Synthesis and Characterization of Some Organic Semiconductors and Investigations on the Effect of Swift Heavy Ions on Their Properties

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Cochin University of Science and Technology
in partial fulfilment of the requirements for the award of the degree
of ***Doctor of Philosophy***

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Synthesis and Characterization of Some Organic Semiconductors and Investigations on the Effect of Swift Heavy Ions on Their Properties

A Ph.D. Thesis in the Field of Materials Science

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November 2003

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and
my Teachers...

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26.Nov.2003.

Certificate

Certified that the work presented in this thesis entitled "***Synthesis and Characterization of Some Organic Semiconductors and Investigations on the Effect of Swift Heavy Ions on Their Properties***" is based on the authentic record of research work done by ***Mr. S. Saravanan*** under my guidance in the Department of Physics. Cochin University of Science and Technology. Cochin - 682 022 and has not been included in any other thesis submitted previously for the award of any degree.

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Declaration

Certified that the work presented in this thesis entitled "*Synthesis and Characterization of Some Organic Semiconductors and Investigations on the Effect of Swift Heavy Ions on Their Properties*" is based on the original research work done by me under the guidance and supervision of ***Dr. M. R Anantharaman,*** Sr. Lecturer, Department of Physics, Cochin University of Science and Technology, Cochin - 682 022 and co-guided by ***Dr. S. Venkatachalam,*** Sci./Engr. SG. Head, Elastomers & Special Chemicals Section, Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Trivandrum - 695 022 has never been included in any other thesis submitted previously for the award of any degree.

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Preface

The history of polymers dates back to the early 20th century. Since then, conventional polymers have been finding innumerable applications in the day-to-day life of human beings. Conventional polymers are excellent insulators. They are inexpensive, lightweight, durable, flexible and hence polymers and polymer based devices slowly replaced other conventional materials.

The quest for a conducting polymer was on for many years and this culminated in the accidental discovery of conducting polyacetylene in the year 1978. Immediately after the discovery of polyacetylene physicists and chemists embarked on an hectic research activity, while physicists concentrated on the mechanism of conduction, chemists dealt with synthesis of novel conducting polymers. They also predicted new applications for conducting polymers. Nowadays devices based on conducting polymers are a common sight and they find extensive applications as Light Emitting Diodes, super capacitors, sensors, high-density storage batteries and electromagnetic shielding.

The class of conducting polymers include, among others, polyaniline, polyacetylene, polypyrrole and polythiophene. They are of interest from the application point of view. They are either prepared in the bulk form by employing electrochemical techniques or by novel synthesis routes. Some of the applications of these polymers necessitate the preparation of this polymeric materials in the form of thick and thin films. Understanding the mechanism of conduction, modification of optical and electrical properties and evaluation of the structure of this polymers have been the hallmark of research during the late 80 and 90's. This enabled scientists to correlate the properties with the structure of the polymer and this has eventually lead to the development of new devices for various applications.

So understanding the mechanism of conduction and correlation of properties assume significance in this context.

Plasma polymerisation is a novel technique for the preparation of polymer thin films. Plasma polymerisation includes ac, dc and rf. In this technique, monomers are injected into the chamber and thin films of the polymer are coated on the substrates. Thus it is possible to prepare thin films of various polymers and they are pinhole free, chemically inert, adhesive and thermally stable. However the structure of a plasma polymerised thin film does not exactly resemble the structure of their bulk counter parts. This means that they differ in their properties very much. Moreover the properties of these films are preparation specific, in the sense that RF plasma polymerised thin films exhibit superior properties with respect to AC plasma polymerised thin films. So understanding the structure and the properties of the plasma polymerised thin films presents an altogether different scientific challenge. The modifications of the various physical properties by different techniques like doping or implantation/irradiation of ions have been a known technique. It is known that the bombardment of swift heavy ions on polymeric thin films induces irreversible changes and they modify the properties considerably.

