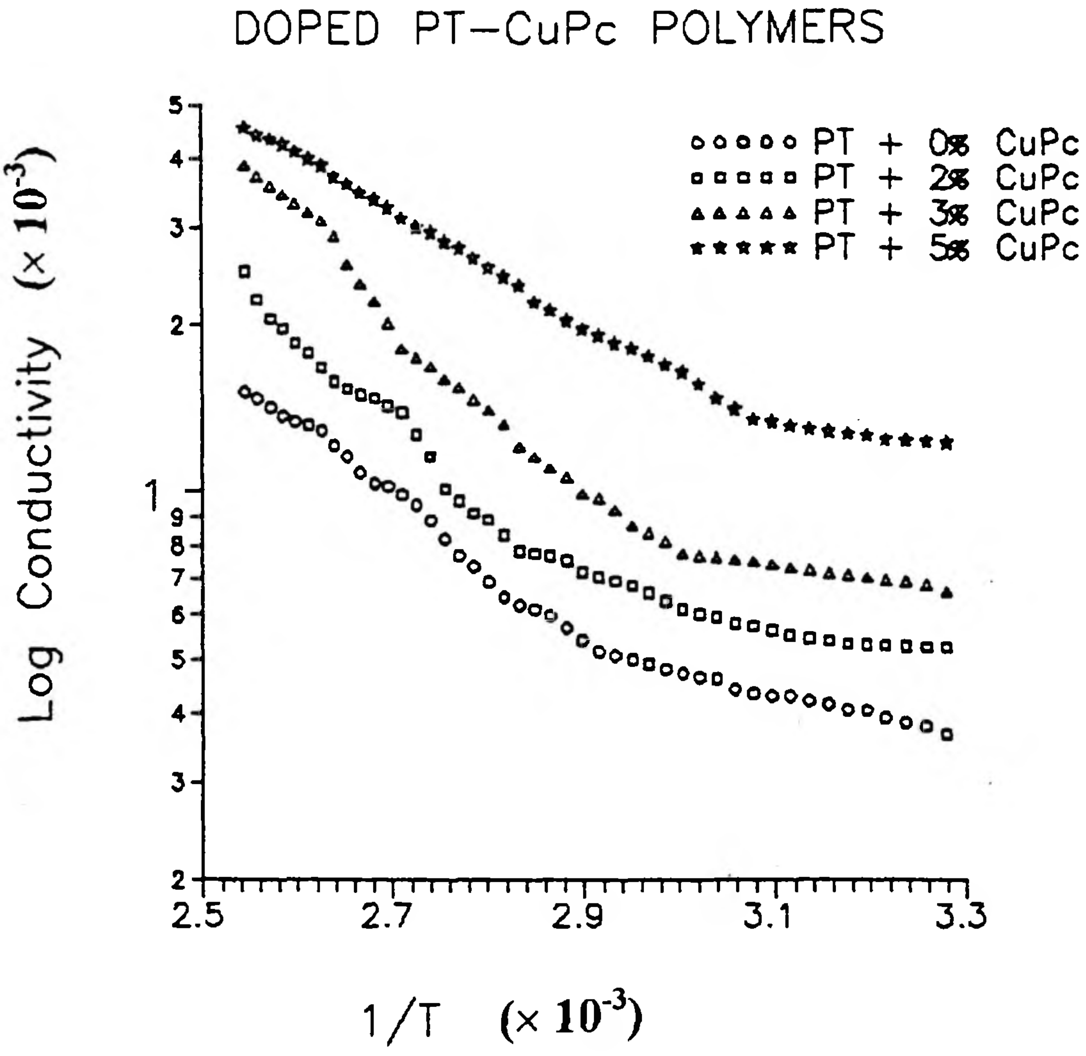
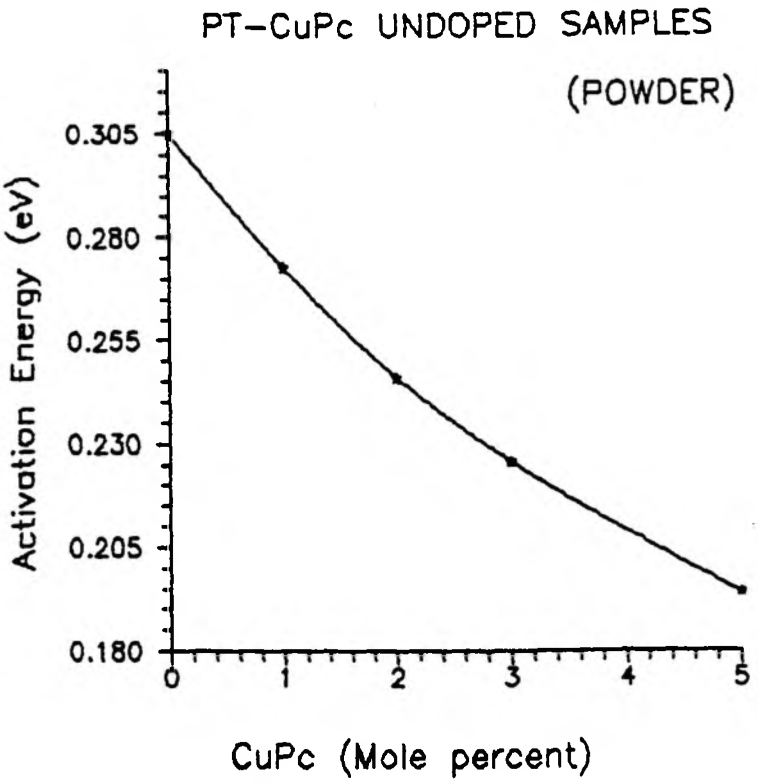


Figure 5.11 : Plots of log conductivity versus reciprocal of temperature For PT-CuPc iodine doped powder samples



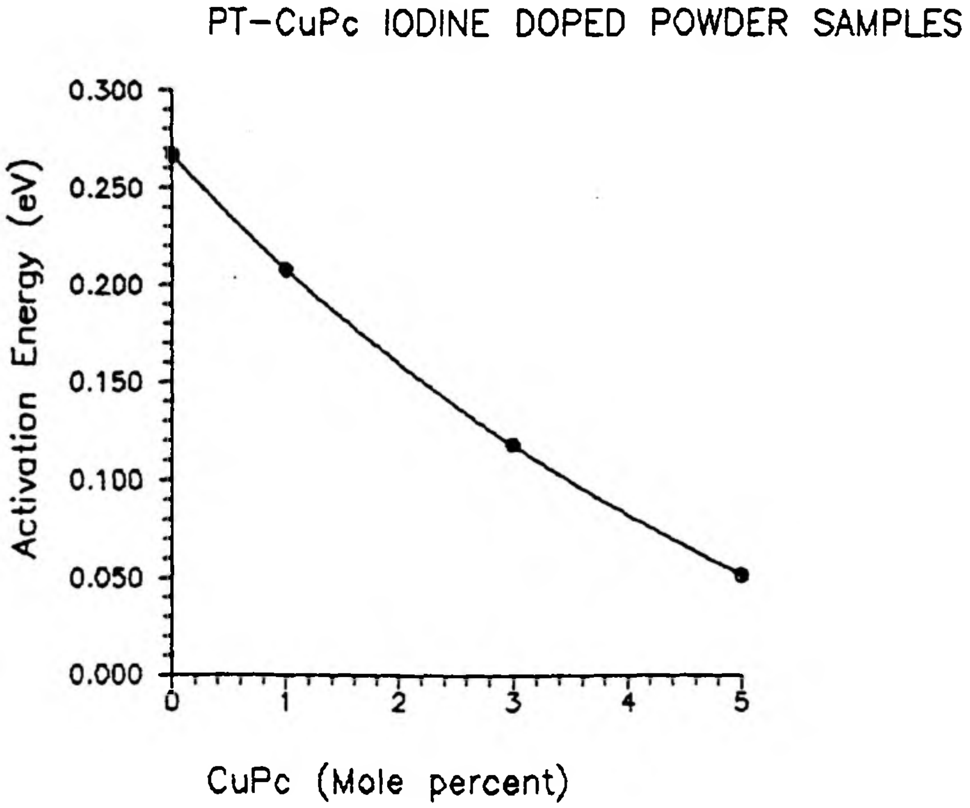


Figure 5.12 : Plots of activation energy versus CuPc concentration for Doped and undoped PT-CuPc powder samples

the undoped state, the activation energy was found to be 0.19 eV. As the CuPc concentration increases, the difference in the activation energy becomes much prominent in their doped and undoped conditions. Iodine doped phthalocyanine is reported to have an activation energy of 0.13 eV.[281] The doping of polymer reduces the band gap, which results in decrease in the activation energy. The other factor, which is responsible, is the presence of phthalocyanine. It is well known that iodine has strong affinity towards binding the metal atom of phthalocyanine. As the CuPc content in the polymer increases, it is expected that the doping level should also increase, which in turn results in low activation energy. The results of activation energy versus CuPc concentration show the similar trend.

The electrical conductivity in these materials is associated with the thermal excitation of mobile π electrons from the valance band containing the highest occupied molecular orbital to the conduction band containing the lowest unoccupied molecular orbital. This mechanism has been described in detail in the earlier chapter. The chemical characterization of thiophene polymers by $FeCl_3$ reveals that the iron impurities exist in the form of an iron (III) octahedral complex. The possibility exists that the complex is coordinated to the polymer backbone[282-283]. Thus, charge transfer between the conjugated polymer and the Fe^{+3} complex might possibly be the origin of charge carriers. These authors found no evidence for migration of impurities, which might be due to the bulkiness of the complex and hence, slow migration of octahedral Fe-complex. In the earlier reports, the polymers prepared by the Grignard route showed impurity migration due to mobile iodide species.

Two energetically equal structures at a point where they couple to give a surface effect known as a 'soliton'. The soliton excitations present in the phthalocyanine polymers probably interact with each other or with neighboring chains leading to free or delocalized electron or hole states, depending upon the coulombic forces between the interacting moieties. Soliton type excitations within these polymers are possible because they possess degenerate ground states. When there is transition from one phase to another, the system has to pass through soliton bound states and therefore, the electronic transport in both heated and unheated polymers containing phthalocyanine could be explained via hopping of soliton-bound states from one chain to another.

(b) CYCLIC VOLTAMMETRIC MEASUREMENTS

In order to study the effect of phthalocyanine on the properties of PT, cyclic voltammetric study was carried out. The sample preparation for this study was described earlier in Chapter-II (**Section 2.2.c**). Cyclic voltammetric studies were carried out with and without illumination i.e. photo electro chemical (PEC) mode as reported earlier[284]. **Figs.5.13, 5.14** and **5.15** shows the cyclic voltammograms (C-V) in aqueous sodium sulfide electrolyte for pure PT, PT with 2% CuPc and PT with 5% CuPc respectively. The C-Vs were recorded in dark and under illumination.

Various energy levels associated with such a PEC configuration cell are indicated in **Fig. 5.16**. It is to be noted that PT is in doped state and hence additional bipolaronic levels are also shown. The different energy levels associated with the chemicals present in the system are taken from standard literature. It can be seen that the presence of CuPc in the polymer gives rise to additional electronic levels, which provide easier path for the electron transport from electrode to S/S^{--} level in the electrolyte. One can now consider the mechanism of sensitization of photocurrent. In dark, the electrons are in the valance band of PT as well as CuPc and it is difficult for their transport to the electrolyte since there is a barrier of almost 1 eV from Ev to S/S^{--} levels. On the other hand, under illumination the electrons are excited to A_F levels in CuPc (photo excited states) which lie much above the S/S^{--} levels. Thus these samples have much higher currents in the cathodic region under illumination than in dark giving rise to sensitization of photocurrent in the presence of CuPc. It may be noted that PT by itself has little photosensitivity due to recombination of photo generated carriers at the bipolaronic levels. The presence of CuPc is essential for observing photosensitive effects.

