A Thesis on

SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYMER POLYANILINE

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Dr. Dwijendra P.Singh

BY

GURPREET KAUR BHULLAR

(Roll No: 30704004)

SCHOOL OF PHYSICS AND MATERIAL SCIENCE

THAPAR UNIVERSITY

PATIALA-147004

INDIA

CERTIFICATE

This is to certify that Ms. Gurpreet kaur bhullar, Roll No. 30704004 has worked on this thesis report as a partial fulfillment for award of the degree of MASTERS OF SCIENCE in physics. I certify that the matter embodied in this report is of candidate's own record and not submitted to any other university in any part or full form for the award of such a degree.

(Dr. Dwijendra P.Singh)
Supervisor
SPMS, Thapar University
Patiala

Countersigned by:

Dr. O.P. Pandey
(Prof. & Head)
School of Physics and Materials Science
University, Patiala.

Dr. R.K. Sharma
Dean of academic Affairs
Thapar University Thapar
Patiala.

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Gurpreet Kaur Bhullar

Roll no. 30704004

Date: 11-07-2009

ABSTRACT

The polyaniline (insulating and conducting) has been synthesized by chemical polymerization technique. The synthesized samples of polyaniline have been characterized by using Fourier Transform Infrared, Ultraviolet-visible spectroscopy, Thermogravimetric analysis and Cyclic voltammetry techniques. The vibration band at 1169.25 cm^{-1} observed in undoped polyaniline is due to presence C-N double bond and indicative of protonation. After doping this vibration band has been shifted to 1129.28 cm^{-1}. Two electronic transitions at 325.24 nm (3.9 eV) and 638 nm (2 eV) have been found in Ultraviolet-Visible spectrum, which correspond to diphenyl paraphenylene diamine and diphenyl paraphenylene diimine structure respectively. Large weight loss in Thermogravimetric analysis and results at 400˚C suggests that polymer degrades after 400˚C. The cyclic voltammetric of polyaniline exhibit two redox peaks at 0.18 and 0.75 volts which are characteristics to the polyaniline. Moreover, the increase in intensity of voltammetric current with the increasing number of scanning cycles might be attributed polymer forming on the electrode surface.

CONTENTS

LIST OF FIGURES

CHAPTER-1

CHAPTER-2

CHAPTER-3

LIST OF TABLES

CHAPTER- 1

INTRODUCTION

Chapter 1

Introduction

1.1 Introduction

Conducting polymers has been observed as frontier area of research and prospective materials for technological applications since last decade [1-5]. The importance of conducting polymer was celebrated in the form of Nobel Prize in chemistry to MacDiarmid, Heeger and Shirakawa [6, 7, 8]. The polymerization mechanism [9], processability [10], and transport mechanism [11] are the point of academic and scientific attractions. Technological applications include biosensors [12], gas sensors [13], electrochromic [14, 26], electromagnetic shielding [15], light emitting devices [16] and photovoltaic applications [17]. The class of conducting polymers is consisting of various polymers such as polythiophene [18], polypyrole [19], polyparaphenylene [20], [21] etc. The polyaniline is extensively studied polymer because of its high electrical conductivity, oxidative properties, environmental stability and ease of preparation etc. [22, 23].One of the surprising quotation given by Prof. A.G. MacDiarmid that ”there are as many different types of PANI as there are people who synthesise it.” [24]. Therefore the way of synthesis decides the conductivity, band gap, chemical structure, polymerization mechanism and ease of attachment and detachment of different functional groups.

1.2 Conducting Polymers and their structures

Conducting polymers are increasing replacing natural and inorganic materials application requiring excellent mechanical properties and lightweight. The mechanical properties of polymers can be tailored to provide strong materials with high toughness and low resistance. Polymers are insulators because the atoms in the polymer chain are covalently bonded. In the

covalent bonded molecules of the saturated carbon compounds, there is no scope of delocalization of the valence electrons and consequently, neither charge carriers nor path for their movements are available. Since in the conjugated molecule of carbon compound, delocalization of electron may occur through the interaction of - bonded electrons, such molecule may be conducting.

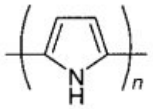
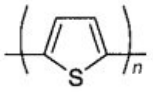
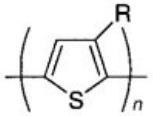
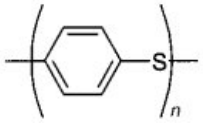
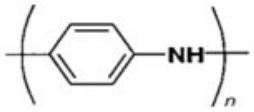
Polymer	Structure	Doping Materials	Approximate Conductivity (S/cm)
Polyacetylene	$(CH)_n$	I_2, Br_2, Li, Na, AsF_5	10,000
Polypyrrole		BF_4^-, ClO_4^-, tosylate[b]	500–7,500
Polythiophene		BF_4^-, ClO_4^-, tosylate[b], $FeCl_4$	1,000
Poly(3-alkylthiophene)		BF_4^-, ClO_4^-, $FeCl_4$	1,000–10,000
Polyphenylene sulfide		AsF_5	500
Polyaniline		HCl	200

Fig. 1.1: The chemical structure and conductivities of some polymers.

The conductivity of polymers can be made to vary over a very wide range, starting from insulating to semiconductor and towards metallic, by varying the concentration of the do-pant.

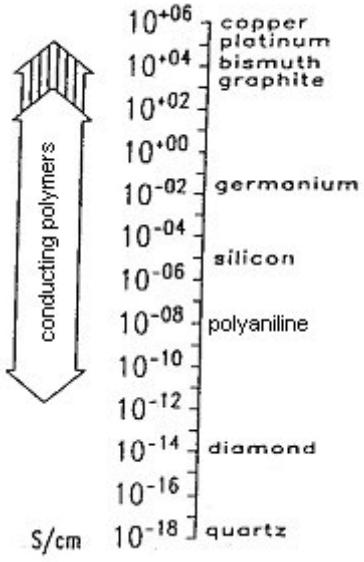


Figure1.2: Conductivity Chart of Various Conducting Polymers

1.2.1 Conduction Mechanism in Conducting Polymers

The conducting polymers are a class of organic semiconductors having a negative temperature coefficient of conductivity and hence the theory of the conventional semiconductors was used to discuss the conduction mechanism. A key requirement for a polymer to become intrinsically conducting is that there should be overlap of molecular orbitals to allow the formation of delocalized molecular wave functions. Besides this molecular orbitals must be partially filled, so that there is free movement of electrons throughout the lattice. [25] In the band theory, the atomic orbitals of each atom overlap with the same orbitals of their neighborhood atoms in all directions to produce molecular orbitals similar to those in small molecules. When these orbitals are spaced together in a given range of energies, they form what looks like continuous energy bands. The electrical properties of conventional inorganic semiconducting materials depend on the band structure. When the bands are filled or empty, no conduction occurs. If the band gap is narrow, at room temperature, thermal excitation of electrons from the valence band to the conduction band gives rise to conductivity. This is what happens in classical semiconductors. When the band gap is too wide, thermal excitation at room temperature is insufficient to excite electrons across the gap and the solid is an insulator. The high conductivity of metals is due to partially occupied bands, a partially filled conduction band, a partially empty valence band, or a

zero band gap. In order to understand the behavior of conducting polymers, it is essential to know about the type of charge carriers and band structure. Molecularly doped polymers represent a genuine molecular system where in; the charge transport is carried out by a hopping mechanism between the dopant molecules which act like hopping site. [11]This mechanism can be visualized using two centers model [27] where the carriers hope from one center to other. Different factors such as temperature (T), separation between centers (R), distribution of hopping energy and electric field (f) would govern this type of charge transport by increasing the hopping probability. By considering these factors, corresponding conduction parameters can be obtained. The subsequent subsections will explain about charge carriers and band gap of conducting polymers.

1.2.1.1 Charge Carriers and Band Gap in Conducting Polymers

Conductive polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Their electrical conductivity cannot be explained well by simple band theory. The electronic phenomena in these electronic polymers cannot be explained by using the theory of conventional inorganic semiconductors. The mechanism of conduction and behavior of charge carriers in the conducting polymers have been explained using the concept of polarons and bipolarons. From the point of view on the binding energy, borrowed from the inorganic semiconductors physics; it is assumed that a band edge exists, and that beyond this energy the holes/electrons are "free". At this energy range the free carriers move in an un-correlated manner, meaning that the knowledge of the position of either an electron or hole does not yield any information about the location of the other. Any energy state that lies below the band edge is known as excitonic state (or polaronic state if it is charged). In these states the motion of the electrons is correlated, and the electrons (holes) are bound. The energy difference between the band edge and the excited state is the binding energy; and the fast excitation before the surrounding configuration could react, described in the former paragraph, is to an un-bound state. The different excitations in the conjugated polymers differ in the charge they carry: A positive/negative Polaron is an excitation that carries a single positive/ negative electron charge. A Bipolaron is a double charged excitation. An exciton is a neutral excited state, which in simplistic way, can be described as carrying a dipole.

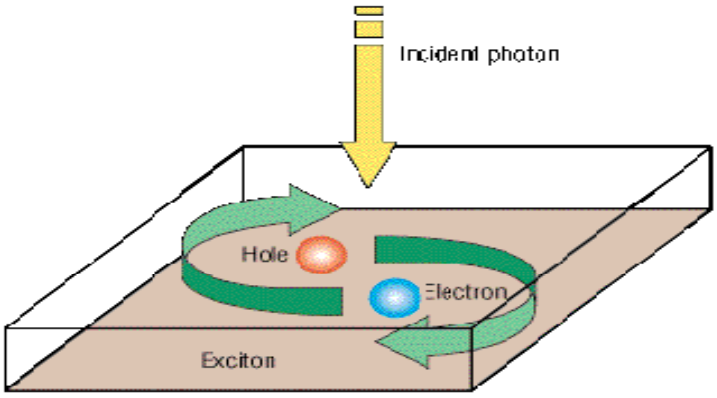


Figure1.3: Schematic view of how an exciton is formed.

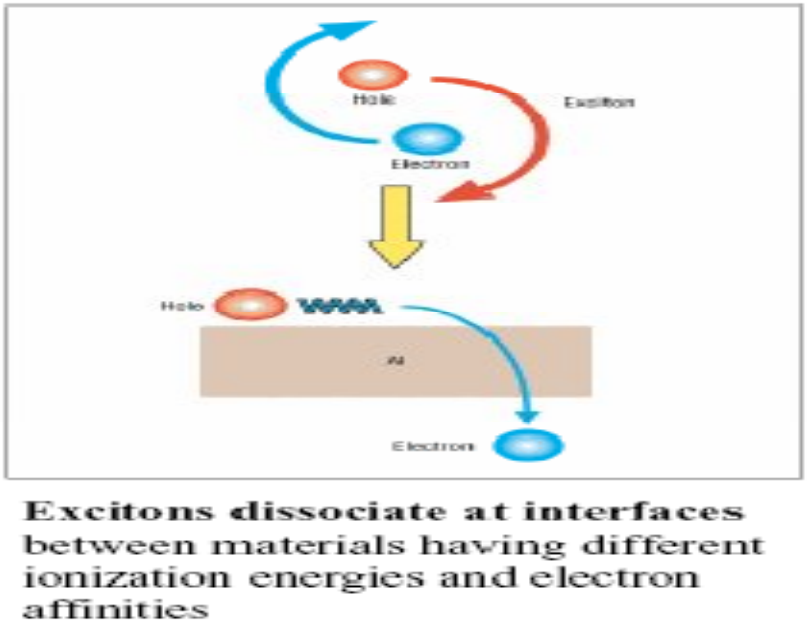


Fig1.4: Exciton generation and separation mechanism in conducting polymers.

A radical cation that is partially delocalized over some polymer segment is called a polaron. It stabilizes itself by polarizing the medium around it. It is really a radical cation and has a spin of ½. When electron is removed from the top of the valence band of a conjugated polymer, a vacancy (hole or radical cation) is created that does not delocalize completely, as would be expected from classical band theory. Only partial delocalization occurs, extending over several monomeric units and causing them to deform structurally. The energy level associated with this radical cation represents a destabilized bonding orbital and thus has a higher energy than the

energies in valence band. This rise in energy is similar to the rise in energy that takes place after an electron is removed from a filling bonding molecular orbital.

If another electron now is removed from the already oxidized polymer containing the polaron, two things can happen: This electron could come from either a different segment of the polymer chain, thus creating another independent polaron, or from the first polaron level (remove the unpaired electron) to create a special dication, which is called a bipolaron. Low doping levels give rise to polarons, whereas higher doping levels produce bipolarons. Compared to polaron, bipolaron is doubly charged but spin less. The bipolaron also has structural deformation associated with it. The two positive charges of the bipolaron are not independent, but act as a pair.

Both polarons and bipolarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds in the conjugated system that occurs in an electric field. If many bipolarons are formed, say as a result of high doping, their energies can start over lapping at the edges, which creates narrow bipolaron bands in the band gap.