In this work, polymers belonging to polyaniline and polyaniline doped with camphor sulphonic acid are synthesised. Cobalt phthalocyanine is an interesting candidate belonging to the tetramers. Studies on the composites containing cobalt phthalocyanine tetramer and polyaniline doped with camphor sulphonic acid for various concentration are also undertaken in order to understand the mechanism. RF plasma polymerised aniline and furfural are prepared. The structural and electrical properties are evaluated. The bombardment of swift heavy ions of these films are carried out and the effect of irradiation on their properties is also investigated.

This proposed thesis is entitled " ***Synthesis and Characterization of Some Organic Semiconductors and Investigations on the Effect of Swift Heavy Ions on Their Properties*** " and consists of eight chapters.

Chapter I contains a brief history of polymers including conducting polymers and polymeric thin films. Importance of swift heavy ions in modifying the various properties of polymers is briefly touched upon in this chapter.

Chapter II deals with the fundamental theory and phenomenon that are central to this thesis. Various experimental techniques including methods of preparation and analytical tools employed for characterisation of the samples at various stages are discussed. This chapter also deals with the theory of conduction in conducting polymers.

Chapter III gives the detailed elemental analysis, structure of tetrameric cobalt phthalocyanine, morphological studies, dielectric and conductivity studies. The electrical conduction of this material is explained on the basis of Mott's Variable Range Hopping Conduction Mechanism.

The preparation of polyaniline with and without camphor sulphonic acid is described in the ***Chapter IV***. They are characterised using XRD, SEM, permittivity measurements and the results are correlated.

Investigations carried out on polyaniline doped with camphor sulphonic acid and oligomeric cobalt phthalocyanine composites are discussed in detail in ***Chapter V***. The electrical properties and morphology of these composites are dealt with in this chapter.

Chapter VI deals with the comparison and correlation of optical, morphological and electrical properties of irradiated polyaniline with swift heavy ions with respect to their pristine samples.

Similarly ***Chapter VII*** describes the results of optical, electrical and morphological studies of irradiated polyfurfural with swift heavy ions and the properties are compared with respect to their pristine samples.

Chapter VIII is the concluding chapter where in the conclusions drawn out of the present investigations are highlighted. The scope for further work is also listed.

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1. Dielectric and conductivity studies on tetrameric cobalt phthalocyanines. ***S Saravanan***, C Joseph Mathai, M R Anantharaman, S Venkatachalam, P V Prabhakaran: Journal of applied polymer science [In Press]
2. Conduction mechanism in plasma polymerised aniline thin films. C Joseph Mathai, ***S Saravanan,*** M R Anantharaman, S Venkatachalam, S Jayalekshmi: Material letters Vol 57 Issue 15 (2003) 2253 - 2257
3. Effect of iodine doping on the bandgap of plasma polymerized aniline thin films. C Joseph Mathai, ***S Saravanan,*** M R Anantharaman, S Venkatachalam, S Jayalekshmi: J. Phys. D: Appl. Phys. 35 (2002) 2206 - 2210
4. Characterization of low dielectric constant polyaniline thin film synthesized by ac plasma polymerization technique. C Joseph Mathai, ***S Saravanan***, M R Anantharaman, S Venkatachalam, S Jayalekshmi: J. Phys. D. Appl. Phys. Vol 35 (2002) 240 - 245

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5. Effect of Swift Heavy Ions on the Structural and Optical Properties of RF Plasma Polymerized Aniline Thin Films ***S Saravanan***, C Joseph Mathai,