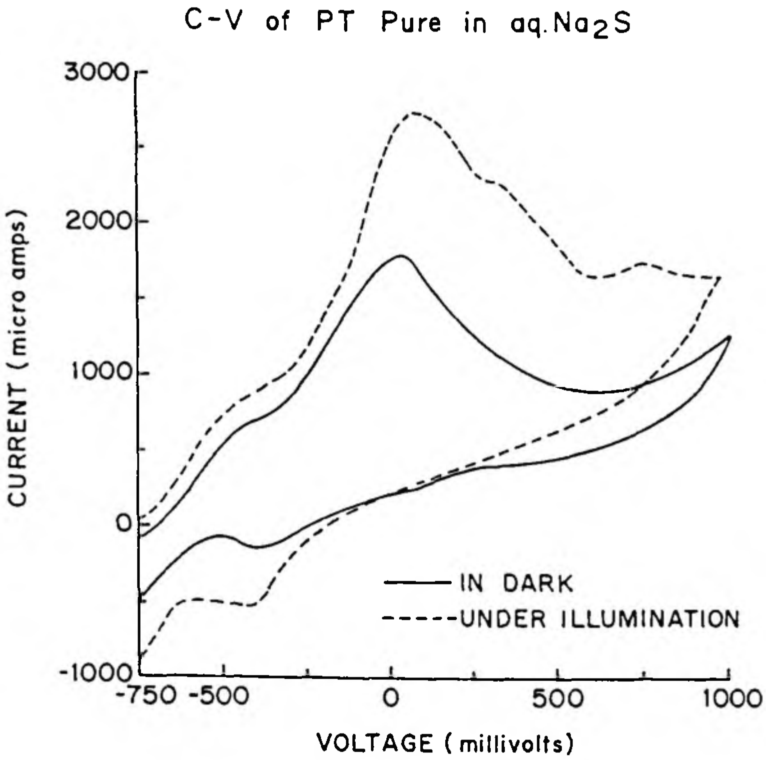


Figure 5.13 : C-V Measurements of pure PT pellet in 0.1 N aq. Na_2S in dark and under illumination

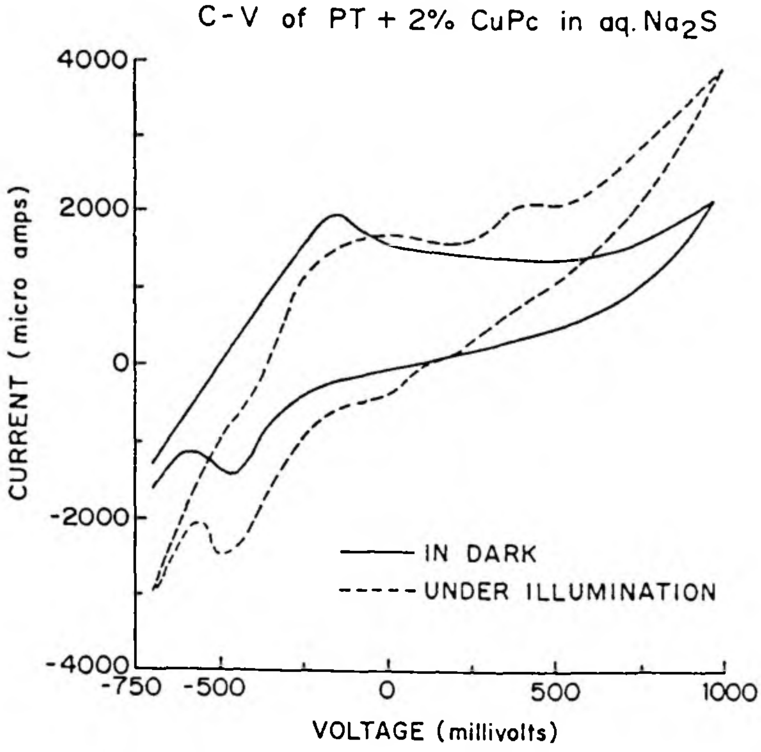


Figure 5.14 : C-V Measurements of PT + 2% CuPc pellet in 0.1 N aq. Na_2S in dark and under illumination

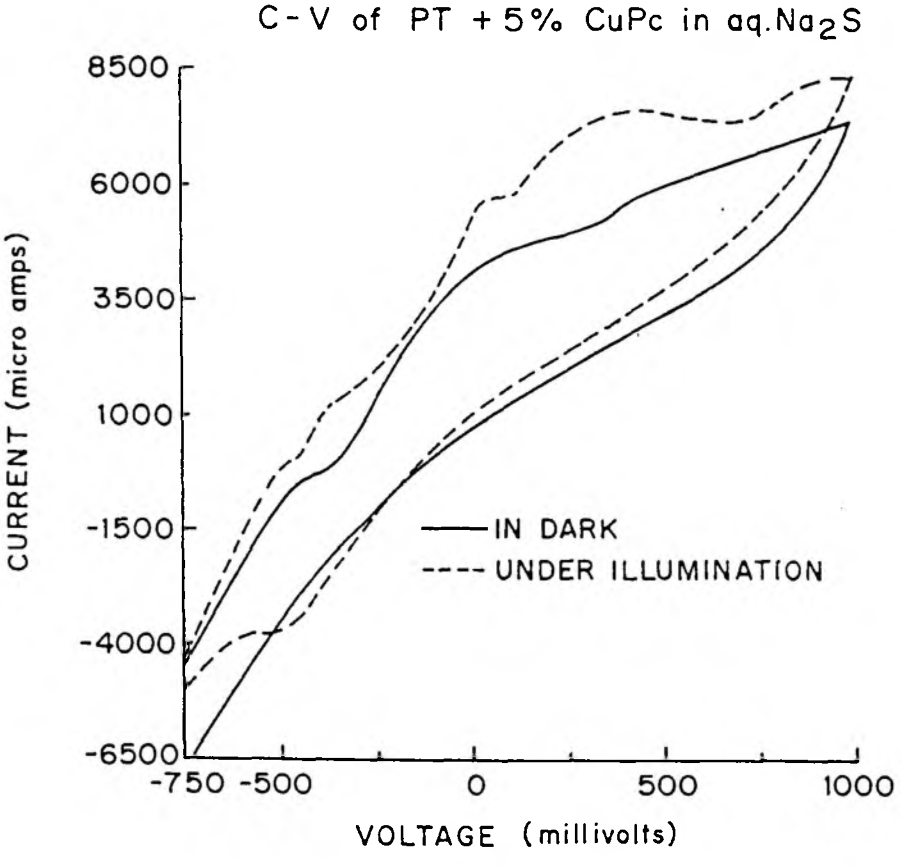


Figure 5.15 : C-V Measurements of PT + 5% CuPc pellet in 0.1 N aq. Na_2S in dark and under illumination

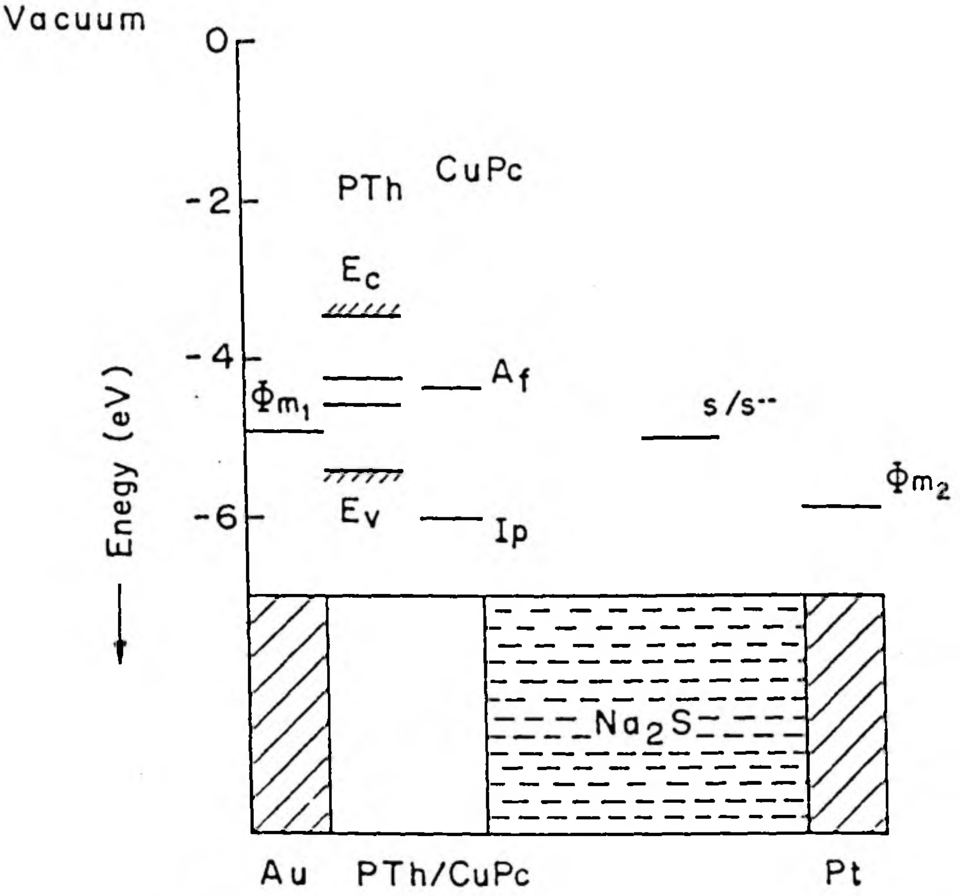


Figure 5.16 : Energy level diagram for PT-CuPc films In aq. Na_2S electrolyte

In case of pure PT, the electrons have to be transported from the gold backing electrode to PT and then to S^{--} levels in the electrolyte. This may occur via bipolaronic states (mid-gap) which are known to be present in doped PT at 1.0 to 1.1 eV above the valence band. However, these are higher than the Fermi level of Au (ϕm) by about 0.4 eV and hence experience a barrier. The incorporation of CuPc in PT leased to the additional impurity/defect sites in the mid-gap region; the electron affinity of CuPc being 4.3 eV and the ionization potential of 6.1 eV. This causes trapping of carriers and decrease in current in the dark. However, under illumination, CuPc absorbs the photon and generates photo-excited charge carriers in its conduction levels. These are then easily transported to the S^{--} levels without any barrier. The photo generated 'holes' in CuPc valence levels also do not experience any barrier and get transported via PT to gold. Thus one can obtain high photosensitivity in the samples containing CuPc which acts as functional group for photon harvesting.

(c) THERMAL STABILITY

The PT-CuPc polymers were tested for their thermal stability using thermo gravimetric analysis. The thermograms obtained for various polymers are shown in **Fig 5.17** in which A corresponds to the pure PT powder sample, whereas B and C corresponds to PT with 3% CuPc and 5% CuPc respectively. The percentage weight loss at different temperatures is represented in **Table- 5.8** for the different samples. From the table, it is evident that up to 500°C the thermal stability for PT-CuPc samples increases as the concentration of phthalocyanine increases. The degradation of phthalocyanine then starts after this temperature (i.e. above 500°). The thermograms mainly show the degradation in two stages. The first stage degradation is up to 200°C, where the moisture/solvent and or low molecular weight species may evolve out of the samples. The second stage of degradation occurs in the range 200-500° C, which can be assigned, to the degradation of polymer.