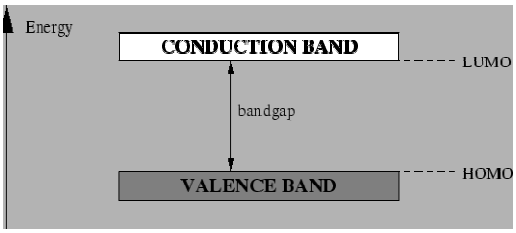


Fig.1.5 Band structure in an electronically conducting polymer

The energy spacing between the highest occupied and the lowest unoccupied bands is called the band gap. The highest occupied band is called the valence band, and the lowest unoccupied band is the conduct ion band. Conducting polymers either have a zero energy band gap or a very low band gap.The optical band gap controls the electronic and the optical properties of conducting polymers. A reduction in the optical band gap increases the conductivity of the polymers. So, attempts have been made to reduce the band gap in conducting polymers by various methods. The band gap of any of the well -suited conducting polymers are greater than 2.0 eV.

1.2.2 Influence of Doping and Dopants on Conductivity

The conductivity of polymers depends on the method of polymer synthesis, isolation and purification techniques, and physical treatment of the polymer. [28-29] Presence of moisture and oxygen in the electrolytic medium affect the conductivity of the doped polymer [30]. Electrical conductivity increases with increasing degree of crystallinity. Generally the degree of crystallinity may be induced in polymers by mechanical stretching or in a better way by simultaneous mechanical stretching and heat treatment. Amount of dopants influences the conductivity to a large extent.

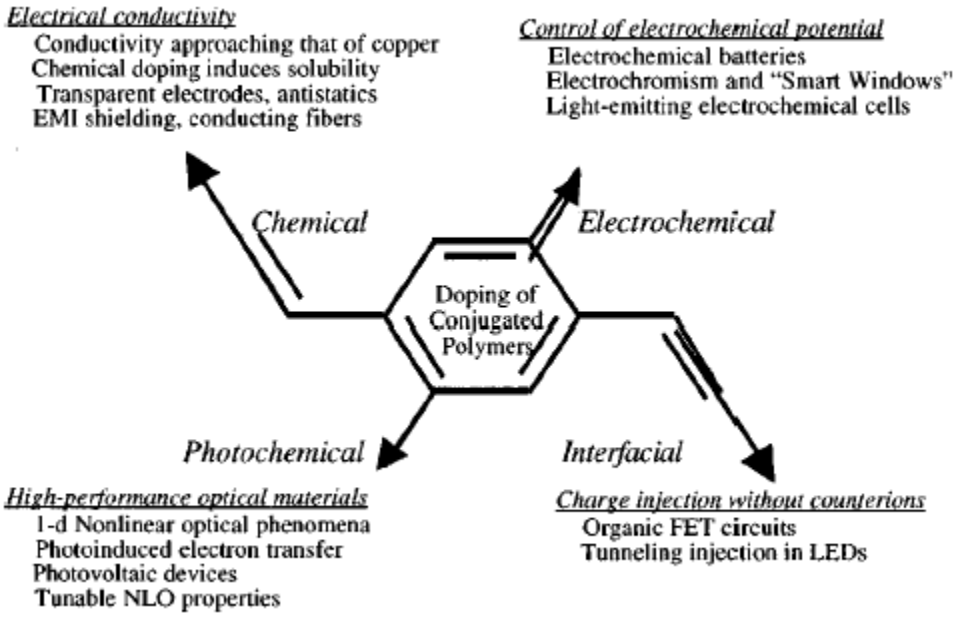


Fig. 1.6: Doping mechanisms and related applications [7].

1.2.2.1 Doping in Conducting Polymers

The process of transforming a polymer to its conductive form via chemical oxidation or reduction is called doping. The extent of enhancement of electric conductivity of a polymer primarily depends on the chemical reactivity of the dopant with the polymer. The same dopant cannot be effective for different polymers. The nature of dopant plays an important role in the stability of conducting polymers. Conductivity of polymers depends directly on the doping level. The doping level increases with exposure time of the polymer to the dopant vapor. Sometimes a sharp rise in conductivity is observed for a very small increment of the dopant level

[31]. This sharp increase may be due to the rapid increase in mobility of the charge carriers, which in turn is due to interchain interaction. The doping is usually quantitative and the carrier concentration is directly proportional to the dopant concentration. On doping, positive or negative charge carriers are developed in the polymers [31-34].

Polymer + Dopant = $(\text{Doped polymer})^{+}$ + Dopant^{-}

Polymer + Dopant = $(\text{Doped polymer})^{-}$ + Dopant^{+}

Doping results in rearrangements of the polymer chains and thereby new ordered structures are formed. The dopant concentration may be as high as 50% [34]. Also incorporation of the dopant molecules in the quasi one-dimensional polymer systems considerably disturbs the chain order leading to the reorganization of the polymer [35]. Thus the ultimate conductivity in polymeric semiconductors depends on many factors, viz., nature and concentration of dopants, homogeneity of doping, carrier mobility, crystallinity and morphology of polymers. Doping agents or dopants are either strong reducing agents or strong oxidizing agents [31, 32].

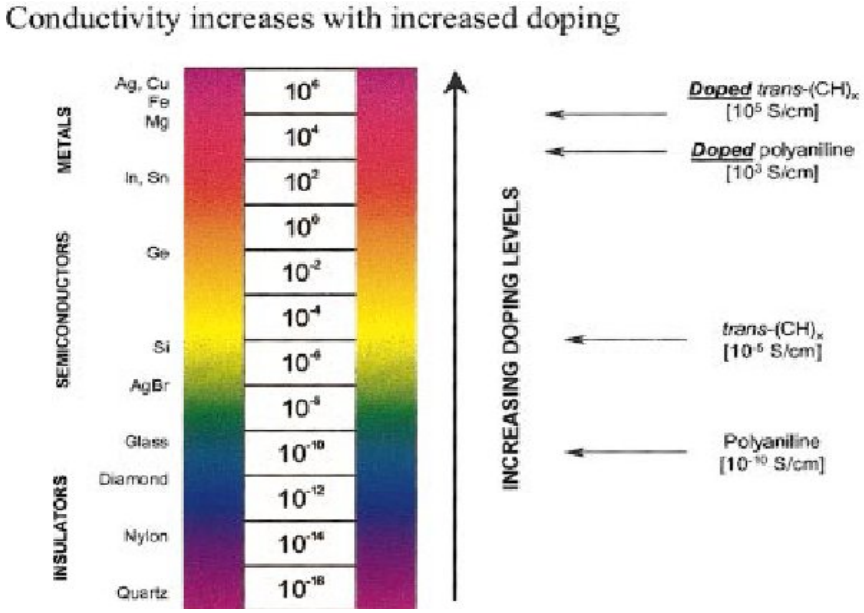


Fig.. 1.7 Conductivity of electronic polymers with doping [6].

1.2.3 Processability of Conducting Polymers

Conducting polymers possess poor processability. Due to the extended conjugation chain structure, these polymers are insoluble and hence are not easily processable.

A number of general techniques have been developed for improving the processability of conducting polymers.

Chain flexibility can be improved by incorporation of flexible centers and flexible linkages in the chain. Blends of rigid conducting polymers with processable polymers are reported to have improved processability. Blending or mixing the conducting polymers with their non-conducting processable counterparts offers not only enhanced processability, but also increases necessary mechanical strength, adhesion and environmental stability [36-37]. The rigidity of the conjugated chain may be reduced and thereby its processability improved by block copolymerization technique.

1.3 Polyaniline

Polyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties. [38-41]. Depending on the method of preparation, polyaniline bases may exist in a fully reduced form (leucoemeraldine), partially reduced form (emeraldine), and fully oxidized form (pernigraniline).

1.3.1 Chemical Structure of Polyaniline

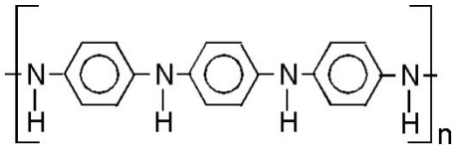


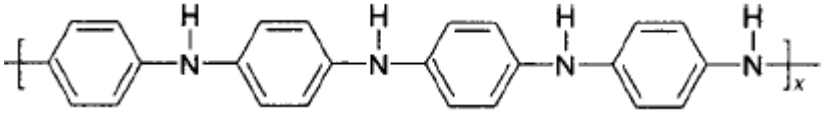
Fig. 1.8: Generalized formula of Polyaniline base

Table1.1 Colors of each four oxidation state of Polyaniline

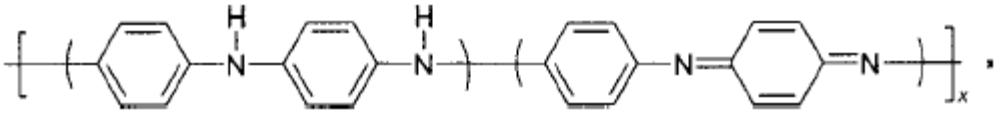
Oxidation state	leucoemeraldine	photoemeraldine	Emeraldine	nigraniline	pernigraniline
Color	pale yellow or colorless	light green	green or dark green	blue or dark blue	violet

The polyanilines refer to a very important class of electronic/conducting polymers. They can be considered as being derived from a polymer, the base form of which has the generalized composition shown in Fig. 1.8 and which consists of alternating reduced and oxidized repeat

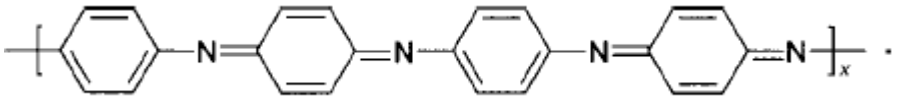
units. The *average* oxidation state (1-*y*) can be varied continuously from zero to give the completely reduced polymer



to 0.5 to give the ‘‘half-oxidized’’ polymer



to one to give the completely oxidized polymer.



The terms ‘‘leuco-emeraldine,’’ ‘‘emeraldine,’’ and ‘‘pernigraniline’’ refer to the different oxidation states of the polymer where (1-*y*)=0, 0.5, and 1, respectively, either in the base form, e.g., emeraldine base, or in the protonated salt form, e.g., emeraldine hydrochloride .In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depending on its oxidation state and on the *p*H of the aqueous acid. Complete protonation of the imine nitrogen atoms in emeraldine base by aqueous HCl, for example, results in the formation of a delocalized polysemiquinone radical cation and is accompanied by an increase in conductivity of $10^{10.}$ [6].

The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 10^0 S cm^{-1} , many orders of magnitude higher than that of common polymers ($<10^9$ Scm^{-1}) but lower than that of typical metals ($>10^4$ S cm^{-1}). Protonated PANI, (e.g., PANI hydrochloride) converts to a nonconducting blue emeraldine base when treated with ammonium hydroxide [39] (Fig. 1.9).

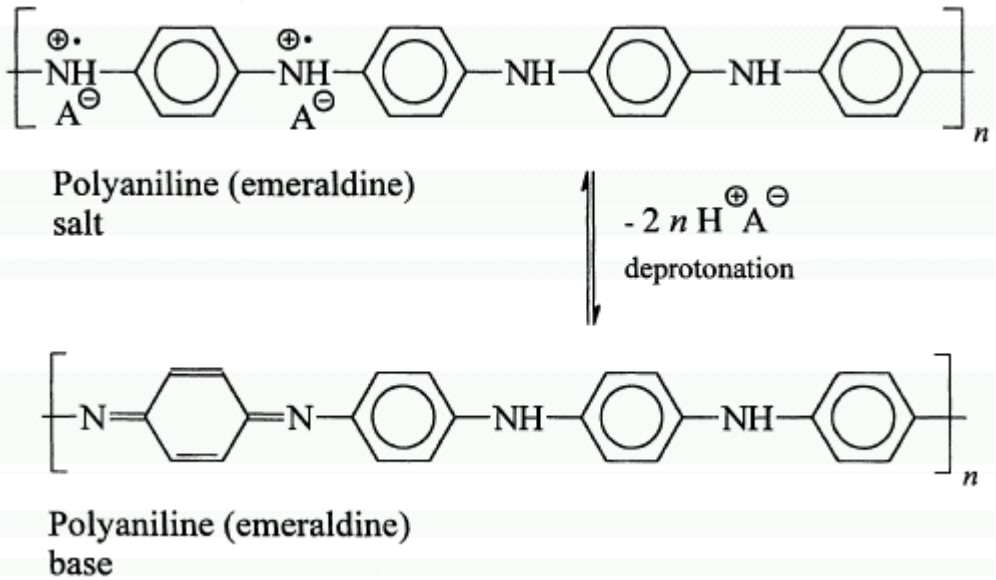


Fig. 1.9 Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to polyaniline (emeraldine) base. A^- is an arbitrary anion, e.g., chloride.