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Conference Contributions

1. Effect of Swift Heavy Ions on the Structural and Optical Properties of RF Plasma Polymerized Aniline Thin Films ***S Saravanan***, C Joseph Mathai, D K Avasthi, S Venkatachalam, M R Anantharaman AVS 50th International Symposium held at Baltimore, MD, USA during Nov. 2 - 7, 2003.
2. Low dielectric constant materials based on plasma polymerised aniline thin films. ***S Saravanan***, C Joseph Mathai, M R Anantharaman, S Venkatachalam, P V Prabhakaran 45th DAE Solid State Physics Symposium - 2002 held at Punjab University, Chandigarh during December 26-30,2002.
3. Conductivity Studies on Oligomeric Cobalt Phthalocyanine. ***S Saravanan***, C Joseph Mathai, M R Anantharaman, S Venkatachalam, P V Prabhakaran Proceeding of the International Seminal on Advances in Polymer Technology held at Department of PS & RT Cochin University of Science and Technology Cochin during December 12-14, 2002.
4. Structural and Dielectric Properties of Polyaniline Doped with Camphor Sulphonic Acid. ***S Saravanan***, C Joseph Mathai, M R Anantharaman, S Venkatachalam, P V Prabhakaran Proceeding of the Seventh International Symposium on advances in Electrochemical Science and Technology held at Chennai during November 27 - 29, 2002.
5. The Optical and Electrical Properties of Polyaniline Thin Films Deposited under rf and ac Plasma Polymerization U S Sajeev, C Joseph Mathai, ***S Saravanan***, S Venkatachalam, M R Anantharaman Proceeding of the DAE-BRNS symposium on application of Plasma, Laser and Electron

beam in Material processing held at Babha Atomic Research Centre, Mumbai during September 23-26, 2002.

6. Plasma assisted deposition technique for synthesis of low dielectric constant polyanisidine thin films. C Joseph Mathai, ***S Saravanan***, M R Anantharaman, S Venkatachalam. S Jayalekshmi held at the 29th IEEE International Conference on Plasma Science, Banff. Alberta, Canada, during May 26-30, 2002.
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Chapter 1

Introduction

1.1. Polymers

"Polymers are high molecular weight, long chain components comprising of much simpler low molecular weight, identical units connected by covalent bonds" [1]. Conventional polymers are excellent electric insulators both at high voltage and high frequencies. Owing to their low cost of synthesis and fabrication, flexibility, lightweight, durability, impact resistance with respect to their inorganic counter parts, polymers are preferred to the conventional materials. Active research in the field of polymers began only in the 50s.

In the year 1950 polymer synthesis was dominated by Karl Ziegler and Ginio Natta [1] and they were awarded the Nobel Prize in chemistry in 1963 for their discoveries in the field of chemistry and technology of polymers [1]. Paul Flory took over and he created the modern polymer science through his studies on macromolecules [1]. The polymers studied by Staudinger, Flory, Ziegler and Natta were insulators and saturated. From the application point of view, the saturated polymers were uninteresting materials. But in 1964, Little [2] gave the chemical formula of a polymer on the basis of theoretical data and predicted exhibition of super conductivity at room temperature. Though this polymer could not be synthesised, but the potentialities of this material stimulated research in the field of organic conductive and super conductive materials.

1.2. Conducting Polymers

Polymers have been considered, as insulators and nobody then believed that a polymer could conduct as good as copper. But the discovery of conducting polymers in 1976 brought a break through and opened the floodgates to achieving a new generation of polymers. Moreover, conducting polymers provided the necessary platform for understanding the fundamental chemistry and physics of the π bonded macromolecules [3]. During the initial days, scientists were interested in studying the electrical properties of these polymers because of the first and stimulating success in the field of electrically conducting polymers. Also these polymers belong to the novel class of semiconductors that combines the optical and electronic properties of inorganic semiconductors with the added advantages of processing and mechanical properties. In 1978, it was demonstrated that polyacetylene becomes highly conducting when it was treated with oxidising or reducing agents [4-6]. This discovery, though accidental, laid the foundation of further developments in the area of conducting polymers.

Basically there are three different approaches for inducing conductivity in the base polymer. The first method involves pyrolysis to produce conductive residue. The second method is to produce a composite structure from a conducting material and organic polymers. The third and the most important of the three deals with organic conjugated polymers. The obstacles in the first generation of conjugated polymers were their insolubility, infusibility and instability. As far as the application point of view is considered, a material must be stable and should have excellent electronic and mechanical properties and it should be soluble. The delocalised electronic structures of π conjugated polymers are responsible for their unusual electronic properties. This electronic delocalisation in conjugated polymers paved the way for charge mobility along the backbone of the polymer chains. The electronic structure in conducting polymers is determined by the chain symmetry and because of this chain symmetry, polymers exhibit semi conducting or even exhibit metallic characteristics.

