A THESIS

On

CONDUCTING POLYMERS: POLYANILINE, ITS STATE OF THE ART AND APPLICATIONS

Submitted in the partial fulfillment of requirement for the award of the degree of

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Submitted by
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CERTIFICATE

This is to certify that the thesis entitled **CONDUCTING POLYMERS: POLYANILINE, ITS STATE OF THE ART AND APPLICATIONS** submitted by **Miss Himani Sharma** in the partial fulfillment of the requirement for the award of the degree of **M. Tech** in **Materials Science and Engineering** from the **School of Physics and Materials Science, Thapar Institute of Engineering and Technology (Deemed University), Patiala,** is a record of candidate's own work carried out by her under my supervision and guidance. The matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.

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Himani Sharma

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Dedicated To My Parents

CONTENTS PAGENUMBER

LIST OF ACRONYMS

ESR	electron spin resonance
GPC	gas permeable chromatography
HOMO	highest occupied molecular orbital
IR	infra red
LUMO	lowest unoccupied molecular orbital
MO	molecular orbital
NMP	N, N'- dimethyl pyrrolidone
PANI	polyaniline
PPy	polypyrrole
UV	ultra violet
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

LIST OF SYMBOLS

c	concentration (molar)
d	interplaner distance
K	Kelvin
nm	nanometer
μ	mobility
Ω	ohm
R	resistance
ρ	resistivity
σ	conductivity
t	time
^{0}C	temperature

ABSTRACT

Polymers seem to provide a solution to almost every deed in life, from preparing daily commodities, the highly sophisticated to, artificial heart valve. Till recently, heat resistant, electrically conducting, ferromagnetic, semiconducting and superconducting polymers were a dream, but today, all these miracles are coming true, at least on laboratory stage, few of them have also been commercialized.

Since desirable properties can be conveniently attained by tailoring the polymer structure and also by incorporating additives, scientists have been enthusiastic to explore the possibility of transforming insulating polymers into conducting or semiconducting materials envisaging such special characteristics like low density, low cost, ease of fabrication, flexibility of design, low energy and labour requirements for fabrication and processing, which make polymers a class of versatile materials capable of meeting even the most stringient specifications of modern technology.

In the present work, an attempt has been made to review the most interesting and fascinating aspects of conducting polymers. We also propose to synthesize and characterize polyaniline as one of the important conducting material and explore its uses as molecular materials in electronic/electrical devices.

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CHAPTER I

INTRODUCTION TO CONDUCTING POLYMERS

1.1 INTRODUCTION

Discovery of polymers has given a new dimension to the present era. Polymers are known so far as a class of heat sensitive, flexible, electrically insulating amorphous materials.Electrically Conducting Polymers appear to be ideal candidates for various applications, as many of their properties circumvent problems prevalent with traditional RAM (ferrites,carbon black), including corrosion, weight, matrix incompatibility, and environmental integrity [1]. In addition to being corrosion resistant and light weight, many critical properties of conducting polymers may be tailored for various applications. The strength to weight, possibility, resistance to corrosion, has given conducting polymers advantage over metals.

Polymers are generally known for their insulating property because of covalent bond present in saturated carbon compounds. Since desirable properties can be conveniently attained by tailoring the polymer structure and also by incorporating additives; scientists have been enthusiastic to explore the possibility of transforming insulating polymers into conducting or semiconducting materials envisaging such special characteristics like low density, ease of fabrication, flexibility of design, low energy and labour requirements for fabrication and processing.

Conducting polymers were first discovered in **1976**. In the mid 1970s, the first polymer capable of conducting electricity, polyacetylene, was reportedly prepared by accident by Shirakawa [2]. The subsequent discovery by Alan Heeger and Alan MacDiarmid that the polymer would undergo an increase in conductivity of 12 orders of magnitude by oxidative doping quickly reverberated around the polymer and electrochemistry communities, and an intensive search for other conducting polymers soon followed [3]. In **1976**, Alan MacDiarmid, Hideki Shirakawa, and Alan Heeger, along with a group of young students found that conductivity of polyacetylene increased by up to 6 orders of magnitude when reacted with iodine (from 10^{-4} S/cm to 10^{2} S/cm); this phenomenon, known as doping, is as a result of charge carriers. In addition, it was discovered that varying the level of doping yielded polymers exhibiting wide range of electrical properties, from insulator, or semi-conductor, to metal [4].

Although polyacetylene is not stable in air, the fact that it could be become conductive upon doping led to further experimentation with other known conjugated polymers. Since 1976, a number of conducting polymers, namely polypyrrole, polythiophene, and polyaniline, have become the focus of much study. The importance of conducting polymers is exemplified by the awarding of the **2000 Nobel Prize** in Chemistry to MacDiarmid, Shirakawa, and Heeger, for the discovery and development of conducting polymers.

This was particularly exciting because it created a new field of research and a number of opportunities on the boundary between chemistry and condensed-matter physics. As the commonly known polymers in general are saturated and so insulators, these were viewed as uninteresting from the point of view of electronic materials. Conducting polymers are polymers containing an extended pi conjugated system, made up of overlap of singly occupied p orbitals in the backbone of the polymer chain. Although conducting polymers possess a relatively large number of delocalized pi electrons, a fairly large energy gap exists between the valence band and the conducting band (greater than 1 eV), thus these polymers are considered to be semi-conducting, at best. These polymers must be doped (usually meaning altering the number of pi electrons) in order to order to render the polymers truly conducting. In conjugated polymers the electronic configuration is fundamentally different, where; the chemical bonding leads to one unpaired electron (the electron) per carbon atom. Moreover, bonding, in which the carbon orbitals are in the sp^2pz configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer.

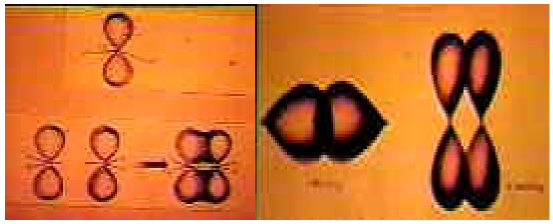


Figure 1.1 Pi and sigma bonding

This electronic delocalization provides the highway for charge mobility along the backbone of the polymer chain. Therefore, the electronic structure in conducting polymers is determined by the chain symmetry, i.e. the number and kind of atoms within the repeat unit, with the result that such polymers can exhibit semiconducting or even metallic properties.

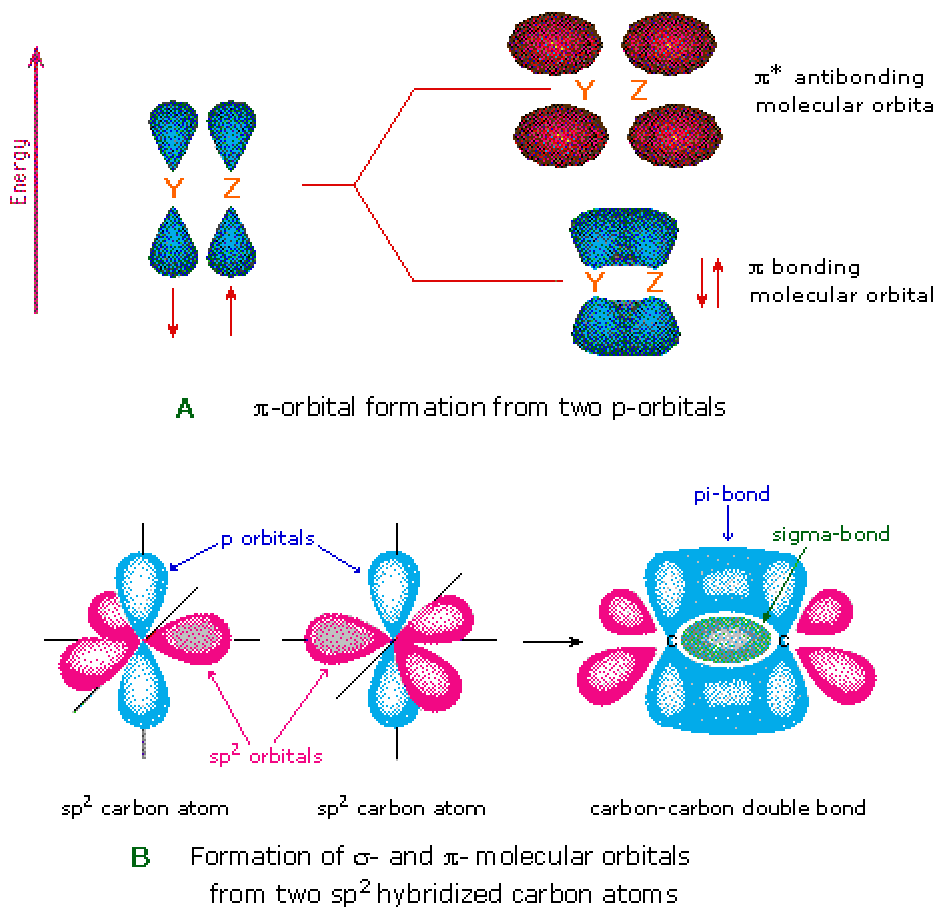


Figure 1.2 Formation of molecular orbitals

Electrically conducting polymers are designated as the fourth generation of polymeric materials. Electronically conducting polymers are extensively conjugated in nature and therefore it is believed that they possess a spatially delocalized band-like electronic structure. These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of the band structure of solid-state semiconductors. It is generally agreed that the mechanism of conductivity in these polymers is based on the motion of charged defects within the conjugated framework. The charge carriers, either positive p-type or negative n-type, are the products of oxidizing or reducing the polymer respectively. The simplest possible form of conducting polymer is of course the arche type polyacetylene (CH)x. Polyacetylene itself is too unstable to be of any practical value, its structure constitutes the core of all conjugated polymers. Little et al [5] had proposed that properly substituted polyacetylene molecule would exhibit superconductivity at room temperature. Hatano et al [6] are the first to report the electrical conductivity of the order of 10^{-5} S/cm for trans polyacetylene sample.

Since late seventies, a large number of polymers have been added to the list of conducting polymers such as polypyrrole, polythiophene, polyparaphenylene, polyphenylene sulphide, polyaniline, polyphenylene vinylene etc.

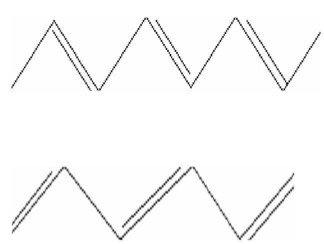


Figure 1.3 Polyacetylene chain

Polyacetylene was the first polymer to be reported. This conjugated organic polymer, could attain high levels of electronic conductivity when oxidized by suitable reagents initiated a significant research. Doping the polymers creates new states (donor or acceptor states), which exist within the band gap, and are energetically accessible to the pi electrons, resulting in significant increase in conductivity. In fact, the conductivity of doped polymers may be up to 10 orders of magnitude greater than that of the neutral polymers. The concept of conductivity and electronegativity of conjugated polymers was quickly broadened from poyacetylene to include a conjugated hydrocarbon and aromatic heterocyclic polymers, such as poly (p-phenylene), polypyrrole and polythiophene. The conductivity of various doped and undoped polymers, some common semiconductors, and metals is presented in Table 1. As the conducting polymers may be doped to various degrees, there is an element of control in doping level, hence the conductivity. This ability to tailor the polymer's electrical properties exemplifies the versatility of conducting polymers.

Table 1.1 Conductivities of Various Conducting Polymers, Semiconductors, and Metals

MATERIAL	CONDUCTIVITY (S/cm)
Gold, Silver, Copper	$\sim 10^{6}$
Doped trans- polyacetylene	$\sim 10^{5}$
Doped polyaniline	$\sim 10^{1}$
Germanium	$\sim 10^{-2}$
Silicon	$\sim 10^{-6}$
Undoped trans- polyacetylene	$\sim 10^{-6}$
Undoped polyaniline	$\sim 10^{-10}$
Glass	$\sim 10^{-10}$
Quartz	$\sim 10^{-12}$

1.2 TYPES OF CONDUCTING POLYMERS

Conducting polymers can be classified in to different types on the basis of conduction mechanism that renders electrical conductivity to polymers.

- Conducting polymer composites
- Organometallic polymeric conductors
- Polymeric charge transfer complexes
- Inherently conducting polymers.

Brief description of the conducting materials have been given here but as present study deals with the inherently conducting polymers, detail discussion have been done for this type of conducting material.

- **Conducting Polymer Composites**

  Conducting polymer composites are mixture or blends of conductive particles and polymers. Various conductors have been used in different forms together with large number of conducting and engineering plastic. 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 the 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 PP, Nylon, and PVC etc.

  .

- **Organometallic Polymeric Conductors**

  This type of conducting materials is obtained by adding organometallic groups to polymer molecules. In this type of materials the d- orbital of metal may overlap orbitals of the organic structure and thereby increases the electron delocalization. The d orbital may also bridge adjacent layers in crystalline polymers to give conducting property to it.

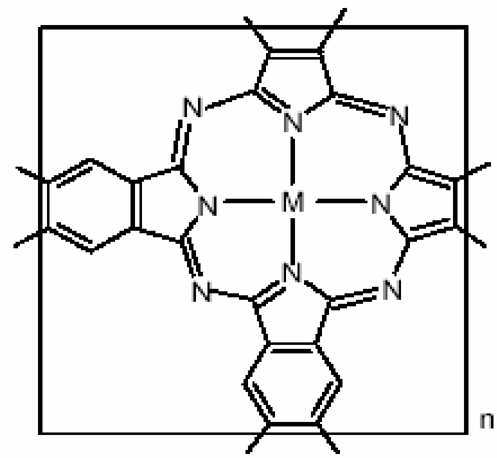


Figure 1.4 Polyphthalocyanines

Metallophthalocyanines and their polymers fall in this class of polymeric material. These polymers have extensively conjugated structures. The bridge transition metal complexes form one of the stable systems exhibiting intrinsic electrical conductivities, without external oxidative doping. Polyferrocenylene is also an example of this type of polymer. These materials possess strong potential for future applications such as molecular wires, antistatic foils and in fibers.

- **Polymeric Charge Transfer Complexes**

Polymeric charge transfer complexes (CTC) are formed when acceptor like molecules are added to the insulating polymers. There are many charge transfer complexes reported in the literature, e.g. CTC of tetrathaifulvalene (TTF) with bromine, chlorine etc is a good conductor. The reason 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.

- **Inherently Conducting Polymers**

Research in the field of inherently conducting polymer started nearly three decades ago when Shirakawa and his group found drastic increase in the electrical conductivity of polyacetylene films when exposed to iodine vapor. The highest crystalline variety of the polyacetylene showed electrical conductivity of the order of 10^{-5} S / cm and was in all possibility the trans-form of polyacetylene. Leading on from this breakthrough, many small conjugated molecules were found to polymerize, producing conjugated polymers, which were either insulating or semiconducting in the oxidized or doped state. The electronic properties of conjugated polymers are due to the presence of electrons. The conjugated polymers are studied as the intrinsically conductive polymers. The conductivity in such polymers arises due to a special type of metallic bonding in which valence electrons are completely delocalized and move almost freely through the crystal lattice. It is therefore necessary for the polymer backbone is necessary for a polymer to behave as an electrical conductor. This delocalization of electrons may occur through the interaction of n-bonded electrons in a highly conjugated chain or by a similar interaction of n-electrons with nonbonded electrons of electron rich hetero-atoms (eg, S, N, etc.) in the backbone. For this the molecular structure of the backbone should be planar. There should be no torsion at the bonds, which would decrease the delocalization of the electron system. Some of the examples of conjugated polymers.

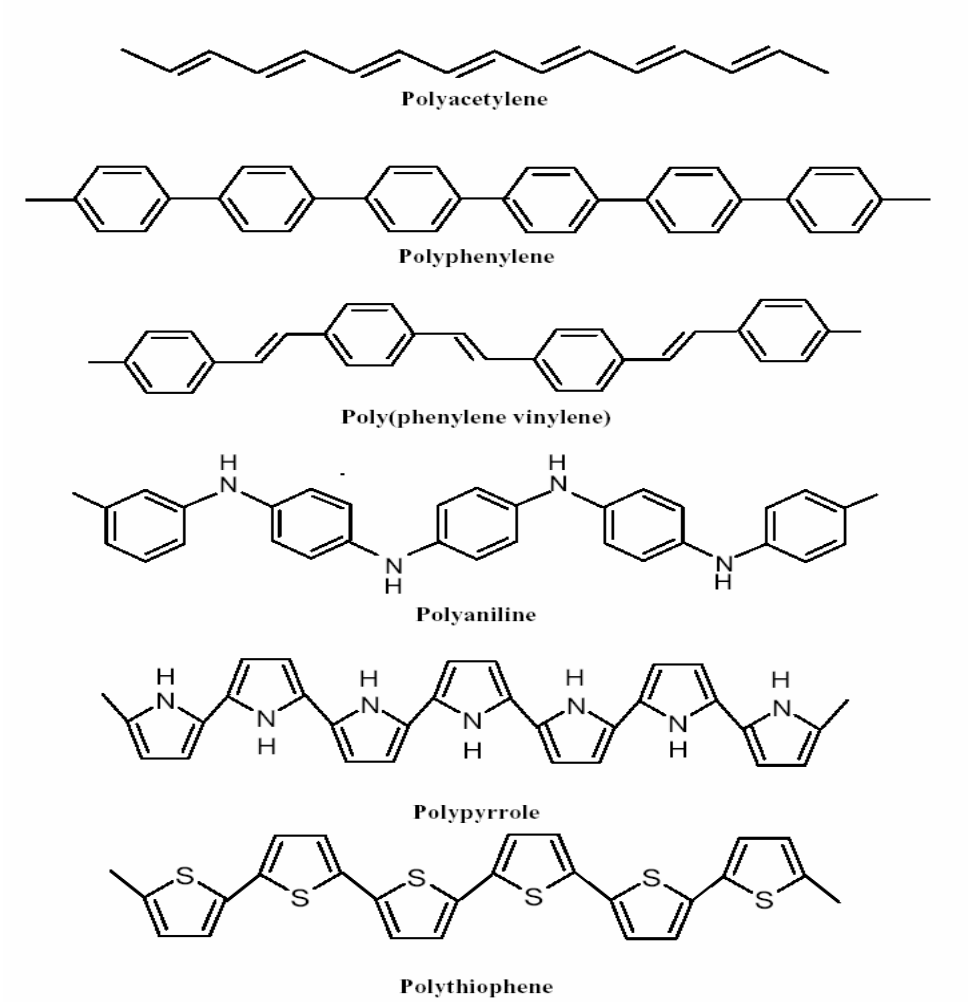


Figure 1.5 Some conducting polymers

1.3 DIFFERENTIATION: Conjugated polymers and Conventional polymers

- Band gap Eg (electronic band gap) is small (~ 1 to 3.5 eV) with corresponding low excitations and semiconducting behavior.
- Can be oxidized or reduced through charge transfer reactions with atomic or molecular dopant species.
- Net charge carrier mobilities in the conducting state are large enough and because of this high electrical conductivity is observed.
- Quasiparticle, which under certain conditions, may move relatively freely through the material.

