A thesis on

Synthesis And Characterisation of Poly(aniline-co-fluoroaniline)

Thesis submitted in partial fulfillment of the requirement for
The award of the degree of
Masters of Science
In
PHYSICS

Under
the supervsion of
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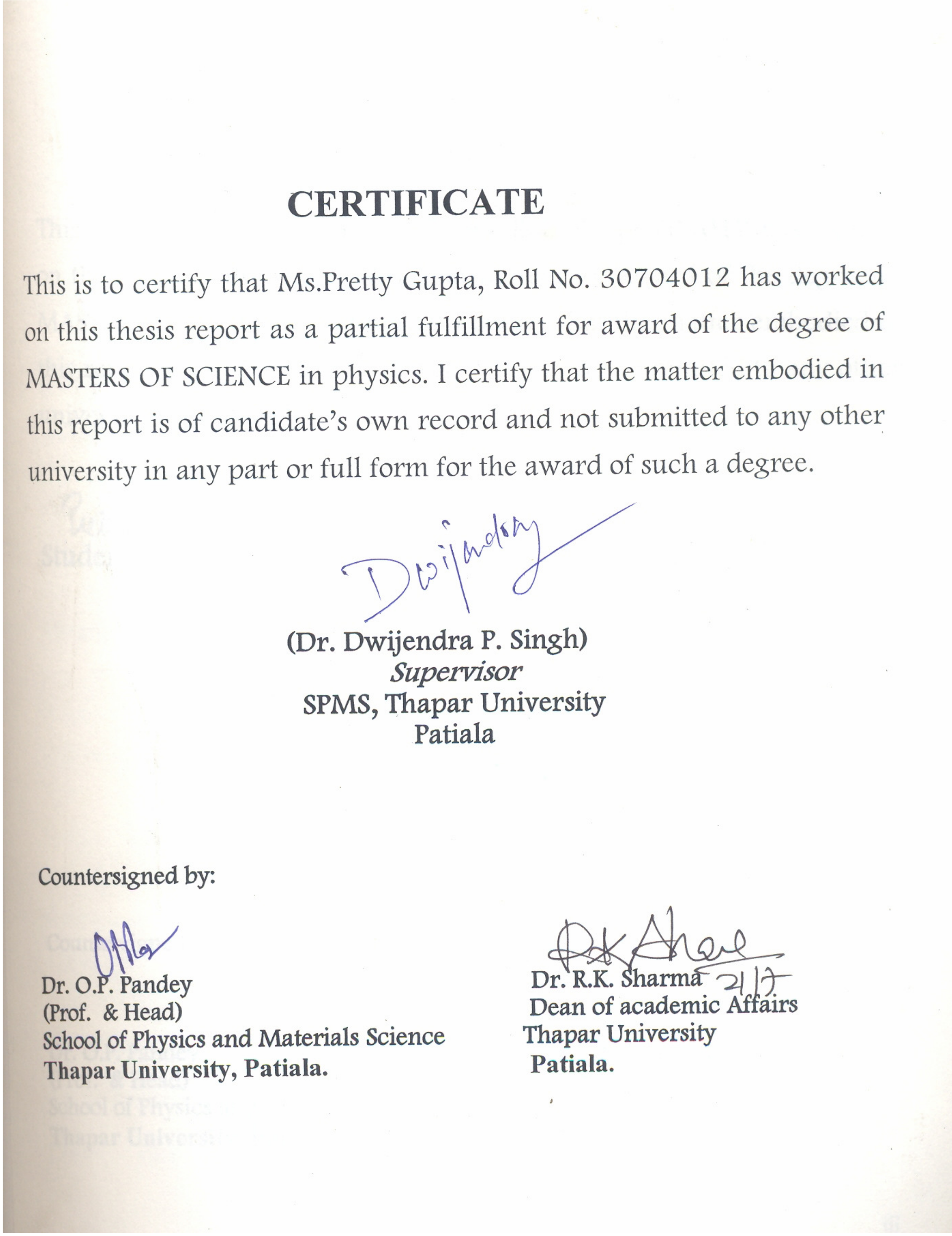
Dedicated
To My
Loving Family



CERTIFICATE

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ABSTRACT

The polyaniline is widely study conducting polymer due to its application in several devices such as biosensor, gas sensor etc. The polymer based on substituted aniline has been found to show better solubility, modified interfacial property and polymerization. The studies in the present work are related with synthesis, characterization and polymerization of poly (aniline-co-fluoroaniline). The poly (aniline-co-fluoroaniline) has been synthesized by using copolymerization of aniline and fluoroaniline monomers. The FT-IR studies has shown vibration band at 1128 cm^{-1}, which confirms the attachment of fluoro group. The fluoro maxima in UV-visible spectroscopy have been observed at 321 nm and 579 nm for the poly (aniline-co-fluoroaniline), which is slightly less as compared to polyaniline. The redox peaks in cyclic voltammetry is coming at 0.28 V respectively and in the subsequent scans the increased anodic current has confirmed the polymerization of poly (aniline-co-fluoroaniline).

LIST OF FIGURES

LIST OF ABBREVIATIONS

PANI	Polyaniline
$(\text{-B-NH-B-NH-})_n$	"B" Benzoid rings
$(\text{-B-N=Q-N=})_n$	"Q" Quinoid rings
THF	TETRAHYDROFURAN
NMP	N-Methylpyrrolidone
DMF	DIMETILFORMAMIDA
DMSO	Dimethyl Sulfoxide
Cl	Chlorine
F	Fluorine
PCIANI	Poly(2-chloroaniline)
PIANI	Poly(2-iodoaniline)
Poly(An-FAn)	Poly(aniline-co-fluoroaniline)
FT-IR	Fourier Transform Infra Red
UV-visible	Ultra Voilet Visible Spectroscopy
CV	Cyclic Voltammetry
APS	Ammonium Persulphate
NMP	N-Methylpyrrolidone
IR	Infra Red
A	Absorbance
T	Transmittance
I	Intensity
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Occupied Molecular Orbital
Epa	Anoidic Peak Potential
Epc	Cathodic Peak Potential
HCl	Hydrochloric Ac
SN	Signal to Noise Ratio

CONTENTS

CHAPTER-1 INTRODUCTION

CHAPTER-2 EXPERIMENTAL

CHAPTER-3 RESULTS AND DISCUSSIONS

CHAPTER-4 CONCLUSIONS AND FUTURE SCOPE

CHAPTER-1
INTRODUCTION

1.1 Introduction

Conducting polymers have drawn scientific, academic and technological interest since last decade [1, 2]. These polymers could be noble electronic material in various applications such as electromagnetic shielding [3], thin film transistor [4], light emitting devices [5], sensors [6] etc. Among the class of conducting polymers, polyaniline has become of particular interest due to its outstanding properties [7-11]. Polyaniline becomes conducting after doping due to partial oxidation and reduction. The conductivity of polyaniline based polymers can be tailored to achieve required conductivity for a given purpose. The resultant blend can be as conducting as metals and as insulating as glass [12]. Therefore, polyaniline based product are easy to fabricate in required shape. To increase the solubility of polyaniline in various inorganic solvent has also been a challenge for the scientists. The polymer of substituted aniline has shown better solubility. The substituent group in the units of polymer chain causes a decrease in the stiffness of polymer chain and result in better salvation. These substituted groups may also affect markedly the polymerizability of aniline [13-16].

1.2 Structure of Polymers

The structure of polymers includes physical and chemical structure of polymer. They have been described in following subsections.

1.2.1Physical structure

Segments of polymer molecules can exist in two distinct physical structures. They can be found in either crystalline or amorphous forms. Crystalline polymers are only possible if there is a regular chemical structure (e.g. homo-polymers or alternating copolymers), and the chains possess a highly ordered arrangement of their segments. Crystallinity in polymers is favored in symmetrical polymer chains; however, it is never 100%. These semi-crystalline polymers possess a rather typical liquefaction pathway, retaining their solid state until they reach their melting point at T_m.

Amorphous polymers do not show order. The molecular segments in amorphous polymers or the amorphous domains of semi-crystalline polymers are randomly arranged and entangled.

Amorphous polymers do not have a definable T_m due to their randomness. At low temperatures, below their glass transition temperature (T_g), the segments are immobile and the sample is often brittle. As temperatures increase close to T_g, the molecular segments can begin to move. Above T_g, the mobility is sufficient (if no crystals are present) that the polymer can flow as a highly viscous liquid. The viscosity decreases with increasing temperature and decreasing molecular weight. In a semi-crystalline polymer, molecular flow is prevented by the portions of the molecules in the crystals until the temperature is above T_m. These effects can most easily be seen on a specific volume versus temperature graph in fig 1.1.