The efficient polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. A variety of inorganic and organic acids of different concentration have been used in the syntheses of PANI; the resulting PANI, protonated with various acids, differs in solubility, Conductivity, and stability [40]. For the present study, we have selected hydrochloric acid in equimolar proportion to aniline, i.e., aniline hydrochloride was used as a monomer. The handling of solid aniline salt is preferred to liquid aniline from the point of view of toxic hazards. Peroxydisulfate is the most commonly used oxidant, and its ammonium salt was preferred to the potassium counterpart because of its better solubility in water. The concentration of aniline hydrochloride was set to 0.2 M. Various oxidant/monomer ratios have been used in the literature [42]. To minimize the presence of residual aniline and to obtain the best yield of PANI, the stoichiometric peroxydisulfate/aniline ratio 1.25 is recommended [42]. Reduced reaction temperature and increased acidity of the polymerization medium influence the polyaniline conductivity. The conductivity changes occur during the storage of polyaniline. The density of polyaniline hydrochloride 1.329 gm^{-3}. The average conductivity of corresponding polyaniline bases was 1.4×10^{-8} S cm^{-1}, the density being 1.245 cm^{-1}.

Polyaniline refers to a general class of conducting polymers composed of benzoid and quinoid character, connected by nitrogen. Polyaniline is built up from reduced (B-NH-B-NH-) n and

oxidized (-B-N=Q-N=) n repeat units, where “B” denotes benzoid and “Q” denotes quinoid rings. Thus the changing ratio of amine to imine yields various structures, such as leucoemaraldine, a reduced form of emeraldine base.[45] Only one form, called the emeraldine salt, is electrically conducting. Protonic doping is accomplished by dipping the emeraldine films in acid or passing a gaseous acid over them to protonate the imine nitrogen atoms in the backbone of the polymer. The conductive emeraldine salt becomes the insulating emeraldine base when treated with aqueous alkali. Polyaniline has good environment stability [46]. The polyaniline of ideal emeraldine base form contains alternating amine and imine repeat units.[47,48] When the emeraldine base is doped with a protonic acid, the protonation occurs at the imine nitrogen sites to yield polysemiquinone in which polarons delocalize along the chain. Aqueous hydrochloric acid has been used most frequently for protonation studies of emeraldine base because, unlike many other strong acids, it is volatile and excess acid wetting the solid polymer can readily be removed from the vacuum. Polyaniline has a chemically flexible –NH- group in its backbone which is responsible for interesting chemistry and physics [49]. The electrochemical stability of polyaniline depends on the pH conditions as well as the counter-ion of the Bronsted acid used for doping.

1.4 Significance of Polyaniline

Amongst the various conducting polymers polyaniline [PANI] has rapidly become the subject of considerable interest for physicists, chemists and material scientists. Polyaniline exists in several oxidation states with electrical conductivity varying progressively from 1-10S/cm. However, only one form, called emerlaldine salt is electrically conducting. It can be synthesized easily by electrochemical or chemical oxidation of aniline in aqueous acidic media, using common oxidants, such as ammonium peroxidisulphate.

Conducting polymer are increasingly replacing natural and inorganic materials application requiring excellent mechanical properties and lightweight .The mechanical properties of polymers can be tailored to provide strong materials with high toughness and low resistance. Until recently, the low electrical conductivity of the polymer had limited their use in electronics. Polymers are insulators because the atoms in the polymer chain are covalently bonded. In the covalent bonded molecules of the saturated carbon compounds, there is no scope of

delocalization of the valence electrons and consequently, neither charge carriers nor path for their movements are available. Since in the conjugated molecule of a carbon compound, delocalization of electron may occur through the interaction of - bonded electrons, such molecule may be conducting .Thus it was thought that a chain conjugated molecule, such as the polymer of acetylene, may prove to be conducting.

Among conducting polymers, polyaniline has been a significant interest due to its high conductivity, good redox reversibility, and swift change in film color with potential and high stability in air. Research in electroactive polymers, particularly in aromatic conducting polymers, has received considerable attention worldwide in the past few years because of their potential applications in the fields of microelectronics, optics and optoelectronics (Bernard et al 1998, 2001; Schultze et al 1999; Mousty et al 2001). Among these polymers, polyaniline (PANI) is one of the most widely studied conducting polymer because of its good conductivity that can be influenced both by the charging level and degree of protonation, its well defined electrochemical (redox) response, easy preparation and possible applications in rechargeable batteries, corrosion protection, light emitting diodes, molecular sensors, electrochromic devices and microwave screening (Inzelt et al 2001). Polyaniline is not charge conjugation symmetric, i.e. the valence and conduction bands are asymmetric to a great extent (Ghos et al 2001). A partial oxidation of PANI usually leads to the reorganization of bonds, resulting in an increase in electronic conductivity. The physic-chemical properties of PAni are strongly related to the proportion of aryl amine and quinone imine units present (Genies et al 1988). PANI possesses two voltammetric redox pairs including three stable oxidation states, with the half-oxidized state (emaraldine) being highly conductive in its protonated state. Existence of different oxidation states of PANI makes it useful as an electrode material in electrochemical capacitors [43].

Among conducing polymers polyaniline attracts many attentions due to its outstanding properties. It is one of the so-called doped polymers, where the conductivity results from a process of partial oxidation and reduction. The conductivity of polyaniline is easily controllable. One of the most frequently tried applications for polyaniline is as the electrochromic material [14]. Polyaniline also has environmental stability. Unlike the other conducting polymers, polyaniline is also processable by melting or by making solution [53]. It means that polyaniline products can easily be shaped into any required form. Polyaniline films can easily be obtained by

polymerization of aniline using some polymerizing agents such as ammonium persulphate [22] or benzoyl peroxide [54]. Also a UV photo processing can be used for the polymerization [55]. Therefore, the polyaniline could be obtained by selecting a proper processing method among those available choices according to the purpose. For the organic material the oxidation and reduction reaction can be explained differently from inorganic materials. Polyaniline shows typical electrochromic behavior, and it is related with different phases of polyaniline which are formed by oxidation and reduction of the material.

As oxidation proceeds, polyaniline changes its phase from completely reduced phase leucoemeraldine to completely oxidized phase pernigraniline. During the oxidation and reduction, polyaniline changes its color. The colors of each oxidation state of polyaniline were summarized in Table 1.

From theoretical point of view, PANI is interesting in the sense that it shows degenerate and non- degenerate ground states. Conjugated system degenerate and non- degenerate ground states exhibit non-linear optical behavior [44]. Extensive studies on theoretical modeling have demonstrated that polyaniline differs from other conducting polymers because of the important role of phenyl rings along with the presence of nitrogen hetero-atom within the conjugation path [38].

1.5 Motivations and Aim of thesis

The statement of Nobel laureate Prof. A.G. Macdiarmid that" there are as many different types of PANI as there are people who synthesize it." has been a wide source of motivation. This statement elaborate that different properties of polyaniline such as optical and electronic property, thermal and environmental stability changes with method and condition in which has it been synthesized.

Therefore the method and condition in which PANI has been synthesized may affect the electrical and optical property, thermal and environmental stability, processibility etc. Thus, the aim present thesis is as follows:

1. To synthesize polyaniline (conducting and insulating) by chemical polymerization.
2. To characterize the polyaniline.
3. To check the stability and the polymerization of polyaniline.

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CHAPTER - 2

EXPERIMENTAL

Chapter 2

Experimental

2.1 Introduction

This chapter presents the details of experimental techniques for synthesis, spectroscopic characterization, electroanalytical characterization and thermogravimetric analysis of polyaniline. The conducting and insulating polyaniline has been prepared by chemical polymerization technique. A thorough investigation about the chemical properties and structural properties can be obtained by several characterization techniques. The Fourier Transform Infra Red technique has been used for finding out the different functional groups. The Ultraviolet- visible spectroscopy has been used for determining the polymerization and band gap of the polymer. The Thermogravimetric analysis (TGA) employed for determining the thermal stability of the polyaniline.

2.2 Synthesis

There are different methods by which conducting polymers can be synthesized. Conducting polymers can be synthesized in the presence of different protonic acid media by different methods [1-8]. The most widely accepted methods are chemical oxidative polymerization method and electrochemical methods [9-11]. Chemical oxidative methods are preferred over electrochemical polymerization because of its cost effectiveness and bulk quantity of the polymer that can be prepared during the onset of the reaction. Other techniques include solid state polymerization, plasma polymerization, precursor polymer route, template polymerization etc. But in the present work, polyanniline has been synthesized by chemical polymerization technique, which has been discussed in detail in following subsection.

2.2.1 Chemical Polymerization of Polyaniline

Polyaniline salts are prepared from an acidic solution containing HCl by adding monomer aniline and APS. The efficient polymerization of aniline is achieved in an acidic medium. When aniline is dissolved into aqueous solution containing HCl, aniline will exist as an anilinium cation. In the acidic solution, aniline hydrochloride is a starting monomer for the polymerization reaction. When APS is added to the solution, the oxidative polymerization starts soon. The overall reaction where polyaniline hydrochloride, i.e. emeraldine salt is produced can be given as Fig.2.1. The Fie oxidation of aniline is exothermic and acid is a by-product (Fig.2.1).

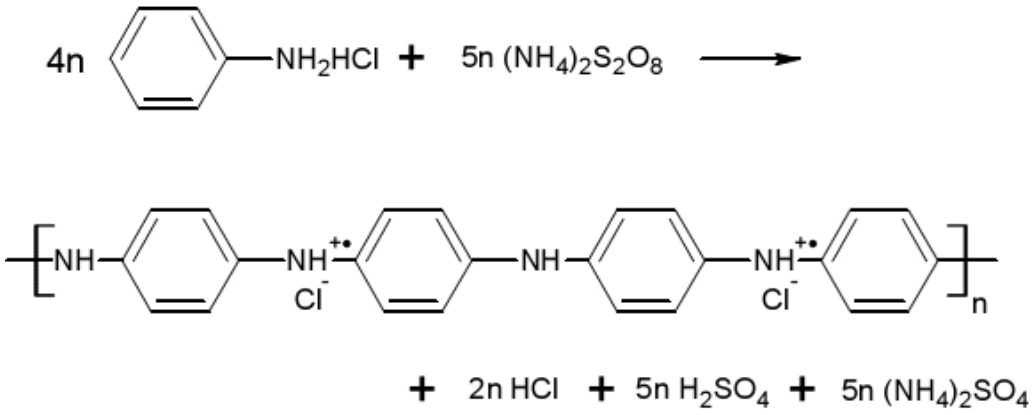

Fig.2.1Stoichiometry of aniline oxidation with ammonium peroxydisulfate to polyaniline hydrogen sulfate in an acidic medium. [12] Sulfuric acid and ammonium sulfate (or ammonium hydrogen sulfate) are by-products.

Oxidative polymerization of aniline consists of following steps:

1. Oxidation of monomer to radical action.
2. Dimerization of radical cation followed by proton loss to form a neutral dimer.
3. Oxidation of neutral dimer to radical action.
4. Oxidation of dimer radical action with another cation to form dication.

In this way the reaction proceeds and consequently trimer, tetramer and finally polymer are formed. An aniline dimer, *N*-phenyl-1,4-phenylenediamine (*p*-semidine), could be a molecule generated in the induction period (Fig. 2.4) [13]. The rate-determining step in the oxidation is the

reaction with the next aniline molecule, producing an aniline trimer [14] which triggers the polymerization and ends the induction period. Later additions of aniline molecules were then found to proceed at a rate exceeding, by orders of magnitude, the rate of trimer formation [15, 16]. The concept of the initial fragment as p-semidine corresponds to the experimental observation that aniline molecules are linked in their para positions [17].

It does not fit, however, into the more general polymerization concept because it does not explain the kinetic rules of the process. It is difficult to understand why the rate of addition of the third aniline molecule, and any later molecule, should be so different. In addition to linear para-linked structures, the oxidation of such units yields heterocycles of the phenazine type [18-21]. Several authors have assumed that such a cyclization is a post-polymerization process only [18-22].Many studies, however, have predicted[14,23]Materials Sciences of the Russian Academy of Sciences and experimentally confirmed that the phenazine units appear in the early stages of aniline oxidation [24][25].

The oxidative polymerization of aniline is based on the following two principles:

• The first initiating fragment of the PANI Chain is based on the oligomeric phenazine-containing structure. Phenazine containing oligomers are produced during the induction period of aniline oxidation. Such species serve as the initiation centres for the subsequent growth of PANI chains with para-linked aniline molecules. The PANI macromolecules are thus composed of initial heterocyclic phenazine fragments attached to linear PANI chains (Fig. 2.5).

• The second principle is associated with the role of medium acidity, pH, as a crucial factor determining the chemistry of oxidation. In various pH ranges of aniline oxidation, the amino and imino groups of the monomer, oligomers and polymer are protonated to various extents; the reactivities of non-protonated and protonated species are different, and their oxidations proceed to give different reaction products.