The electrical and optical properties of these kinds of materials depend on the electronic structure and on the chemical nature of the repeated units. The electronic conductivity is proportional to both density and the drift mobility of the charged 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. To enhance the electrical conductivity of polymers, an increase in the carrier mobility and the density of the charge carriers is required.

As the present work deals with conducting material polyaniline, a brief history of this material is given here.

1.4 POLYANILINE (PANI)

The continuously growing interest in the study of **PANI** over the years is mainly because of its diverse, but unique properties of PANI, allowing its potential applications in various fields.

Among all the conducting polymers, polyaniline is known for it's

- Ease of synthesis
- Environmental stability and
- Easy to dope by protonic acids.

Polyaniline is well- known as an environmentally stable and highly tunable conducting polymer, which can be produced as bulk powder, cast films, or fibers. This, in conjunction with the feasibility of low- cost, large- scale production, makes it an ideal candidate for various applications. The term Polyaniline corresponds to a class of polymers having up to 1000 repeat units (also called mers) and was first reported in 1862 [7]. Much of the structural characterization of polyaniline has taken place in the last 20 years or so, and is fairly well established, although the large number of papers published in the last five years would indicate that polyaniline is still under much scrutiny.

Polyaniline is a typical phenylene based polymer having a chemically flexible –NH- group in a polymer chain flanked either side by a phenylene ring. It can also be defined as the simple 1, 4- coupling product of monomeric aniline molecule. The protonation and deprotonation and various other physico-chemical properties of polyaniline is due to the presence of the –NH- group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black. There are several reports of polyaniline found in the literature over the decades about the structure and constitutional aspect of aniline polymerization [8]. In the year 1968, Surville et al [9] reported the proton exchange and redox properties with the influence of water on the conductivity of polyaniline. Polyaniline can be synthesized by both chemical and electrochemical oxidative polymerization.

Structure and Morphology

There are many levels of polymer structure, and one can categorize the levels loosely using terms used to describe protein structure. The primary structure describes the connectivity of the atoms. The secondary structure describes the three dimensional shape due to short range non- bonded interactions, such as backbone twisting. The tertiary structure describes the shape, also called conformation, of the polymer chains due to long-range non- bonded interactions, which may be interchain or intrachain. The term quaternary structure could be used loosely to describe the polymer in terms of degree of order, for example crystalline, semicrystalline, or amorphous.

Morphology is defined as the study of the form**.** However, when applied to polymers, morphology generally describes the three- dimensional chain conformation and the relationship between chains, as well as the aggregates. Furthermore, morphology includes the physical appearance of polymer particles such as rice grains, spheres, tubules, and fibrils.

Polyaniline exists in four main oxidation states viz.

- Leucoemeraldine base,
- Emeraldine base
- Emeraldine salt and
- Pernigraniline,

Derivatives

The presence of non-hydrogen substituents, on the ring or nitrogen atom, has a dramatic effect on the polymer properties. In general, the solubility increases and the conductivity decrease. In terms of solubility, the increase depends on the nature of the substituents. For example, alkyl and alkoxy substituents result in increased solubility in organic solvents, whereas hydroxyl, carboxylic and sulfonic groups result in increased solubility in water.

It is believed that the decrease in conductivity is a result of two factors: the difference in both size and electronic character of the non- hydrogen substituents. In addition, the electronic nature of the substituents can also affect the conductivity.

Some substituents, such as carboxylic or sulfonic moieties, if substituted on the ring impart a very interesting property to the polymer.

Synthesis of Polyaniline

The most common synthesis of polyaniline involves oxidative polymerization, in which the polymerization and doping occurs concurrently, and may be accomplished either **electrochemically** or **chemically.** Electrochemical methods tend to have lower yields than chemical yields [10].

- **Chemical Synthesis**

Synthesis of polyaniline by chemical oxidative route involves the use of either hydrochloric or sulfuric acid in the presence of ammonium peroxo-di-sulfate as the oxidizing agent in the aqueous medium. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong co-ordination bond either with the substrate / intermediate or with the final product. However smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed. In the review article by Gospodinova et al. [11] they had reported that the propagation of polymer chains proceeds by a redox process between the growing chain (as an oxidant) and aniline (as a reducer) with addition of monomer to the chain end. The high concentration of a strong oxidant, $(NH4)_2S2O8$, at the initial stage of the polymerization enables the fast oxidation of oligo and polyaniline, as well as their existence in the oxidized form.

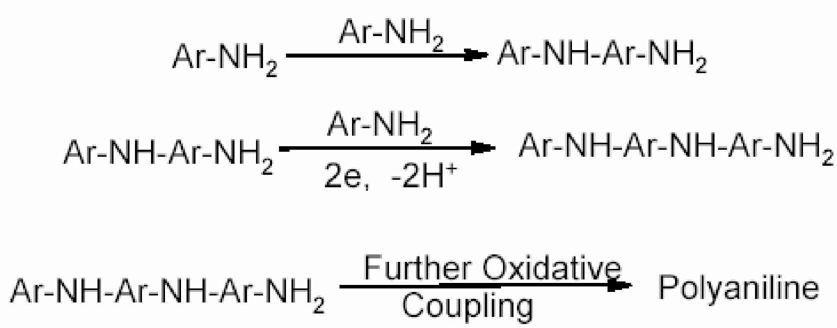


Figure 1.6 Formation of polyaniline

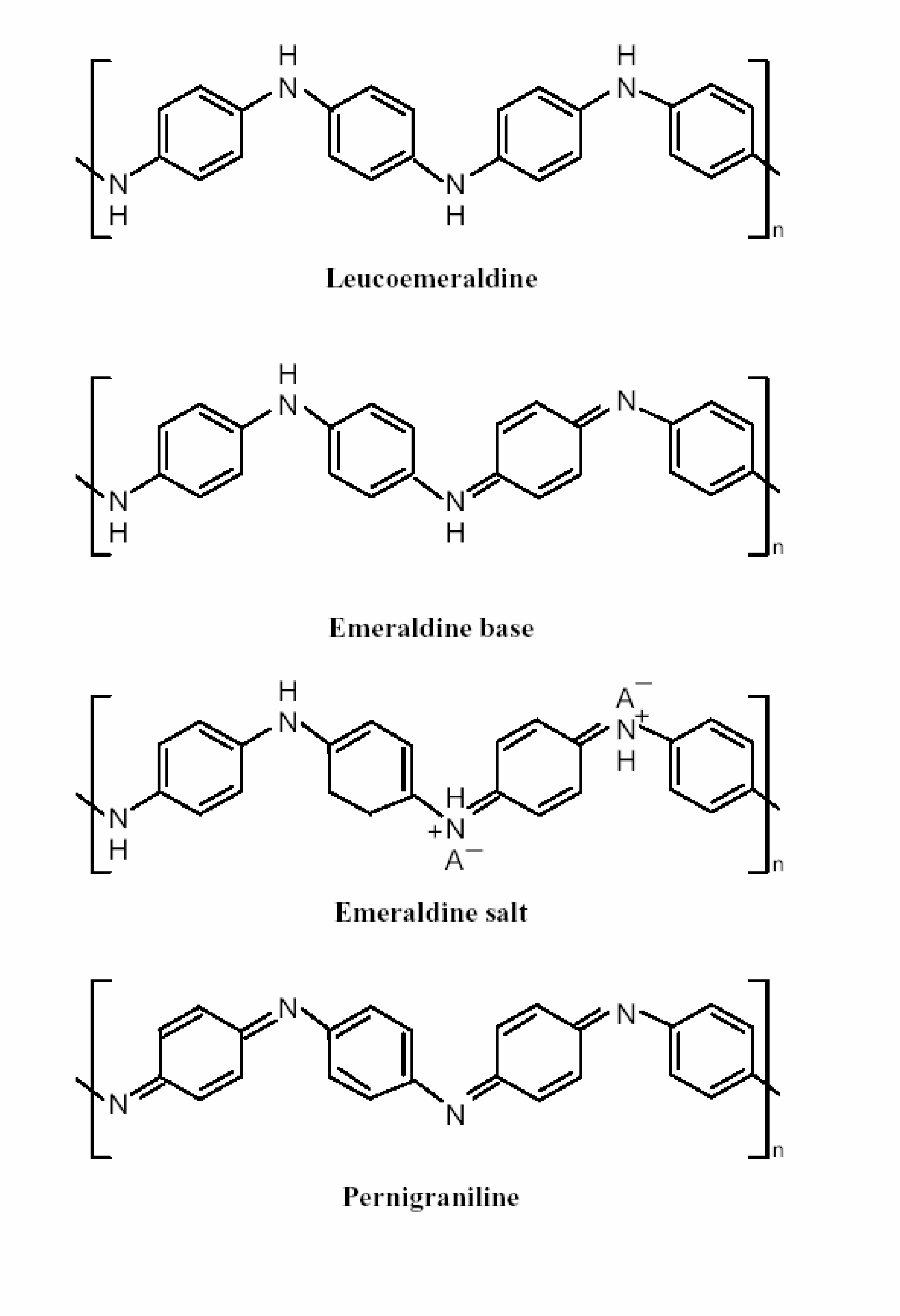


Figure 1.7 Oxidation states of polyaniline

- **Electrochemical Synthesis**

The electrochemical preparation of conducting polymer dates back to early attempts of Dall'olio and coworkers [12], who obtained "pyrroleblack" as it was called at that time, on electrochemical oxidation of pyrrole in aqueous sulphuric acid as a powdery, insoluble ppt on a platinum electrode. Electrochemical polymerization is regarded as a simple and novel method for synthesis of conducting polymers.

The beauty of this method is that polymerization in suitable electrolytic medium gives directly the directly doped polymer as a flexible freestanding film. In this method, films are produced on the electrode surface by oxidative coupling. In this respect this method is somewhat similar to the electrochemical deposition of metal.

The first electrochemical synthesis of polyemeraldine salt was reported by Letheby [13] in the year 1862. In the year 1962 Mohilner et al [14] reported the mechanistic aspects of aniline oxidation. 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 conducting film. Electrochemically prepared polyaniline is the preferred method to obtain a clean and better ordered polymer thin film.

1.5 CHARGE TRANSPORT IN CONDUCTING POLYMER

It is well known that polymers with conjugate bonding system, 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 characteristics, 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 valence 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 valence band. 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 loc 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 the 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.

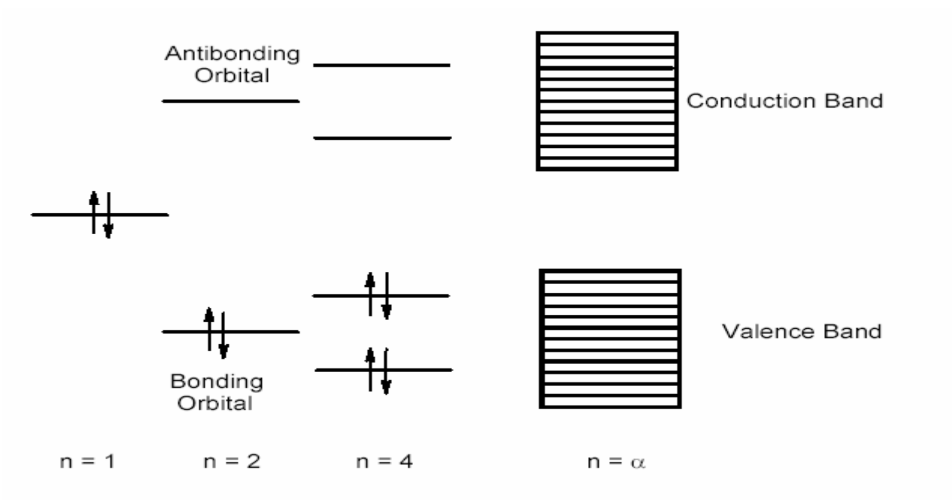


Figure 1.8 One electron band model for electrical conduction

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 in to the lower energy orbital. The (now filled) lower energy orbital is a bonding orbital and the high energy (empty) orbital is an antibonding orbital. The magnitude of the conductivity is determined by the number of charge carriers at which they move. In order to consider the effect of temperature on the electrical conductivity of the three main 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. 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 increase in temperature. 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.

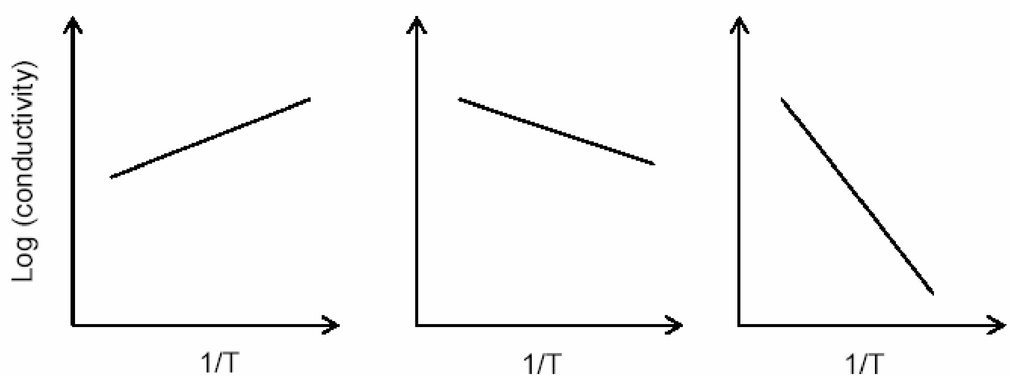


Figure 1.9 Conductivity behaviour of metal, semiconductor and insulator as function of reciprocal of temperature.

Conducting polymers are amorphous in nature with short conjugation lengths. Therefore it has been suggested that electrical conduction take place by charge hopping between polymeric chains. The electrical conductivity in homogeneous systems can be well explained by quasiparticles such as polaron, bipolaron and solitons.Therefore, transport phenomenon leading to high electrical conductivity. 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 take place by hopping.

1.6 DOPING OF POLYMERS

Conductive polymers generally exhibit poor electrical conductivity ($\sigma \leq 10^{-12}$ S/cm) in the virgin state and behave as insulators. These virgin polymers need to be treated with a suitable oxidizing or reducing agents to remarkably enhance their conductivities to the metallic region. This phenomenon has been termed as "**doping**". Doping can be simply regarded as the insertion or ejection of electrons. Doping process results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer. Doping of polymeric semiconductors is different from that in inorganic or conventional semiconductors. Inorganic semiconductors have three dimensional crystal lattice and on incorporation of specific dopant, n-type or p-type in ppm level, the lattice becomes only highly distorted.

The dopant is distributed along specific crystal orientations in specific sites on a repetitive basis. Whereas, doping of conducting polymer 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%. Also incorporation of the dopant molecules in the quasi one dimensional polymer systems considerably disturbs the chain order leading to reorganization of the polymer. Doping process is reversible, and it produces the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counterions which stabilize the doped state, may be carried out chemically or electrochemically. Doping of inorganic semiconductors generates either holes in the valence band or electrons in the conduction band.

On the other hand, doping of polymer leads to the formation of conjugation defects, viz. solitons, polarons or bipolarons in the polymer chain. 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. By controllably adjusting the doping level, conductivity anywhere between that of the non-doped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained. The various oxidation states of Pani obtained by different doping is given in the. Generally in conducting polymers p-type doping is conducted with an electron acceptor, such as p and n-type doping is conducted with donor specie, such as Li. In the doped state, the backbone of a conducting polymer consists of a delocalized system. In the undoped state, the polymer may have a conjugated backbone such as in trans- $(CH)_x$ which is retained in a modified form after doping, or it may have a nonconjugated backbone, as in polyaniline (leucoemeraldine base form), which becomes truly conjugated only after p-doping, or a nonconjugated structure as in the emeraldine base form of polyaniline which becomes conjugated only after protonic acid doping.

1.7 DOPANTS

Dopants are either strong oxidizing or reducing agents. On doping, either positive or negative charge carriers are created in polymers.

Polymer + Dopant → [Polymer^{+}- Dopant^{-}]
(Acceptor) charge transfer complex

Polymer + Dopant→ [Polymer^{-}- Dopant^{+}]
(Donor) charge transfer complex

Figure 1.10 Action of a dopant on polymer

1.8 DIFFERENT TYPES OF DOPING

The expression doping is ambiguous and refers to an uptake into pure material of some other material. This uptake may be diffusion of dopants in to the fibers, a chemical reaction with internal or surface chains or simple adsorption on the surface. Doping is accomplished by chemical methods of direct exposure of the conjugated polymer to a charge transfer agent in the gas or solution phase, or by electrochemical oxidation or reduction. The dopant concentration can be determined by chemical or spectroscopic analysis, or simple weight uptake. Doping of polymers may be done by the following methods including [15]:

Redox doping

Redox doping is the most common method of doping. This is also known as oxidative doping and accomplished by removing pi electrons from the conjugated pi electrons. All conducting polymers e.g., PPy, PT, Pani etc undergo p- and/ or n- redox doping by chemical and/ or electrochemical processes during which the number of electrons associated with the polymer backbone changes.

p-doping is accompanied by partial oxidation of the backbone of the polymer. It was first discovered by treating trans- (CH)x with an oxidizing agents such as iodine. p-doping can also be done by electrochemical anodic oxidation by immersing a trans-(CH)x film in a solution of $LiClO_4$ and attaching it to the positive terminal of a DC power source, the negative terminal being attached to an electrode also immersed in the solution. n-doping, i.e. partial reduction of the backbone system of an organic polymer, was also discovered using trans-(CH)x by treating it with a reducing agents such as sodium naphthalide.