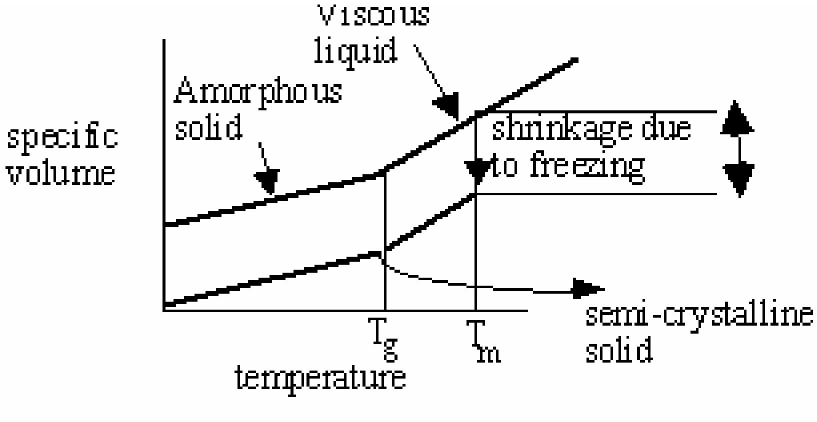


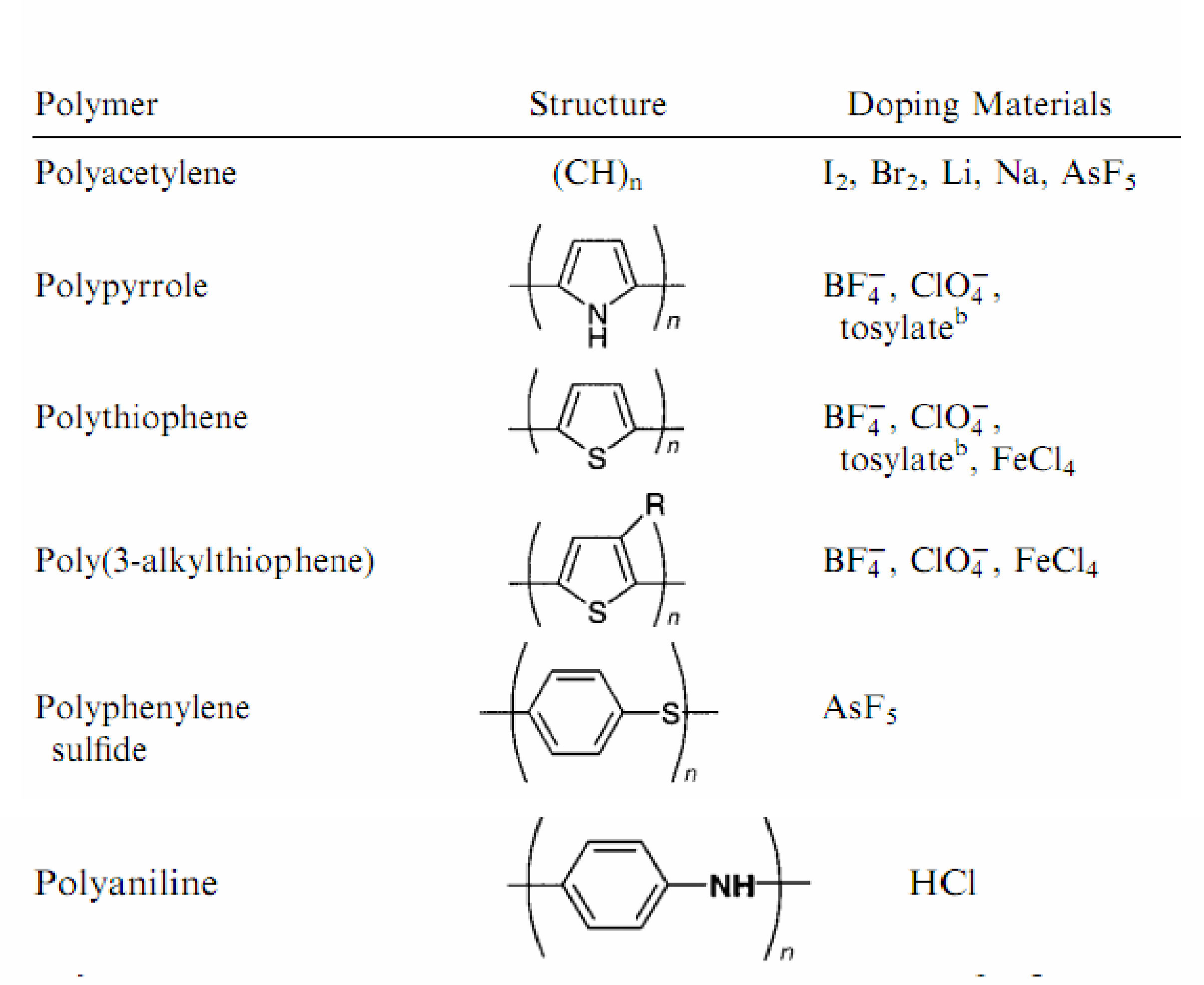
Figure1.1: Specific Volume versus Temperature graph.

In the arc between Tg and Tm, the semi-crystalline polymer is a tough solid. The amorphous material changes to a viscous liquid after Tg. This is when the material can be easily deformed.

1.2.2 Chemical Structure and conductivity of polymer

Figure 1.2 shows the chemical structure of some of the polymers. The polymers are consisting of alternating single and double bonds, such a polymer is called conjugated polymer. Atoms in the polymer chain are covalently bonded so that they are insulator. 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 π- bonded electrons, such molecule may be conducting.

Figure 1.2: The chemical structure and conductivities of some polymers



Polymer	Structure	Doping Materials
Polyacetylene	$(CH)_n$	I_2, Br_2, Li, Na, AsF_5
Polypyrrole		BF_4^-, ClO_4^-, tosylate[b]
Polythiophene		BF_4^-, ClO_4^-, tosylate[b], $FeCl_4$
Poly(3-alkylthiophene)		BF_4^-, ClO_4^-, $FeCl_4$
Polyphenylene sulfide		AsF_5
Polyaniline		HCl

The polymers can be made conducting by doping. Figure 1.2 shows the conductivity of different polymers with various dopants. 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.

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 10^{-8} S/cm to more than 10^{2} S/cm. However, only one form, called emerlaldine salt is electrically conducting.

1.3 Structure of polyaniline

Polyaniline refers to a general class of conducting polymers composed of benzoid and quinoid character, connected by nitrogen. Polyaniline is built up from reduced $(B\text{-}NH\text{-}B\text{-}NH\text{-})_n$ and oxidized $(\text{-}B\text{-}N{=}Q\text{-}N{=})_n$ 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. A 50% oxidized form and a fully oxidized form of pernigraniline was obtained [17].

The polyaniline structure consists of up to 1000 or up to more repeating units, and conductivity 10^{-11} to 10 S/cm. 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. The polyaniline of ideal emeraldine base form contains alternating amine and imine repeat units [18, 19].

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 vacuo. Polyaniline has a chemically flexible –NH- group in its backbone which is responsible for interesting chemistry and physics [20]. The electrochemical stability of polyaniline depends on the pH conditions as well as the counter-ion of the Bronsted acid used for doping.

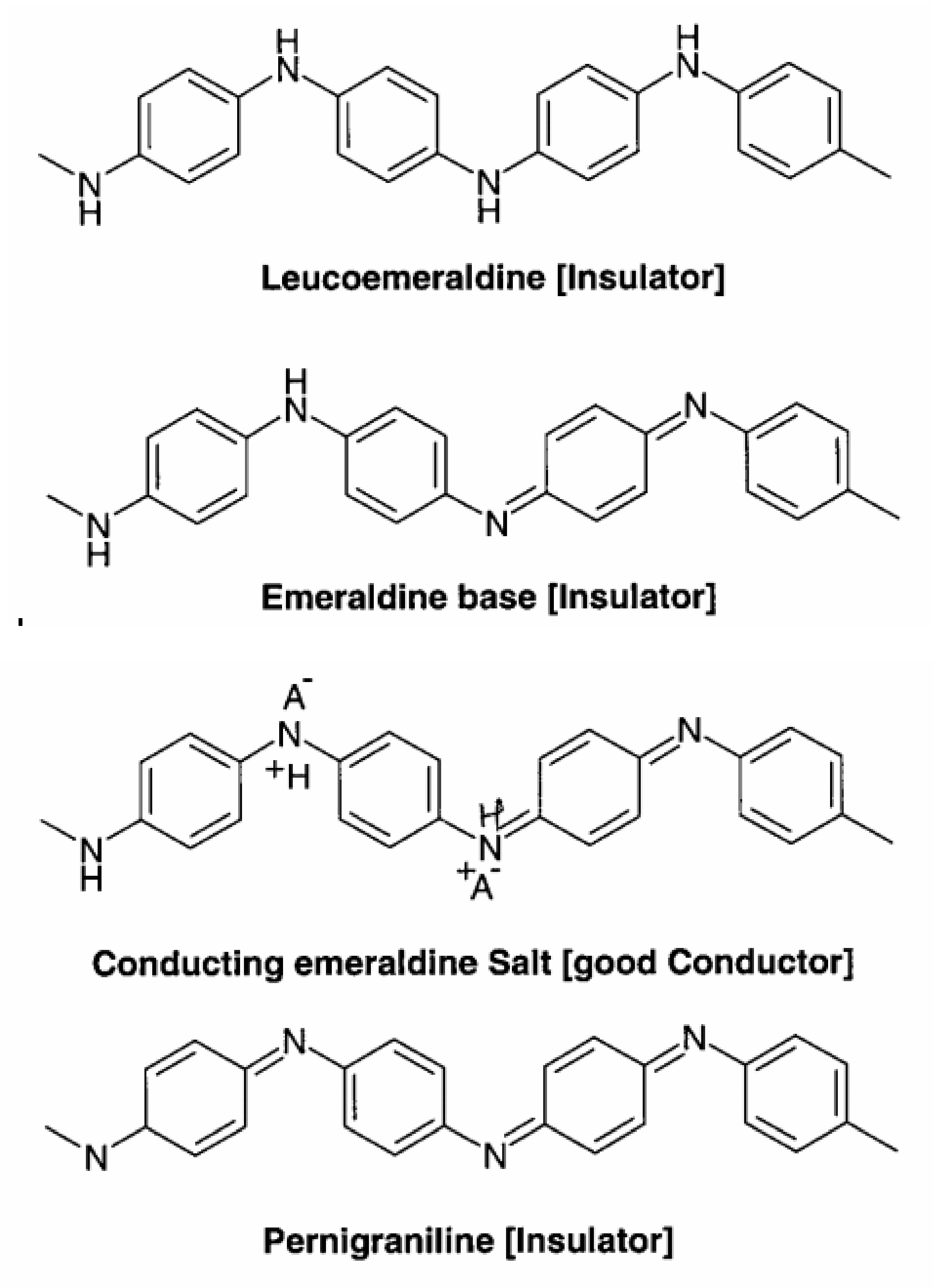


Figure 1.3: Molecular design of four oxidation states of Polyaniline [17].