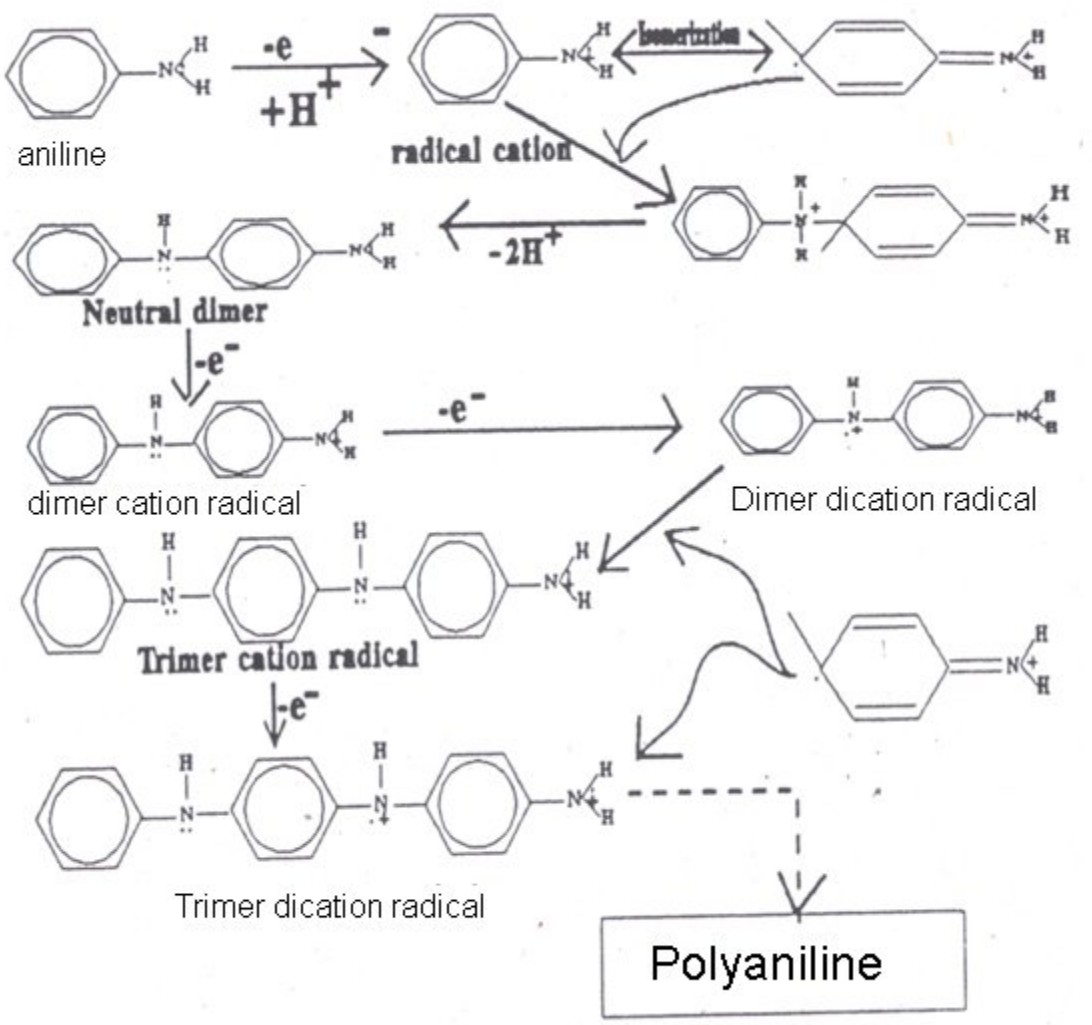

Fig. 2.2: Schematic of polymerization of Polyaniline.

In chemical oxidative polymerization, a monomer is polymerized using ammonium persulphate (APS) as an oxidant. For carrying the polymerization reaction, chilled monomer of definite molarity is added to pre-cooled acidic solution. The reaction is carried out in low temperature range (0-5^{o}c), by placing the beaker in ice bath, to achieve better yield and better quality of polyaniline and to avoid the formation of oligomers. Ammonium persulphate (APS) taken in 0.1 M is added to the above solution slowly (~1ml/min) and the resulting solution is stirred in order to ensure the completion of the reaction. The slower addition of ammonium persulphate (APS) will avoid the formation of oligomers. The reaction mixture is then filtered using vacuum pump and then washed with distilled water to remove the non reacted monomer and oligomers formed

during the course of reaction until the filtrate becomes colorless. The precipitate is then dried under vacuum. The resulting powder is in doped form.

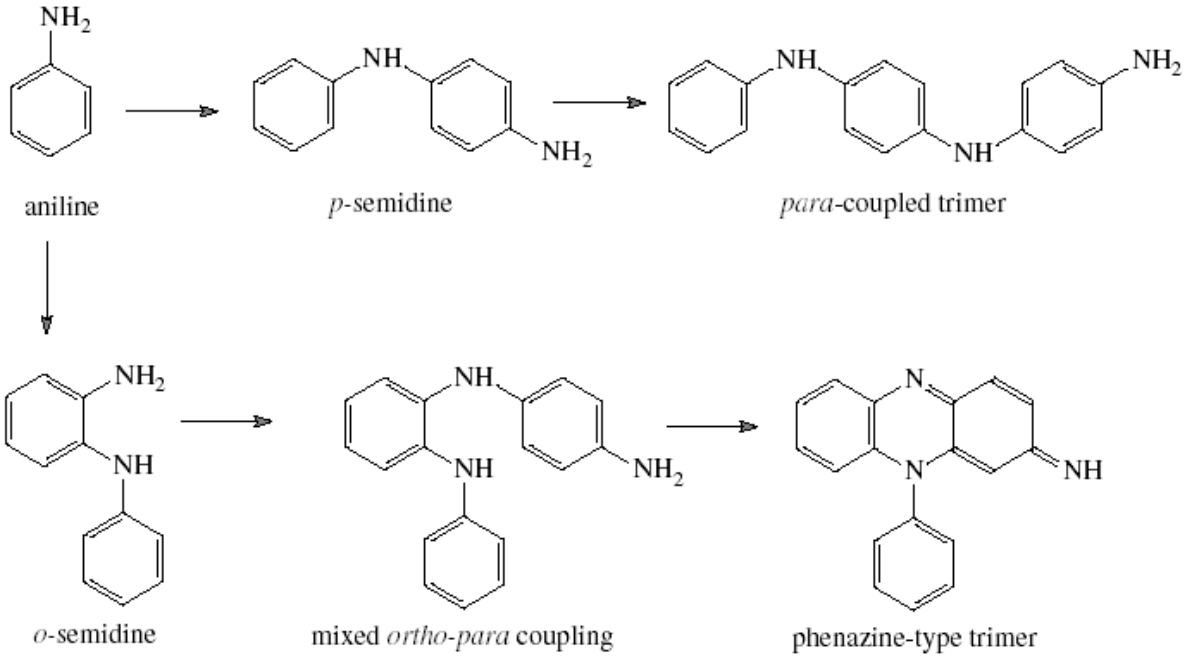

Fig. 2.3: Aniline oligomers: The coupling of aniline molecules in *ortho* and *para* positions yields corresponding semidines. Aniline trimers may be linear or the coupling is mixed. The oxidation of the latter type may lead to the formation of phenazine cycles. All structures can be present in reduced or oxidized states, and as protonated or base forms.

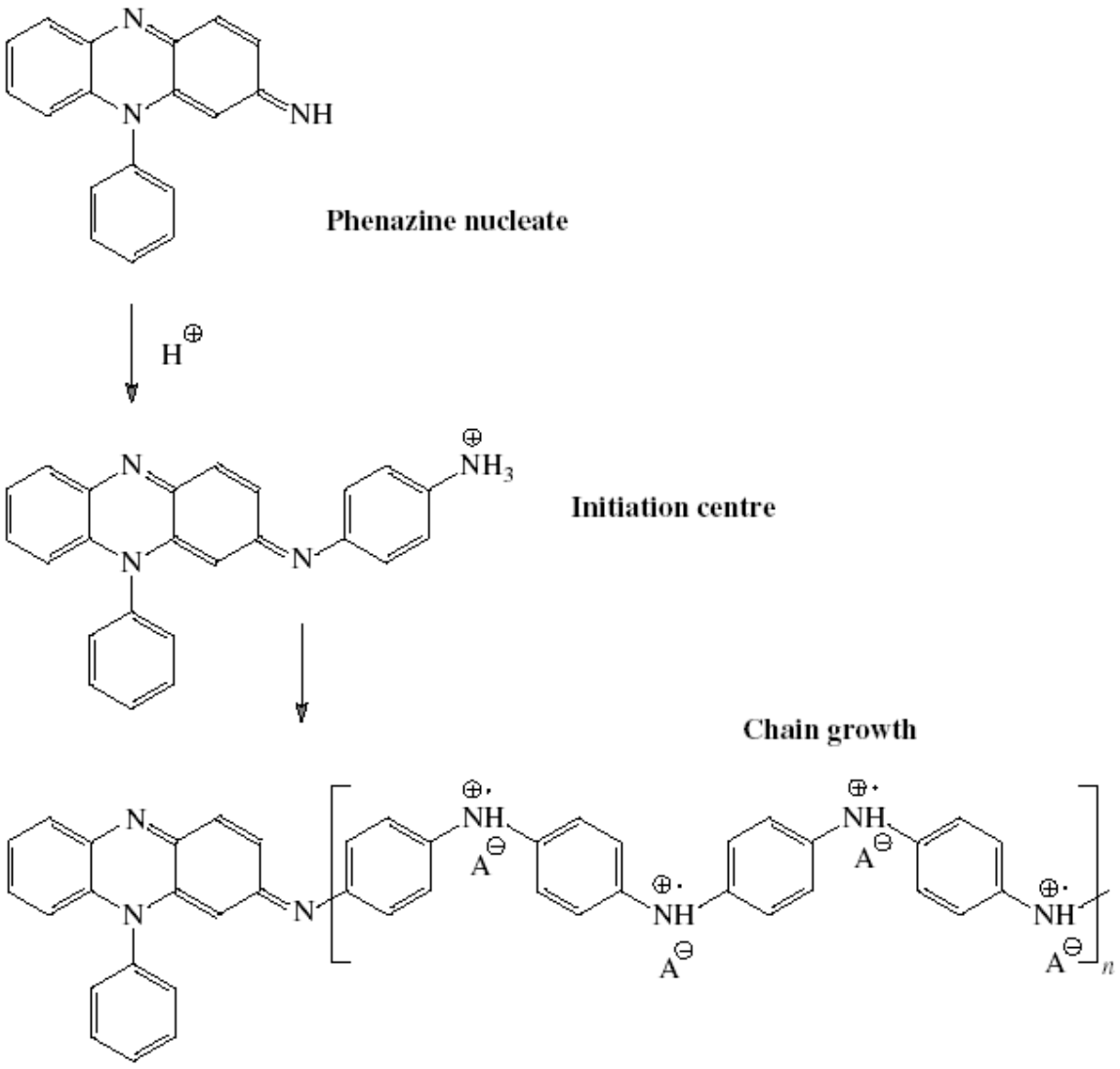

Fig. 2.4: Transformation of the phenazine nucleate to the initiation centre is a limiting step of aniline oxidation. Linear *para*-coupled PANI chains in the protonated pernigraniline form grow from the initiation centre at a high rate.

2.3 Characterization

Characterization of a material is an important step after its synthesis because it gives useful parameters in determining the properties of polymers. Chemical characterization consists of determination of oxidation states. Physical characterization consists of spectroscopic analysis using Fourier Transform Infra Red (FT-IR) and UV-visible spectrometer, thermal analysis (Thermo Gravimetric Analysis). Physico-chemical methods involve the application of electroanalytical techniques like cyclic voltammetry (CV). This technique is performed to determine the redox behavior of conducting polymers.

The characterization of synthesized material includes spectroscopic characterization, electrochemical characterization and Thermo Gravimetric Analysis of Polyaniline. The characterization techniques used for the characterization of polyaniline is described in following sections.

2.3.1 Spectroscopic characterization

The spectroscopic characterization of the polymer samples is usually carried out by Fourier Transform Infra Red and Ultraviolet-visible techniques. Ultraviolet-visible gives the energy band gap and defect states, while IR spectroscopy identifies and confirms the structure and presence of various linkages in polymer.

2.3.1.1 Ultraviolet-Visible Absorption Spectroscopy

Ultraviolet-Visible absorption spectroscopy is the measurement of the attenuation of the beam of light after it passes through a sample or after reflection from a sample surface. UV-Vis includes transmittance, absorption and reflection measurements in UV, visible and Near Infra Red region [26].

The absorption of UV radiation by organic compounds in the visible and ultraviolet region involves promotion of electrons in σ, π and n-orbitals from the ground state to higher energy state. These higher energy states are described by molecular orbitals that are vacant in the ground state and are commonly called anti bonding orbitals. The anti bonding orbitals associated with σ bond is called the σ* orbital and that associated with π bond is called the π* orbital. As the n

electrons do not form bonds, their antibonding orbitals are not associated with them. The electronic transitions that are involved in the UV and visible regions are of various types viz; σ σ*, n π*, π π*. Transitions to antibonding π* orbitals are associated only with unsaturated centers in the molecule.

Compounds containing isolated double bond absorb in the range162nm to190nm, whilst conjugated molecules (those containing single and double bond) absorb above 210nm. Extension of conjugated systems intensifies the absorption peaks and shits it further to the higher wavelengths, towards the visible spectrum. This technique not only provides information about the different bonding but also is an excellent tool for determining the band energy, which is an important parameter used in investigating the condution mechanism in the organic conductors.