Photo doping

When trans (CH)x is exposed to radiation of energy greater than its band gap, electrons are promoted across the gap and polymer undergoes "photo-doping".

Charge injection doping

Charge injection doping is most conveniently carried out using a metal/insulator/semiconductor (MIS) configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator. Application of an appropriate potential across the structure can give rise to a surface charge layer. The resulting charges in the polymer, for example, (CH)x or poly (3-hexylthiophene) are present without any associated dopant ion.

Non redox doping

Although oxidative doping is available to polyaniline, a more common method of producing doped polyaniline is known as acid- doping (or proton doping). This type of doping differs from redox doping is that the number of electrons associated with the polymer backbone does not change during the doping process. As with the oxidative doping process, doped polyaniline may be produced in one step. The presence of the acid (HA) results in the protonation of nitrogen atoms. Once protonated, the polymer chain is now positively charged, and has associated counter- anions. The degree of protonation depends on the oxidation state of the polymer and the pH of the acid solution [7]. The energy levels are rearranged during doping. The emeraldine base form of Pani was the first example of the doping of an organic polymer to a highly conductive regime by non-redox type doping.

Neutral (or undoped) polyaniline exhibits conductivity on the order of 10^{-10} S/cm; as with oxidative doping, protonic, or acid, doping can result in a significant increase in conductivity (up to 10 S/cm – 11 orders of magnitude) [16]

1.9 TYPES OF DOPING AGENTS

Dopants may be classified as:

- Neutral dopants: I_2, Br_2, AsF_2, Na, K, H_2SO_4, $FeCl_3$ etc.
- Ionic dopants: $LiClO_4$, $FeClO_4$, CF_3SO_3Na, $BuNClO_4$ etc.
- Organic dopants: CF_3COOH, CF_3SO_3Na, p-$CH_3C_6H_4SO_3H$
- Polymeric dopants: PVS, PPS

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. Organic dopants are anionic dopants, generally incorporated into polymers from aqueous electrolytes during anodic deposition of the polymer.

1.10 DOPING TECHNIQUES

Doping in polymers can be done by following ways,

- *Gaseous doping*
- *Solution doping*
- *Electrochemical doping*
- *Self doping*
- *Radiation induced doping*
- *Ion exchange doping*

Gaseous, solution and electrochemical doping methods are widely used because of the convenience in carrying out and of low cost. In gaseous doping process, the polymers are exposed to the vapor of the dopant under vacuum. 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 acrylonitrile, tetrahydrofuran, nitro methane are used as solvents. The polymer is treated with dopant solutions. In the electrochemical doping technique simultaneous polymerization and doping generally occurs. 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.

1.11 CHARGE APPEARING ON THE POLYMER CHAINS UPON DOPING

In a polymer, just as in a crystal, the interaction of a polymer unit cell with all its neighbours leads to the formation of electronic bands. The highest occupied electronic level s constitute the valence band (VB) and the lowest unoccupied levels, the conduction band (CB).the width of the forbidden band , or bandgap (E_g), between the VB and CB determines the intrinsic electrical properties of the material. In organic molecule, it is usually the case that equilibrium geometry in the ionized state is different from the ground state. On ionization of an organic molecule the geometry of the molecule is first distorted in the ground state in such a way that the molecule adopts the equilibrium geometry of the ionized state. This costs distortion energy $E_{dis.}$ Then the reduction in the ionization energy i.e. E_{IP-V} - E_{IP-d} upon distortion is larger than the energy E_{dis} required to make that distortion.

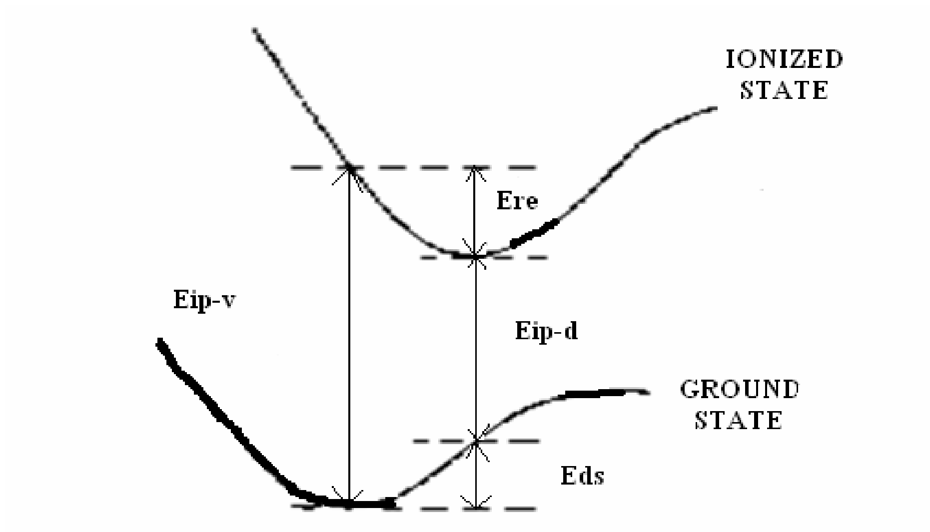


Figure 1.11 Molecular ionization process in conducting polymers

However in an organic polymer chain, it can be energetically favourable to localize the charge that appears on the chain and to have, around the charge, a local distortion (relaxation) of the lattice. This process causes the presence of a localized electronic state in the band gap.Conisdering the case of oxidation, i.e., the removal of an electron from the chain. This causes the formation of radical ion on the polymer chain and around that charge or cation localization occurs. This radical cation which is formed is having more energy then that of the energy of the valance band. This radical cation associated with the lattice distortion is known as *polaron* and the presence of localized electronic state in the gap referred to as polaron state. It is having half (1/2) spin [17].

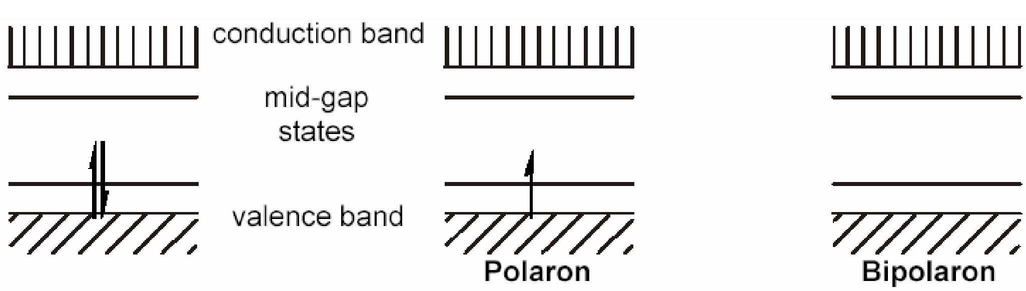


Figure 1.12 Conduction states

A bipolaron is defined as a pair of like charges associated with a strong local distortion. It is spinless.

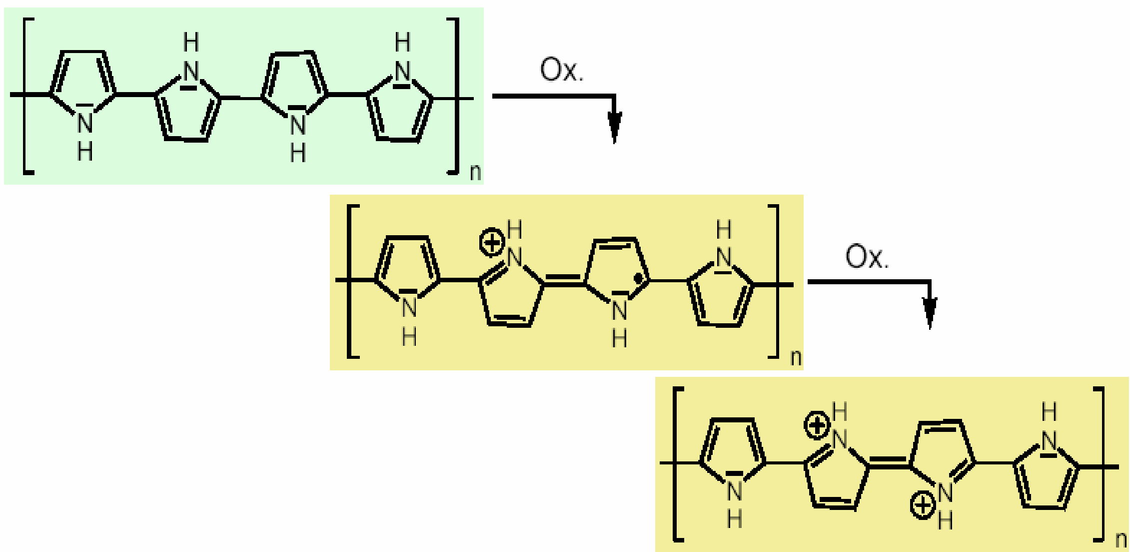


Figure 1.13 Mechanism of charge conduction

The bipolaron charge carrier is of relatively high energy, and thus is short- lived. Redistribution of charge and spin yields a polaron as the more stable charge carrier [18]. A radical, cation, or anion defect on a polyacetylene backbone divides the polymer into sections which are mirror image to each other. The defect can move in either direction without affecting the energy of the backbone. The movement of the defect can be describes as a solitary wave or soliton. The radical defect is referred to as soliton, the anion and cation defects are charged solitons.The neutral soliton is having ½ spin whereas the anion and cation defects are spinless.

1.12 EFFECT OF DOPING ON CONDUCTIVITY

The doping process involves transfer of the charge to or from the bonding system of the conjugated polymer, leaving the system essentially intact and hence the structural identity of an individual chain preserved. However, vibrational, electronic and other properties of the polymer are strongly altered upon doping as well as its supramolecular structure. The most spectacular result of the doping is the increase of the polymer conductivity over several orders of magnitude. In some cases conjugated polymers reach the conductivity of metals with a negative temperature coefficient which is characteristic of metallic behavior. 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. Thus due to the changes in the environment of the chains disorders are created from doping. At low dopant concentration, the dopant molecules occupy random positions between the chains. The effect the electronic properties by their coulomb potential and by hybridization with the polymer p-orbitals. As polarons produced has long lifetime, they are treated as quasi-particles. Polarons have low mobility, which results in obtaining 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 to form bipolaron. At this point in the doping process, conductivity undergoes a marked increase. Once the radical components of the polarons have combined to form bonds, the remaining charges achieve high mobility along the chain. Example showing formation of polarons –bipolarons in polypyrrole chain is given in the *Fig. 1.14*

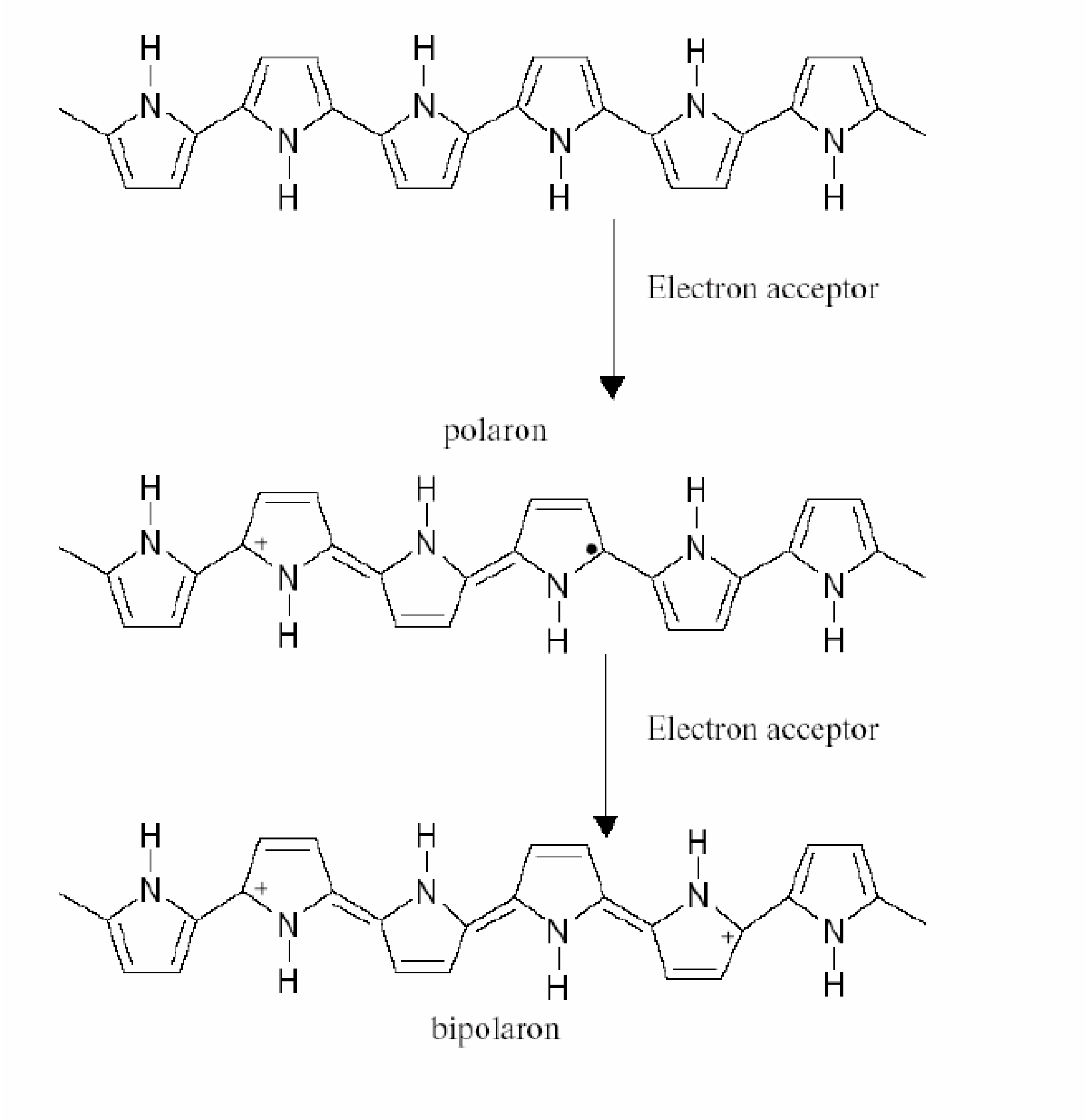


Figure 1.14 Formation of polaron- bipolaron in a PPy chain

1.13 ELECTRICAL PROPERTIES OF CONDUCTING POLYMERS:

It is only the doping which makes most of the conjugated polymers conducting from their insulating state to semiconducting or conducting. Although the charged species are incorporated by doping, the electrical conductivity is not ionic but electronic.

Electronic conductivity of conducting polymers depend upon numerous factors. Significant among these are:

- *Nature or chemical reactivity of the dopant*
- *Process of doping*
- *Doping level*
- *Method and condition of polymer synthesis*
- *Processing of the polymer*

Chemical reactivity of the dopant is of prime importance to obtain a conducting polymer. Not all dopants are equally capable of oxidizing a polymer chain. Iodine is a dopant for increasing the electrical conductivity of polyacetylene by 13 orders of magnitude but is too weak to oxidize PPy or PANI. Similarly HCl is used to conduct PANI. The electrical conductivity of polyaniline hydrochloride observed is 4.4 ± 1.7 S cm–1 (59) samples.

Doping conditions also play an important role. Electrical conductivity usually increases with the doping level due to increase in charge carriers concentration. Rapid increase in mobility of the charge carriers may be responsible for this high rate of increase in conductivity. Development of quantitative model for conduction is hampered by the fact that there are at least three elements contributing to the carrier mobility:

- Single chain or intramolecular transport
- Interchain transport
- Interparticle contact

Electrical conductivity is very much dependent on the method of polymer synthesis, purification of the polymer, physical treatment of the polymer etc.besides nature of the dopants and the process of doping.

1.14 APPLICATIONS

Research shows that conducting polymers exhibit conductivity from the semiconducting range (~10^{-5} S/cm) right up to metallic conductivity (~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. There are mainly two groups of applications for organic conducting polymers which are briefly described as follows:

- **Group I**

These applications just use the conductivity of the polymers. The polymers are used because of either their lightweight, biological compatibility for ease of manufacturing or cost. Electrostatic materials, Conducting adhesives, Electromagnetic shielding, Printed circuit boards, Artificial nerves, Antistatic clothing, Piezoceramics, Active electronics (diodes, transistors), Aircraft structures.

- ***Electrostatic materials**:* By coating an insulator with a very thin layer of conducting polymer it is possible to prevent the buildup of static electricity. This is particularly important where such a discharge is undesirable. Such a discharge can be dangerous in an environment with flammable gasses and liquids and also in the explosives industry. Bayer uses polythiophene as an anti-static layer in film products.

- ***Conducting adhesives**:* By placing monomer between two conducting surfaces and allowing it to polymerize it is possible to stick them together. This is a conductive adhesive and is used to stick conducting objects together and allow an electric current to pass through them.

- ***Electromagnetic shielding**:* Many electrical devices, particularly computers, generate electromagnetic radiation, often radio and microwave frequencies. This can cause malfunctions in nearby electrical devices. By coating the inside of the plastic casing with a conductive surface this radiation can be absorbed.

- ***Printed circuit boards**:* Many electrical appliances use printed circuit boards. These are copper coated epoxy-resins. The copper is selectively etched to produce conducting lines used to connect various devices. These devices are placed in holes cut into the resin. In order to get a good connection the holes need to be lined with a conductor. Copper has been used but the coating method, electroless copper plating, has several problems. This process is being replaced by the polymerization of a conducting plastic. If the board is etched with potassium permanganate solution a thin layer of manganese dioxide is produced only on the surface of the resin. This will then initiate polymerization of a suitable monomer to produce a layer of conducting polymer.
- ***Artificial nerves**:* Due to the biocompatibility of some conducting polymers they may be used to transport small electrical signals through the body, i.e. act as artificial nerves.

- ***Aircraft structures**:* Modern planes and spacecraft are often made with lightweight composites. This makes them vulnerable to damage from lightning bolts. By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft.

- **Group II**:

This group utilizes the electroactivity character property of the materials. Molecular electronics, Electrical displays, Chemical, biochemical and thermal sensors, Rechargeable batteries and solid electrolytes, Drug release systems, Optical computers, Ion exchange membranes, Electromechanical actuators, 'Smart' structures, Switches.