1.4 Processing 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. Polymerization of substituted monomers [21, 22], mixing with processable polymers [23], preparation of molecular composites [24], and copolymerization [25] etc. have been utilized for processability.

Among the various techniques described above copolymerization is the easiest and the effective method of introducing systematic changes in the polymer properties and is widely used in the production of commercial polymers. The copolymerization methodology has been briefly described in the following subsection.

1.4.1Copolymerisation

Copolymerization is usually defined as polymerization in which two or more structural distinct monomers are incorporated into a given polymer chain.

In general, copolymers exhibit physical and mechanical properties far different from those of homopolymers. Thus the characteristics of these conducting polymers are different from those of blends of the same individual homopolymers. The properties of copolymers can also be modified by varying either the ratio of the various constituents or the manner by which these are chemically attached. Such conducting copolymers exhibits improved electrical conductivity compared to that of homopolymers. This method provides a versatile route of systematic modification of physico-chemical properties.

Considerable efforts have been made towards the copolymerization of aniline monomers by some workers in order to improve processability of the polymer [26-28] However, these polymers are unsuitable for device fabrication either due to low conductivity [26], or less crystallinity [27], or due to a number of defects present in these polymers [28].

Polyaniline has been considered to be an important futuristic electronic material due to the unique conduction mechanism, ease of synthesis, yield, good electrical conductivity and good thermo-environmental stability [29, 30]. But the poor processability is the main drawback associated with this polymer. On the other hand, poly (2-fluoroaniline) has poor electrical conductivity due to the presence of electron withdrawing fluoro group but has been found to be soluble in various organic solvents like THF, NMP, DMF, and DMSO etc. The problem of processability of polyaniline can be reduced by block copolymerization [31-34], blend of rigid polymers [35].

1.4.1.1 Copolymers

So far, the discussion has been confined to polymers with only a single type of repeat unit, but in reality, a large and growing number of commercial polymers are actually composed of different types of unit attached together by chemical covalent bonds. They are known as copolymers, and can comprise just two different units (binary copolymers) or three (ternary), and so on [36]. It is one of the common strategies used by molecular engineers to manipulate the properties of polymers to gain just the right combination of properties for a specific application.

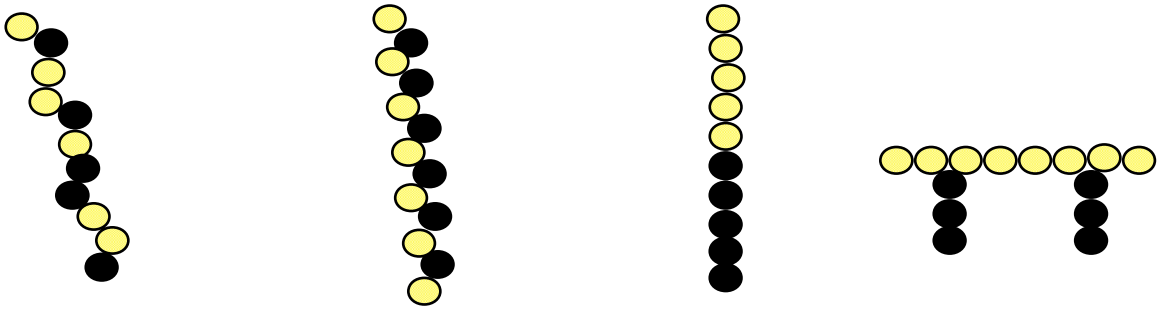
Polymers may contain monomers of identical or different chemical structure. Polymers made up of only one type of monomeric units are called ‘Homopolymers’, whereas those polymeric compounds which are built up of two different types of monomer units in their chain are called ‘Copolymers‘ (or mixed polymers). Polymers with three different types of monomeric units are sometimes called ‘terpolymers‘. The advantage of such polymeric structures is that a single polymer molecule can have the properties of both the entities, which can be selected suiting to the end use of application. Such possibility hardly exists in simple molecules.

Copolymers are further classified as alternating copolymers or statistically regular (where both different repeating monomeric units are joined side by side) and random copolymers or statistically irregular (where there is no regularity in the joining of units of two different monomers). Copolymers can also be of block or graft types.

1.4.1.2 Chemical Structure of Copolymer

The monomers in a polymer can be arranged in a number of different ways. As indicated above, both addition and condensation polymers can be linear, branched, or cross-linked. Linear polymers are made up of one long continuous chain, without any excess appendages or attachments. Branched polymers have a chain structure that consists of one main chain of molecules with smaller molecular chains branching from it. A branched chain-structure tends to lower the degree of crystallinity and density of a polymer. Cross-linking in polymers occurs when primary valence bonds are formed between separate polymer chain molecules.

Chains with only one type of monomer are known as homopolymers. If two or more different type monomers are involved, the resulting copolymer can have several configurations or arrangements of the monomers along the chain [37]. The four main configurations are depicted below:



Random Copolymers: Different monomers are randomly arranged within the polymer chains.

Alternating Copolymers: Different monomers show a definite ordered alternation.

Block Copolymers: Different monomers are arranged in long blocks of each monomer.

Graft Copolymers: Appendages of one type of monomer are grafted to a long chain of the other.

Figure 1.4: Copolymer configurations.

Copolymerization is usually defined as polymerization in which two or more structurally distinct monomers are incorporated into a given polymer chain. It modifies polymer chain, and modulates both intramolecular and intermolecular forces, including the properties such as melting point, glass transition temperature, crystallinity, solubility, elasticity, permeability, chemical reactivity etc.

Thus the characteristics of these conducting polymers are different from those of blends of the same individual homopolymers. The properties of copolymers can also be modified by varying either the ratio of the various constituents or the manner by which these are chemically attached. Considerable efforts have been made towards the copolymerization of aniline monomers by some workers in order to improve processability of the polymer [38-40]. However, these polymers are unsuitable for device fabrication either due to low conductivity [38], or less crystallinity [39], or due to a number of defects presents in these polymers [40].

1.4.1.3 Doping in Conducting Polymers

Doping in polymers is different from that in inorganic or traditional semiconductors [41]. The nature of dopants plays an important role in the stabillity of 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.

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 [42]. 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 [42-45].

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

Doping results in rearrangements of the polymer chains and thereby new ordered structures are formed. The dopant concentration may be as high as 50% [45]. 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 [46]. 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 [44, 45].

1.5 Conductivity of Conducting Polymers

It is just an enigma about the conductivity of conducting polymers, till now there is not any suitable method exist for improving the conductivity of conducting polymers. There are several efforts have been taken for improving the conductivity

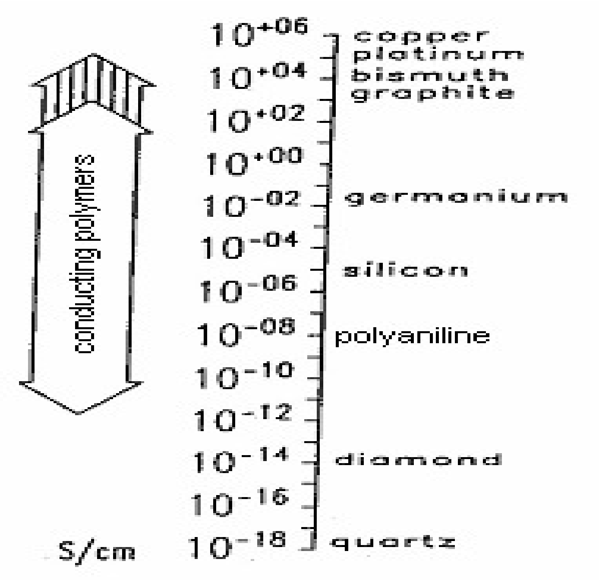


Figure 1.5: Conductivity Chart of Various Conducting Polymers

1.5.1 Charge Carriers 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. 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.

1.5.2 Band Gap in Conducting Polymers

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 conduction 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 [47]. 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 many of the well-suited conducting polymers is greater than 2.0 eV.

1.5.3 Conduction Mechanism and Electrical Behaviour 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 [48]. In the band theory, the atomic orbitals of each atom overlap with the same orbitals of their neighbourhood 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 the conducting polymers, it is essential to know about the type of the charge carriers and the band structure.

The mechanism of conduction and behavior of charge carriers in the conducting polymers have been explained using the concept of polarons and bipolarons.

In degenerate ground state (two equivalent resonance forms), the bipolaron dissociates into two independent cations, which are spinless and are called solitons. Solitons do not form in polymers with nondegenerate ground state.In non-degenerate state. Resonance forms are not identical if they are superimposed.. Doping with a suitable dopant can increase the concentration of charged solitons.

1.6 Halo Derivatives of Aniline

The polymers of substituted anilines have shown better solubility. The substituent groups present in the units of the polymer chain cause a decrease in the stiffness of the polymer chain and result in better solvation. Several substituted PANIs with electron-donating groups (alkoxy, alkyl, etc.) have been reported in the literature; these polymers are soluble in common solvents but exhibit lower electrical conductivity values (10^{-3} to10^{-1} S/cm) than unsubstituted PANI. These results indicate that the side groups may markedly affect the polymerizability of anilines. [49].

The synthesis of different homopolymers and copolymers derived from anilines bearing electron-withdrawing groups has been reported. The electrochemical polymerization of halogen-substituted anilines was done and reported the chemical copolymerizations of aniline with mono-ortho-halogenated anilines (2-chloroaniline and 2-fluoroaniline), and they showed that the presence of Cl- or F-substituted groups in the ortho position did not adversely affect the polymerization.