Principle of UV-visible spectroscopy

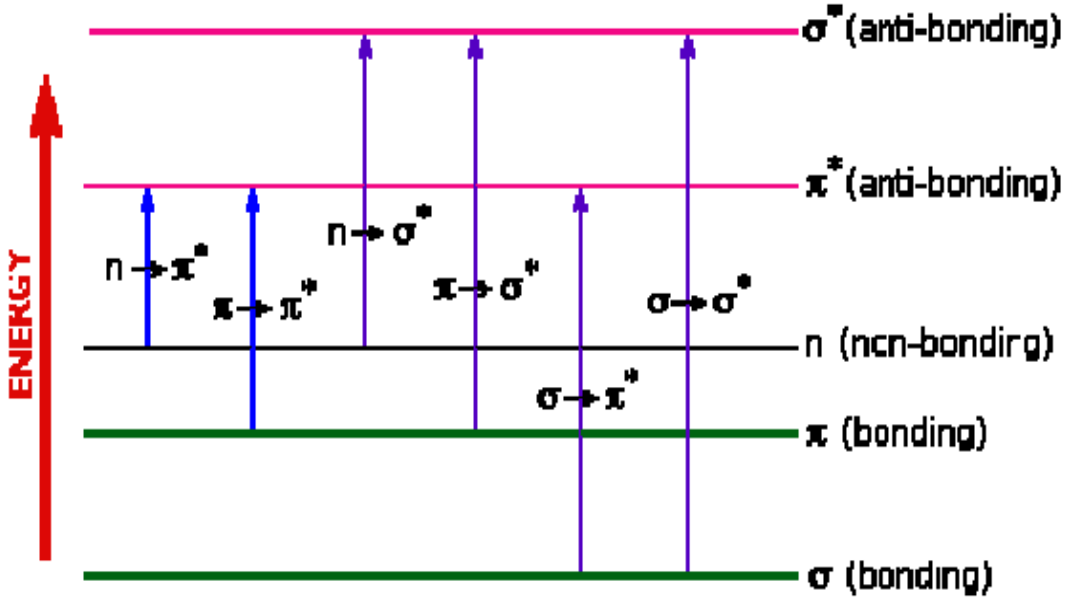

Fig. 2.5. Energy Level Diagram

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes

called “electronic spectroscopy”. A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown in fig. 2.5. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital *(LUMO*), and the resulting species is called an excited state. [27]

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to the higher energy orbital. An optical spectrometer records the wavelength at which absorption occurs, together with the degree of absorption at each wavelength. Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called “molar absorptivity “, and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). Molar absorptivity (ε) is defined as

Molar Absorptivity, $\varepsilon = A / c\, l$, Where A= absorbance,

c = sample concentration in moles/liter & l = length of light path through the sample in cm

The UV-visible spectral data is used for the determination of the band gap (i.e. the difference between the conduction band energy and the valence band) in case of various conducting polymers by using the relation:

$$(\alpha.d) = (h\nu - \varepsilon_g)^{1/2}$$

$$\alpha.h\nu = \alpha\,(h\nu - \varepsilon_g)^{n}$$

Where, α is the absorption coefficient and d is the thickness of the sample, ε_g is the energy band gap n (1/2, 1, 2) is a constant is dependent on the degree of transition, hν is incident photon energy. The band gap can be evaluated by plotting hν versus absorbance and extrapolating the tangent on the X-axis. This tangent is drawn from the peak in the spectrum corresponding to π-π* transition of the polymer. This directly gives the band gap of the desired conducting polymer. UV visible spectroscopic studies are also used for carrying out the distinction between the

conducting and the insulating state of the polymer matrix both in the solution phase as well as in the film form.

A diagram of the components of a typical spectrometer is shown in the following diagram (Figure 4). The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 nm to 400 nm, and the visible portion is from 400 nm to 800 nm.

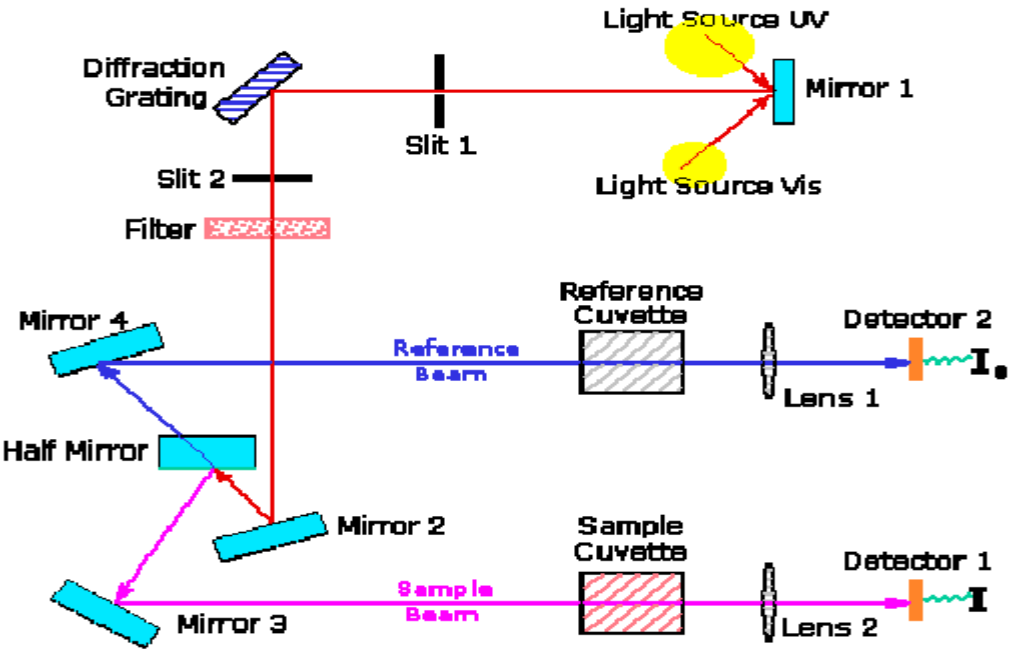

Fig. 2.6: Block Diagram of Ultraviolet-Visible Spectrometer.

If the sample compound does not absorb light of a given wavelength I = Io. However, if the sample compound absorbs light then I is less than Io, and this difference may be plotted on a graph versus wavelength. Absorption may be presented as transmittance (T = I/Io) or absorbance (A = log Io/I). If no absorption has occurred, T = 1.0 and A = 0. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100 % transmittance) to 2 (1 % transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λ_{max} [28].

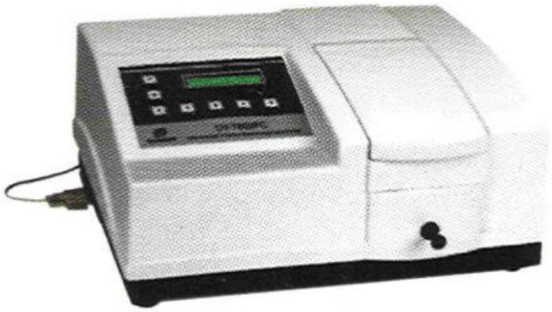

Fig. 2.7: UV-Vis spectrophotometer.

2.3.1.2 Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR spectra of Polyaniline have been taken by using Perkin Elmer spectrometer using the KBr pallets technique. A molecule absorbs radiation only when the natural frequency of vibration of some part of molecule (i.e. atoms or group of atoms comprising it) is the same as the frequency of the incident radiation. After absorbing the correct wavelength of radiation, the molecule vibrates at increased amplitude. This occurs at the expense of the energy of the IR radiation, which has been absorbed [29].

Infrared spectroscopy is one of the most powerful analytical technique , which offers the possibility over the other usual method of structural analysis (X-ray diffraction , electron spin resonance , etc) is that its provides useful information about the structure of the molecules and bonding quickly , without tire-some evaluation method . Moreover, FT-IR provides a very faster of identifying chemical structures especially those of the organic ones. FT-IR spectroscopy employs an interferometer in place of monochromatic (Fig. 2.7). This device generates the

Fourier transform of the infra-red spectrum, which is converted to spectrum itself by a computer. This approach has the advantageous of providing much higher source radiation throughout, increased signals-to-noise (SN) ratio and higher wave number accuracy than is possible with a conventional light dispersive spectrometer [27].

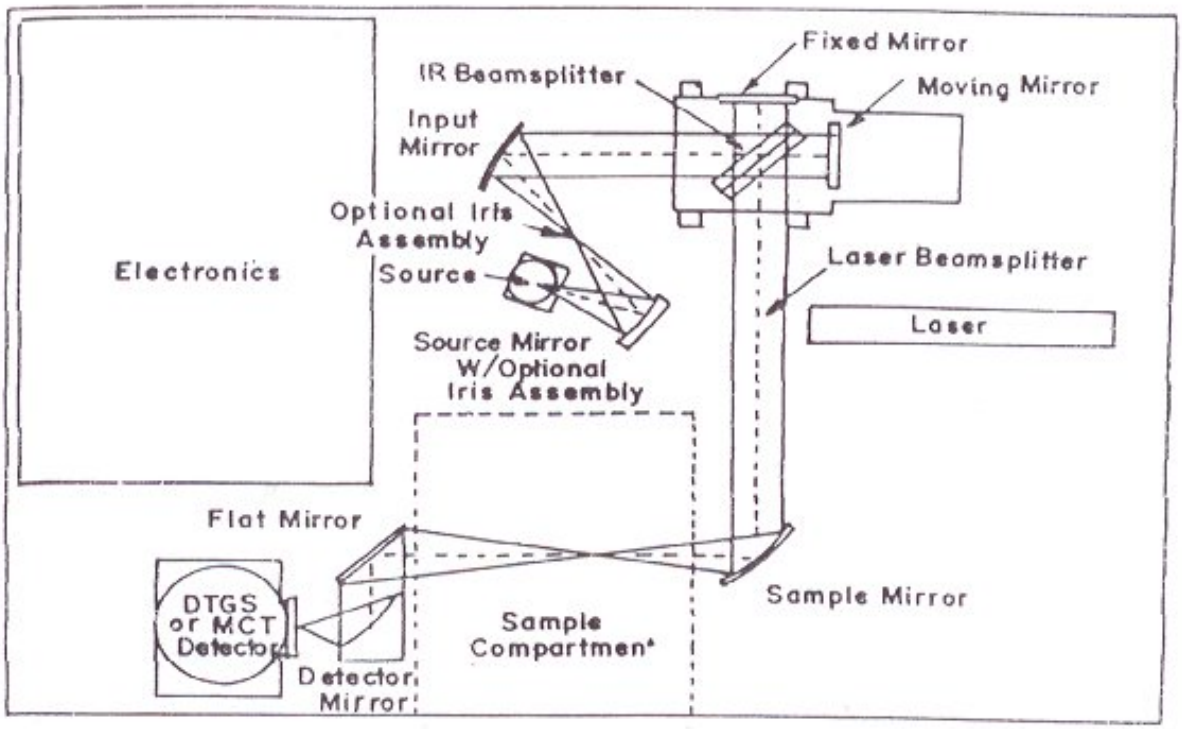

Fig. 2.8: Experimental set-up of Fourier Transform Infrared

The technique is based upon the simple fact that a chemical substance shows marked selective absorption in infrared region giving rise to close-packed absorption bands, called an IR absorption spectrum, which may extend over a wide wavelength range. Various bands in all IR spectrum correspond to characteristic functional groups and bonds present in the chemical substance. IR spectrum of a chemical substance is thus a fingerprint for its identification. Band position in infrared may be expressed conveniently by wave number ν, whose unit is cm^{-1}. The relation between velocity c, wavelength λ and frequency ν is as follows;

$\nu = c/\lambda$ or $\nu/cm^{-1} = l\lambda$

Band intensities in IR spectrum may be expressed either as transmittance (T) or absorbance (A). Transmittance is defined as the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. In most spectra transmittance (T) versus wave number (cm^{-1}) has been plotted.

2.3.2 Thermal Characterization

The thermal characterization of conducting polymers is carried out for determining thermal stability. Thermo Gravimetric Analysis has been employed for this purpose. This technique has been discussed in subsequent subsection.

2.3.2.1 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA is commonly used to determine polymer degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite material compositions.

A sample is placed into a tarred TGA sample pan which is attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight (losses or gains) as heat is applied to the sample. TGA tests may be run in a heating mode at some controlled heating rate, or isothermally. Typical weight loss profiles are analyzed for the amount or percent of noncombusted residue at some final temperature, and the temperatures of various sample degradation process.

2.3.3 Electroanalytical Characterization

The electroanalytical characterization has been used for determining the polymerization and redox behavior of the polymer. Cyclic voltammetry (CV) has been employed for

electroanalytical characterization. The details of this technique have been described in subsequent section.