The development of environmentally stable, processable conducting polymers with good mechanical properties leads to the possibility of new applications. It attracted the attention of researchers because of their electrical, electronic, non-linear optical, electrochemical and photochemical applications.

From a materials science point of view, the design, synthesis, characterisation and processing of polymers assume significance.

Conjugated polymers in the semi conducting form exhibited most of the photonic phenomenon known in inorganic semiconductors. High performance optoelectronic devices including electroluminescent displays [7], photovoltaic solar cells [8], photodetectors and thin film transistors [9] are fabricated from conjugated polymers. Also various researchers have demonstrated that conducting polymers can be utilised as energy storage elements in capacitors [10], secondary batteries [11], as Schottky diodes [12], insulated gate FETs [13], light emitting diodes [7, 14] and also as conductive layers for Electro magnetic interference [EMI] shielding [15]. In addition to this, conducting polymers have also been proved useful for electro chromic displays [16], non-linear optics [17] and as sensors [18,19].

Late seventies saw the emergence of several new conducting polymers. They are polyaniline, polypyrrole, polythiophene, polyparaphenylene, and polyvhenylene (Fig. 1.1.). These conducting polymers can be prepared in the bulk form by using any one of the following processes:

1.2.1. Chain polymerisation

Long chain polymers are formed by a series of consecutive steps. This process is rapid and fast. Also no intermediate products are isolated in this process [20,21].

1.2.2. Step polymerisation

Polymers can be grown from their monomer by the stepwise repetition of a particular reaction over and over again. Unlike chain polymerisation, this process involves condensation of two polyfunctional molecules takes place and produce large molecules with the elimination of small molecules [20,21].