The measured electrical conductivity of the homopolymers, poly (2-chloroaniline) (PClANI) and poly (2-iodoaniline) (PIANI), was less than 10^{-6} S/cm and the electrical conductivity of the copolymers were strongly dependent on the amount of the substituted aniline incorporated.

There is a decrease in the electrical conductivity of the copolymers with respect to polyaniline takes place due to the incorporation of the fluoro- and chloro-substituted anilines into the polyaniline chain.

1.7 Motivation and Aim of Thesis

The various groups have studied the properties of substituted functional group in polyaniline [50-53]. The substituted functional group has been found to improve the different properties useful for the processability and electronic application of polyaniline. The modified properties include protonic doping ability [50], improved surface and interface characteristics [51], improved solubility [52], and polymerization [53]. Therefore synthesis of the substituted group polyaniline is important. Hence, the aim of the work presented in the thesis includes

1. Synthesis of poly (aniline-co-fluoroaniline)
2. Characterization of poly (aniline-co-fluoroaniline)
3. The study of polymerization of poly (aniline-co-fluoroaniline)

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CHAPTER-2

EXPERIMENTAL

2.1 Introduction

Several methods are used to synthesize conducting polymers. Powders of these polymers can be prepared by chemical methods. This chapter presents the details of the experimental techniques applied for synthesis and characterization of PANI (polyaniline) and poly (An-FAn) poly (aniline-co-fluoroaniline). The powdered samples of PANI and poly (aniline-co-fluoroaniline) have been synthesized by using chemical polymerization and copolymerization respectively. FTIR spectroscopy has been used for finding out the presence of various functional groups. UV-visible spectroscopy has been employed for determining the optical band gap. The cyclic voltammetry has been used for studying the redox behavior of synthesized polymers.

2.2 Synthesis

There are different methods by which conducting polymers can be synthesized, depending on the desired applications [1]. In the present work, poly (aniline-co-fluoroaniline) has been synthesized by copolymerization method, which has been discussed in the following section.

2.2.1 Chemical Synthesis of Conducting Poly (aniline-co-fluoroaniline)

In chemical oxidative polymerization, a monomer is polymerized by 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 a low temperature range (0-5^{o}C) by placing the beaker in ice bath, to achieve better yield and better quality of a polymer and to avoid the formation of oligomers [2].

Poly (An-FAn) was chemically synthesized by copolymerization of aniline and 2-fluoroaniline using ammonium persulphate [$(NH_4)_2S_2O_8$] as an oxidant. A mixture consisting of 2.80 mL of aniline (0.1 M) and 2.90 mL of 2-fluoroaniline (0.1 M) was dissolved in 150 mL of 1 M HCl. The temperature of solution was maintained at 0–2°C and constantly stirred for about 1 h. To this solution was added drop by drop another solution of 12.5g ammonium persulphate in 100 mL distilled water. The reaction was continued for 24 h, after which green precipitates were filtered.

The filtrate was washed with 1 M HCl until it became colorless, followed by washing with methanol. The precipitate was dried in vacuum oven at 80°C for about 5 h. The resulting polymer is in doped form and after dissolving in aqueous alkali it becomes undoped.

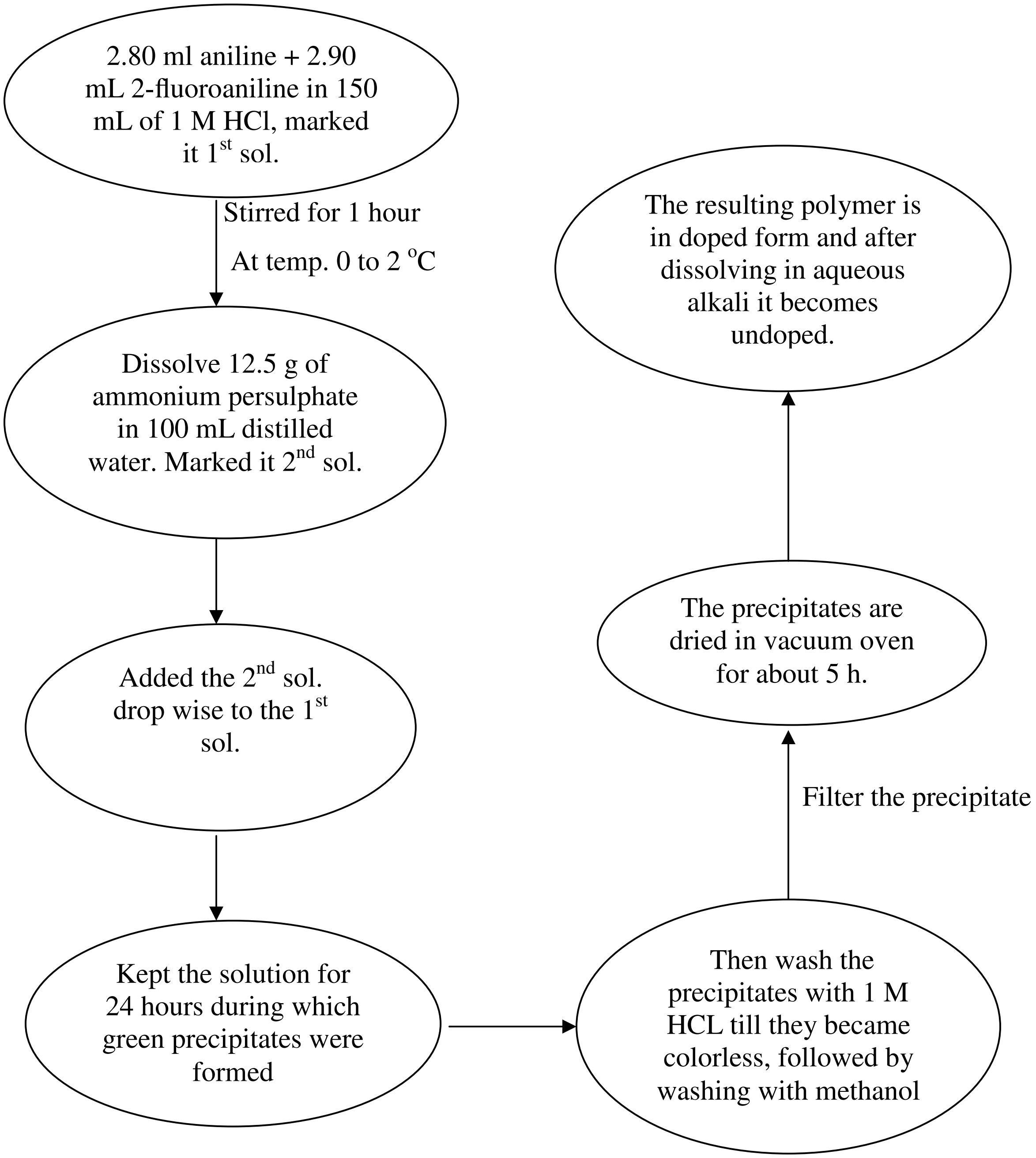

Figure 2.1: Flow chart for the synthesis of the poly (aniline-co-fluoroaniline)

2.2.2 Chemical Synthesis of Insulating Poly(aniline-co-fluoroaniline)

Undoped conducting polymer was obtained by treating the precipitate with aqueous ammonium hydroxide solution and constantly stirring for about 48 h. The powder was then collected on a Buchner funnel and was washed with distilled water several times. The resulting powder was dried at 80°C for about 5 h in a vacuum oven. This form of polymer is an insulator with high resistance. The ultimate conductivity and other properties of conducting polymer depends 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 either in protonic or ionic form yielding polymer powder with required conductivity and morphology [2].

The poly (An-FAn) films were prepared by casting a poly (An-FAn) solution in NMP on a Petridish and drying under dynamic vacuum at 70–80°C. The solution-cast copolymer film was utilized to measure electrical conductivity and tensile strength.

The chemical synthesis was performed using a water bath to maintain the temperature below 5°C of the solution.

The characteristic properties of the Ammonium Persulphate utilized for the synthesis of poly (An-Fan) has been described in the following subsection.

2.2.1.1 Characteristics of Ammonium Persulphate

Ammonium persulfate is a white, crystalline, odourless salt. It is used as initiator for the polymerization of monomers and as a strong oxidizing agent in many applications. It has the particular advantage of being almost nonhygroscopic, of having a particularly good storage of stability as a result of its extremely high purity and of being easy and safe to handle. APS is a suitable initiator for the emulsion or solution polymerization of acrylic monomer, vinyl acetate, vinyl acetate, vinyl chloride etc. And for the emulsion copolymerisation of styrene, acrylonitrile, butadiene etc.

APS is also a kind of oxidizing agent:

(1) Used in cleaning and picking of metal surface.
(2) Used in accelerated curing of low formaldehyde adhesives.
(3) Used in modification of starch, production of binders and coating materials.
(4) Desizing agent and bleach activer
(5) An essential component of bleaching formulations for hair cosmetics.

2.3 Material Characterization Techniques

Powdered form polymer has been characterized by using spectroscopic techniques. The spectroscopic techniques include the FTIR and UV-visible spectroscopy. The cyclic voltammetry has been used for electrochemical characterization. These characterization techniques have been describe in the following subsections

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 polymers. The details of these techniques have been discussed in the following subsections.

2.3.1.1 Fourier Transform Infra-Red Spectroscopy

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 [3].

Infrared spectroscopy is one of the most powerful analytical techniques; which provides useful information about the structure of the molecules and bonding quickly. 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 (Figure 2.2). 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 [4].