- ***Rechargeable batteries**:* Batteries were one of the first areas where conducting polymers promised to have a commercial impact. Conducting polymer batteries were investigated by leading companies like BASF/VARTA and Allied Signal. A number of conducting polymers such as polyacetylene, polyaniline and other polyheterocycles have been used as electrode materials for rechargeable batteries.
- ***Sensors**:* Since electrical conductivity of conducting polymers varies in the

presence of different substances, these are widely used as chemical sensors or as gas sensors. In its simplest form, a sensor consists of a planar interdigital electrode coated with 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

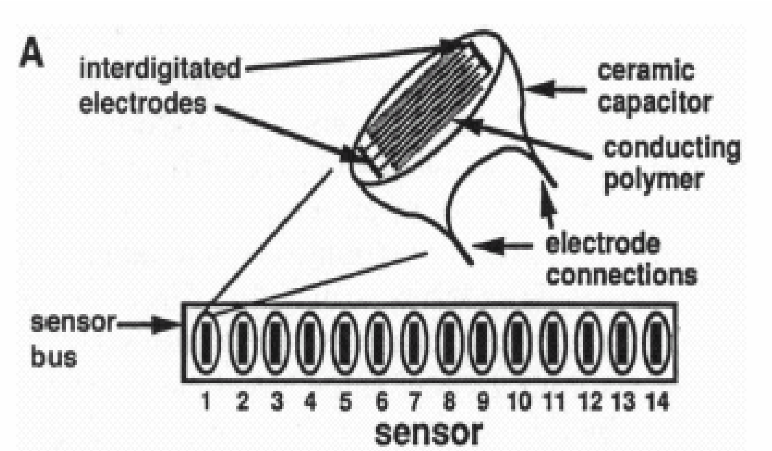


Figure 1.15 Schematic of a sensor array showing an enlargement of modified ceramic capacitors used as sensing elements.

- ***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. Conjugated polymers that can be repeatedly driven from insulating to conductive state electrochemically with high contrast n color are promising materials for electrochromic device technology. Conjugated polymers have an electronic band structure. The energy gap between the valence band and the 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 electrochromic materials first drew interest in large area display panels. In architecture electrochromic devices are used to control the sun energy crossing a window. In automotive industry rearview mirrors are a good application for electrochromic system. With oxidation, polypyrrole turns from yellow to black whereas polythiophene turns from red to blue.

- ***Electromechanical Actuators**:* Conducting polymers also change volume depending on their oxidation state. Therefore it is possible for conducting polymers to convert electrical energy into mechanical work. Conducting polymer actuators were proposed by Baughmann and coworkers [19]. Oxidation induced strain of polyaniline and polypyrrole based actuators has been reported.

- ***Drug release systems*:** Another application for conducting polymers is controlled release devices. Ions can be selectively released, as well as biologically active ions such as adenosine 5-triphosphate (ATP) and Heparin. Principle used in this application is potential dependence ion transport. This potential dependence ion transport is an interesting way to deliver ionic drugs to certain biological systems. One can deliver selective ions depending on the requirement

- ***Catalyst:*** Conducting polymers show redox property; therefore these are expected to behave as redox catalyst. Several reports have been found in the literature on modification of conducting polymers and their use as catalyst for small organic molecules. Conducting polymers in their various oxidation states interconvert each other, which permits to construct redox cycle for catalytic reactions. The catalytic activity has been revealed to be controlled by doping. Coordination of transition metals to the nitrogen atoms (in case of Pani and PPy) affords the complexes, in which transition metals are considered to interact through a conjugated chain. The characteristics of conjugated polymers are reflected on the complexes, which are expected to provide novel catalytic system.

CHAPTER II

LITERATURE REVIEW

2.1 INTRODUCTION

Conductive polymers such as polypyrrole, polyacetylene, etc.continue to be the focus of active research in diverse fields including electronics, energy storage catalysis, chemical sensing and biochemistry.Polyaniline is unique among conducting polymers in its wide range of electrical, electrochemical and optical properties as well as good stability.Polyaniline can be doped to highly conducted state by protonic acids or by electrochemical methods and show moderate conductivity upon doping. The literature survey in this chapter puts into:

- Invention of conducting polymers
- Developments in the field of conducting polymers
- Development of polyaniline
- Synthesis
- Properties
- Applications
- Recent trends

2.2 INVENTION OF CONDUCTING POLYMERS

In 1971, the fist intrinsic conducting polymer was reported by **Shirakawa** *et al.* **[20]** Polyacetylene, a conjugated organic polymer, could attain high levels of electronic conductivity when oxidized by suitable reagents initiated a significant research.

The concept of conductivity and electroactivity was quickly broadened from polyacetylene to polypyrrole; an aromatic heterocyclic polymer by **Diaz** *et al.* **[21]** Polypyrrole due to its stability in air was one of the compounds having highest potential for commercial applications.

According to **Bigg** *et al*. **[22]** Polymers were made conducting with the help of fillers. In that case polymer was regarded as the matrix and some conductive filler was incorporated in to that which made polymer as a conductor. They called that arrangement as a composite.

Yamaguchi [23] after the theoretical study of high T_e superconductors have predicted that a polymeric molecules with –C-N-C-N- type skeleton may have super conductivity. This prediction was done after molecular orbital study of Cu-O bonds in copper oxide super conductors and finding their similarly with C-N bonds.

2.3 DEVELOPMENTS IN THE FIELD OF CONDUCTING POLYMERS

Street *et al***. [24]** in his work compared all reported conducting polymers with that of classical materials. They discussed the mechanism of doping together with the final state of the dopant and polymer. They also made out some of the problems related with the inhomogeneous distribution of dopants.

Solaneck et al. **[25]** have studied that PAN (poly acrylonitrile) can be electropolmerised and adopts a linear conformation.

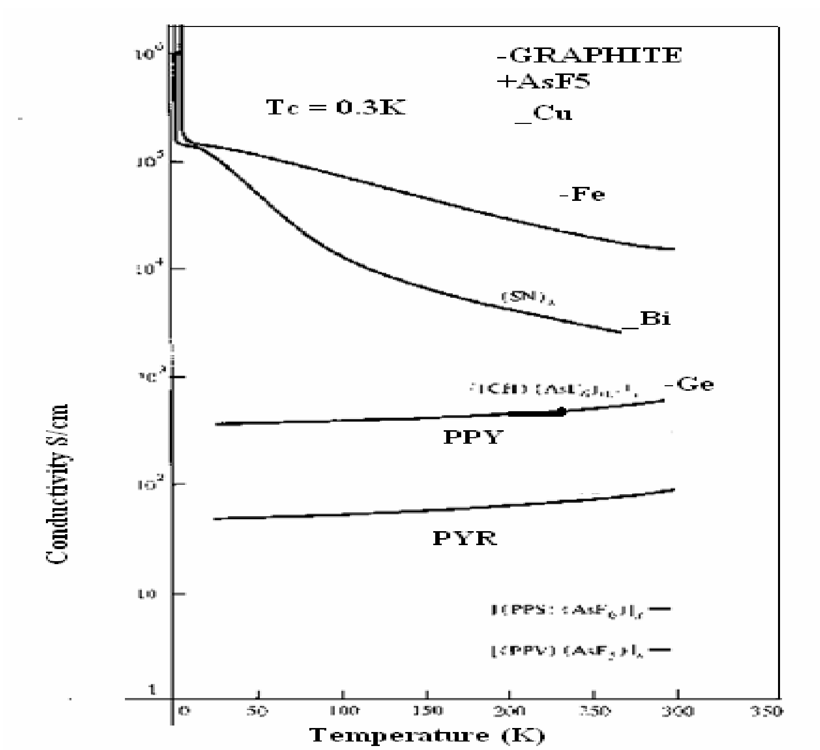


Figure 2.1 Conductivity Vs Temperature for various conducting polymers and classical conductors.

The new feather in the cap of conducting polymers was the invention of polyaniline by **Wu-Song Huang** *et al*. **[26]** who gave new theory of non-oxidative doping of this material. Extensive work has been carried out on this polymer. According to them, the emeraldine salt form of polyaniline, conducting in the metallic regime, could be synthesized electrochemically as a film exhibiting a well defined fibrillar morphology closely resembling that of polyacetylene. Probable chemical changes which occurred and the compounds which were formed when chemically synthesized poly-aniline was electrochemically oxidized and reduced between –0.2 and 1.0 V *vs.* SCE in aqueous HCl solutions at pH values ranging from –2.12 (6.0 mol dm^{-3}) to 4.0 . These were shown to be consistent with previous chemical and conductivity studies of emeraldine base and emeraldine salt forms of polyaniline. It was proposed that the emeraldine salt form of polyaniline has a symmetrical conjugated structure having extensive charge delocalization resulting from a new type of doping of an organic polymer–salt formation rather than oxidation which occurs in the p-doping of all other conducting polymer systems.

According to Hegger *et al*. **[27]** principal goal of the field of conducting polymers was to strive for advances in materials quality that would enable the exploration of the intrinsic electrical properties. In this context, they summarize the requirements for achieving high performance conducting polymers with electrical conductivities greater than that of copper. They investigated that to avoid localization onto one-dimensional polymer chains, interchain charge transfer was required.

Clark *et al***. [28]** carried out that advances in the synthesis of organic conducting polymer systems had increased the electrical conductivity of these systems by several orders of magnitude in the last decade. Several practical applications were envisioned for such systems, but a thorough understanding of the conduction mechanisms and identification of the charge carriers was lacking, making design and implementation for bulk synthesis difficult. They clarified the electrical properties of these systems, the resistivity and magnetoresistivity of various polymers doped near the metal - insulator transition, such as polyaniline protonated by camphor sulfonic acid (PANI-CSA) and polypyrrole doped with PF_6 (PPy-PF_6), was studied down to 25 mK in magnetic fields up to 16 T.

Michael *et* al. **[29]** described a method for generating a variety of chemically diverse broadly responsive low-power vapor sensors. The chemical polymerization of pyrrole in the presence of plasticizers has yielded conducting organic polymer films whose resistivities were sensitive to the identity and concentration of various vapors in air. An array of such sensing elements produced a chemically reversible diagnostic pattern of electrical resistance changes upon exposure to different odorants. They investigated that, this type of polymer-based array was chemically flexible, was simple to fabricate, modify, and analyze, and utilized a 16w-power dc resistance readout signal transduction path to convert chemical data into electrical signals.

Schoch *et al.* **[30]** found out that there had been considerable progress in both processing the conducting polymer materials as well as developing certain applications for them. They a discussed the advances in materials synthesis and processing, the characteristics of these materials, and the applications receiving the most attention at that time. They also compared the conductivity of several conductive polymers with other materials.

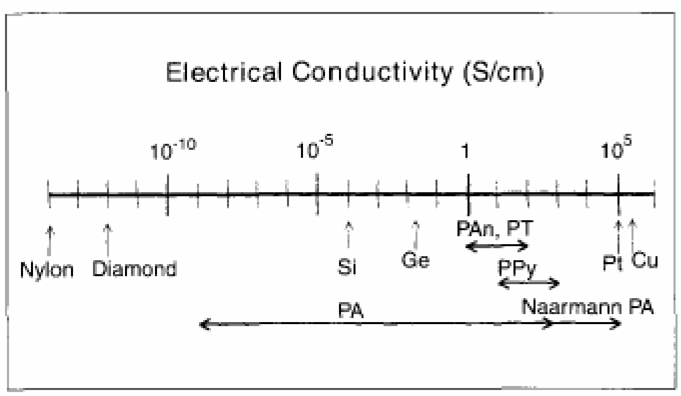


Figure 2.2 Electrical conductivity of selected solids

2.4 DEVELOPMENT OF POLYANILINE

Negi *et al.* **[31]** in their work reviewed, recent research work on polyaniline-type conducting polymers. Research and development work had been reviewed with special interest in chemical, electrochemical, doping processes, and polyaniline-based composite processes. Process development with high accuracy of product results had the direct relationship with structure and properties. According to them, polyaniline based on a variety of structures generated from molecular structural modification could give more interesting results for future applications.

2.5 SYNTHESIS OF POLYANILINE

Mehmet Sacak *et al.* **[32]** proposed that conductive polyaniline was synthesized in aqueous 1.0 M oxalic acid containing 0.1 M aniline by electrochemical and chemical oxidation and characterized by conductivity, solubility, ultraviolet and infrared spectroscopy, and cyclic voltammetry. They found out that electrochemical behaviour of aniline in oxalic acid was similar to that in H_2SO_4. However, the polymerization rate was slower. The use of oxalic acid medium improved the solubility of PANI in dimethylsulfoxide and dimethylformamide to a certain extent.

X.L.Wei *et al***. [33]** found out that sulphonated polyaniline (SPAN) was a self-doped conducting polymer. They investigated that, it had high water solubility and a novel pH-dependent DC conductivity that is of interest for fundamental science and also for applications in such areas as rechargeable battery and pH control technologies. They reported extensive characterization and details of synthesis of a new form of sulphonated polyaniline which showed novel or significantly improved chemical and physical properties

2.6 CHEMICAL SYNTHESIS

Sacak *et al***. [34]** carried out that the conductive form of polyaniline was synthesized by the anodic and chemical oxidation of aniline in malonic acid medium. The conductivity of polyaniline doped with malonic acid changed from 1.62 x 10^{-6} to 2.5 x10^{-5} S cm^{-1} depending on the way it was synthesized. The polymer growth rate was observed to be very slow in malonic acid compared with H_2SO_4. Thermogravimetric data revealed that the maximum thermal reaction rate of PANI doped with malonic acid was at 200^0C and 520^0C compared with 290^0C and 530^0C of the polymer doped with H_2SO_4. A conductive PANI can be synthesized in malonic acid solution using both chemical and electrochemical routes. The electrochemical polymer growth rate in malonic acid media was much slower than that observed in H_2SO_4.

Eight persons [35] from five institutions in different countries carried out polymerizations of aniline. They oxidized aniline hydrochloride with ammonium peroxydisulphate in aqueous medium at ambient temperature. The yield of polyaniline was higher than 90 % in all cases. The electrical conductivity of polyaniline hydrochloride thus prepared was 4.4 ± 1.7 S cm^{-1} (average of 59 samples), measured at room temperature. According to them, a product with defined electrical properties could be obtained in various laboratories by following the same synthetic procedure.

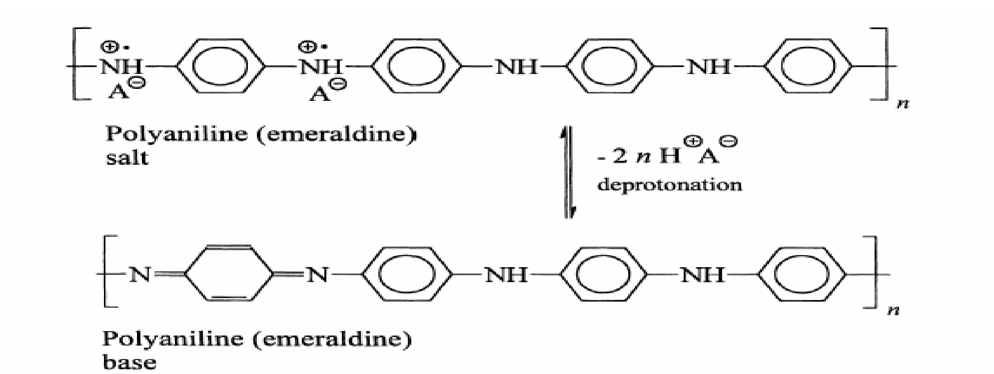


Figure 2.3 Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to polyaniline (emeraldine) base.

.2.7 ELECTROCHEMICAL SYNTHESIS

According the study of **Bekar Sari** *et al***. [36]** conductive homopolymers of o-chloroaniline, p-bromoaniline and N-methylaniline were synthesized electrochemically in perchloric acidic solution and their properties were analyzed. Initially, the maximum oxidation potential values of these monomer solutions were determined by Cyclic

Voltammetry (CV). Their conductive polymers were then synthesized under a nitrogen atmosphere using a potentiostat.

Majjidi et al. [37] worked out tha the synthesis of optically active polyaniline salt films of the type PAn has been achieved via the enantioselective electropolymerization of aniline on indium-tin-oxide (ITO)-coated glass electrodes in the presence of sulphonic acid. They found out that thesimilar results were obtained under potentiostatic, galvanostatic and potentiodynamic conditions. Results suggest that chiral holes might be formed in the polymer matrix during both redox and chemical re-doping cycles with PAn. SA salt films.

2.8 PROPERTIES OF CONDUCTING POLYMERS

E.Fayad et *al.* **[38]** investigated the electrical resistivity, optical properties and morphology of thin solid films of an oligomer of the polyaniline. The oxidative doping processes of these thin films were studied by means of Resonance Raman scattering. The conductivity was also monitored. Combination of these different techniques led to the characterization of the electronic transport that is induced by doping, and finally, a mechanism of the modification of the electronic structure of the oligomer was proposed.

Jakub *et al.* **[39]** discussed the changes in the electrical conductivity of polyaniline suspensions in 1,2,4-trichlorobenzene observed during the freezing and melting of the medium .They explained that by the changes in the organization of conducting particles in an electric field under a varying state of the system. The conductivity of liquid suspension was two orders of magnitude higher by comparison with the frozen one. Polyaniline suspensions were the new class of liquid systems comprising electrically conducting polymers. According to them, their electrical conductivity could be decreased by several orders of magnitude by freezing the suspension, while it was recovered after melting.

Chandrakanthl *et al* **[40]** found that among conducting polymers with metallic characteristics, polyaniline was claimed to have one of the highest environmental stability.They proposed that PANI was stable up to 200^0C.

Mathal *et al* **[41]** prepared PANI films by ac plasma polymerization technique and studied its various properties and parameters like capacitance, dielectric loss, dielectric constant and the ac conductivityin yhe frequency range of 100 Hz to 1 MHz. They investigated that capacitance and dielectric loss decreased with frequency and increased with temperature.

2.9 EFFECT OF DOPANTS ON PANI

Murugesan *et al* **[42]** proposed, how metal oxalate complexes which were inorganic in nature affected the polyaniline.The XRD patterns indicated some crystalline nature in metal oxalate doped doped PANI.