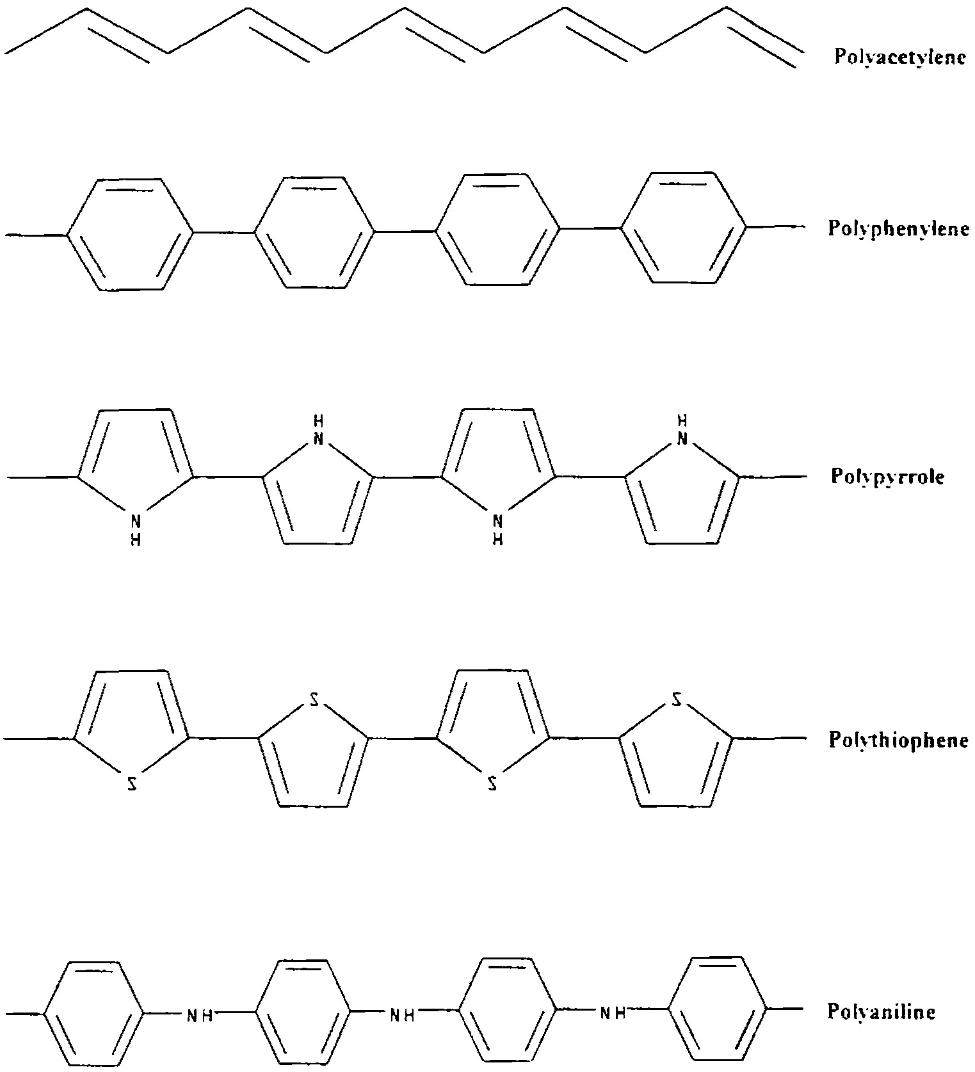

Fig. 1.1. Chemical structure of some conducting polymers

1.2.3. Electrochemical synthesis

The electrochemical synthesis of conducting polymers [22] is an electro organic process rather than organo electrochemical one. This is a radical combination reaction and is diffusion controlled. In electro organic reactions the active species is generated on the electrode surface through electron transfer between a substrate molecule and the electrode in which the substrate molecule is transformed to cation radical or anion radical depending on the direction of electron transfer. Thus the active species is generated through electron transfer between a substrate and an electrode, as this always involves inversion of the polarity of the substrate, this type of inversion is not always easy in organic synthesis.

1.3. Polymer Thin Films

Organic and polymer thin films have received a great deal of interest due to their extensive applications [23-26]. The preparation of polymer thin films can be broadly classified in to two groups. They are

- Preparation of polymer thin films from the bulk polymer and
- Preparation of polymer thin films from the monomer itself

However, formation of polymer thin films from the bulk polymeric materials is difficult because of their insolubility. So the latter is more convenient than the former. Plasma polymerisation is one such convenient technique for preparing polymer thin films from the monomer.

Plasma Polymerisation

Formation of polymer thin films through reactions of the plasma with an organic monomer gas is known as plasma polymerisation [27]. The development of plasma polymerisation began in the 1950s and since then, extensive studies on this technique have been going on. Plasma polymerisation involves both homogeneous and heterogeneous reactions. Homogeneous reactions involve reaction between plasma species and the heterogeneous reactions involve reaction between plasma and surface species and the surface species itself. The two types of reactions are often called plasma-state polymerisation and plasma-induced polymerisation.

Polymers formed by plasma polymerisation are altogether different from conventional polymers [27,28]. These polymers demonstrate chemical and physical properties. Plasma polymers are generally:

1. Amorphous, hard, tough, insoluble in organic solvents and resistant to high temperatures
2. Chemically inert
3. Very adherent to a variety of substrates including polymer, glass and metal surfaces
4. Uniform and pinhole free thin films

A schematic of the processes is shown in Fig. 1.2.

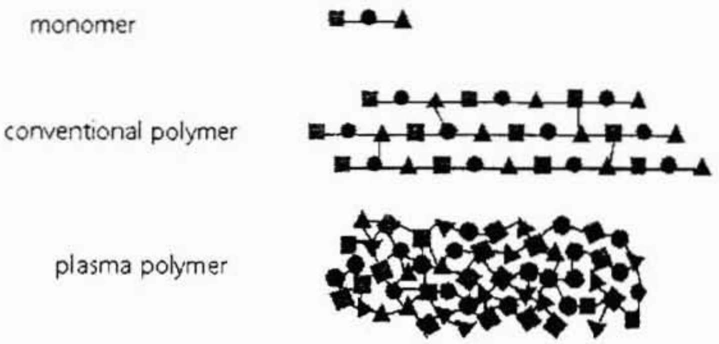

Fig. 1.2. Schematic of conventional and plasma polymers

Though investigations on plasma polymerisation began in the 60s systematic studies on a large scale started only in the 70s. Most of them belonged to the three classes namely hydrocarbon, fluorocarbons and siloxanes.