Another aspect emerges from this data regarding the chemical composition of these co-polymers. One can compare the weight loss observed at any given temperature

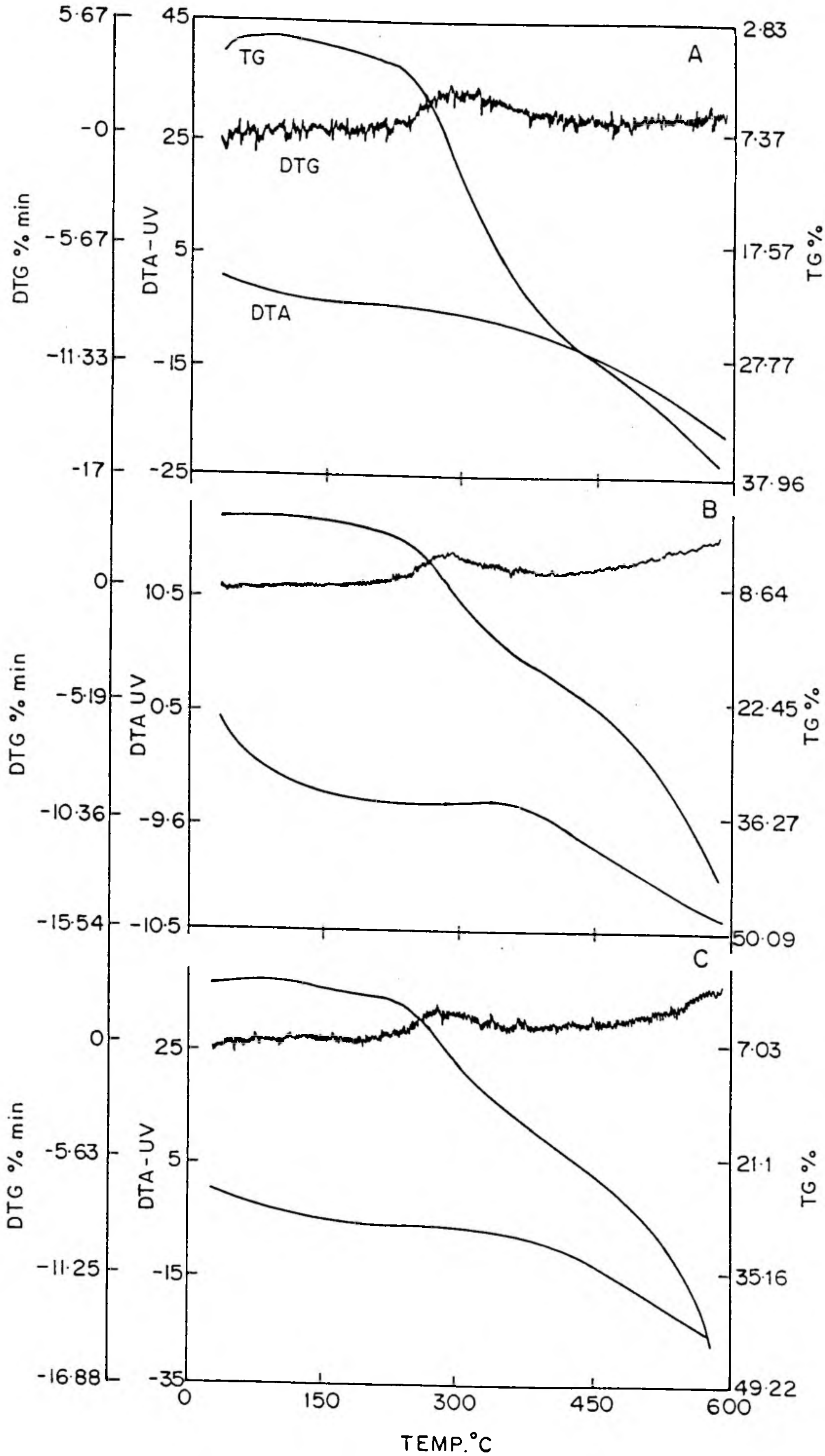


Figure 5.17 : TGA/DTA thermograms of PT-CuPc powder samples In nitrogen atmosphere (A) Pure PT

TABLE- 5.8

THERMAL ANALYSIS DATA OF PT-CuPc POLYMERS (IN NITROGEN)

Temp. ° C	Pure PT % Wt. loss	PT + 1% CuPc % Wt. loss	PT + 2% CuPc % Wt. loss	PT + 5% CuPc % Wt. loss
200	1.60	1.40	1.25	1.00
250	3.00	2.80	2.70	2.50
300	10.80	10.00	9.50	8.00
350	18.80	16.50	14.75	12.40
400	24.10	19.15	18.40	15.15
450	27.80	23.10	22.10	20.10
500	31.20	29.00	27.10	26.20

THERMAL ANALYSIS DATA OF PT-CuPc POLYMERS

CuPc content Wt. %	Wt. loss from 200-500°C	% PT from % T.G.	% PT from actual Wt. add^n
0.0	29.6	100.00	100.00
1.0	27.6	93.24	91.30
2.0	25.5	87.33	77.80
5.0	25.2	85.13	67.80

with that of expected value for a mere physical mixture of PT and CuPc having same composition. These values for the range of composition studied are compared in **Table-5.8** (CuPc does not have significant weight loss below 400°C). It is seen that in every case the value for weight loss is much less than that expected for physical mixture. This clearly suggests that in the present case CuPc participates in the polymerization reaction and the final product is not a mere mixture. It also indicates that thermal stability of the PT-CuPc polymer is higher than pure PT sample.

(d) CHEMICAL SENSITIVITY

The different PT-CuPc polymers obtained were fabricated as a chemical sensor device using interdigited gold films with PEO-$CuCl_2$-Polymer mixture as described in detail in Chapter-II (**section 2.2.d**). This sensor[285] was then subjected to exposure of various chemical vapors such as methanol, ammonia and nitrogen dioxide etc. The results obtained in each case are plotted in **Fig. 5.18** and the data is presented in **Table-5.9** The figure shows the sensitivity factor versus CuPc concentration curves. Here, sensitivity factor (S), is defined by the equation $S = R_v/R_o$, where R_v is the resistance after the chemical exposure and R_o is the initial resistance of the sensor.

The action of chemical vapors, on this composite system would proceed as follows. Firstly, PEO-$CuCl_2$ which is a major component would absorb the vapor, which then diffuses through inter-domain spaces and reach the conducting polymer moieties, where it would interact with the impurity states and transfer electronic charge. Transfer of electron leads to a lowering of the potential barrier at the interface, giving rise to an increase in conductivity.

It is interesting to note that sensitivity increases initially with increasing phthalocyanine content to about 3% concentration for ammonia and nitrogen dioxide vapors but then decreases for higher concentration of phthalocyanine. This peculiar behaviour can be explained as follows: The pure PT is an amorphous polymer. Through this amorphous structure diffusion of these gases would to very easy. Hence they show

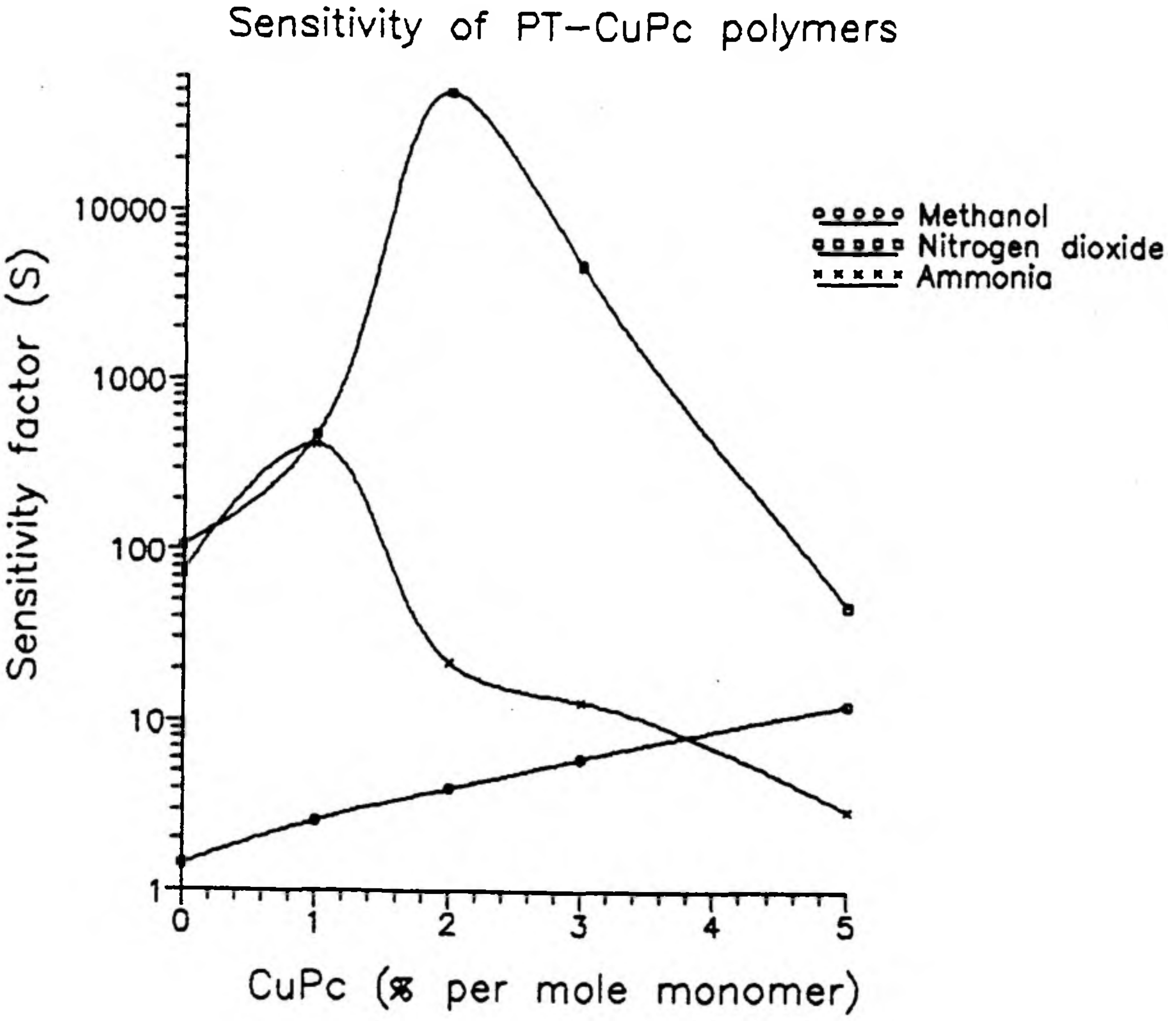


Figure 5.18 : Plots of sensitivity factor versus CuPc concentration for Methanol, ammonia and nitrogen dioxide vapors measured With PT-CuPc/ PEO/ $CuCl_2$ interdigited electrodes

TABLE- 5.9

Sensitivity of PT-CuPc polymers with chemical vapours

Sr. No.	**CuPc content by Wt. %**	**Sensitivity Factor (S)**		
		Methanol	**Ammonia**	**Nitrogen dioxide**
1	0.0	1.43	77.33	105.26
2	1.0	2.60	416.60	476.20
3	2.0	4.00	22.00	50000.00
4	3.0	6.92	13.33	4761.90
5	5.0	12.50	3.00	47.62

greater sensitivity. As the phthalocyanine content in the polymer increases, the polymer becomes more crystalline. The diffusion of the gas molecules through this well ordered crystal lattice is very difficult. Hence after certain level of CuPc concentration there is a sudden drop in sensitivity.