2.3.3.1 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is the most versatile electroanalytical technique for the mechanistic study of redox behavour, number of electrons involved in the redox reaction, electrochemical studies, degradation studies and study of reversibnility of redox couples in the conducting polymer systems. By varying the potential between working electrode and a counter electrode in an electrochemical cell, change of color (according to their oxidation level) from one state to another can be investigated. Redox couples can be characterized from the potentials of the peaks on the cyclic voltammogram (CV) and from the changes caused by variation of the scan rate. The important parameters of a CV are the magnitudes of the peak current, I_{pa} (anodic current) and I_{pc} (cathodic current) and the peak potential, E_{pa} and E_{pc} (anodic and cathodic peak potenial). For electrochemically and chemically reversible system the following equation is applied:

$$\Delta E_p = E_{pa} - E_{pc} = 0.059/n$$

Where, n is the number of electrons transferred and E_{pa} and E_{pc} are the anodic and the cathodic peak potentials (Volts), respectively. ΔE_p is independent of scan rate for a reversible couple. The values of I_{pa} and I_{pc} are similar in magnitude for a reversible couple with the kinetic complications [14]. Peak current (anodic/cathodic) depends on the square root of scan rates in any redox couple. In ideal reversible system anodic peak current should be equal to cathodic peak current or $I_{pa}/I_{pc} = 1$.

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CHAPTER-3

RESULTS AND DISCUSSION

Chapter 3

Results and Discussion

3.1 Introduction

The polyaniline is the most widely studied polymer in the group of conducting polymers [1]. The polyaniline is important from application and academic point of view. The often quoted statement by Prof. A. G. MacDiarmid ” there are as many different types of PANI as there are people who synthesise it. ”[2].This statement consists of lot of mystery to be unraveled in itself such as polymerization mechanism and reason for aniline oxidation, band gap of polyaniline, thermal stability etc.

3.2 Synthesis of Material

The polyaniline (insulating and conducting) has been synthesized by using chemical polymerization technique. The detail of the technique has been described in section 3.2. The subsequent subsection describes the synthesis of insulating and conducting polyaniline.
In chemical oxidative polymerization, a monomer (aniline) is polymerized using ammonium persulphate (APS) as an oxidant. For carrying the polymerization reaction, chilled monomer (15 ml Aniline) of definite molarity is added to pre-cooled acidic solution (250ml water +35 ml HCl conc.)(1N). The reaction is carried out in low temperature range (0-5^{o}c), by placing the beaker in ice bath, to achieve better yield and better quality of polyaniline and to avoid the formation of oligomers. Ammonium persulphate (APS)(2.85 mg APS + 100ml water) taken in 0.1 M is added to the above solution slowly(~1ml/min) and the resulting solution is stirred using magnetic stirring for 5-6 hours in order to ensure the completion of the reaction. The reaction mixture is then filtered using vacuum pump and then washed with distilled water to remove the non reacted

monomer and oligomers formed during the course of reaction until the filtrate becomes colorless. The precipitate is then dried under vacuum. The resulting powder is in partial doped.

3.2.1 Insulating Polyanilne

To get the undoped polymer, ammonia solution (NH_3 25%) is added to the doped polymer powder. This solution is continuously stirred with the help of magnetic stirrer for 4-5 hours and then filtered and washed with distilled water followed by washing with methanol. Distilled water was used; the potential presence of iron (III) ions in tap water may accelerate the aniline oxidation. Washing the PANI precipitate with 0.2 M HCl removes residual monomer, oxidant, and its decomposition products. The treatment with hydrochloric acid solution provides a more uniform protonation of PANI with chloride counterions, although some of the sulfate or hydrogensulfate anions from the decomposition of peroxydisulfate also participate as counterions. A final washing with acetone removes low-molecular-weight organic intermediates and oligomers. It also prevents the aggregation of PANI precipitate during drying, and the product is obtained as a fine powder. The precipitate is then dried in vacuum. This form is an insulator with high resistance. Polyaniline is in the emeraldine salt form, which is conducting. Subsequent deprotonation with ammonium hydroxide transforms the emeraldine salt into the emeraldine base form.

3.2.2 Conducting Polyanilne

The ultimate conductivity and other properties of conducting polymer depend on the nature and concentration of dopants homogeneity of doping, carrier mobility and specific orientation taken by dopant moiety in the polymer structure. This powder in its undoped form is treated by dopants (HCl) either in protonic or ionic form yielding polymer powder with required conductivity and morphology.

3.3Ultraviolet–Visible Absorption Spectroscopy

The Fig 3.1 shows change in optical spectra accompanying doping are significant and these spectral changes play a key role in elucidating the mechanism of doping and the nature of charge storage species in the polymer chain UV Visible spectrum of emeraldine base in n-methylpyrrolidinone (NMP) solution, shows two electronic transitions at 325 nm (3.9 eV) and 635 nm (2 eV).

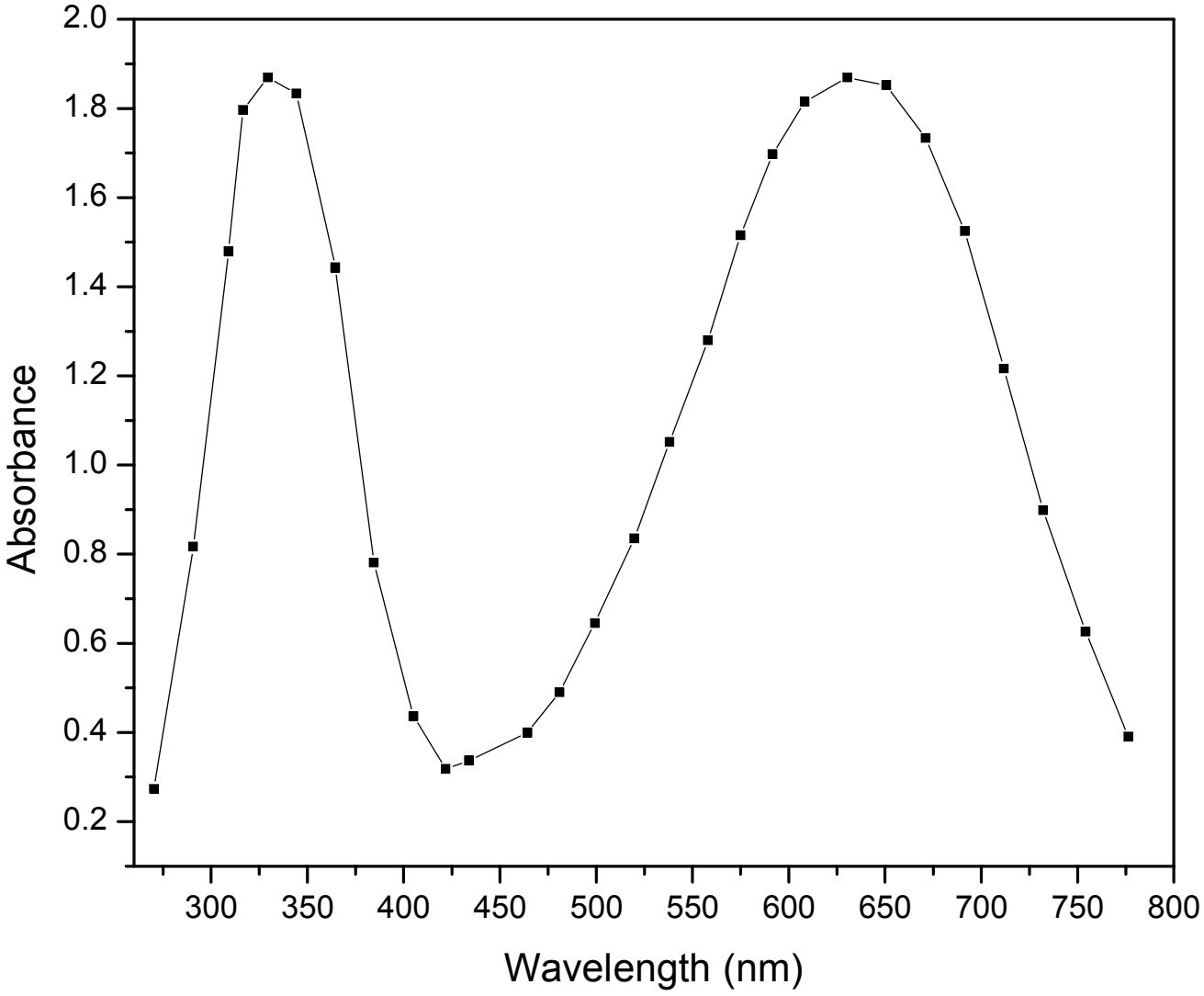

Fig. 3.1: UV-visible spectrum of undoped polyaniline in NMP.

With the view to identify the nature and the origin of these transitions, a soluble oligomer (trimer) diphenyl para phenylene diamine(l) and its oxidized form diphenyl para phenylene diimine(ll) having structure shown in Fig. 3.2 have been suggested [3]. UV Visible spectra of these compounds show principle adsorption peaks at about 302 nm (4.1 eV) and 443 nm (2.8 eV) respectively [4]. A critical analysis of UV Visible spectra of emeradine base and the above

two organic compound suggest that the benzenoid amine units perhaps cause the 3.9 eV adsoption (similar to that of 4.1eV of diamine) where as quiniod imine unit causes the 2.1 eV peaks (similar to the 2.8 eV absorption) for diimine. This interpretation is consistent with the theoretical calculations [5]. The 2 eV absoption peak has been thought to be arise from the excitation occurring from HOMO (π b) of the benzenoid part of LUMO (π q) of the localized quinoid ring and the two surrounding imine nitrogen .The 3.9 eV electeronic transition has been attributed to the both π to π* transition of the benzenoid ring and the low lying orbitals to π q orbitals .

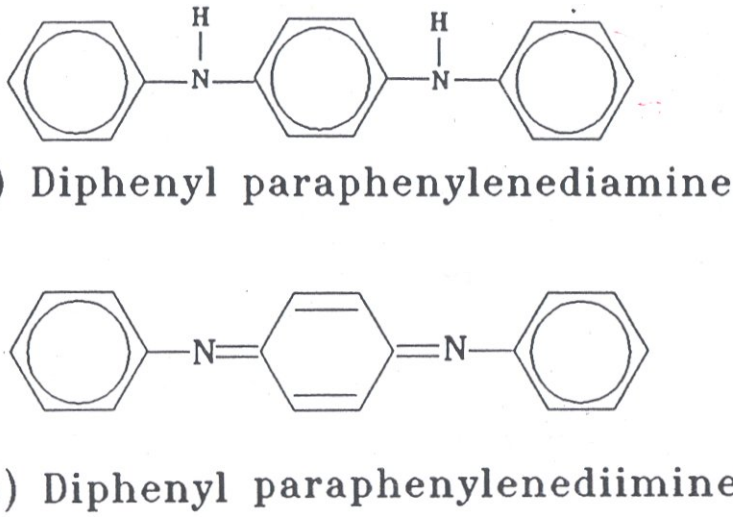

Fig3.2: Structures of model Trimeric compounds, (a) diphenyl paraphenylene diamine and (b) diphenyl paraphenylene diimine

Fig 3.3 shows the UV visible spectrum, (curve a) of the polyaniline doped with sulphuric acid (p_H=0).It shows prominent electronic transition at 762.90 nm (1.63 ev).Curve b is UV-Visible spectrum of the emeraldine base in 98% sulphuric acid that shows two peculiar electronic transition at 479.95 nm (2.6 eV) and 1043 nm (1.19 eV).The 2.6 eV and 1 eV (curve b) peaks are understood to arise from a transition from a polaron to a bipolaron lattice. The 1.6eV peak is significantly absent in the UV-Visible spectra observed for polyaniline doped with concentrated H_2SO_4. These results are in accordance with the theoretical prediction that the over protonation may perhaps break the conjugation resulting in the transformation of lattice structure from polaron to bipolaron [10].