Valsangiacom *et al* **[43]** studied the effect when PANI was doped with iron. They also analyzed the mossbauer spectroscopy which showed that by applying the UV exposure, electrons from the polymer chains were trapped by the Fe ions, changing their from Fe^{3+} to Fe^{2+}**.**

2.10 APPLICATIONS

Spinks *et al*. **[44]** described the effects of conducting polymer coatings on the corrosion rate of ferrous alloys (iron, steel and stainless steel). This literature was interpreted in terms of the proposed mechanisms of corrosion protection: barrier, inhibitor, anodic protection and the mediation of oxygen reduction. The most intriguing aspect of the reported literature was the studies demonstrating corrosion protection when deliberate defects were introduced into the coating to expose the bare metal. The studies showed that protection afforded by conducting polymer coatings is not due to simple barrier protection or inhibition alone. The studies supported the proposed anodic protection mechanism.

J.H.Jung *et al* **[45]** proposed that lithium doped polyaniline could be used as the applications to the secondary batteries. They reported the results of temperature dependence of dc conductivity, the electron paramagnetic resonance and the thermoelectric power, for polyaniline samples doped with various lithium **salts.**

2.11 FURTHER MORE DEVELOPMENTS

C.Valsangiacom *et al* **[46]** carried out that the major target of conductive polymer technology development has been to combine the electrical and optical properties of conducting materials with the mechanical and processability properties of commodity bulk polymers. Polyaniline was synthesized at – 15°C using a polyethylenglycole / ice bath and doped with Fe^{3+} ions. Polyaniline films (tenths of mm) were prepared by the gravity method. The dried films were exposed to UV (300nm <l< 500nm, 10mW/cm2), up to 25 min. The conduction mechanism vs. the exposure time was analyzed by resistively measurements and Mössbauer spectroscopy.

E.Erdem *et al.* **[47]** gave the idea that the chemical polymerization of aniline was carried out in media containing different linear dicarboxylic acids with the use of oxidants such as $K_2Cr_2O_7$, $KMnO_4$, $K_2S_2O_8$, KIO_3 and $FeCl_3$. The highest yield and the conductivity was observed with $K_2Cr_2O_7$. The yield and the conductivity of the polyaniline (PAn) synthesized were observed to decrease in the order of oxalic acid> malonic acid > succinic acid > glutaric acid > adipic acid > phthalic acid.

Table 2.1 Showing how an Oxidant Affects the Yield

Oxidant	An/oxidant (mol/mol)	Yield (%)					
		OX	MA	SA	GA	AA	FA
$K_2Cr_2O_7$	6	46.84	36.00	31.82	26.60	10.00	8.99
$K_2S_2O_8$	2	43.03	42.00	22.92	17.18	7.62	3.86
$KMnO_4$	5	17.42	15.77	14.43	19.97	4.55	–
KIO_3	6	10.92	0.88	0.10	–	–	–
$FeCl_3$	6	–	–	–	–	–	–

2.12 RECENT TRENDS

According to **Habberg** *et al***. [48]** contact molding and other related techniques of imprint lithography have recently received much attention as inexpensive and versatile methods for the replication of sub-100 nm features.They recently reported the use of contact molding for the accurate replication of structures as small as 60 nm. In this technique, they employed an inexpensive, reusable stamp is to mold a photopolymer resin. The resin, then cured in contact with the stamp resulting in a highly reproducible positive copy of the stamp.

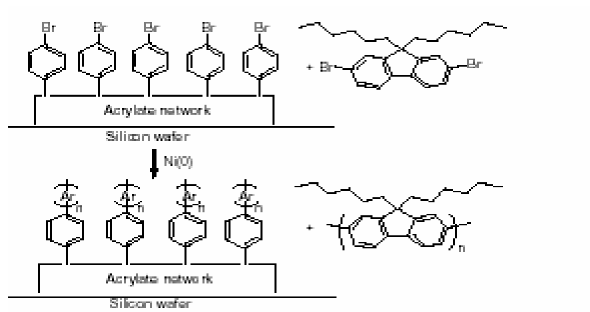


Figure 2.4 Polyfluorene brush growth under Ni (0) coupling conditions from bromoarene functionalized substrates.

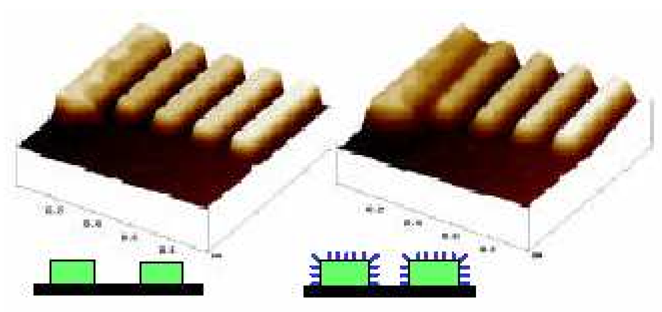


Figure 2.5 AFM topographs of substrates patterned by contact molding priorto polyfluorene brush growth (left) and after polyfluorene brush growth (right).

According to **Sadik** *et al*. **[49]** advances in conducting electroactive polymers (CEPs) have driven the design of novel chemical and biochemical sensors. The redox properties of CEPs have been intensely studied for more than two decades with emphasis on their synthesis and characterization. Little attention has been paid to the importance of mechanism in sensor designs. They considered that, in order to design robust and stable sensors, it was important to understand how the polymer structure, morphology, adhesion properties and microenvironment affect sensor performance.

Huang *et al.* **[50]** carried out that Conducting polymer nanostructures combine the advantages of organic conductors and low dimensional systems and therefore should yield many interesting physicochemical properties and useful applications. In their work, polyaniline was used as a model material to systematically investigate the syntheses, properties and applications of nanofibers of conjugated polymers. To begin, a conceptually new synthetic methodology has developed that readily produced high αquality, small diameter nanofibers in large quantities.

2.13 CONCLUSION

From the literature survey, it can be inferred that polyaniline has given fire to the research of conducting polymers. There are various synthesis processes to obtain polyaniline.They can be synthesized chemically as well as electrochemically. Certain new methods have been developed to synthesize polyaniline to have better mechanical properties. Polyaniline exists in a variety of forms that differ in chemical and physical properties. The most common is green protonated emeraldine which has conductivity on a semiconductor level. When aniline hydrochloride was oxidized with ammonium peroxydisulate in aqueous medium at ambient temperature, the yield was quite high of all the cases. Other than this, polyaniline can be used in various applications such as textile fibers, photovoltaic devices etc.One of the biggest achievement with the polyaniline is that, even they are not at back in the race of nano's. Recent work deals with synthesis of nanofibers.

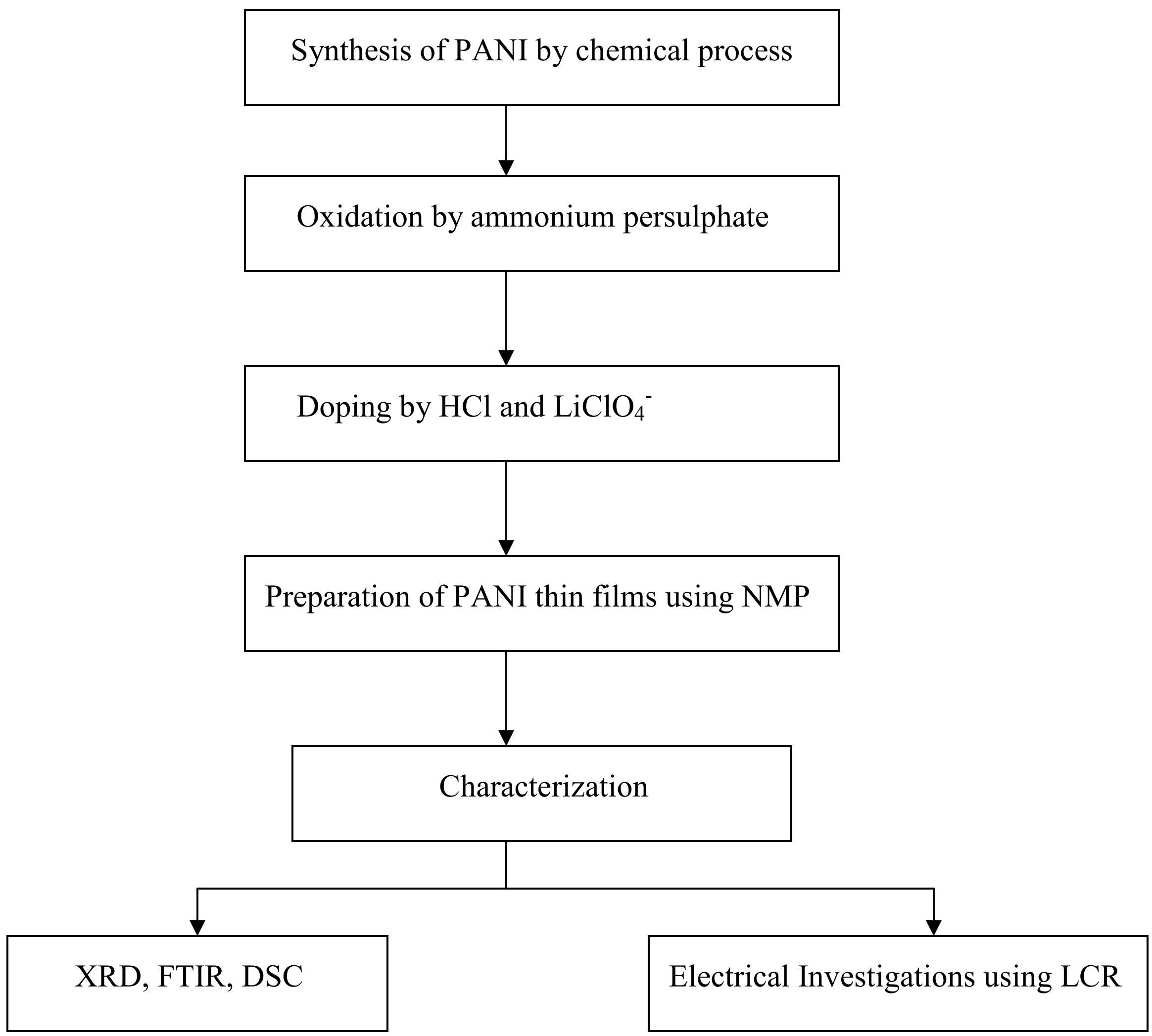
2.14 AIM OF THE PRESENT WORK

The aim of the present work is to understand and prepare conducting polymer materials having improved conductivity so that they can be used in electrical and electronic devices.

We have focused on the novel PANI and characterized it for structural and electrical properties to validate the theoretical results.

Very sophisticated experimental tools have been used for characterization of these materials. This can be shown in the form of flow chart.

Flow Chart for synthesis of characterization of PANI



CHAPTER III

EXPERIMENTAL AND RESULTS & DISCUSSION

3.1 INTRODUCTION

Present investigation deals with the synthesis of conducting polymers, their characterization, activity towards oxidation and reduction of organic molecules, their conductivity and also the identification of products. The conducting polymer chosen was polyaniline.Its synthesis, purification and modification was done by chemical method.

- **Why Polyaniline**

  - Polyaniline is chosen because of its *better electrical, electrochemical, physical, optical properties and good stability* than other conducting polymers.

  - Its ease of preparation and low cost allows one to get in to the field of polyaniline.

  - Polyaniline can be classified into three kinds (luecoemeraldene base, emeralidine base and pernigraniline base) by its oxidation state.

  - This investigation can contribute to the developing of polyaniline with higher conductivity, yield and processability.

3.2. CHEMICALS USED

The chemicals used in the present study along with the sources are given in *Table 3.1*. The chemicals as obtained were used for synthesis purpose.

3.3. SYNTHESIS AND PURIFICATION OF CONDUCTING POLYMER

Chemical Synthesis of Conducting Polymers

Synthesis of conducting polymer involves the oxidation of the monomer viz. aniline with oxidizing agents such as APS in acidic medium. Solvents used for the polymerization reaction is distilled water or NMP-water (1:1) mixture. Detailed procedure for the synthesis is given below.

Table 3.1 Table of chemicals used with their formulae and sources

CHEMICALS	ACRONYM	Source
Aniline	Ani	s.d. fine- Chem. Ltd
Ammonium persulphate	$(NH_4)_2S_2O_8$	s.d. fine- Chem. Ltd
Lithium perchlorate	$LiClO_4$	LOBA Chemie
Hydrochloric Acid	HCl	s.d. fine- Chem. Ltd
N- Methyl Pyrrolidine	NMP	s.d. fine- Chem. Ltd

Synthesis of Polyaniline.

Synthesis of Polyaniline involved various steps:

Preparation of 1 molar HCl solution, 0.2 molar aniline solution and 0.2 molar ammonium persulfate solution was done. 0.2 molar aniline solution was dissolved in 100 ml of 1 molar HCl solution. Both the solutions were stirred on a magnetic stirrer for 1 hour at 0-2^0C. After complete mixing of both the solutions, ammonium persulphate which acted as an oxidant was dissolved in 100 ml of HCl solution. The solutions were mixed and then kept on stirring for about 4-5 hours. The reaction was then kept for 2 days for complete polymerization. Purification of the samples was done. Doping of the PANI samples was done with HCl and lithium salts. After doping thin films of PANI were prepared between two ITO coated glasses.

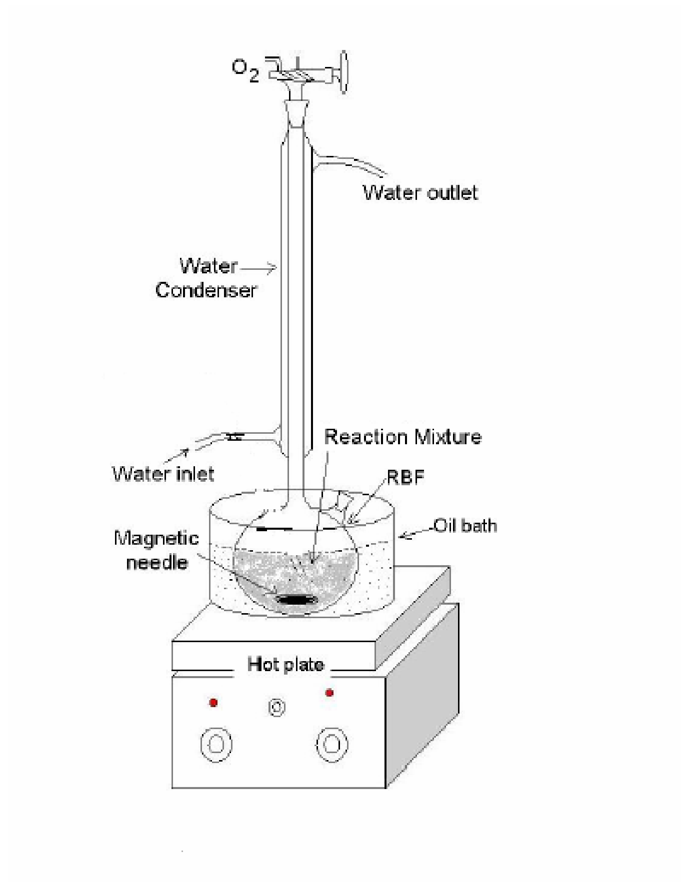


Figure 3.1 Reaction set up for chemical synthesis

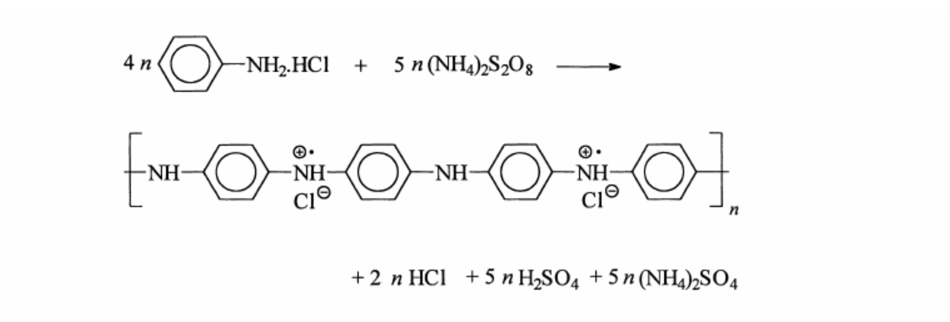


Figure 3.2 Oxidation of aniline hydrochloride with ammonium persulphate yields polyaniline (emeraldine) hydrochloride

Purification of the polymers

After the reaction was over, polyaniline in the form of flakes or powder was obtained which was blue in colour. The precipitated polyaniline was filtered by conventional method. The polymer was washed with distilled water several times till the filtrate obtained was colorless and neutral in nature. The polyaniline samples obtained in powder form were dried first at room temperature for few hours and then finally dried in an oven kept at 60ºC- 90^0C for 4-5 hours. The dried polymer powder was then preserved for sample preparation.

Figure 3.3 Reaction set up used in the lab for synthesis of PANI

Doping of Polyaniline

PANI powder thus obtained was doped with different doping agents viz., HCl, $LiClo_4^-$. Prior to doping these powders were undoped completely by dumping into 1M NH_3 solution for 4 hours. These were then washed thoroughly with distilled water to remove ammonia. The blue colored powder was then dried in ambient followed by vacuum drying. Doping of these powders were done with dopants mentioned above with concentrations 1M, 2M, 5M solutions of which were prepared in the aqueous medium. Doping was done by two ways. In one case the required concentration is immersed in the powder and then the powder was kept for 72 hours for doping .After 72 hours the thin film was prepared which was then kept in vacuum oven for 15 hours. In another case thin film was prepared, doped with the solution of required concentration and was kept for 15 hours in the vacuum oven.

3.4 CHARACTERIZATION

The material thus synthesized was characterized for molecular, structural and thermal studies using:

(i) IR Spectroscopy

(ii) X- Ray Diffraction (XRD)

(iii) Differential Scanning Calorimetory (DSC)

3.4.1 Infrared (IR) Spectroscopy

IR spectroscopy is and important and useful technique for determining functional groups present in a compound. Studies were carried out in order to confirm the presence of lithium perchlorate in the polyaniline/doping concentration of polyaniline with different dopants. The powder samples were dissolved in chloroform to record the spectra. For PANI, it is most useful for obtaining qualitative information regarding the average oxidation states. IR spectroscopy can distinguish between benzenoid rings and quinoid rings in the 1300 to 1600 cm^{-1} region of the spectrum; this region of the spectrum is most useful for distinguishing between oxidation states in the undoped polymer, as the quinoid stretches disappear on doping.