5.3.B: PT-CuPc Polymers synthesized by electrochemical technique

The electrochemical deposition of PT and PT-CuPc films were carried out using electrolyte containing tetra butyl ammonium perchlorate (TBAP) in dry nitrobenzene, thiophene monomer and phthalocyanine blue. The experimental details are described in **section 5.2.B**. The films were obtained on gold-coated glass and PET film substrates. In order to investigate the UV- VIS studies, the films were deposited on ITO substrates. The color of pure PT film was reddish brown whereas PT films functionalized with phthalocyanine were bluish-violet in color. Good qualities of the films were obtained at deposition time of 600 to 900 seconds under potentiostatic conditions. The sharp change in the physical appearances of these films is a first indication of the incorporation of phthalocyanine molecules in the polymeric chain.

5.3.B.1: CHARACTERIZATION OF ECP FILMS

(a) FT-IR STUDIES

The FT-IR spectrum recorded in the reflection mode for the films of PT and PT with 2% CuPc are shown in **Fig. 5.19**. The spectrum A corresponds to pure PT film, whereas the spectrum B corresponds to PT with 2% CuPc film respectively. The various possible assignments for the different absorption bands observed in each spectrum are given in **Table-5.10**. The observed peaks match well with the reported values[286]. It is seen that there are prominent changes in the spectra in the region of 800 cm^{-1} to 1600 cm^{-1}. The appearance of absorption at 825 cm^{-1} and 1250 cm^{-1}, which can be associated with the presence of CuPc group in the polymer, is noteworthy. Further, there is shift in the

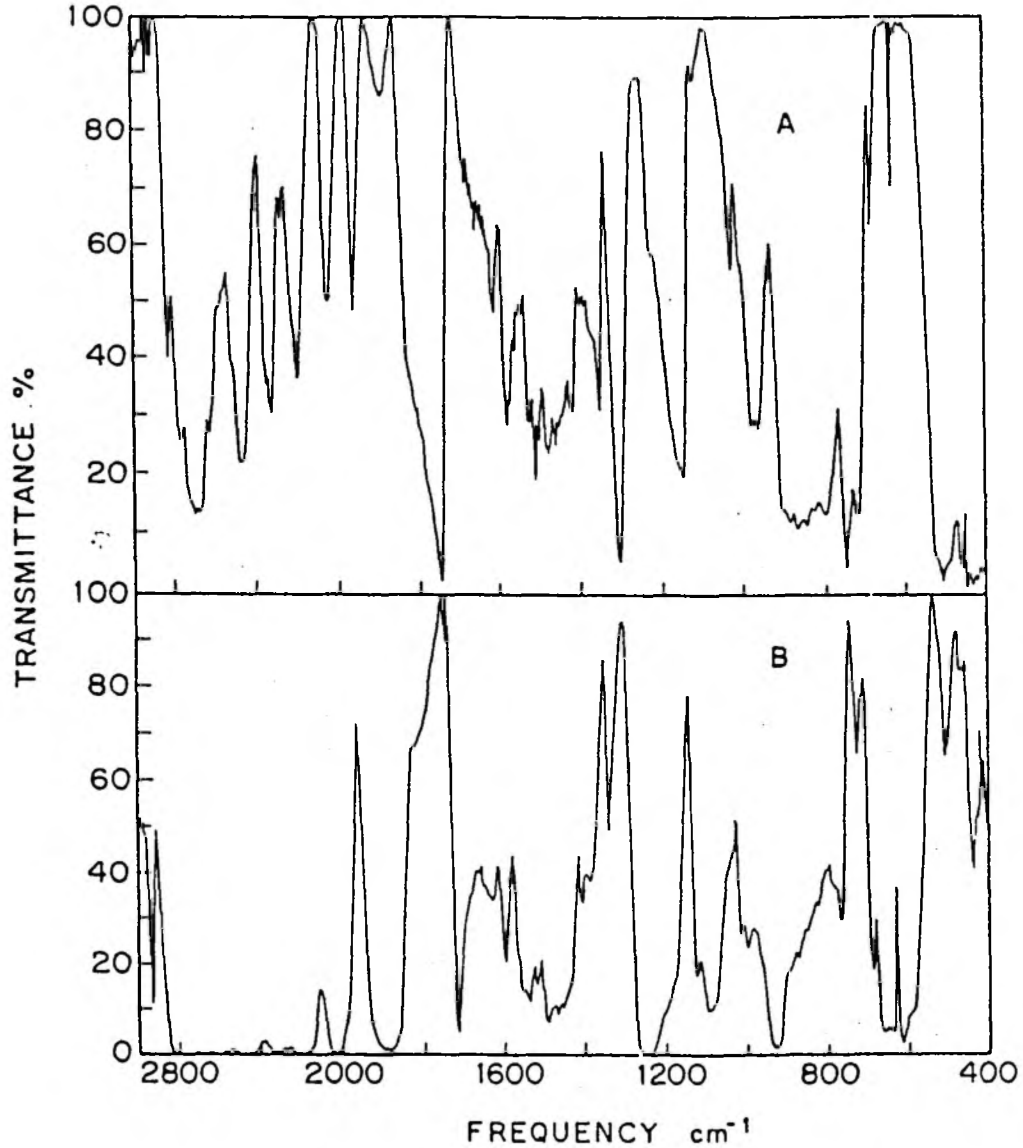


Figure 5.19 : FT-IR absorption spectrum of PT-CuPc films. (A) Pure PT and (B) PT + 2% CuPc

TABLE- 5.10

FT-IR DATA OF PT-CuPc POLYMERIC FILMS.

Polythiophene (PT) Peak cm^{-1}	PT + 1% CuPc Peak cm^{-1}	PT + 2% CuPc Peak cm^{-1}	Possible Assignments.
2900.0 (w)	2907.0 (s)	2930.0 (s)	C-H str.
2669.3 (s)	2669.3 (s)	--------	
2462.9 (s)	2462.9 (s)	--------	
2318.3 (s)	2316.3 (s)	--------	
2192.9 (s)	2191.0 (s)	2192.9 (br)	
2038.6 (s)	2038.6 (s)	2038.6 (s)	
1959.5 (s)	1961.5 (s)	--------	
1888.2 (w)	1884.3 (m)	1886.3 (br)	
1743.5 (vs)	1743.5 (s)	1743.5 (w)	
--------	1716.5 (w)	1716.5 (vs)	Pc skeleton
1612.4 (w)	1610.0 (w)	1610.0 (br)	
1577.0 (m)	1577.7 (m)	1596.9 (m)	Vib. C-C
1415.7 (w)	1415.7 (m)	1415.7 (m)	Sym. str. C=C
1350.1 (m)	1350.1 (m)	1338.5 (s)	
1301.9 (vs)	1299.9 (m)	--------	Th. skeleton
--------	1240.0 (w)	1247.9 (br)	C-N str.
1145.6 (s)	1145.6 (s)	1145.0 (w)	Pc skeleton
1090.0 (w)	1090.0 (s)	1089.7 (s)	C-H def.
962.4 (s)	958.6 (s)	925.8 (br)	
796.5 (w)	765.0 (w)	765.7 (s)	Pc skeleton
742.5 (m)	742.5 (m)	--------	
717.5 (w)	711.7 (m)	723.3 (m)	Th. skeleton
680.8 (w)	680.8 (w)	680.0 (w)	C-H out of plane def.
632.6 (s)	632.6 (s)	642.3 (br)	
507.2 (m)	507.2 (m)	507.2 (m)	

absorption bands associated with C-S-C out of plane deformation (706 cm^{-1}) and in plane vibration modes (1026 cm^{-1}) of the thiophene ring of pure PT to the new positions (725 cm^{-1} and 958 cm^{-1} respectively) in PT film containing CuPc. This clearly shows that the CuPc groups are linked by thiophene in the main chain causing restrictions to the normal free modes due to the bulky planar nature of CuPc molecules.

(b) X-RAY DIFFRACTION STUDIES

The X-ray diffraction patterns obtained for PT and PT with CuPc films are shown in **Fig. 5.20**. The curves (A) and (B) correspond to pure PT and PT functionalized with CuPc films respectively. In all cases, the films were essentially amorphous with very little crystallinity (less than 5%). However, there are a few distinct (though weak but sharp) reflections, which are observed especially when the XRD is recorded at high sensitivity. These peak correspond to various reflections from the orthorhombic structure (a = 7.8 A°, b = 4.55 A° and c = 8.03 A°) reported for PT[272].

On the other hand, when CuPc is incorporated, the crystalline structure is apparently changed since there are few new peaks observed at low 2θ regions in these samples. The detailed analysis of the various diffraction patterns suggest that the structure could be hexagonal type with a = 10.9 A° and c = 14.3 A°. **Table-5.11** represents the d-values and the assignment of the observed peaks in the X-ray diffraction. These findings clearly suggest the stiffening of the PT chains and different packing due to the incorporation of CuPc.

5.3.B.2: MEASUREMENT OF PROPERTIES

(a) ELECTRICAL CONDUCTIVITY

The results of variation in electrical conductivity at room temperature with the concentration of CuPc for synthesized films and those doped with iodine are shown in