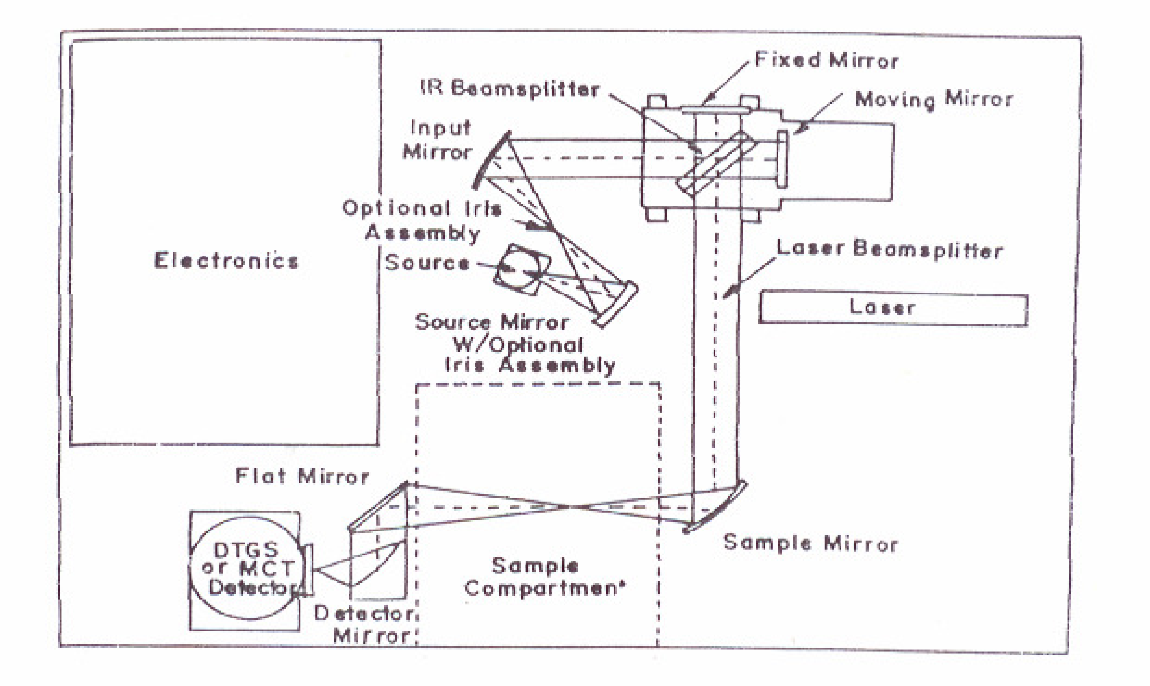

Figure2.2: Set-up of Fourier Transform Infra-Red Spectroscopy

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;

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

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 spectrum transmittance (T) versus wave number (cm $^{-1}$) has been plotted.

Optical spectroscopy has been widely used for the characterization of nanomaterials, and it can be categorized into two groups: absorption and emission spectroscopy. The absorption and emission spectroscopy determines the electronic structures of atoms, ions, molecules or crystals through exciting electrons from the ground to excited states (absorption) and relaxing from excited to ground states (emission).

2.3.1.2 Ultra-Voilet Visible Spectroscopy

UV-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 [5].

Light Range: 190-900 nm

Lower wavelength limit exists because of the absorption of <180 nm by atmospheric gases. We can get a limit of 175 nm if we purge the spectrometer with nitrogen gas. For working to <175 nm we need a vacuum spectrometer. The upper wavelength limit is determined by the wavelength response of the detector in the spectrometer.

Information:

- Quantative measurement of an analyte.
- Optical and electronic properties of the materials can be determined. Since UV and visible photons can promote electrons to higher energy states in the molecules and materials.

The absorption of UV radiation by organic compounds in the visible and ultraviolet region involves promotion of electrons in σ, л 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 л bond is called the л* orbital. As the n electrons do not form bonds, their antibonding orbitals are not associated with them. Transitions to antibonding л* orbitals are associated only with unsaturated centers in the molecule.

Principle of UV-visible spectroscopy

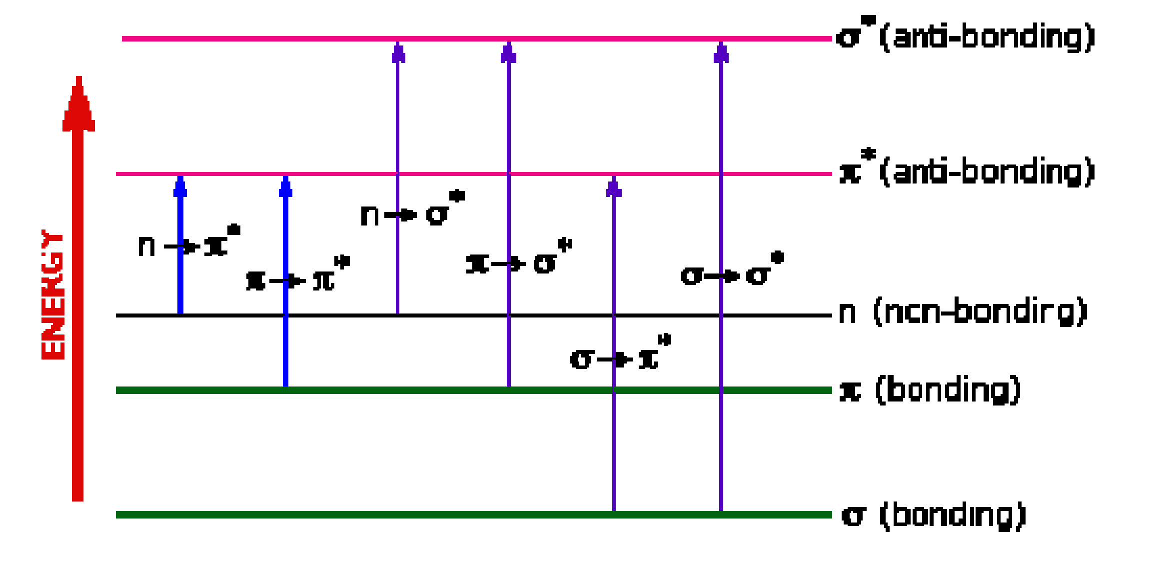

Figure 2.3: Energy Level Diagram

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 figure (energy label diagram). 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. [4].

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

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

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, $h\nu$ is incident photon energy. The band gap can be evaluated by plotting $h\nu$ 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 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.

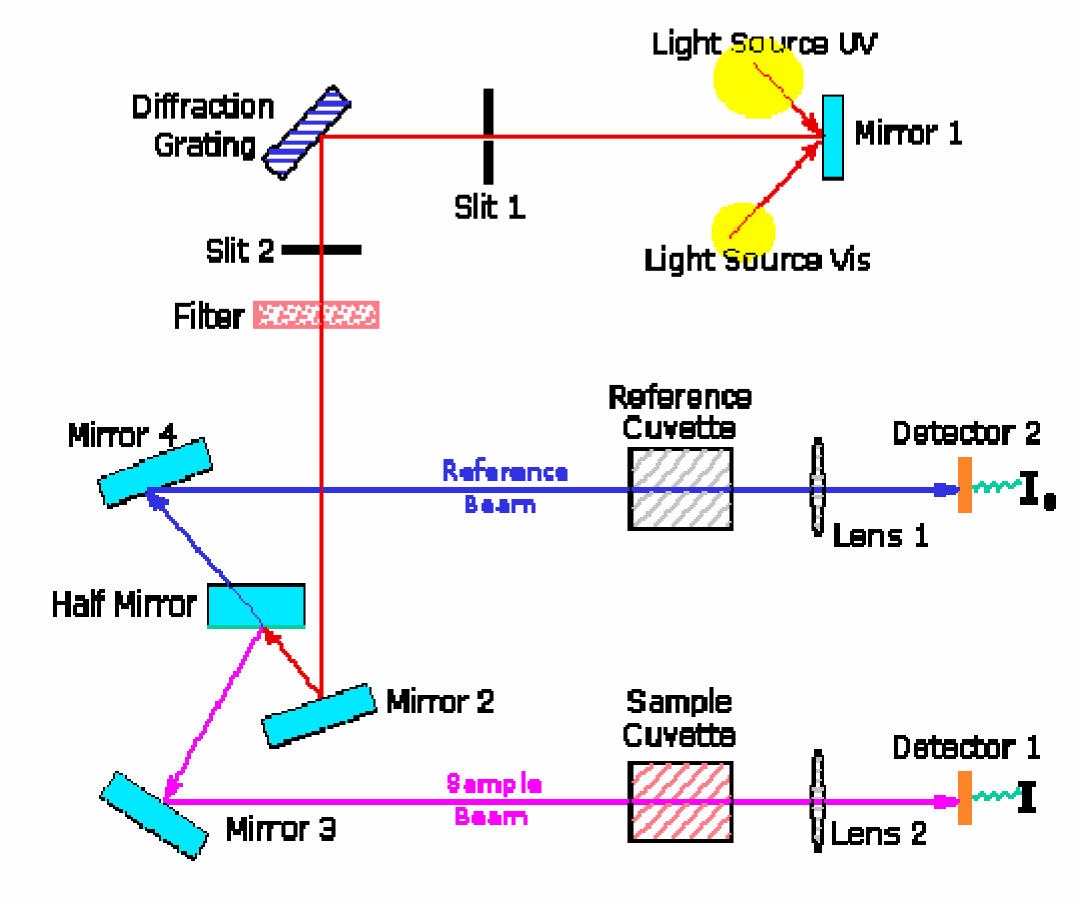

Figure 2.4: Block Diagram of Ultravoilet-Visible Spectrometer

If the sample compound does not absorb light of a given wavelength $I = I_o$. However, if the sample compound absorbs light then I is less than I_o and this difference may be plotted on a graph versus wavelength. Absorption may be presented as transmittance ($T = I/I_o$) or absorbance ($A = \log I_o/ I$). 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} [6].