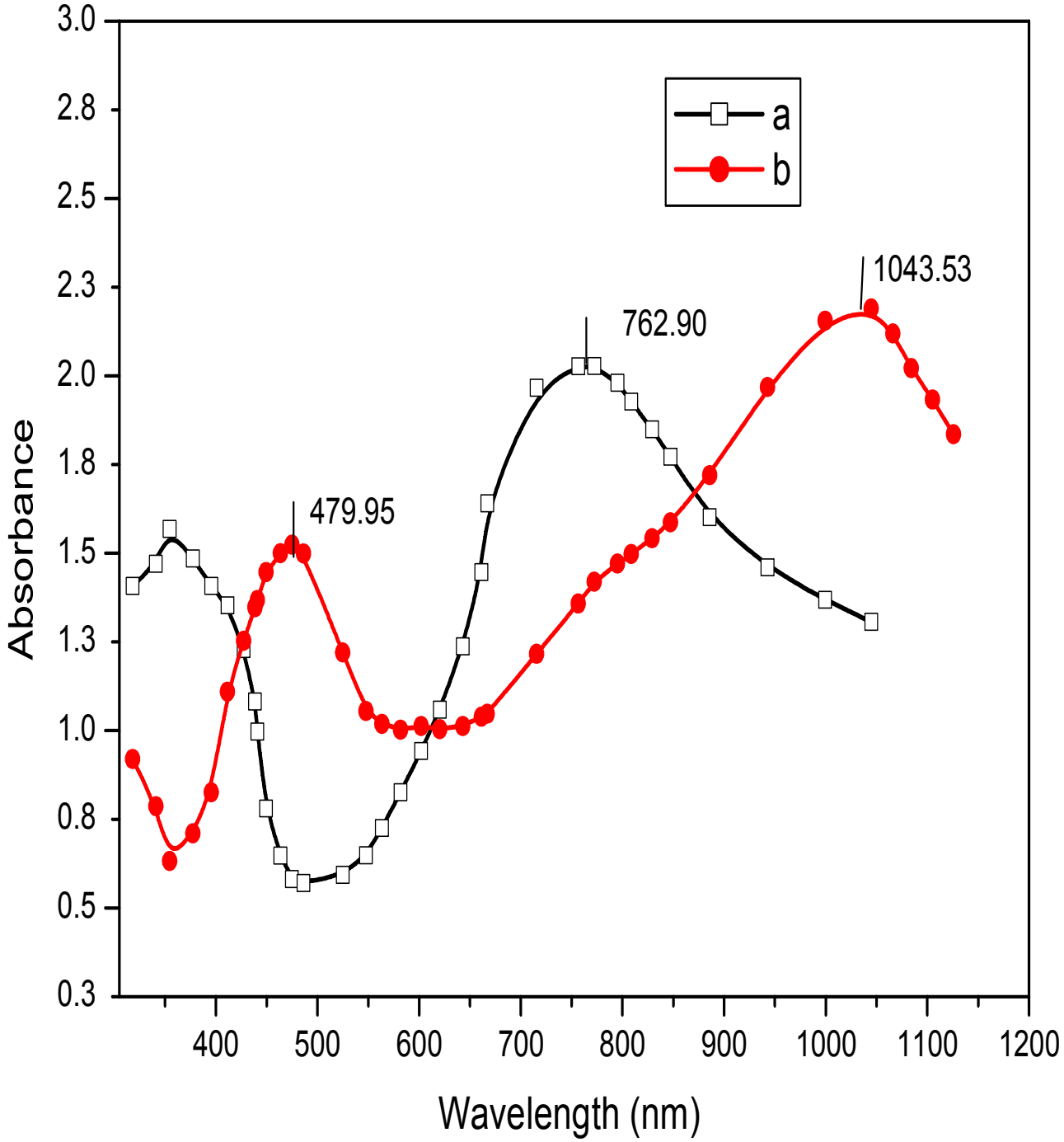

Fig. 3.3: UV-visible spectra of polyaniline doped with (a) sulphuric acid with at pH=0 and (b) concentrated sulphuric acid.

The shift of observed peak from 2 eV to1.6 eV during protonation indicates that both 1.6 eV and 2 eVhave the same origin and are associated with the presence of defects (polarons) resulting as a consequence of doping (polaron band). The peak 2.6 eV have been assigned to the electronic transition from the benzenoid ring to the quinoid ring [11]. The schematic representation of the evolution of a polaron and bipolaron in polyaniline is shown in Fig. 3.4

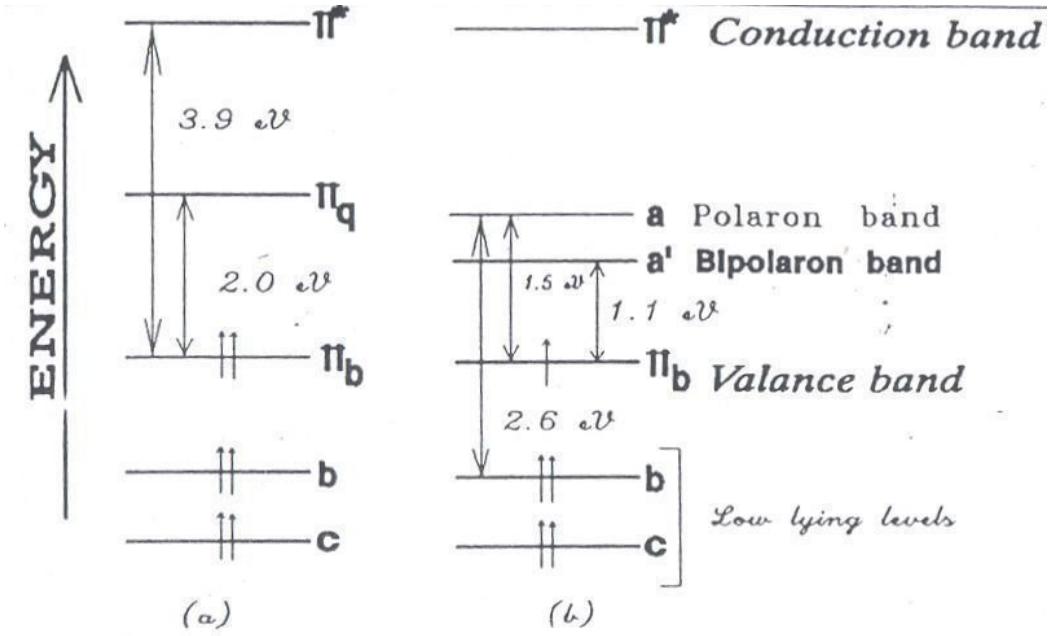

Fig. 3.4 : Energy level diagram, (a) emeraldine salt (b) emeraldine base form of Polyaniline.

3.4 Fourier Transform Infra-Red (FT-IR) Spectroscopy

FTIR spectra were measured by Perkin Elmer spectrometer using the KBr pallets technique. For structural characterization FTIR is an important physical tool. An FTIR spectrum of a chemically synthesized polyaniline in its respective doped and undoped state is shown in figure. Fig 3.6 shows vibration bands at 3445, 2981.88, 1492.314, 1292.90, 1125.68 and 793.45 cm^{-1} etc. These values are characteristic of polyaniline chain and are in agreement with theoretical predictions [6]. The

3445 m^{-1} vibration band has been attributed to the stretching vibration of secondary amine. The vibration band seen around 2981cm^{-1}has been ascribe to the aromatic C-H vibration. The 1600cm^{-1} vibration band is due to the C = C double bind of quinoid rings whereas 1492.32cm^{-1} vibration band arises due to vibration of C = C double bond associated with the benzenoid ring. The peak at 1500 may be due to strong symmetrical bending band and it may be due to secondary aromatic amines.The origin of 1292.90 cm^{-1} as yet completely understood. It has never been thought but it perhaps linked with various stretching and bending vibrations associated with C-N single bond. The vibration band at 1125.25 cm^{-1} is due to presence of C-N double bond and indicative of protonation. Significantly, the 1125.25 cm^{-1} is much pronounced in case of FTIR spectra (fig 3.6) of doped polyaniline. The vibration band at 793.45 cm^{-1} is attributed to C-H vibration band of paralinked phenyl ring. It confirms the predominance of para coupling in polymerization of aniline.

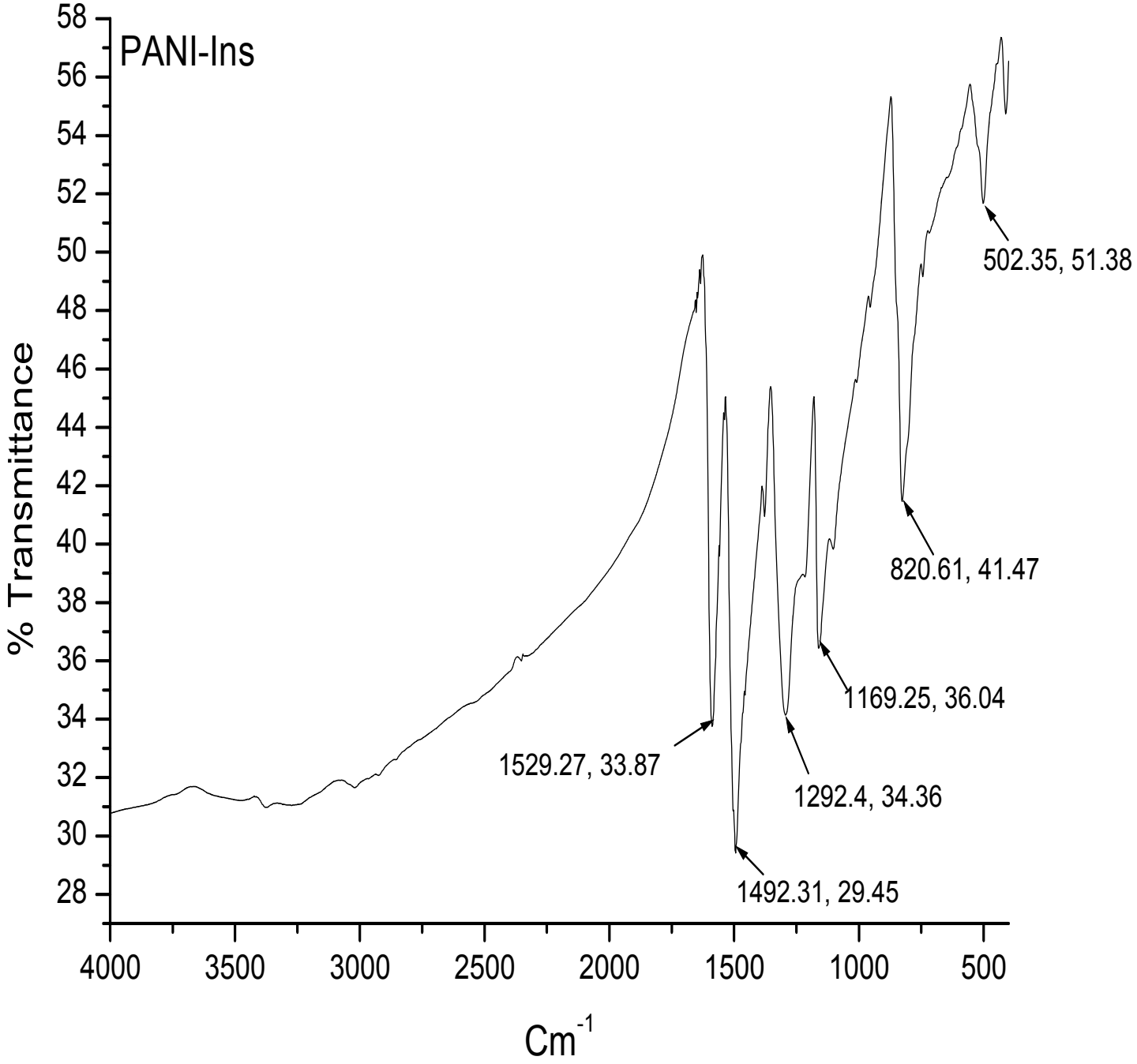
PANI-Ins
% Transmittance
Cm-1
502.35, 51.38
820.61, 41.47
1169.25, 36.04
1529.27, 33.87
1292.4, 34.36
1492.31, 29.45