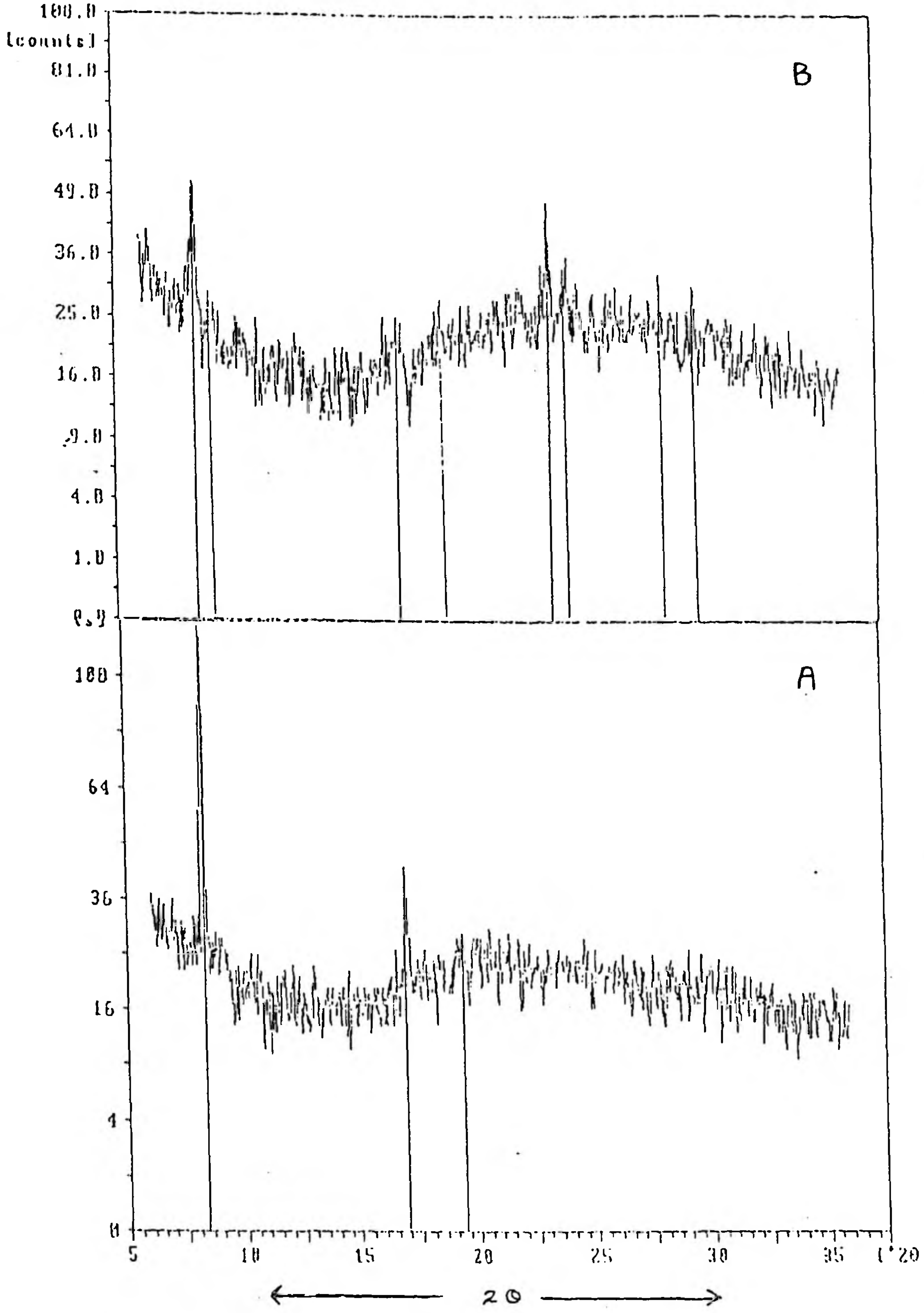


Figure 5.20 : X-ray diffraction patterns of PT-CuPc films deposited on gold glass (A) Pure PT and (B) PT + 2% CuPc

TABLE- 5.11

X-ray Diffraction Analysis of PT-CuPc Films

d expected	d calculated*	h k l
9.41	9.43	1 0 0
7.90	7.89	0 1 1
7.18	7.15	0 0 2
4.82	4.77	0 0 3
3.66	3.59	1 1 3
3.49	3.46	1 2 1
3.11	3.19 2.99	2 1 2 1 1 4
2.83	2.85 2.86	2 1 3 0 0 5

*** as per hexagonal lattice a = 10.9 A° and c = 14.3 A°**

Fig.5.21. It is interesting to note that even with small incorporation of the CuPc, the conductivity increases considerably. This can be due to the structure modification and more planar configuration of the PT in presence of CuPc. It is also likely that the CuPc gives better charge transfer interaction with the dopant molecule and holds the same in the close proximity of the PT chains[287]. The electrochemical polymerization of thiophene monomer was carried out using tetra butyl ammonium per chlorate (TBAP); the PT films obtained were doped weakly with ClO_4^- ions. When these films are de-doped using reverse potential and finally doped with iodine solution in benzene, tremendous changes in conductivity were observed. The conductivity of iodine doped films was about four orders of magnitude greater than that for ClO_4^- doped ones. The data on conductivity are shown in **Table-5.12** and depicted in **Fig. 5.21**. Both the PT[288] and CuPc[289] have reported to have greater affinity towards iodine molecules, which results in higher doping level and more electrical conductivity.

The electrical conductivity for the PT films containing CuPc was found to be at least two orders of magnitudes higher than that in pure PT film. **Fig. 5.22** shows the graph of conductivity as a function of temperature for these films. The curves A to D correspond to the CuPc concentrations of 0%, 0.5%, 1.0% and 2.0% with respect to thiophene monomer respectively. It may be mentioned that the conductivity has been measured with aluminum as one of the electrodes, which is known to be blocking type[290]. This was essential because the sample resistance was otherwise quite low and often there was shorting of the films observed due to sudden high currents. It is evident from the plots of log σ versus 1/T that there is very little variation of conductivity with temperature suggesting that the activation energy for conduction is very low and the material behaves as a heavily doped semiconductor[291].

The activation energy was calculated from the plots of log conductivity versus 1/T as described in detailed in chapter-II. The ΔE values of CuPc incorporated PT films as a function of CuPc concentration are shown in **Fig. 5.23**. It is observed that as the CuPc concentration increases the activation energy decreases. The pure PT film has

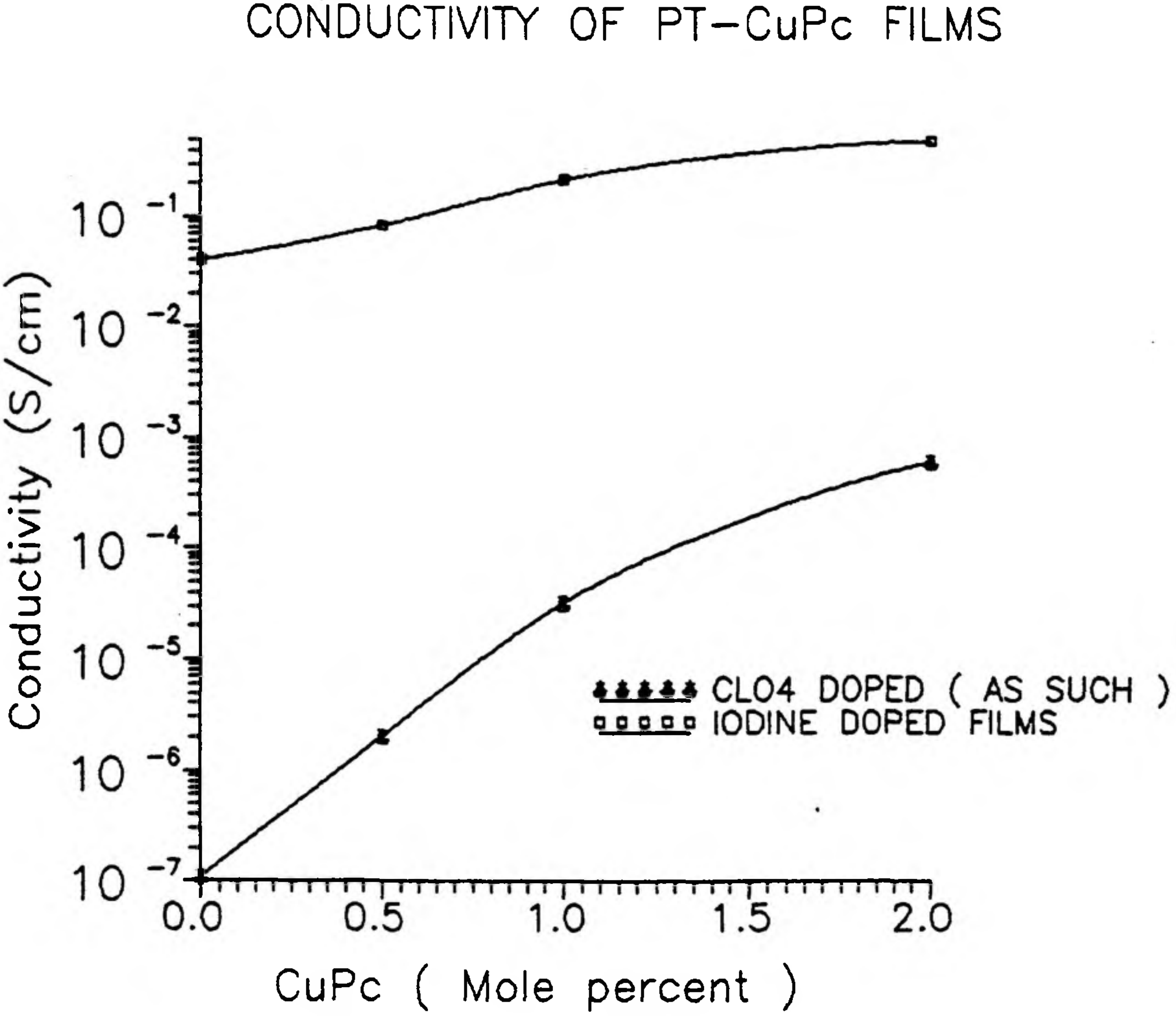


Figure 5.21 : Plots of conductivity versus CuPc concentration for As synthesized and iodine doped PT-CuPc films

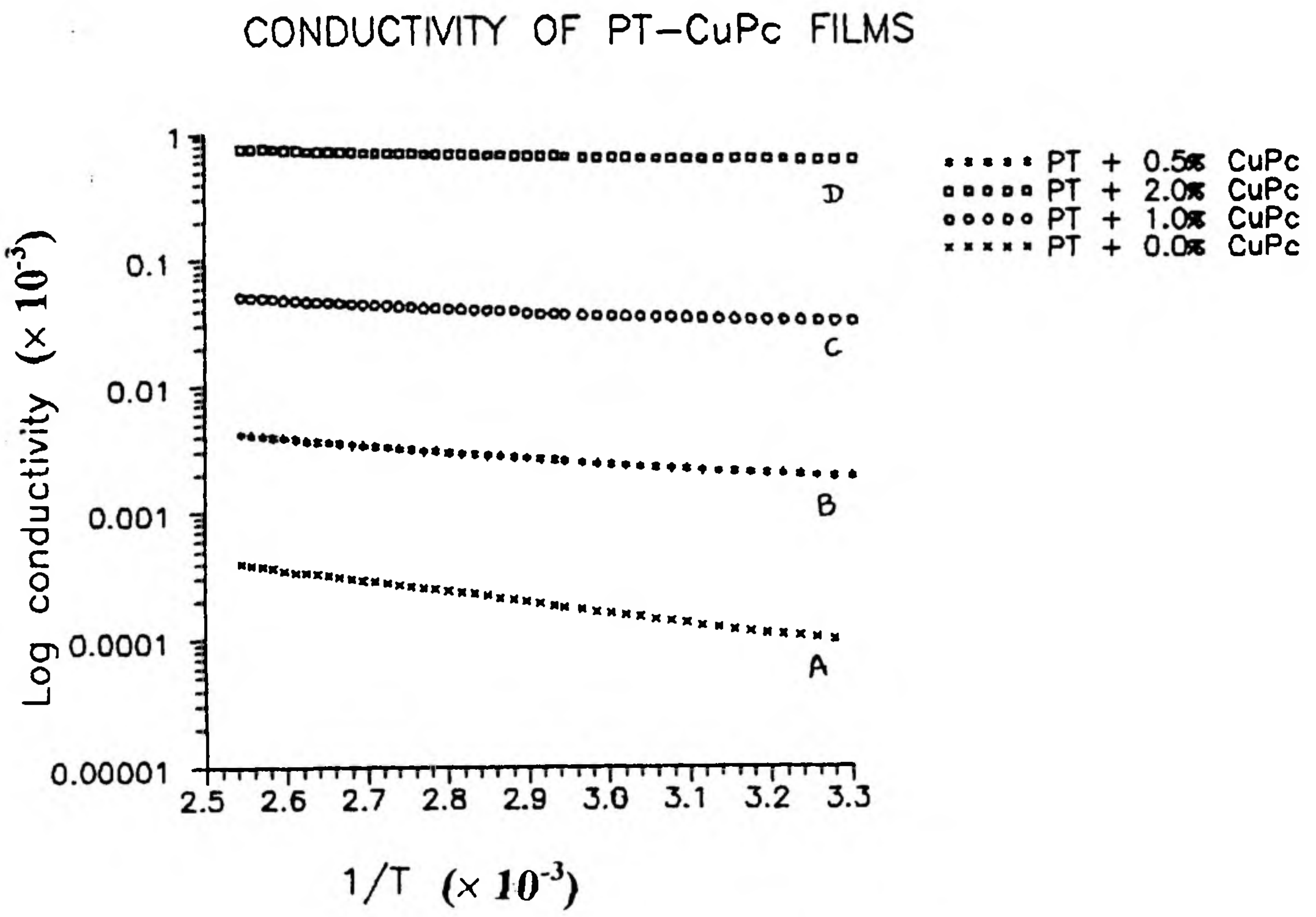


Figure 5.22 : Plots of log conductivity versus reciprocal of temperature For PT-CuPc films