N-Methylpyrrolidone (NMP) is the lactam of 4-methylaminobutyric acid and a very weak base. NMP is a chemically stable and powerful polar solvent. These characteristics are highly useful in a variety of chemical reactions where an inert medium is of concern. Despite the stability of NMP, it can also play an active role in certain reactions: hydrolysis, oxidation, condensation, conversion with chlorinating agents, polymerization and o-alkylation, and related reactions. NMP has desirable properties such as low volatility, low flammability, and relatively low toxicity.

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

2.3.2.1 Cyclic Voltammetry

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 reversibility 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} (anoidic current) and I_{pc} (cathodic current) and the peak potential, E_{pa} and E_{pc} (anoidic 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 [7]. 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

3.1 Introduction

Polyaniline is one of the most studied conducting polymer due to high electrical conductivity, redox and ion exchange property and various applications [1-5]. But the solubility of polyaniline in various organic solvents has posed a challenge. The solubility of PANI (polyaniline) in organic solvent decides its ease of processing in various forms for the application. The polyaniline with different type of functional group has been synthesized [6]. The presence of SO_3H groups on the polymer chain enables the sulfonated copolymer to possess intrinsic protonic doping ability. The polyaniline with substituted benzene diazonium ions controls the surface chemistry [7]. In this way substitutional functional group in polyaniline has been found to modify interfacial chemistry. Wang et. al. [8] have synthesized chlorinated polyaniline and found that it is soluble in THP both in doped and undoped form. Chemical synthesis and successful polymerization of polyfluoroaniline has been accomplished [9]. This substituted polyaniline has been found to modify the various properties. Therefore haloderivative of polyaniline has been synthesized in order to enhance its solubility in solvent. The attempt has been made for synthesizing the polyfluoroaniline. The substituted functional group by fluorine has been characterized by UV-visible spectroscopy, FT-IR spectroscopy and Cyclic Voltammetry.

3.2 Synthesis of poly (aniline-co-fluoroaniline)

Poly (An-FAn) was chemically synthesized by copolymerization of aniline and 2-fluoroaniline using ammonium persulphate $[(NH_4)_2S_2O_8]$ as an oxidant. A mixture consisting of 2.80 mL of aniline (0.1 M) and 2.90 mL of 2-fluoroaniline (0.1 M) was dissolved in 150 mL of 1 M HCl. The temperature of solution was maintained at 0–2°C and constantly stirred for about 1 h. To this solution was added drop by drop another solution of 12.5g ammonium persulphate in 100 mL distilled water. The reaction was continued for 24 h, after which a green precipitate was filtered. The filtrate was washed with 1 M HCl until it became colorless, followed by washing with methanol. The precipitate was dried in vacuum oven at 80°C for about 5 h. The resulting polymer is in doped form and after dissolving in aqueous alkali it becomes undoped.

3.3 Spectroscopic characterization

The spectroscopic characterization of polyaniline and poly (anile-co-fluoroaniline) has been carried out by using FTIR and UV-visible spectroscopy. The subsequent section will describe the result of FTIR and UV-visible spectroscopy.

3.3.1 Fourier Transform Infra-Red Spectra

Figure 3.1 and Figure 3.2 shows the infra-red spectra of chemically synthesized doped poly (An-FAn) and polyaniline powder. The curve of poly (aniline-co-fluoroaniline) shows the characteristic peaks at 3420, 1555, 1474, 1301, 1237, 1119 and 792 cm^{-1}, respectively. The peak at 1555 cm^{-1} is due to C=C double bond of quinoid rings, whereas the peak at 1474 cm^{-1} arises due to vibration of C=C double bond associated with the benzenoid ring. The peak at 1301 cm^{-1} has been attributed to a combination of C-N in quinoid and benzanoid sequences.

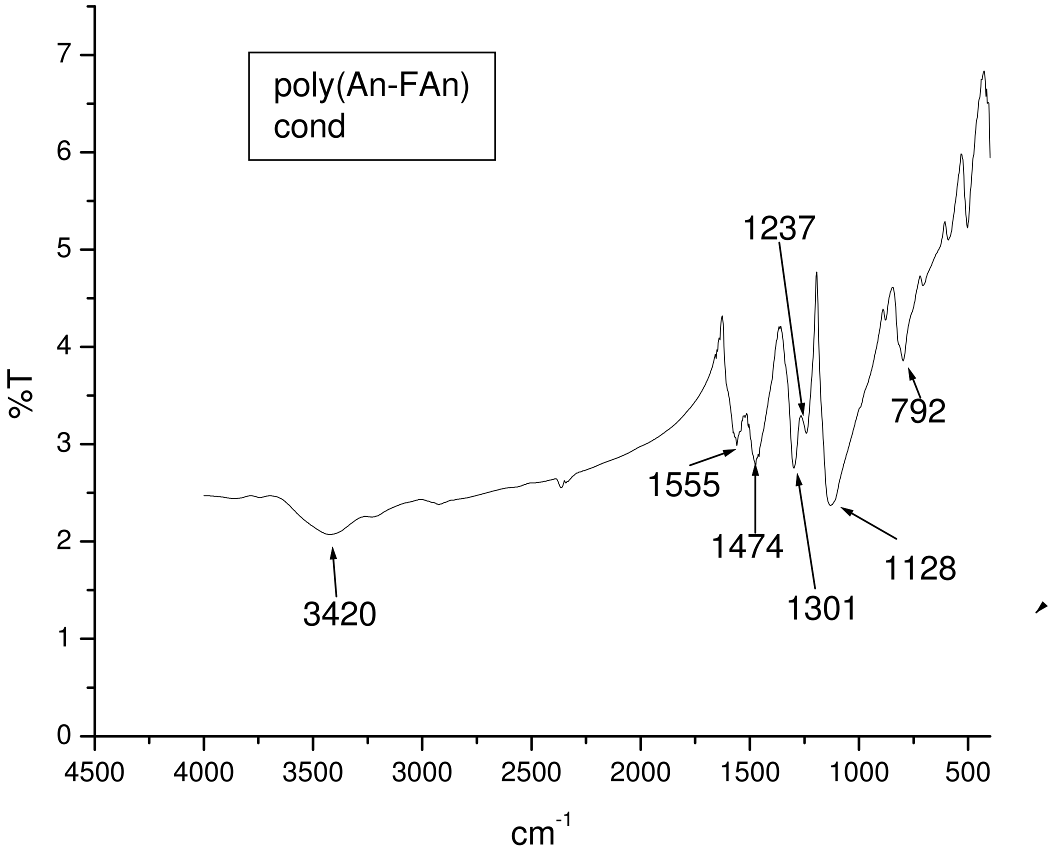

Figure 3.1 Fourier Transform Infra-Red Spectra of chemically synthesized doped poly (aniline-co-fluoroaniline).

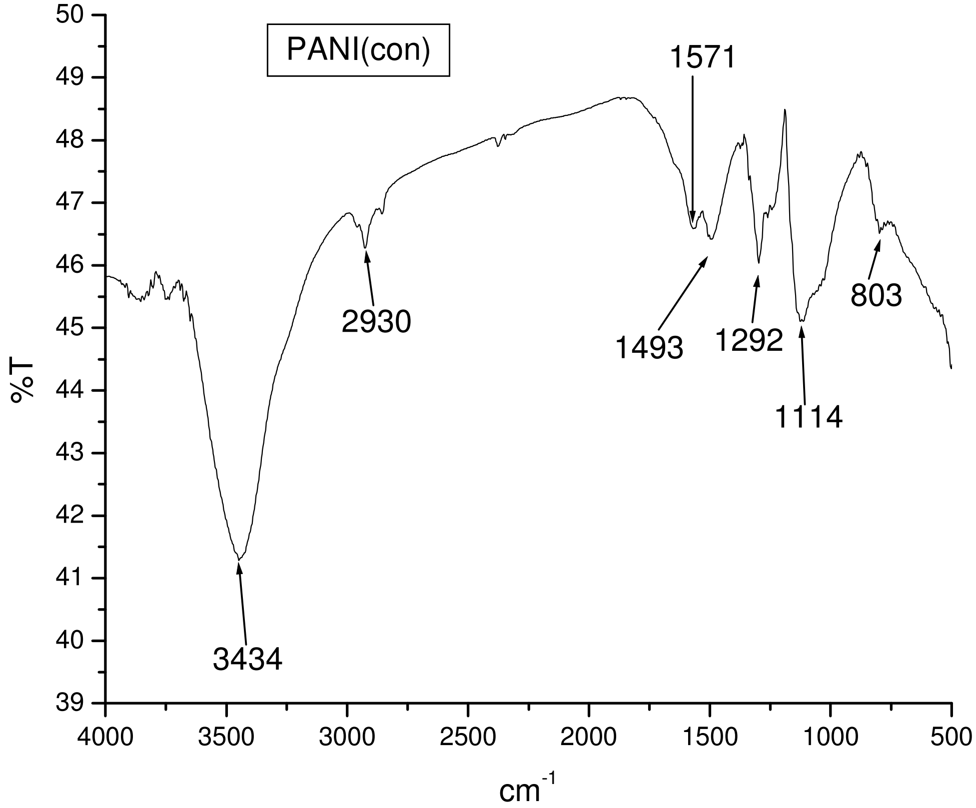

Figure 3.2 Fourier Transform Infra-Red Spectra of chemically synthesized doped polyaniline.

The absorption peak observed at 1128 cm^{-1} has been associated with the presence of halogen (fluoro) group [10] in the copolymer. The peaks at 792 cm^{-1} are the characteristic peaks of polyaniline backbone.

The absorption peak observed at 1128 cm^{-1} has been associated with the presence of a halogen (fluoro) group in the copolymer. These vibration bands are also present in the infrared spectrum of PANI [11]. However, a shift observed in the spectrum of Poly (An-FAn) indicates the presence of fluoro moieties in the polymer chain.