IR spectra of the samples was taken using a spectrometer (Perkin Elmer).The characteristic absorption bands thus obtained are tabulated in *Table 3.2.* These values were also compared with standards [40] and were found in good agreement. The profile of the PANI IR spectra as detected through spectrometer was recorded and given in *Fig. 3.4 to 3.8*. Our results show that no pronounced peaks have been observed in the spectra region 2000 – 3500 cm^{-1}, but there is a shift in the responses after doping the samples with HCl and $LiClO_4^-$ giving rise to a good comparison between the doped and undoped polymer.

Table 3.2 Assignment of the FTIR spectra of PANI -EB

Wave Number(cm^{-1})	Peak Assignment
3024	Combination N-H str and C-H atomic str
1302	C-N str. QB, QBB, and BBQ
1507	Str. Of N=Q=N
807	C-H out of plane bending C-H bending
1174	Mode of N=Q=N

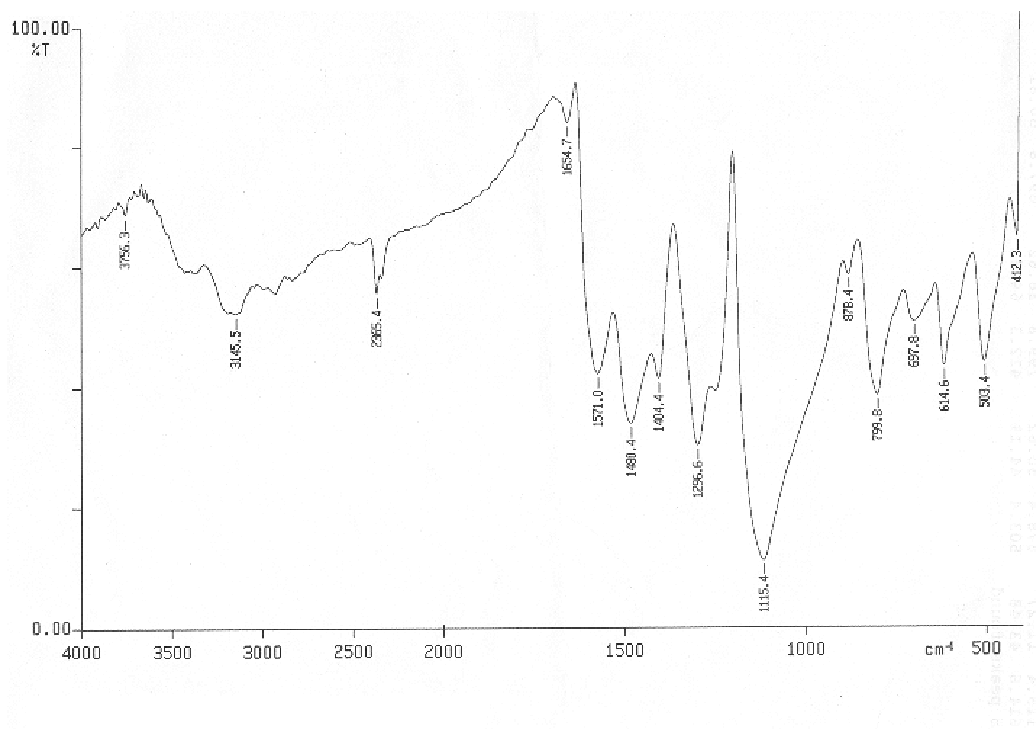


Figure 3.4 FTIR of Undoped polyaniline

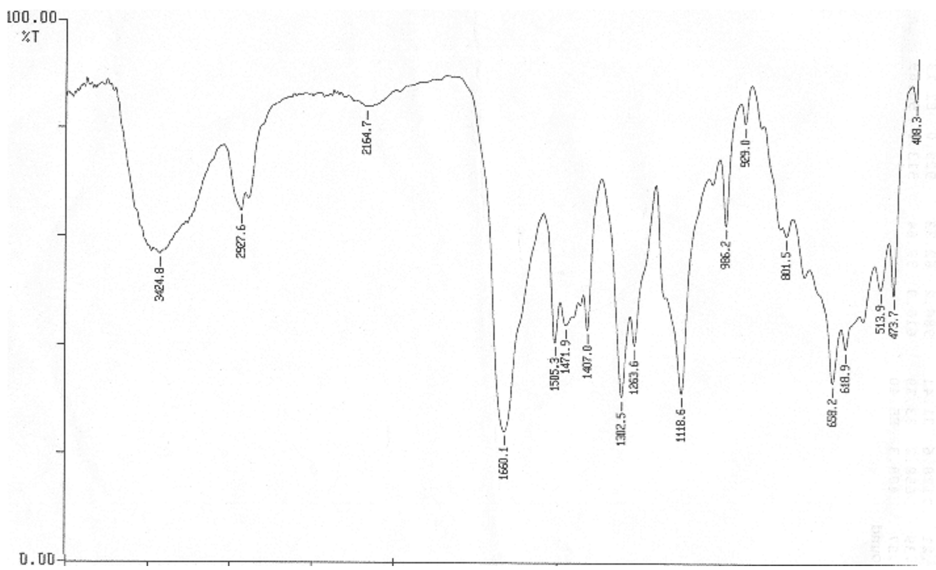


Figure 3.5 FTIR of HCl doped Polyaniline

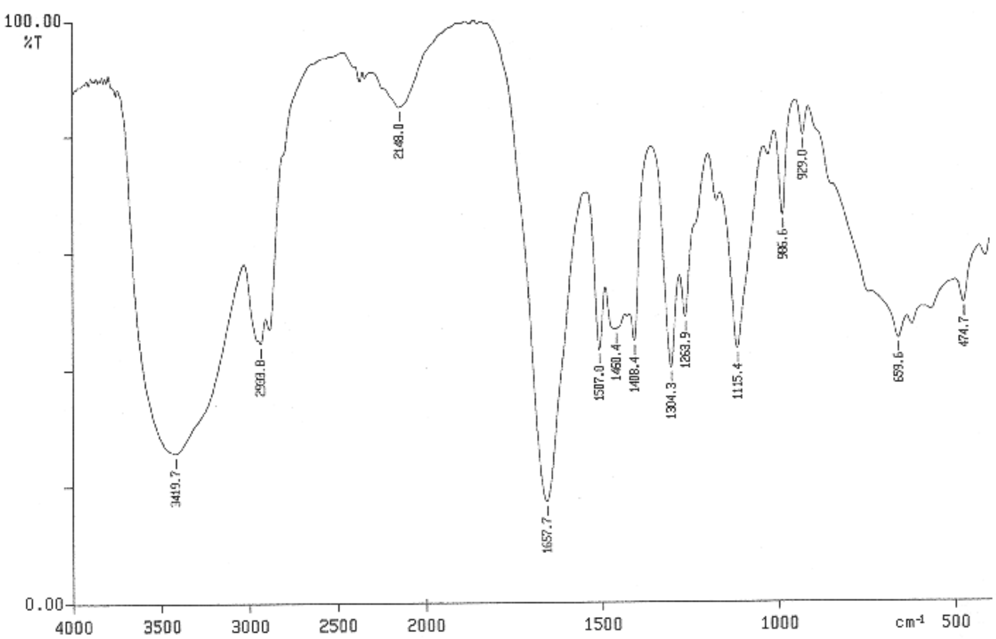


Figure 3.6 FTIR of 1% lithium doped Polyaniline

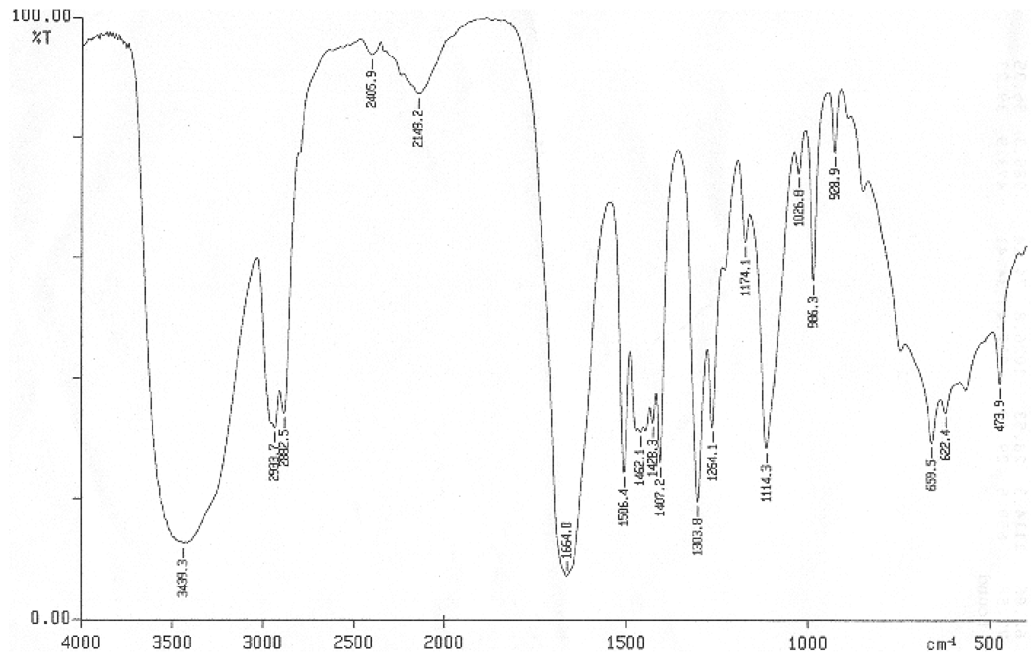


Figure 3.7 FTIR of 2% Lithium doped Polyaniline

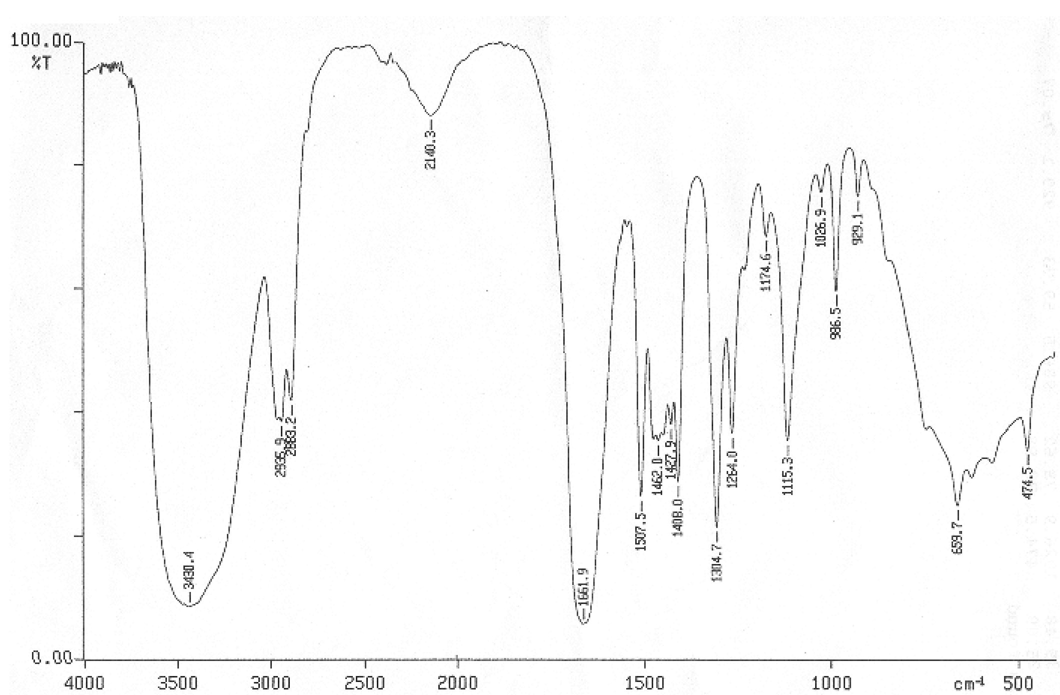


Figure 3.8 FTIR of 5%Lithium doped polyaniline

3.4.2 X-Ray Diffraction

The conducting polymers synthesized by chemical route are generally semicrystalline in nature, whereas the conducting polymer prepared by electrochemical route is usually amorphous in nature. The structure of the various modified polymer was investigated by powder X-ray diffractometer (Rigaku, Japan) using CuKα source and Ni filter. All the scans were recorded in the 2θ region of 20-25 ^{0} at a scan rate of 5 ^{0} /min. From the 2 θ value for the reflections, d values were calculated using Bragg's equation.

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

The results are tabulated in *Table 3.3*. The X-Ray profile as shown in *Fig. 3.9 to 3.13*, do not show sharp peak thus suggests an amorphous nature to polymer samples. It is interesting to observe certain well diffused peaks in doped samples at 20-25 ^{0}.

The d- spacing was calculated from 2θ value and is reported to be the characteristic distance between the ring planes of benzene ring in adjacent chains or the close contact distance between the two adjacent chains.

However some sharp peaks also have been found in some doped samples which show the semi crystalline nature of the sample. No sharp peaks were found in undoped sample which showed that the sample was amorphous.

Table 3.3 XRD data of Polyaniline Samples

Sample	**2θ (^{0})**	**d- space (A^0)**
Pani HCl doped	22.5	3.948
Pani - lithium 2% doped	21.8	4.074
Pani – lithium 5% doped	21.8	4.074