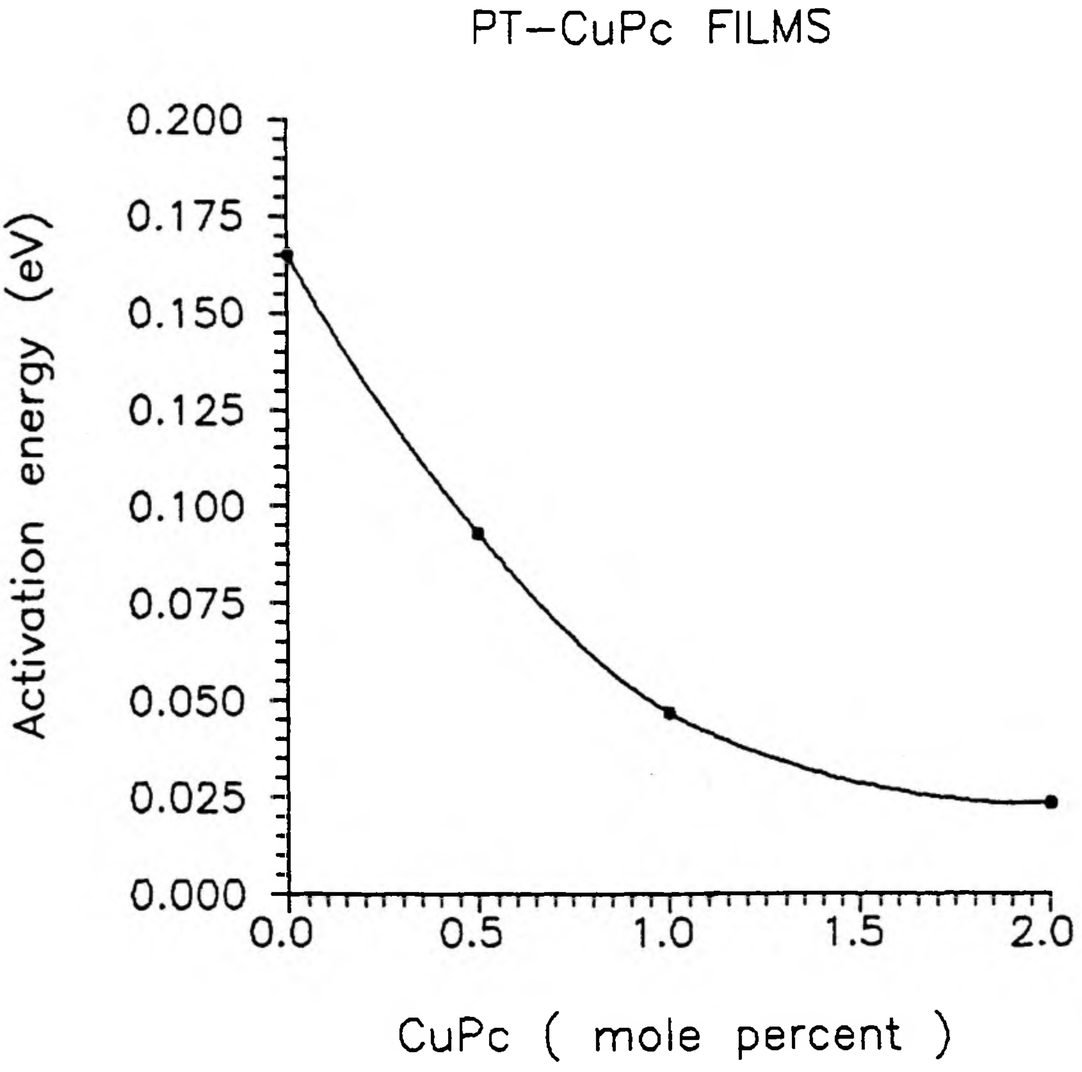


Figure 5.23 : Plot of activation energy versus CuPc concentration for PT-CuPc films

TABLE- 5.12

CONDUCTIVITY DATA OF PT-CuPc FILMS

CuPc conc. Mole % in PT	Conductivity ClO_4 doped film (As synthesized) S/cm	Conductivity I_2 doped film S/cm
0.0	1.1×10^{-7}	4.0×10^{-2}
0.5	2.0×10^{-6}	8.0×10^{-2}
1.0	3.3×10^{-5}	2.2×10^{-1}
2.0	6.2×10^{-4}	6.0×10^{-1}

activation energy value as 0.165 eV and the film of PT containing 2% CuPc shows this value as low as 0.023 eV.

(b) CYCLIC VOLTAMMETRIC MEASUREMENTS

Cyclic voltammetry experiments were frequently used for obtaining information on the mechanism of polymer growth, redox behaviour as well as mode of electronic transport. In order to study the effect of the functional group (CuPc) on the properties of PT, cyclic voltammetry (C-V) with and without illumination i.e. PEC mode experiments were carried out on different electrolytes.

Fig. 5.24, 5.25 and **5.26** show the C-Vs in Na_2S aqueous electrolyte in dark (a) and under illumination (b) for the PT films containing 0%, 0.5% and 2% CuPc respectively. It is seen that PT by itself does not exhibit much photosensitivity. There is an oxidation peak at 0.4 V SCE, the height of which increases slightly under illumination. On the other hand, for the samples containing CuPc, the currents in the dark decreases but under illumination it increases considerably (compare **Fig 5.24** and **5.26** D and L each). Further, there is an additional peak (shoulder) in the C-V at about 0.6 V SCE for the CuPc containing samples. This can be associated with the charge transport from the additional mid-gap states (impurity/defect) to the appropriate levels ($S/S^{-\ -}$) in the electrolyte.

The exact mechanism for photosensitized electrochemical process taking place in PT-CuPc electrodes in the PEC mode has been already discussed in **section 5.3.A.3 (b).** The current values in the present case are much higher and the sensitivity is enhanced than for the samples prepared by chemical route. This can be understood as follows. The ECP films have much lower thickness as compared to pellets of chemically prepared PT-CuPc polymer. The uniformity also is higher than the pellets since the latter contains large number of inter-particulate defects, which act as trapping and recombination centers for photo generated, charge carriers. The sharp peak in the cathodic region also suggests a well-defined level for transfer of charge from the solid polymer electrode to that in liquid