Fig 3.3 and Fig.3.4 shows the FT-IR spectra of undoped poly (An-FAn) and polyaniline respectively. All the vibration bands are also present in the infra red spectrum of undoped poly

(An-FAn). The FT-IR spectra of polyaniline show the characteristic peaks at 3434, 2930, 1571, 1493, 1292 and 1114 cm^{-1}. The peaks at 1571 and 1493 cm^{-1} are due to the C=C vibrations of quinoid and benzoid rings, respectively. The peak found at 1292 cm^{-1} is due to the C-N vibration bands. Whereas the peaks found at 1114 and 803 cm^{-1} are due to the C-N double bond and C-H vibration bands, respectively.

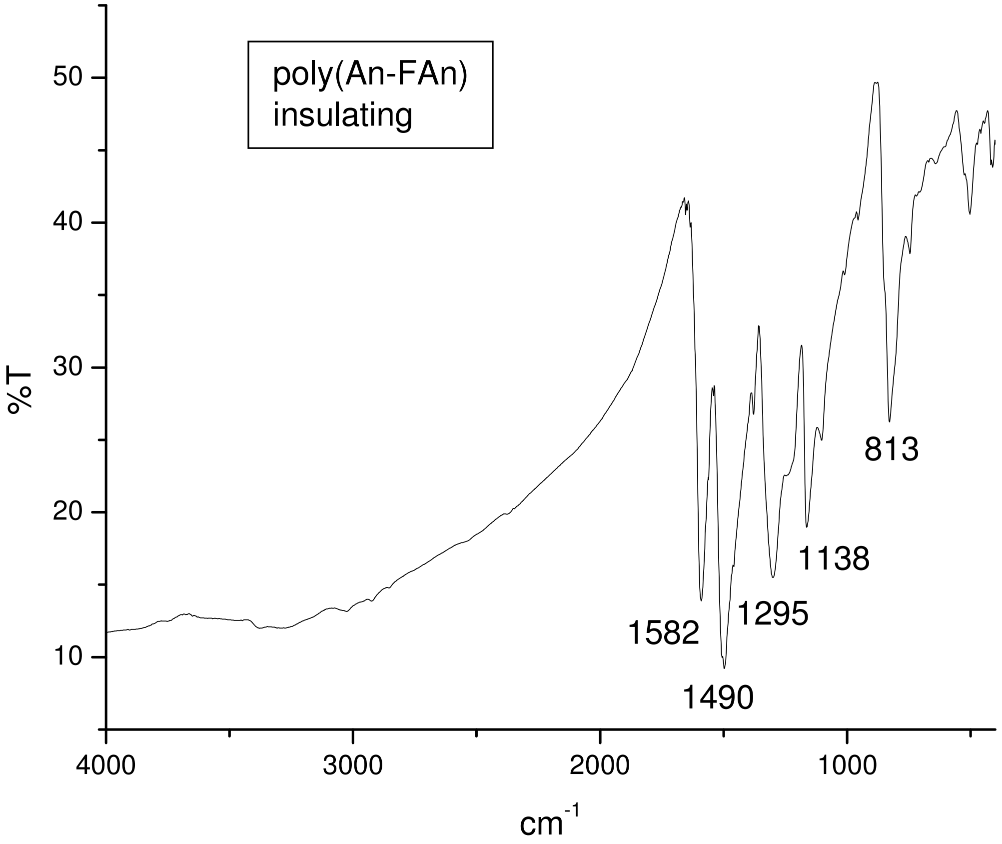

Figure 3.3 Fourier Transform Infra-Red Spectra Spectra of powders of insulating poly (aniline-co-fluoroaniline).

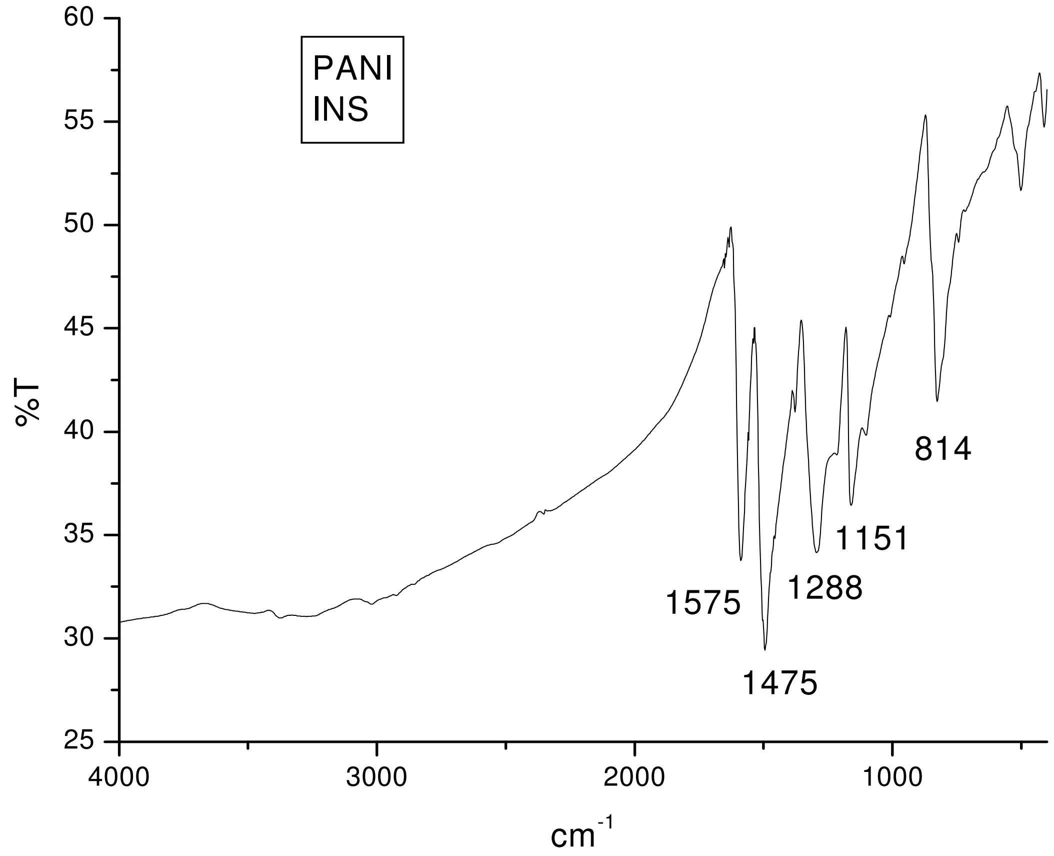

Figure 3.4 Fourier Transform Infra-Red Spectra Spectra of powders of insulating polyaniline.

3.3.2 Ultra violet visible spectra

The UV-vis spectra of poly (An-FAn), polyaniline, in their undoped form, recorded at room temperature are shown in fig 3.5 and 3.6. The spectra were obtained after dissolving these samples in their undoped states n NMP. The reference cell was filled with NMP. A shift is observed in the case of poly (An-FAn) [Fig. 3.5] in comparison with PANI [Fig. 3.6]. The absorption band in UV-visible spectrum at 321 nm is assigned to π-π* transition, whereas the absorption band at 579 nm corresponds to the quinoid ring of in the chain of poly (aniline-co-fluoroaniline) [12, 13]. A new absorption peak has been found in poly (aniline-co-fluoroaniline) has been found in absorption spectrum. This peak may be attributed to the enlarged energy difference between the orbits after attaching the fluoro group to the polyaniline. This may perhaps be attributed to the presence of electron withdrawing group (fluorine) present in the polymer backbone. In the case of poly (An-FAn), absorption peaks such as 321 nm and 579 nm are attributed to π-π* transition and polaronic band, respectively, whereas PANI shows the absorption peaks at 314 nm and 590 nm. This fact also suggests that the synthesized material is a copolymer.

We know that heavily doped polyaniline exhibits metallic behavior [14, 15]. In the present study a low-level doping has been done, and hence, this exhibits a band gap. The band gap for chemically synthesized doped poly (An-FAn) has been calculated from the plot of $(\alpha h\nu)^{-2}$ vs photon energy, shown in Figure 3.7. The energy band gap has been estimated to be 2.3 eV, which is higher than that of PANI [16].

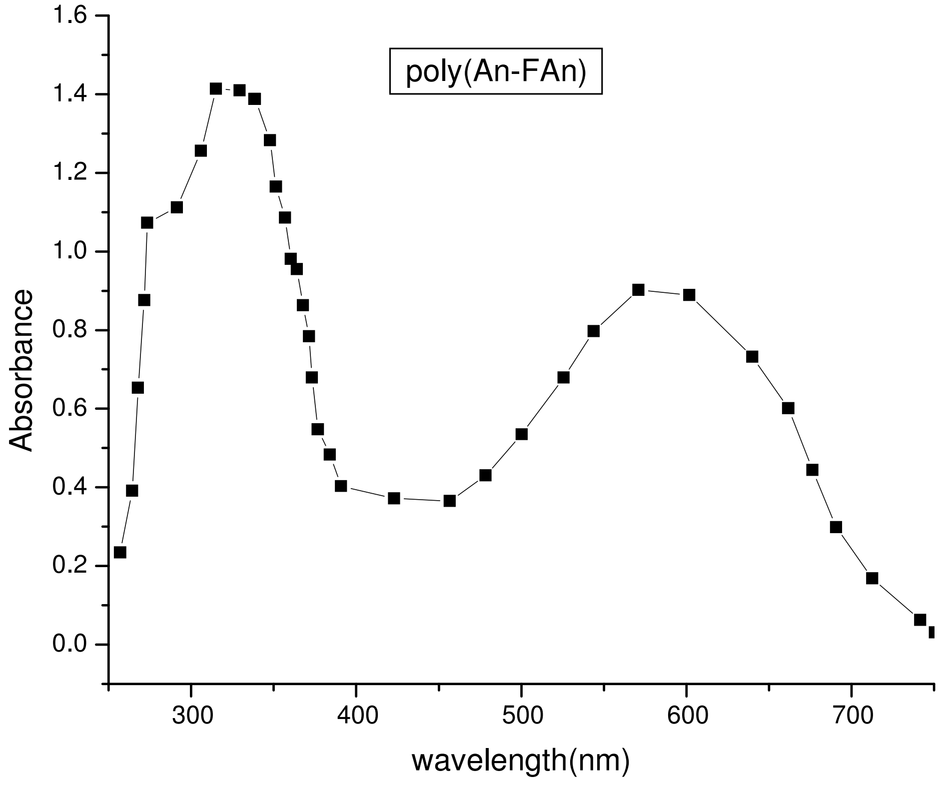

Figure 3.5 UV-visible spectra of powders of Poly (aniline-co-fluoroaniline)