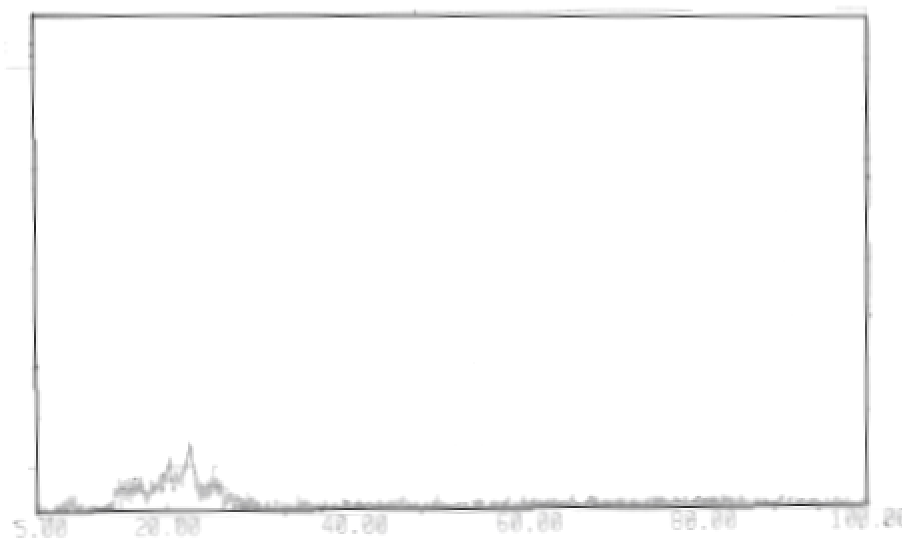


Figure 3.9 XRD of undoped Pani

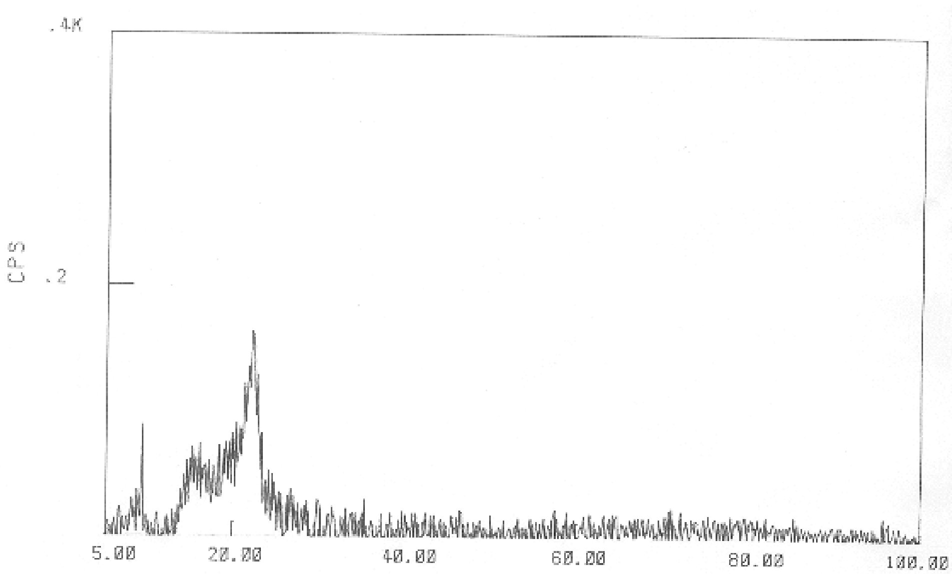


Figure 3.10 XRD of HCl Doped Pani

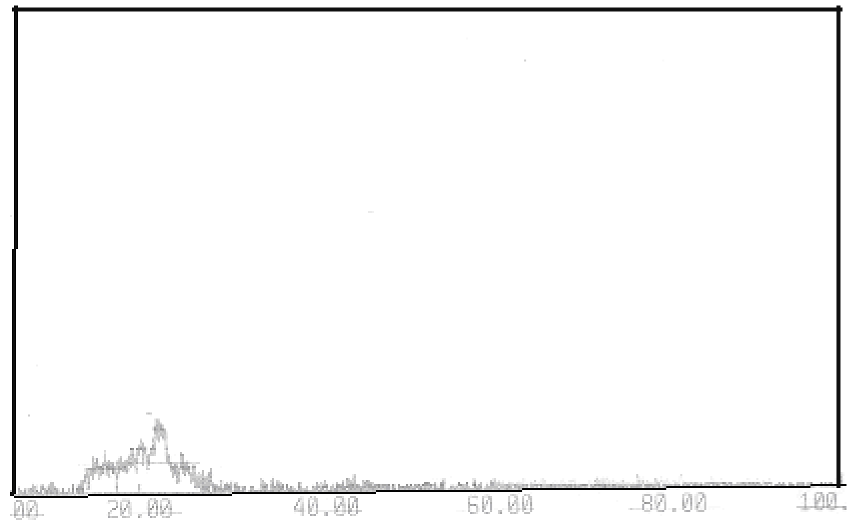


Figure 3.11 XRD of 1% Lithium Doped Pani

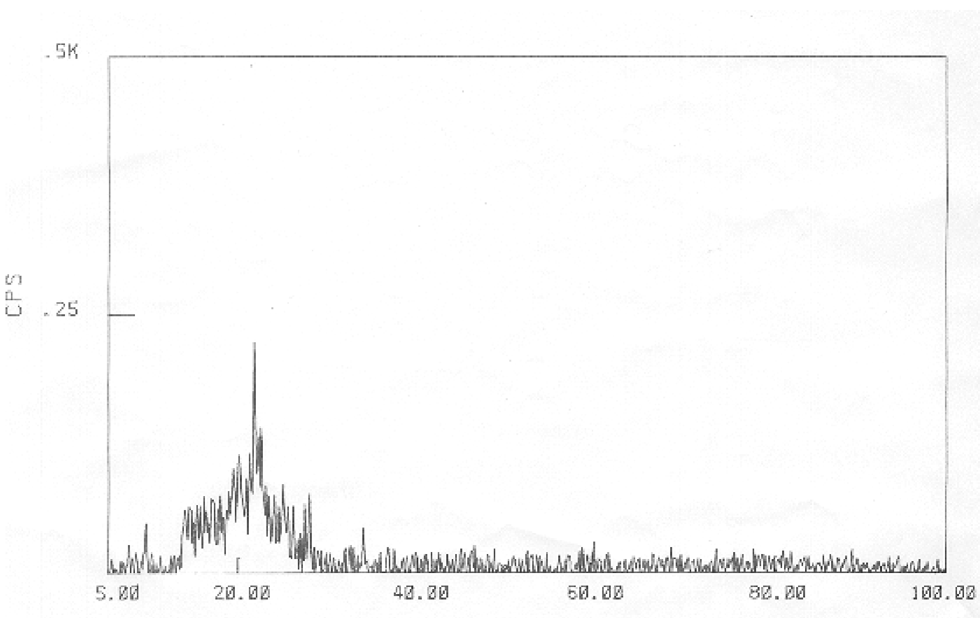


Figure 3.12 XRD of 2% Lithium doped Polyaniline

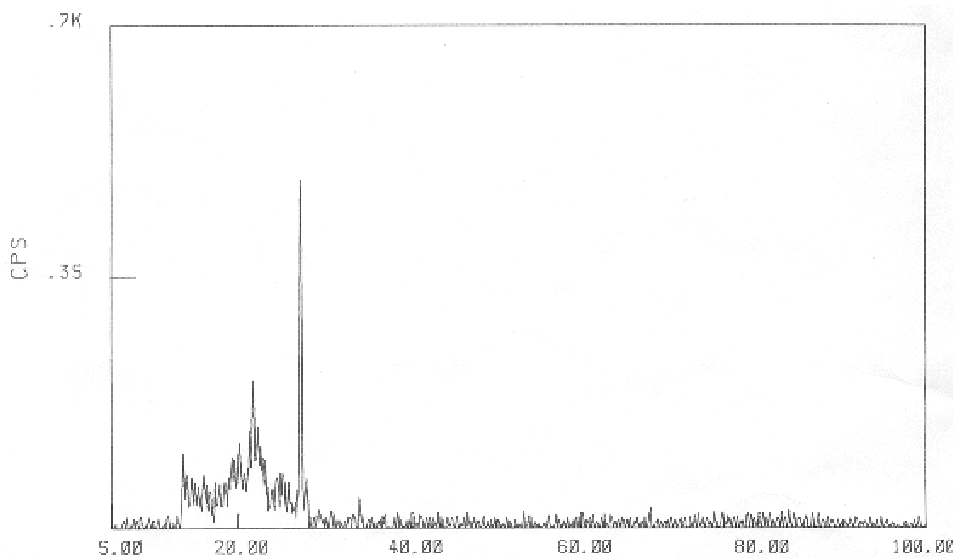


Figure 3.13 XRD of 5% lithium doped Polyaniline

3.4.3 Differential Scanning Calorimetory (DSC)

Thermal studies in PANI samples were carried out with Differential Scanning Calorimetory (DSC) (LINESIS model L63) of PANI samples. Among the conducting polymers, PANI is claimed to have one of the highest environmental stability. The study of the thermal properties was carried out to examine the thermal stability of these materials as well.

DSC of all the polymer samples was done in the temperature range between 30 – 200 ^{0}C. We reported that emeraldine base shows a high stability. The protonated polyaniline is significantly less stable than emeraldine base form. PANI shows a slow decrease in electrical conductivity when treated at temperatures below 200 ^{0}C, the electrical conductivity decreased very rapidly at temperature above 200 ^{0}C.

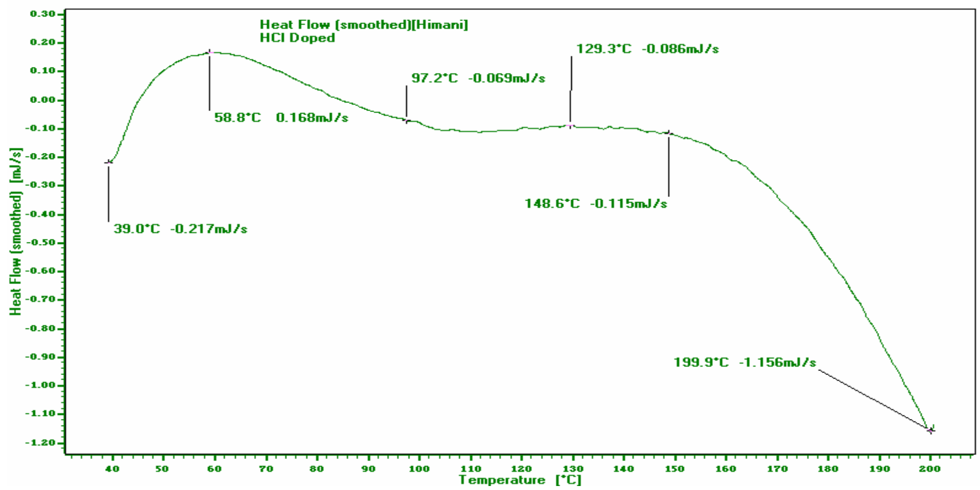


Figure 3.14 DSC of Undoped Sample

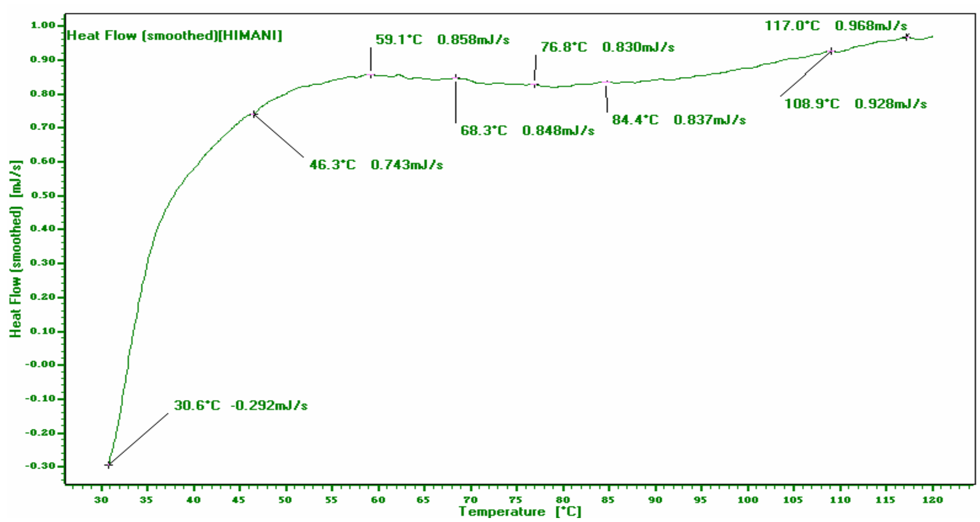


Figure 3.15 DSC of HCl doped Sample

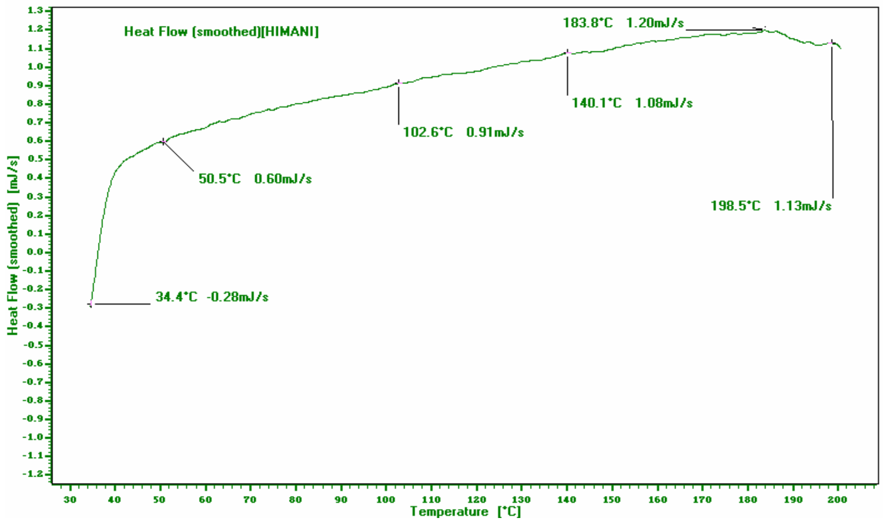


Figure 3.16 DSC of 1% Lithium doped Sample

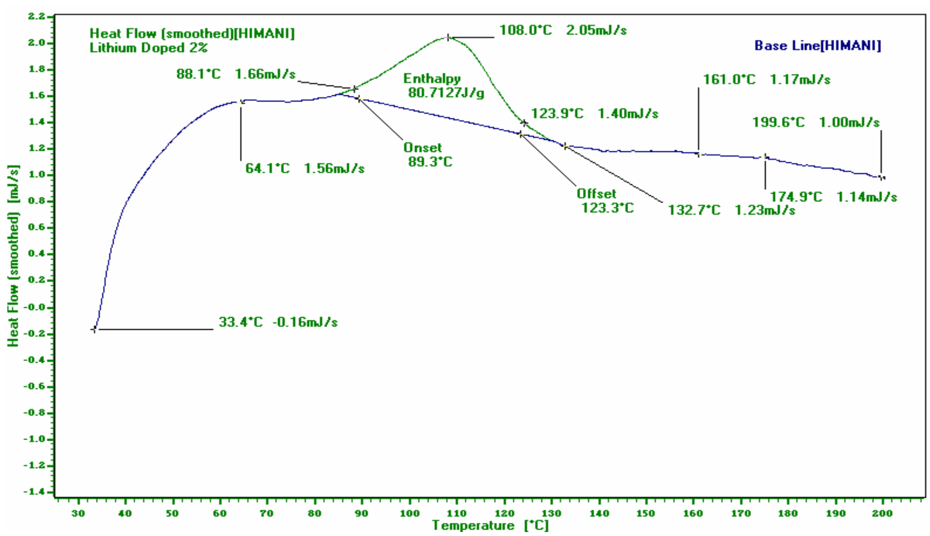


Figure 3.17 DSC of 2% Lithium doped Sample

DSC of PANI –EB powder samples does not exhibit any pronounced specific thermal transitions below 200 ^{0}C. This observation also seems to indicate that PANI is thermally stable up to 200 ^{0}C, with little, if any, weight loss other than water.

3.4.4 Electrical Investigations

It is one of the most important characteristic of a conducting polymer especially to explore their use in electrical devices. We have attempted to measure resistivity, conductivity, capacitance and dielectric constant of PANI under different conditions.

Resistivity and Conductivity measurements

The conductivity measurements were carried out by a two-probe technique recorded by a multimeter (Keithley model 2001). The thin films (~ 7μm) of the samples were prepared and sandwiched between the two ITO coated glass plates. The conductivity of the ITO coated glasses was measured by using the multimeter (DM - 453). The connections for measuring electrical parameters were made with ITO substrates using indium solder. The cell with its connections is shown in *Fig3.18*. The methodology followed for cell assembly is given in flow chart.

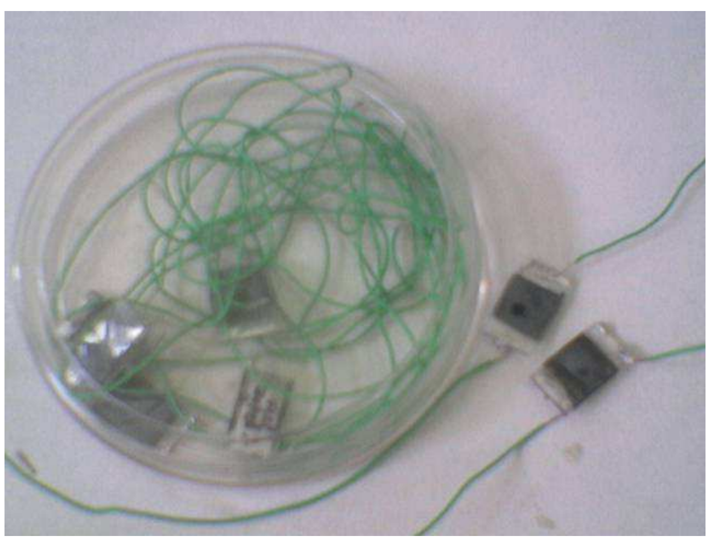
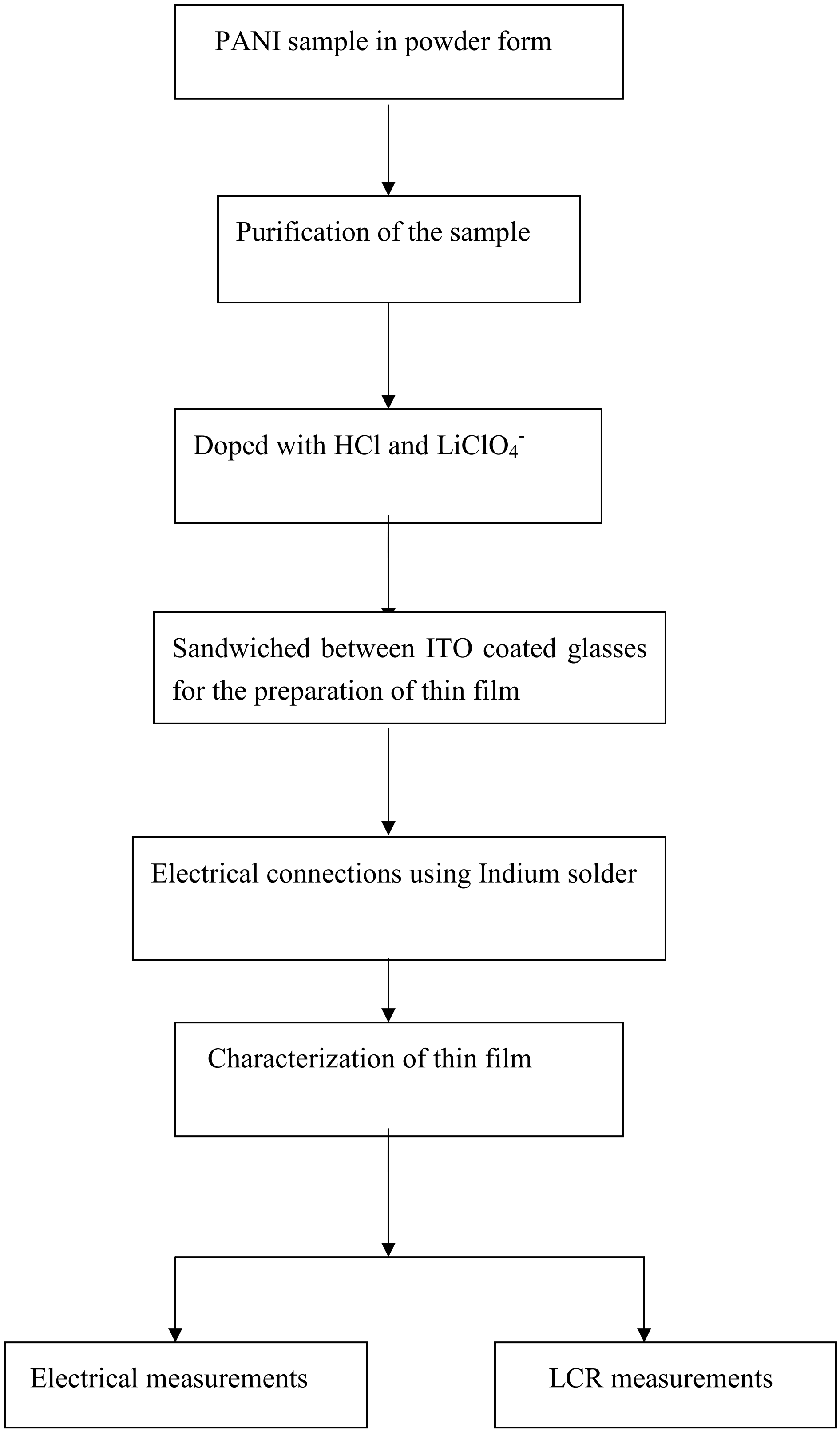


Figure 3.18 Cells with thin film sandwiched between ITO coated glasses

Flow Chart for preparation of thin PANI film



The specific resistivity has been evaluated as,

$$\rho = RA/L \quad (1)$$

or conductivity, $\sigma = 1 / \rho$ (2)

Where ρ is its resistivity, A is the cross sectional area of the sample and L is its thickness. The effect of dopant ion on the overall conductivity behaviour of PANI was observed. The room temperature conductivity for undoped sample was found to be 6.4×10^{-4} S/cm for undoped samples while it increased to a value of 0.10S/cm for HCl doped samples and 5.77 S/cm for 5% lithium doped samples. The temperature dependence of conductivity for these films was also measured in the temperature range of 30 to 70^0C.

The increase in conductivity with temperature was obvious for conducting polymer, which might be due to thermal activation process. The electrical conductivity in the doped PANI powders might be associated with excitation of the mobile p-electrons from the valence band containing highest occupied molecular orbital (HOMO) to the conduction band containing lowest unoccupied molecular orbital (LUMO) and the charge hopping between the polymer chains. The conduction mechanism in PANI as observed in our case can be explained on the concept of polaron and bipolaron formation. Low level of oxidation of the polymer gives polaron and higher level of oxidation gives bipolaron. Both polarons and bipolarons are mobile and could move along the polymer chain by the rearrangement of double and single bonds in the conjugated system.