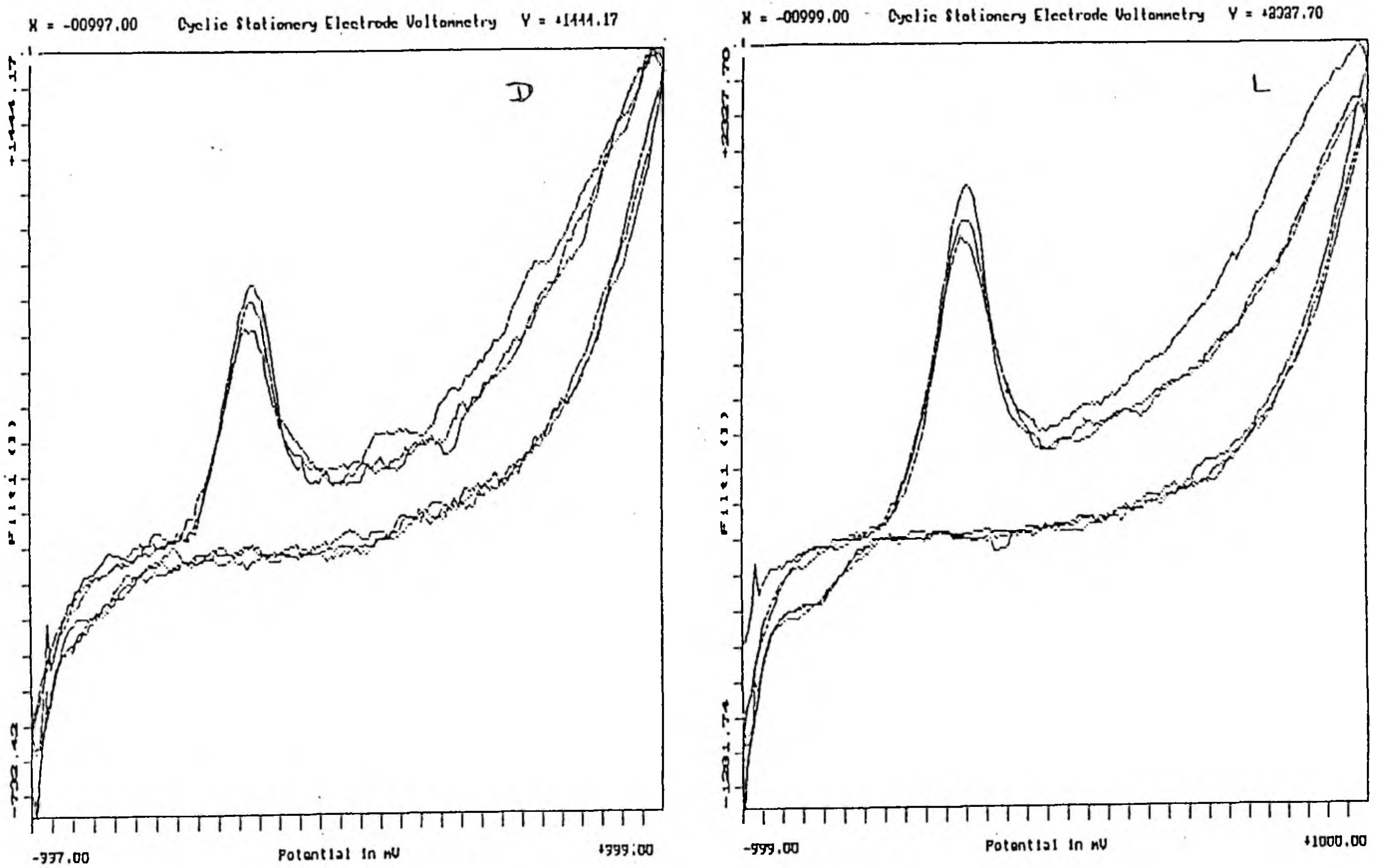


Figure 5.24 : C-V Measurements of pure PT film in aq. 0.1 N Na_2S electrolyte

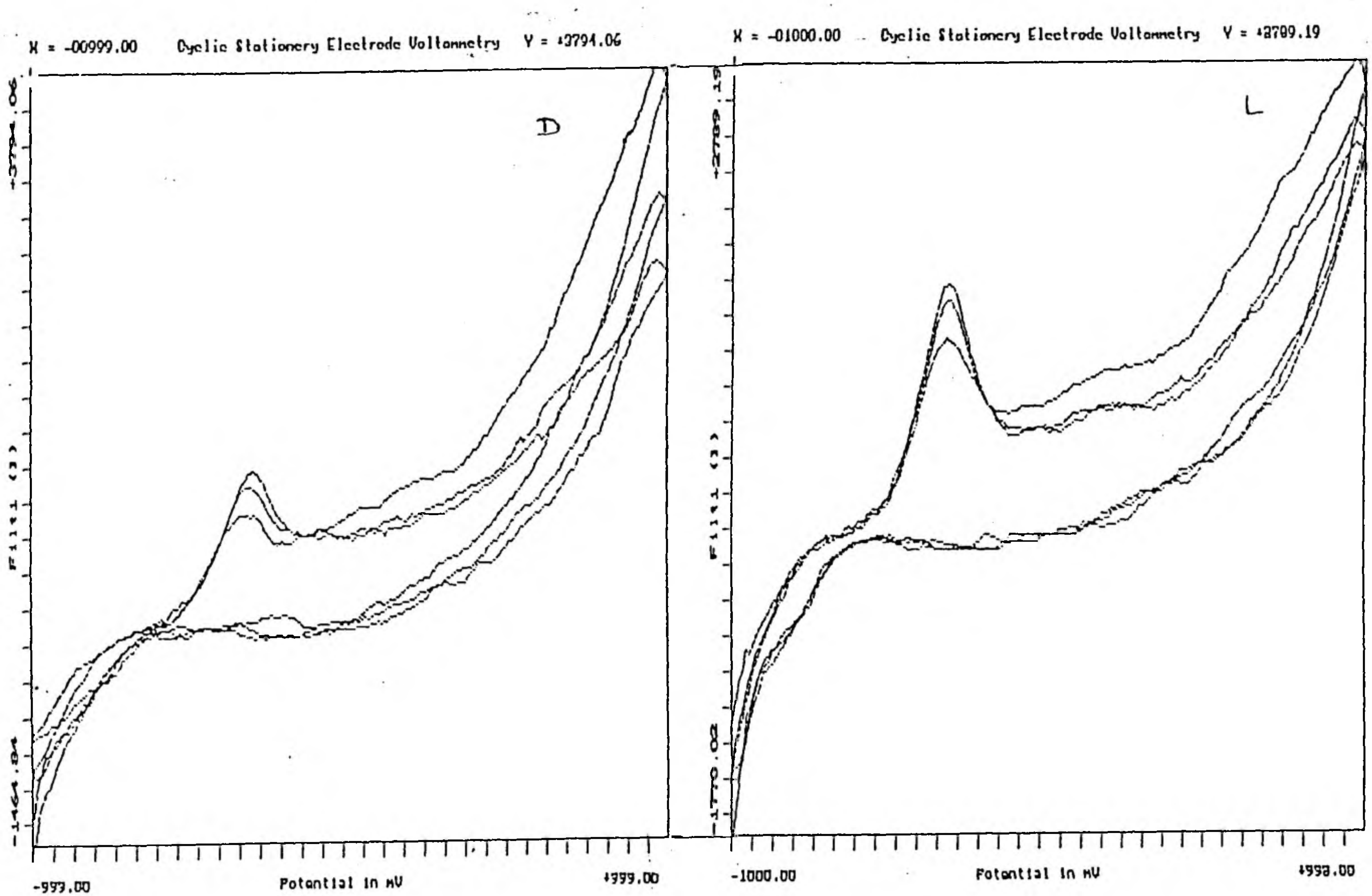


Figure 5.25 : C-V Measurements of PT + 0.5% CuPc film

in aq. 0.1 N Na_2S electrolyte

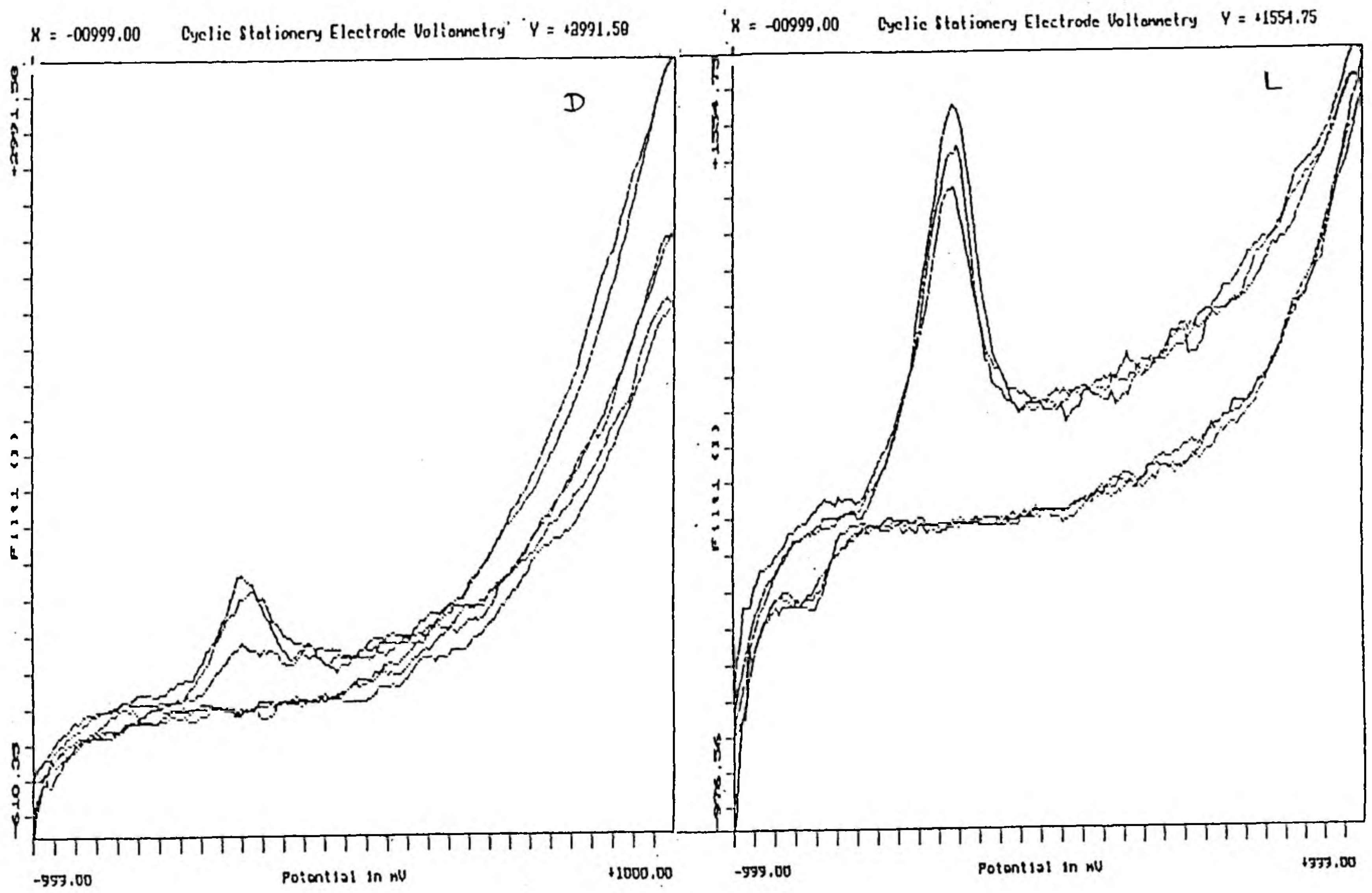


Figure 5.26 : C-V Measurements of PT + 2% CuPc film in aq. 0.1 N Na_2S electrolyte

electrolyte. Thus the presence of CuPc in the polymer gives rise to photo-assisted electrochemical reactions which are not prominent in normal homopolymer.

5.4: CONCLUSIONS

The incorporation of phthalocyanine in polythiophene was successfully achieved by both the chemical and electrochemical method of polymerization. The change in the physical appearance is the first indication of incorporation of phthalocyanine into these polymers. The incorporation of phthalocyanine was confirmed by using conventional techniques such as FT-IR, UV-VIS and microanalysis. The presence of Cu_{2p} core-level peak in the ESCA studies confirmed the CuPc incorporation into polythiophene chains. The iodine core-level spectra show the distribution of dopant ions among the PT and CuPc molecules since both of them have strong affinity towards iodine molecules.

The electrical conductivity of chemically synthesized polymers was found to increase by 7-8 orders of magnitude in the presence of phthalocyanine, after doping with iodine. Even in as synthesized weakly doped polymers, the electrical conductivity was found to be 3 to 4 orders of magnitude higher in the phthalocyanine containing polymers than that of pure polythiophene homopolymer. The thermal stability of polythiophene increases with the increase in concentration of phthalocyanine. The polythiophene obtained as such by $FeCl_3$ route is mainly amorphous in nature, but PT containing phthalocyanine does show some crystallinity. The chemical vapor response of these PT-CuPc polymers shows selectivity and better sensitivity towards nitrogen dioxide and ammonia gas than the homopolymer. The cyclic voltammetric studies indicate more photochemical response for the PT-CuPc polymers than the pure PT.

The polymeric films obtained by electrochemical method exhibit higher electrical conductivity with the increase in concentration of phthalocyanine used in the electrolyte during deposition. The increase in electrical conductivity was associated with decrease in the activation energy for conduction. The detailed x-ray analysis of the synthesized films shows a hexagonal type structure with lattice parameter as a = 10.9 A° and c = 14.3 A°. Cyclic voltammetric measurements in different electrolytes of these films indicate that CuPc gives sensitized photocurrent in cathodic region as compared to pure PT films.

It is interesting to compare the oxidation data of pyrrole and thiophene using $FeCl_3$ as oxidizing agent. The oxidation product of pyrrole and thiophene showed much difference in their behaviour. The former gave a polymer with electrical conductivity as high as 10^{-2} S/cm, whereas the latter gave a polymer with its electrical conductivity very low i.e. 10^{-11} S/cm. These results could be attributed to the oxidation potential of the starting monomers. The oxidation potential of pyrrole and thiophene are 0.7 V and 1.8 V respectively. Thus, pyrrole gets oxidized more easily as compared to thiophene. The C.V. measurement data shows the oxidation peaks for PPy and PT at –0.1 V and +0.4 V respectively. The phthalocyanine incorporated samples of PPy and PT exhibits the oxidation peaks at +0.2 V and +0.6 V, which indicates that the incorporation of phthalocyanine can be achieved much more easily in case of PPy than in PT. As stated above that the oxidation product of PT has a lower conductivity value, to achieve better conductivity these polymers are further doped with I_2 solution. The iodine doped PT-CuPc polymers showed the electrical conductivity in the range of 10^{-4} to 10^{-3} S/cm depending upon the CuPc concentration in the reaction mixture. Thus, iodine doping yields a product with its electrical conductivity almost 8 fold higher than the as synthesized PT polymer.

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION.

In the present investigations, the incorporation of phthalocyanine into various conducting polymer viz. polyaniline, polypyrrole and polythiophene was successfully carried out using chemical as well as electrochemical methods. The chemical method involves oxidative polymerization of monomers such as pyrrole and thiophene, using $FeCl_3$ as an oxidizing agent, while aniline monomer was oxidized using ammonium persulfate. The colour of the polymer changes after incorporation of phthalocyanine from red to greenish brown for PT while the color of PANI and PPy changed from blue/ green to dark greenish black. The change in the physical appearance of the polymers is the first indication of incorporation of phthalocyanine into these conducting polymers. The incorporation of phthalocyanine was also confirmed using conventional techniques such as FT-IR, UV-VIS and elemental analysis.