Fig3.5: Fourier transform Infrared spectrum of polyaniline insulating

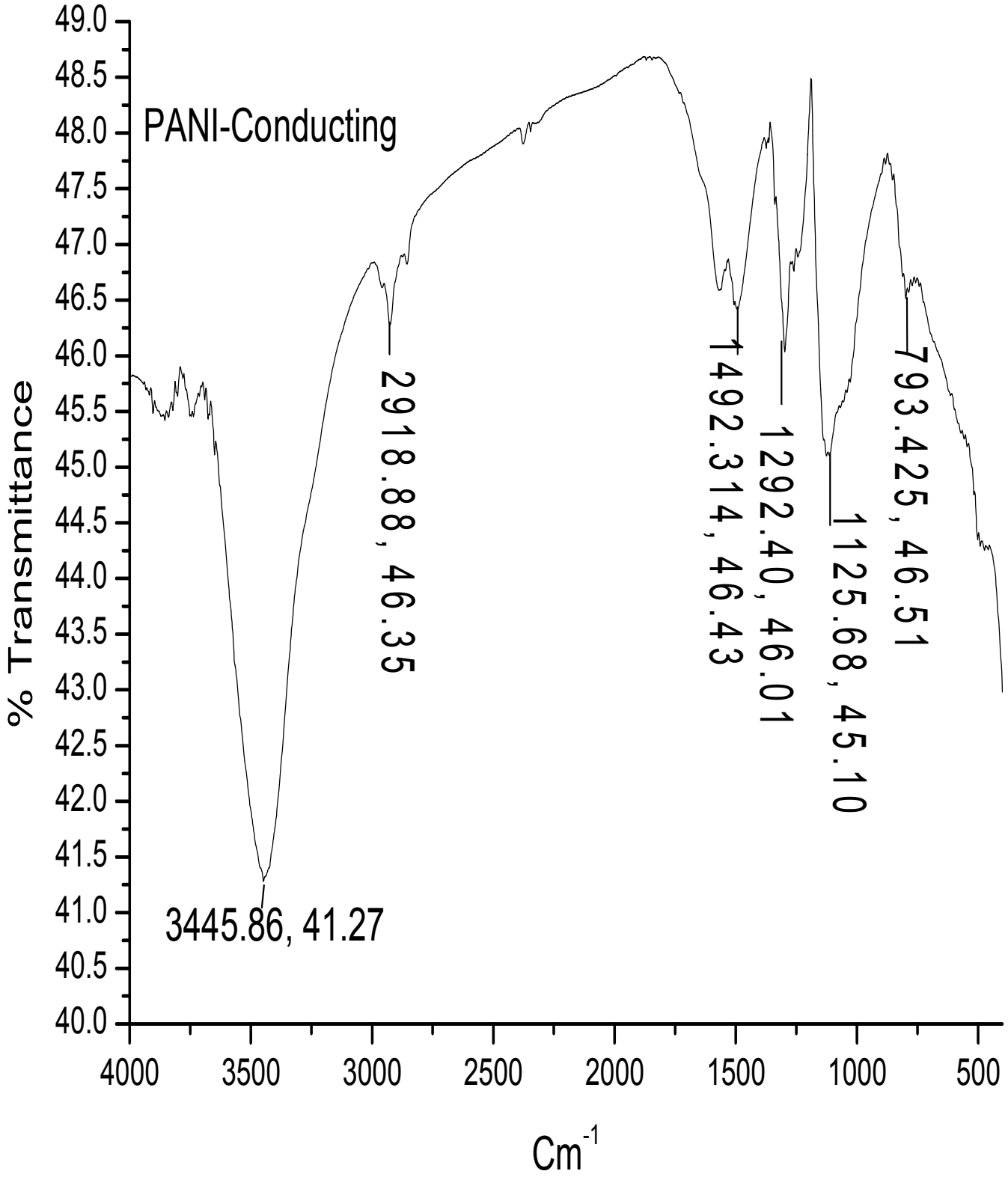

Fig. 3.6: Fourier transform Infrared spectrum of polyaniline conducting

3.5 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA is commonly used to determine polymer degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite material compositions.

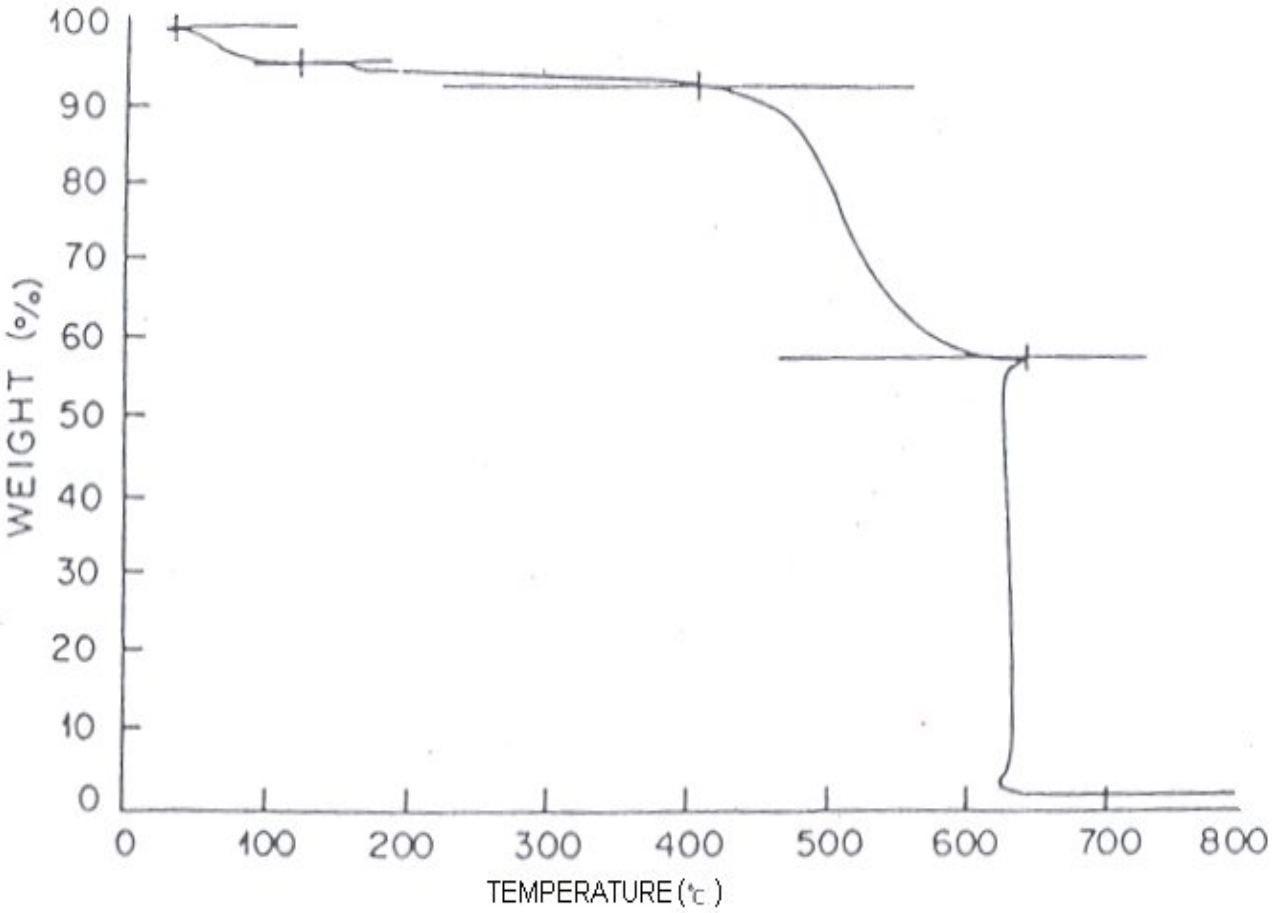

Fig. 3.7: TGA thermograph of undoped polyaniline

The weight loss from 125^0C to 400^0C is 3%.soon after the sample reaches 400^0C there is a tremendous weight loss (more than 35%). The very small weight loss (only 3%) cannot be due to polymer degradation. Large weight loss after 400^0C suggests that degradation of polymer starts after 400^0C. It can be concluded that the 260^0C exothermic peak arises as a consequence of inter chain cross-linking. This cross-linking is further supported by the observation that upon heating (300^0C in vacuum**),** solubility of undoped polyaniline decrease tremendously.

3.6 Cyclic Voltammetry

Fig 3.8 shows Polarization studies upon polyaniline have been performed by taking 0.2M aniline in 1M in a single compartment cell for setting the anodic potential limit both for electro synthesis as well as electroanalytical characterization. It shows that at 0.8V versus Ag/AgCl reference electrode there is a sharp rise in the current showing oxidation of aniline monomer. Polyaniline undergoes a reversible redox reaction. A cyclic voltammogram recorded for polyaniline at 20mV/s scan rate in 1M HCl medium has been shown in Fig.3.9

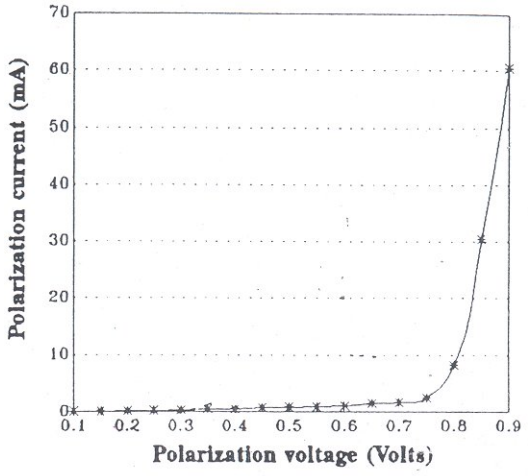

Fig.3.8. Polarization curve obtained for Polyaniline.

For recording CV potential have been cycled between -0.2V to 0.8V versus Ag/AgCl. The CV of ployaniline shows two redox paks at 0.18V and 0.75V versus Ag/AgCl. These redox peaks are

characterization of polyaniline. These peaks basically arise due to polyaniline deposits. The first peak is associated with the oxidation of aniline to radical cation whereas a second peak is due the oxidation of radical cation to the radical dication [7] as shown in Fig.3.10

It appears that the degradation of polyaniline starts due to increased anodic potential. Lower scan also accelerates both degradation and loss in elecrtroactivity. The degradation can be visualized by the loss of electroactive sites as well as appearance of the third peak at around 0.5V versus Ag/AgCl.this peaks become more and more preminent with increase of time.

Fig 3.9 shows that cyclic voltammogram of polyaniline. In the chemical polymerization mechanism, the dimer formation on is rate determining step, which is accompanied by the loss of electrons (e^-) and a proton of every aniline molecule [8, 9]. The dimer is then oxidized in one step to diimmine from with participation of two electrons due to its low oxidation potential in comparison with aniline. The redox couple situated within the range of less positive potentials has a progressive evolution (intensities of voltammetric currents increase with increasing the number of scanning cycles) and might be attributed to the dimer and , subsequently, to the polymer forming on the electrode surface.

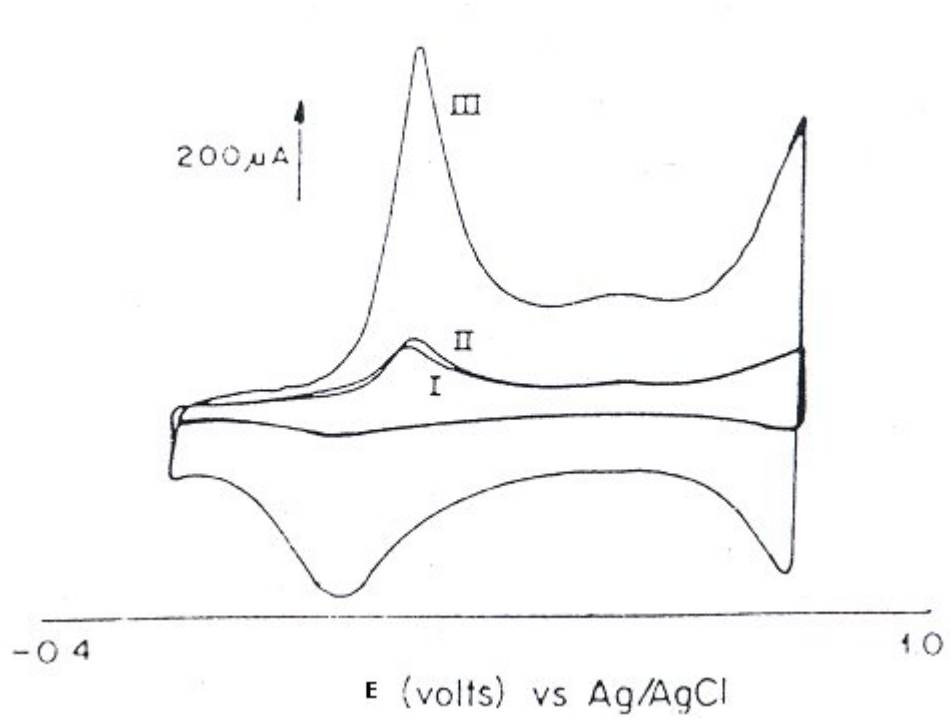

Fig3.9: Cyclic-voltammogram of polyaniline

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CHAPTER - 4

CONCLUSIONS AND FUTURE SCOPE

Chapter 4

CONCLUSION AND FUTURE SCOPE

1.1 Conclusion

The important conclusions of the present study are summarized as follows:

- Synthesis of polyaniline (insulating and conducting) has been successfully brought about.
- Results of UV-visible conducted on this conducting polymer poyaniline have revealed that the two electronic transitions at 325.24 nm (3.9eV) and 638nm (2eV) has been found in UV-Visible. The shift of peak from 2ev to 1.6eV during protonation is associated with the presence of defects (polarons) resulting as a consequence of doping.
- The results of FTIR spectroscopic investigations have been found to be consistent with the tentatively proposed structure of polyaniline in its oxidation states. Results of FTIR conducted on this conducting polymer poyaniline have revealed that the vibration band at 1169.25 cm^{-1} observed in undoped polyaniline due to presence C-N double bond has been shifted to vibration band 1129.27 cm^{-1} after doping.
- It has been shown that undoped polyaniline is thermally stable up to 400^0C.
- The cyclic voltammetric of polyaniline shows two redox peaks at 0.18 and 0.75 volts which are characteristics to the polyaniline.

1.2 Future Scope

The studies presented in this thesis further suggest some area of academic and technological importance as follows.

1. The conductivity of polyaniline varies with various dopants, but the mechanism of conduction in polymer is not still very clear. Therefore the mechanism of conduction in polyaniline with various dopants needs to be investigated.
2. The polyaniline and its composite with nanotube and several other nano particles such asTiO_2, $BiFeO_3$, Ferrites etc. are of technical importance. The applications of polyaniline -nanocomposite for technological applications need to be explored.
3. The composite of polyaniline with some new class of materials such as multiferroics is of academic interest. Therefore the microstructural, structural, dielectric, magnetic and transport properties of polyaniline-multiferroic composite need to be investigated.