Conduction by polarons and bipolarons was supposed to be the dominant factors which determine the mechanism of charge transport in polymer with non-degenerate ground states. The magnitude of the conductivity was determined by the number of charge carriers available for conduction and the rate at which they move i.e. mobility. In conducting polymers which could be considered as semiconductor the charge carrier concentration increased with increasing temperature. Since the charge carrier concentration was much more temperature dependent than the mobility, therefore it was the dominant factor and conductivity increased with increase in temperature. Hence, it may be summarized that the conduction is associated with thermal excitation of charge carriers from the impurity levels. The room temperature electrical conductivity and resistivity of PANI samples is shown in the *Table 3.4.*

Table 3.4 Calculated Resistivity and Conductivity of the samples

Sample	Resistivity (Ω/cm)	**Room Temperature Conductivity(S/cm)**
Pani Undoped	1560	6.4×10^{-4}
HCl doped	9.41	0 .10
1% lithium doped	0 .31	3.24
2% lithium doped	0 .29	3.46
5% lithium doped	0.17	5.77

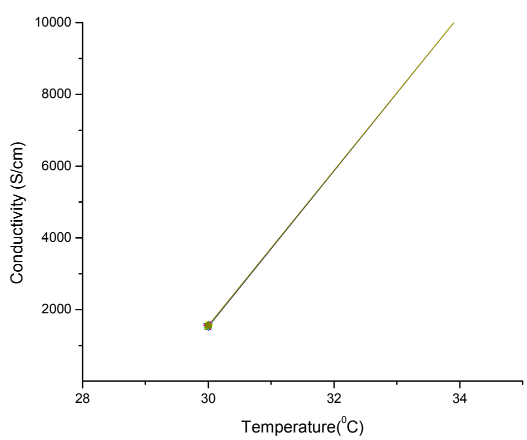


Figure 3.19 Behaviour of conductivity of PANI sample with increase in temperature

Dielectric Constant as a function of frequency and temperature:

The dielectric constant of PANI thin films was measured from the capacitance data using the LCR meter (Fluke model PM 6306), shown in figure 3.20 in the frequency range of 50 Hz – 1 MHz.

The dielectric constant was computed using

$$\epsilon_r = C\, d / \epsilon_0 A \qquad (3)$$

Where ϵ_r is the dielectric constant, C is the capacitance, d is the thickness of the film, A is the cross sectional area and ϵ_0 is the permittivity of free space.

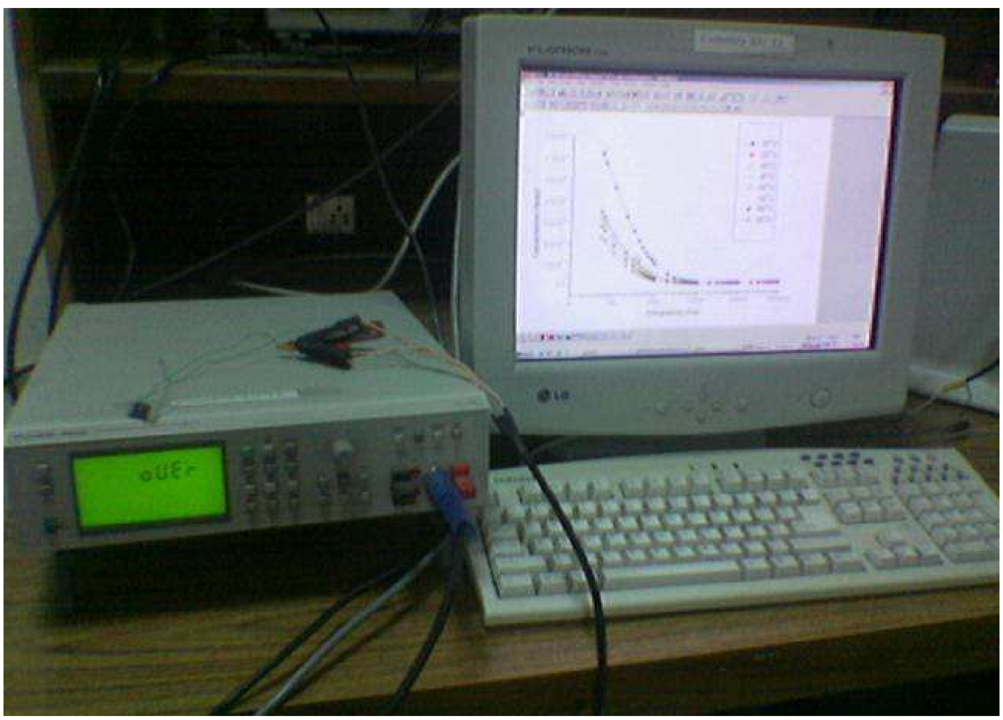


Figure 3.20 LCR meter set up used for electrical measurement

Table 3.5 Dielectric Constant of different PANI samples at 1 MHz

Sample	Dielectric Constant
Pani Undoped	82.5
HCl doped	1.7
1% lithium doped	3.8
2% lithium doped	2.5
5% lithium doped	1.6

The value of dielectric constant was obtained in the frequency range from 50 Hz to 1 MHz and temperature varying from 30 – 70 ^{0}C. The temperature was varied using temperature controller as shown in *Fig. 3.21*. The variation of dielectric constant as a function of frequency at different temperatures is shown in *Fig 3.22 to 3.25.* It is found that in the whole frequency and temperature range scanned, the dielectric constant lies between 3.8 and 1.62 which is very low. For the undoped PANI the value for dielectric constant is very high. The observed frequency dependence of the dielectric constant is due to the interfacial polarization, which is usually observed in sandwich type configurations.

Figure 3.21 Temperature controller

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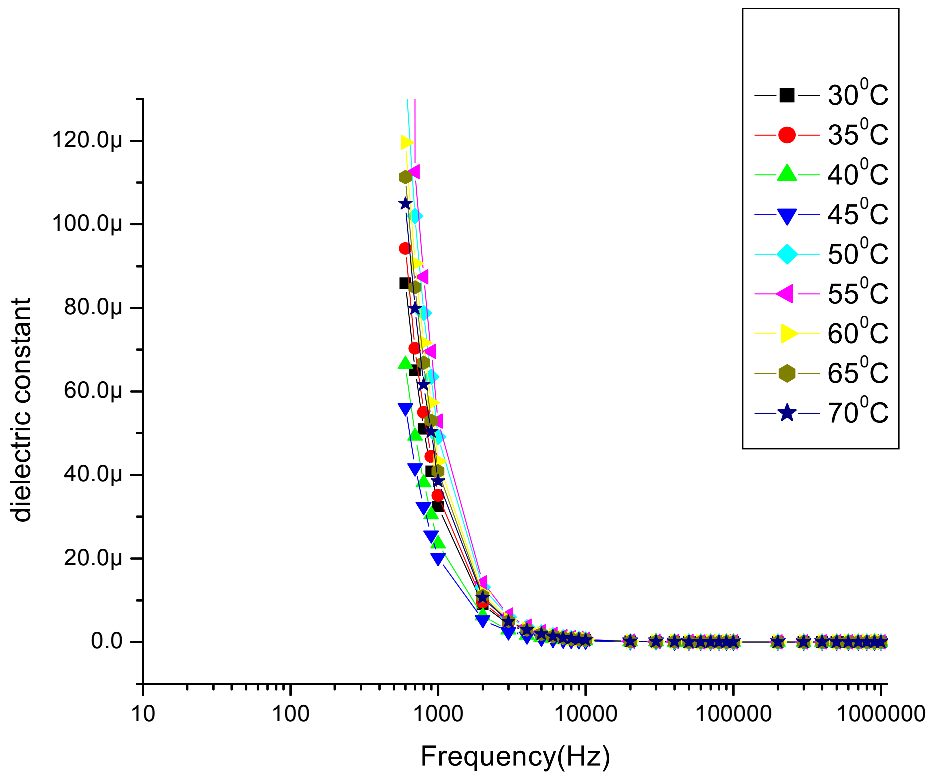

Figure 3.22 Dielectric Constant of Undoped PANI thin film as a function of frequency at different temperatures

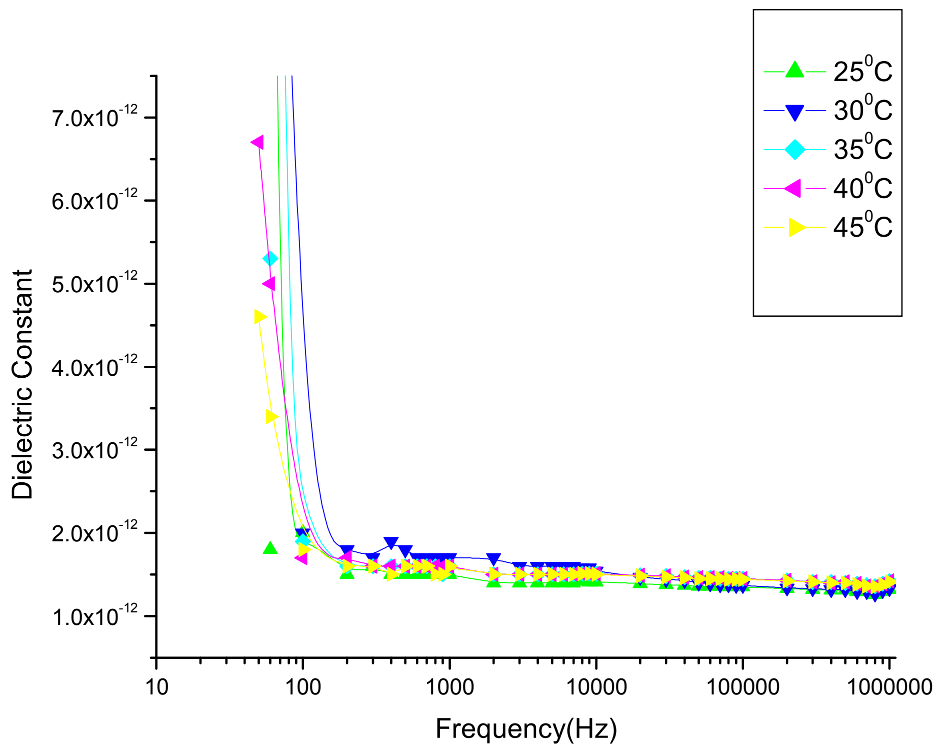

Figure 3.23 Dielectric Constant of HCl doped PANI thin film as a function frequency at different temperatures

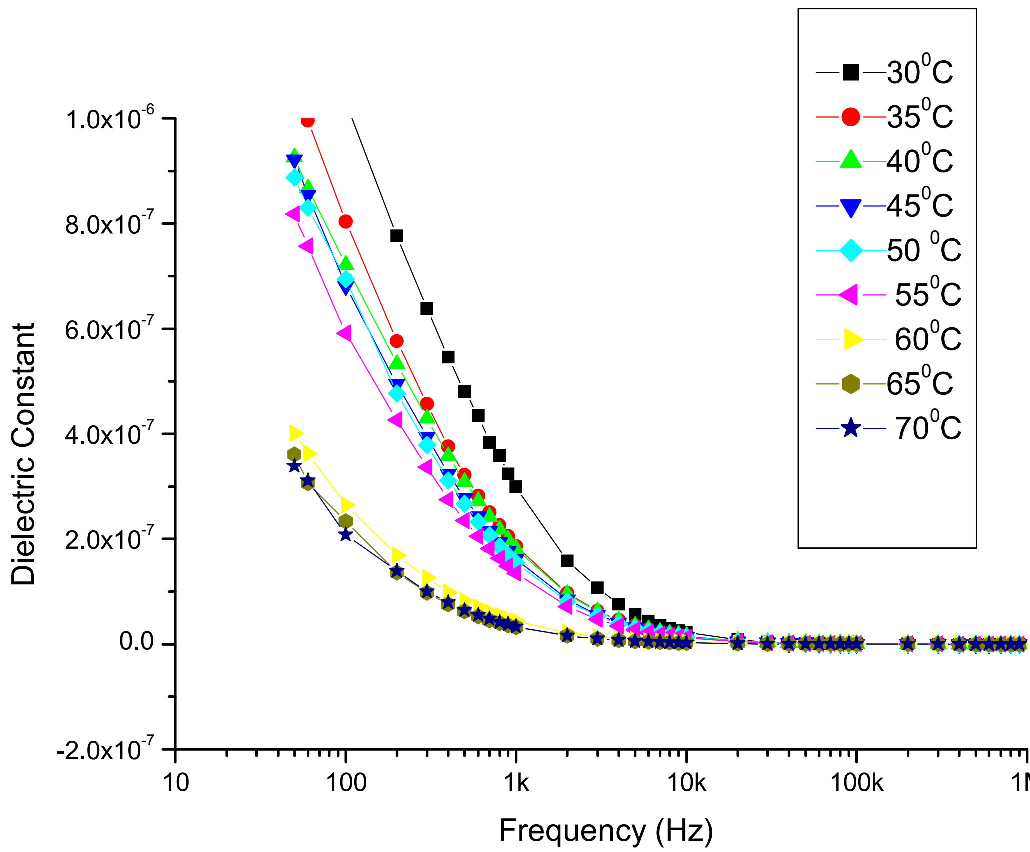

Figure 3.24 Dielectric Constant of 1% Lithium doped PANI thin film as a function of frequency at different temperatures

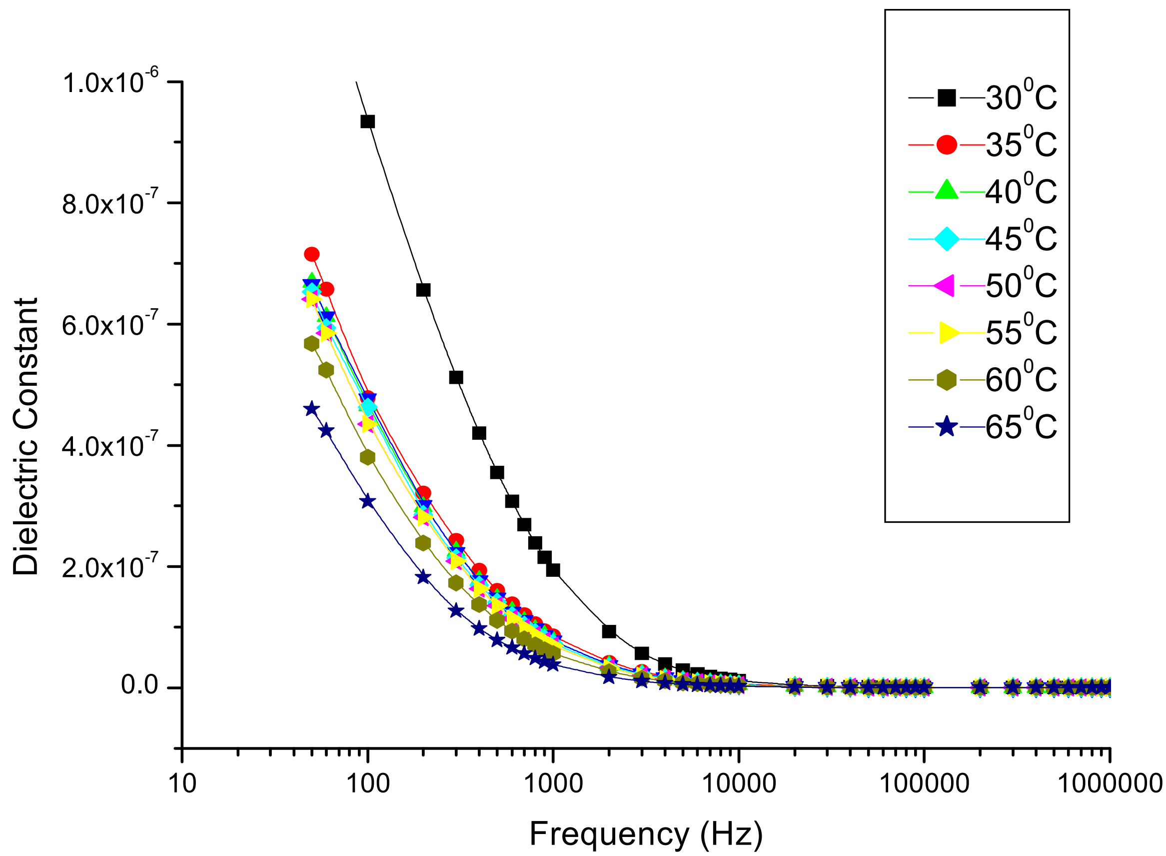

Figure 3.25 Dielectric Constant of 5% Lithium doped PANI thin film as function of frequency at different temperatures

CHAPTER IV

CONCLUSIONS AND THE FUTURE SCOPE

The present work was an attempt to understand the synthesis and characterization of PANI based conducting polymer. Polyaniline after synthesis did not exhibit a very good conductivity of its own. Therefore, we used dopants as materials modification agents to gauge the enhancement of its conductivity. HCl and $LiClO_4^-$ were added as dopants. We observed that the dopants do contribute to increase in conductivity especially with the $LiClO_4^-$ addition. The conductivity with $LiClO_4^-$ has shown many fold increase than HCl and other Li dopants

The work also exposed us to get familiarized with several instruments used in the present study.

Future Scope

Among conducting polymers which have emerged as a new class of materials of current research interest world-wide, polyaniline occupies a prominent place owing to its possible wide spread applications as compared with other polymers. Polyaniline is an attractive material because of its environmental stability, controllable electrical conductivity, and easy processability. PANI exists in variety of forms that differ in chemical and physical properties. The present work can be enhanced by various ways:

- The catalytic activity of PANI towards oxidation and reduction process can be studied.
- Metal oxalate complexes which are inorganic in nature can be used as dopants and their effect on PANI can be studied.
- PANI can be doped with various lithium salts other than that of $LiClO_4^-$.These salts can be $LiPF_6$, $LiAsF_4$, and $LiBF_4$. By doping with these salts PANI can become applicable for lithium batteries.
- Aging of PANI can be done at various temperatures and their FTIR's can be compared.
- Different characterizations like XPS, ESR, UV-Vis spectroscopy and GPC can be done.

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