The incorporation of phthalocyanine into various conducting polymers has shown profound effect on its electrical conductivity. The polymers obtained as such after chemical synthesis, were in partially doped states in case of PANI and PPy, whereas for PT, it was practically not in doped state. The electrical conductivity was found to be at least 2 to 3 orders of magnitude higher for the functionalized conducting polymers than the pure polymers. For example, the PANI homopolymer sample has an electrical conductivity of 4.2×10^{-5} S/cm, whereas PANI – CuPc (5%) sample exhibits a value of 7.25×10^{-2} S/cm. This increase in the electrical conductivity was more dramatic in PT-CuPc after iodine doping. The results of temperature dependence of electrical conductivity showed that as the concentration of CuPc in the conducting polymer increases, the slope of the Arrhenius curves ($\log \sigma$ vs $1/T$) decreases. In other words, the thermal activation energy decreases as the phthalocyanine content in the conducting polymer increases. This is mainly because of the creation of additional electronic states in the band gap region which can arise from extended conjugation of the electrons due to addition of phthalocyanine in the main chain of the conducting polymer.

In PT-CuPc polymers doped with iodine, the electrical conductivity increases tremendously by about 5 to 8 orders of magnitude (10^{-11} to 10^{-3} S/cm). The doping of conducting polymers involves dispersion / complex formation of dopant molecules in the inter-chain domains of the polymer, which considerably disturbs distribution of charge along the chain leading to reorganization of the polymer. Thus, polymer doping leads to the formation of conjugated defects viz. solitons; polarons or bipolarons in the polymer chain ultimately resulting in sharp increase in the conductivity. In doped PT-CuPc samples, the iodine atoms are mainly associated with the phthalocyanine moieties due to strong charge transfer interaction between them leading to the formation of phthalocyanine-iodine complex. The dopant concentration levels in CuPc incorporated conducting polymer can be higher than that in corresponding homopolymers due to the additional sites for complexation available in the former than the latter case. Thus, the increase in electrical conductivity of the conducting polymers, due to phthalocyanine incorporation, can also be due to increase of dopant concentration levels that can be accommodated in these polymers

Although there is an increase in the electrical conductivity with the incorporation of phthalocyanine, the values obtained for each of the conducting polymers studied are slightly lower than those expected from the reported ones for the homopolymer. This was explained on the basis of NMP- H_2O interactions i.e. hydrogen bonding effect. Amongst the conducting polymers studied in the present investigations, PPy-CuPc had conductivity value at higher side (2.1×10^{-1} S/cm) and the PT-CuPc at the lower end (7.2×10^{-10} S/cm) while PANI-CuPc shows the intermediate values of 4.2×10^{-5} S/cm. In other words, the conducting polymers containing phthalocyanine show the conductivity values in the following order: PPy-CuPc > PANI-CuPc > PT-CuPc. These results are quite in agreement with their oxidation potential value of 0.7 V, 1.2 V and 1.8 V for pyrrole, aniline and thiophene respectively. There may be additional reasons for these observations. The phthalocyanine molecule can be considered as a cyclic compound made from substituted pyrrole units and hence its compatibility with the PPy matrix may be better than the other cases. The dopant ion distribution in this case would be more uniform in this polymer leading to its higher conductivity than PANI-CuPc or PT-CuPc.

The XRD analysis of these functionalized conducting polymers showed that, the super-molecular structure was modified by the incorporation of phthalocyanine. In polyaniline, the incorporation of CuPc not only showed improvements in the crystallinity but also a modified structure. These polymers have an orthorhombic crystal structure with lattice parameters of a = 15.3 A°, b = 16.5 A° and c = 20.8 A° as derived from the XRD data. The structural changes in the PPy polymers due to incorporation of phthalocyanine indicated more planar configuration for the chains. Pure polypyrrole shows amorphous nature but crystalline structure was seen in the PPy sample, which contains phthalocyanine. The d-value calculations for PPy-CuPc shows the orthorhombic crystal structure with lattice parameters as a = 6.80 A°, b = 5.33 A° and c = 12.62 A°. The formation of crystalline structure was due to the addition of crystalline moiety (phthalocyanine) into these polymers. The microanalysis data for these polymers show that as the CuPc concentration in the reaction mixture increases the number of monomer units in the chains decreases, which can result into the formation of "dendrimers". These dendrimers which are type of molecular assemblies in which oligomers are attached to four active sites of central unit (phthalocyanine in present case) can be more crystalline than random co-polymers or cross-linked polymers.

The electrochemically deposited polymeric films of PANI, PPy and PT are amorphous in nature. On the other hand, conducting PT films incorporated with phthalocyanine show appearance of new peaks and the structural assignments fit with hexagonal type of structure with lattice parameter as a = 10.9 A° and c = 14.3 A°. The slow rates for electrochemical deposition / polymerization (due to high oxidation potential) for the PT-CuPc as compared to PPy-CuPc and PANI-CuPc could lead to formation better ordered structures in the same.

The different possible oxidation levels formed due to dopant incorporation lead to changes in the chemical environment of the polymer, which were revealed by studies on XPS /ESCA of these polymers. These studies showed the presence of different components in the core-level spectra for C_{1s}, N_{1s}, Cl_{2p}, Cu_{2p}, S_{2p} and I_{3d} in these polymers. Also, the Cu_{2p} peaks, which were totally absent in the original conducting polymer samples, were clearly evidenced in the polymers containing CuPc. The different components in the core-level spectra were associated with corresponding charged species. The lower B.E. component in the respective core-level was assigned to the neutral species, whereas the higher B.E. was associated with charged species and the intermediate core-level was assigned to partially charged species. It was observed that in the doped state the contribution from the charged species was much higher than in its undoped state. Interestingly, iodine doped PT-CuPc samples showed the dopant distribution on both the polymeric chains as well as on phthalocyanine molecules, resulting in the appearance of doublet for the I_{3d} peak at 621 eV and 632 eV respectively. Thus, XPS studies showed that, CuPc incorporated polymers exhibit higher doping level, which consequently gives higher electrical conductivity in these polymers.

In order to check chemical reactivity of phthalocyanine with these conducting polymers, the results of thermal analysis was used. The weight loss for different polymers at certain temperature was estimated from TG/DTA thermograms. The results tabulated in **Tables 3.9, 4.9** and **5.8** showed remarkable improvements in the thermal stability for all the polymers at least up to 300° C by incorporation of CuPc. Further, the extent to which this improvement is obtained depends on the polymer matrix used. This increase in thermal stability is maximum for PPy in which the weight loss decreased from 29% to 5.5 % at 400 ° C by incorporation of just 5% CuPc. The specific improvements in properties of PPy-CuPc could be due to the better compatibility between CuPc and PPy than other cases, which has been discussed above. In conclusion, it can be said that the overall thermal stability of all the three conducting polymers studied was found to increase with the incorporation of phthalocyanine.

In order to exploit the possibility of employing these polymers in chemical sensors, their response characteristics were studied after exposure to various chemical vapors such as methanol, ammonia and nitrogen dioxide. The results obtained showed that these polymers have moderate sensitivity towards the methanol as well as ammonia vapors. It is quite interesting to note that all these polymers containing CuPc show tremendous sensitivity towards nitrogen dioxide vapors. The sensitivity factor of as high as 50,000 was obtained for PT-CuPc polymers. The sensitivity factor of 1600 was obtained in the case of PPy-CuPc polymers, whereas PANI-CuPc polymers exhibit a value of 1100 for nitrogen dioxide vapours. In comparison to this, the sensitivity factors of about 100 and 40 were obtained, when these polymers were exposed to ammonia and methanol vapors.

The very high selectivity towards the nitrogen dioxide may be explained on the basis of charge transfer complex formed between, the phthalocyanine donor and nitrogen dioxide acceptor molecules. On the other hand, ammonia becomes a competing electron donor in CuPc containing conducting polymers. The very low response towards the methanol may be explained on the basis very little charge transfer / interaction between CuPc containing polymers and methanol. Thus, CuPc incorporated conducting polymers have much higher selectivity than their original homopolymers.

The electrochemical response of conducting polymers functionalized with phthalocyanine was determined using cyclic voltammetric measurements. Additionally the effect of the functional group (CuPc) on the photo-response of conducting polymers in electrochemical cells i.e. photo-electrochemical (PEC) mode was carried out. The different electrolytes used in these investigations were HCl, Na_2S, $LiClO_4$ and TBAP etc. The incorporation of phthalocyanine into PANI enhances its electrochemical activity. When the C-V measurements were carried out under illumination, PANI-CuPc polymers exhibit considerable photosensitivity, especially in the cathodic regions. The PPy-CuPc polymers show more electrochemical activity as compared to pure PPy polymer. In fact in this case photocurrent increases tremendously in both anodic as well as cathodic regions. This implies that there is an overall increase in the photo-induced electrochemical activity for PPy-CuPc polymers. The C-V studies on PT-CuPc polymers, also shows tremendous increase in the currents under illumination thus leading to much higher photosensitivity than PT by itself. These various results have been explained on the basis of charge transport across the electrode / electrolyte interface with CuPc acting as an intermediate photo-sensitizer. Under illumination, CuPc absorbs the photon and generates photo-excited charge carriers in its conduction levels. Since, CuPc groups are bonded to conducting polymer chains there is efficient transfer of charge carriers from CuPc groups to conducting polymers. Thus, there is an over all increase in the current under illumination. These results may be useful in developing efficient photo-electrochemical cells having wider response over the whole visible range of spectrum.

It would be of interest to compare the results of both the, chemical and electrochemical methods used for the synthesis of these functionalized conducting polymers. The electrical conductivity is at least 2 to 3 orders of magnitude higher in electrochemically synthesized polymers than the chemically synthesized polymers having same composition. The electrochemically deposited polymers are thus, in their highly oxidized state and are in pure form, whereas the chemically synthesized polymers need further purification with distilled water, methanol and acetone etc. Obviously, these are in slightly lower oxidation states resulting in giving lower conductivity. When these chemically synthesized polymers are doped further with the doping agents, they showed remarkable increase in the conductivity (up to 7-8 order of magnitude high). The time required for electrochemical deposition ranges from as low as 1 minute to 10 minutes, depending upon the polymer. However, the chemical synthesis method requires the reaction period of 1 hr. to 24 hrs. The chemicals/reactants required for electrochemical deposition are very less, but chemical synthesis requires a quite high quantity of chemicals. The advantage in the chemical synthesis is that it gives large quantity of material in a single run. Generally, the chemically synthesized materials show better crystallinity than the electro-chemically-synthesized counterparts. In the electrochemical synthesis one can have better control over the reaction parameters to get the desired geometry for the materials. The chemical synthesis methods are slightly difficult to control especially oxidation with strong oxidizing agents such as $FeCl_3$. The direct incorporation of macro cyclic moieties such as phthalocyanine into various conducting polymers is being reported here probably for the first time and it opens out various possibilities for synthesis of conducting polymers coupled with other macro-cyclic groups.

Thus, the incorporation of phthalocyanine into conducting polymers such as polyaniline, polypyrrole and polythiophene has led to development of new materials which have better electrical conductivity, thermal stability, higher sensitivity / selectivity to certain chemical vapours and improved photo-response. Considering the recent developments in molecular electronics wherein molecules are made to switch from conducting to non-conducting states and this information is transferred to macro-levels, the CuPc containing polymers may find wide ranging applications in near future. The present studies have already demonstrated their improved performance in the field of chemical sensors, photo-electrode and electro catalysis. Thus, this work has shown the initial steps to the numerous possible applications for these novel materials.

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