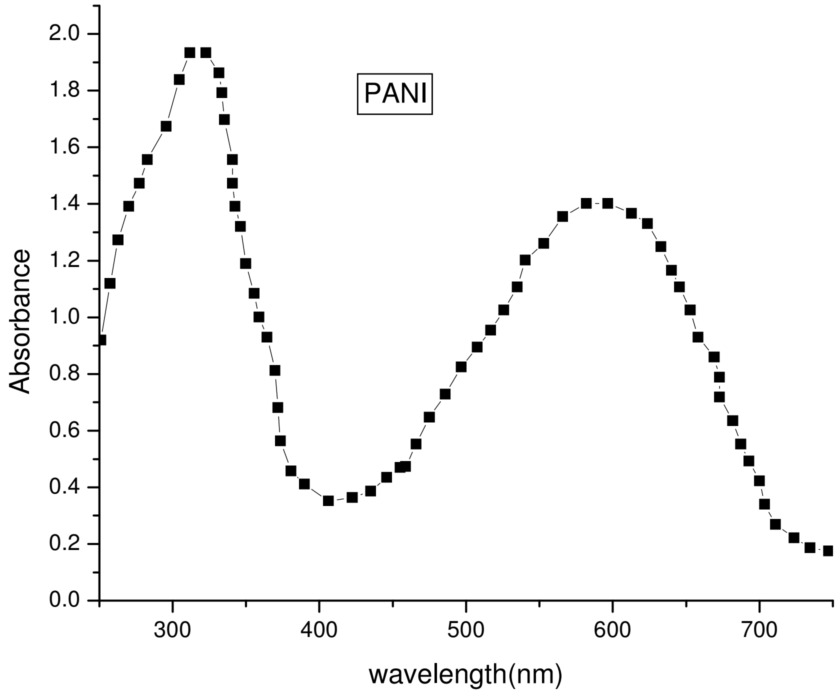

Figure 3.6 UV-visible spectra of powders of Polyaniline [12].

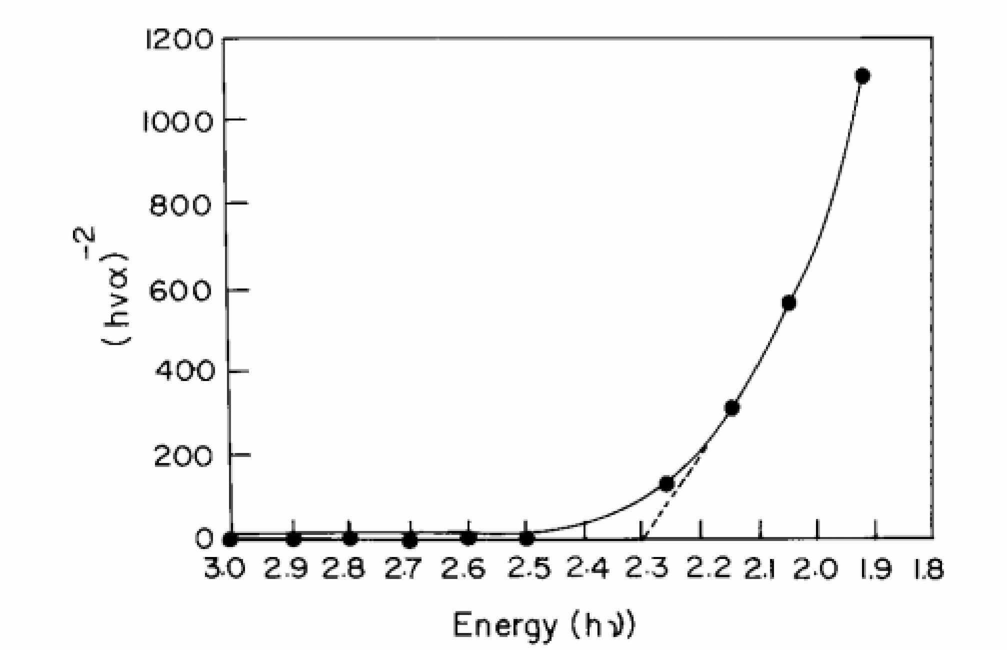

Figure 3.7 $(\alpha h\nu)^{-2}$ vs $(h\nu)$ for the band gap of poly (aniline-co-fluoroaniline).

Comparing the absorption spectra of poly (An-FAn) with PANI, a notable blue shift was observed. This may be due to the presence of electron withdrawing group in the copolymer backbone.

3.4 Cyclic Voltammetry

Fig. 3.8 shows the growth pattern of poly (aniline-co-fluoroaniline) at the scan rate of 50 mV/s in 1 M HCl. During the scanning of sample in cyclic voltammetry, the anodic current has been found to increase in subsequent voltammogram, which confirms the (formation of monomer, dimer, trimer etc.) [17, 18] polymerization of poly (aniline-co-fluoroaniline).

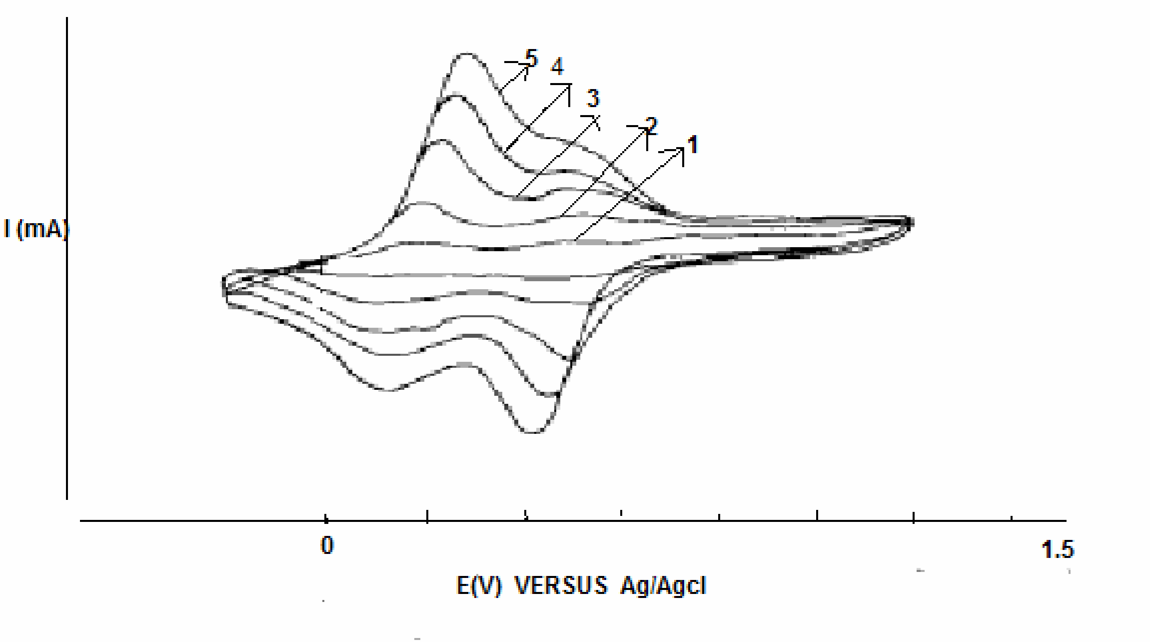

Figure 3.8 Electrochemical growth curve of poly (An-FAn) film.

The cyclic voltammetry (CV) of this copolymer at the same scan rate (50 mV/s) shows a shift in first oxidation peak (0.28 V) in comparison to polyaniline (0.12 V) [12]. This suggests that the conjugation length of the copolymer decreases as compared to the polyaniline and polyfluoroaniline. Therefore one may also expect that the other physical properties of poly (aniline-co-fluoroaniline) will lie between polyaniline and polyfluoroaniline.

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CHAPTER -4

CONCLUSION AND FUTURE SCOPE

4.1 Conclusions

The important conclusions drawn from present study are as follows:

1. The copolymer, poly (aniline-co-fluoroaniline) has been synthesized by chemical method, both in doped and undoped form.
2. The processability (solubility) of the copolymer has been checked in 1-methyl 2-pyrrolidone (NMP) and it has been found that the poly (aniline-co-fluoroaniline) shows better solubility as compared to polyaniline in NMP.
3. The vibration bands of FT-IR at 1128 cm^{-1} confirm the presence of fluoroaniline group.
4. The UV-vis measurements showed a band gap of 2.3 eV for chemically synthesized copolymer. This behavior of the copolymer is perhaps due to the incorporation of fluoroaniline moieties in polyaniline chain.
5. The oxidation peak occurs at 0.28 V and with the subsequent scans the anodic and cathodic current increases.

4.2 Future Scope

The studies mentioned in the present work further suggest some areas of interest from academic and technological point of view. They are as follows:

1. Other halo derivatives can be synthesized in order to check solubility and processability in various forms e.g. thin film and bulk etc.
2. The interfacial properties of poly (aniline-co-fluoroaniline) should be checked in order to apply it for different electronic applications [1].
3. The nano composite of poly (aniline-co-fluoroaniline) need to be synthesized. Moreover, a thorough characterization is also required to find out its possibility in electronic applications.