The quality of the films deposited by plasma polymerisation is dependent on various parameters and they are the following.

1. Minimization of the Yasuda parameter, W/FM
   [W: power coupled into the plasma, F: monomer Flow rate and M: Monomer molecular weight]
2. Use of monomers with polymerisable double bonds
3. Sample position
4. Use of cold substrate
5. Pulsed plasma excitation to reduce the plasma on time

Plasma polymerised thin films are employed for a variety of applications and they are shown in Table 1.1.

Table 1.1.

Some important applications of conducting polymers

	Monomer/Polymer	Application
1.	Hydrocarbons, Halocarbons & Organometallics	Thin film capacitors
2.	Polystyrene, Polytetrafluoroethylene, Polypropylene	Protective coatings for cans, Plastic films, Steels
3.	Hydroperfluoropropane, dibromodifluoromethane, & ethylene	Coatings on cutting surfaces of Knife and tools
4.	Xylene, divinylbenzene	Insulators for microelectronic devices
5.	Polyacetylene, Polyaniline, Polypyrrole	LEDs, Sensors, Solarcells
6.	Polythiophene	Optical memory element in opto electronic devices

1.4. Polymeric Phthalocyanines

Phthalocyanines are a class of organic semiconductors. Metallophthalocyanines and their polymers possess extended conjugated structures and show interesting optical, electrical and electrochemical properties [29-32]. Organometallic polymer backbones such as polymeric phthalocyanines have excellent thermal stability and stable in the presence of moisture and oxygen and hence it is a suitable candidate for making environmentally stable, electrically conductive materials. By varying the substituents on the ring of the phthalocyanine moiety, it is possible to control the properties of the system [33,34]. Their unique electrical and chemical properties are due to their large π electron systems. The possibility of the excitation of π electrons by optical and thermal means gives scope for various applications.

Apart from the use of dyes, pigments and catalysts, phthalocyanines are also employed in electronic, optoelectronic and molecular electronic applications. These include energy conversion cells [35-37], electrophotography [38], photosensitizers [39], gas sensors [40,41], electrochromic devices [42], rectifying circuits [43], optical data recording [44] and liquid crystals [45].

1.5. Polyaniline

Polyaniline is a typical phenylene based polymer having flexible - NH - group in a polymer chain flanked on either sides by a phenylene ring [46]. The protonation, deprotonation and other physico chemical properties of polyaniline is due to the presence of this -NH- group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and is known as aniline black since 1862 [47]. In 1907 and 1909 Willstatter and co workers proposed an indamine structure for aniline black. In 1910, Green and Woodhead reported the constitutional aspects of aniline polymerisation. Though reports envisaged that organic compounds are insulators, Mecoy and Moore mooted the idea of making organic solids conducting. Almost 50 years later, in 1968, Suville reported for the first time that polyaniline can be made conducting. But it was only after the discovery of the metallic conductivity in iodine-doped polyacetylene [4], polyaniline received much greater attention.

Among all the conducting polymers. polyaniline occupies a special position due to its ease in synthesis. environmental stability and the possibility of simple non redox doping.

Non - redox doping by protonic acids is an important aspect in which a number of electrons in a polymer chain remain unchanged during the doping process. This protonated form is electrically conducting and the order of conductivity increases with increase of level of protonation as well as functionalities present in the dopant. Structure and orientation of functional group of doping acid play an important role [48.49] in conductivity.

One such dopant is aromatic sulphonic acids [50.51]. They are strong acids comparable to sulphuric acid and phosphoric acid. They decompose upon distillation. The advantages of using organic sulphonic acid as dopants are

1. The physicochemical properties of conducting polymers can be altered by introducing the Functional groups of acids
2. Induce solubilization of polyaniline by micellar action
3. Induce optical activity of polyaniline

Some of the potential applications of conducting polyaniline are in batteries [52], LEDs [53.54]. solid state transistors [55]. liquid crystal displays [56.57]. capacitors [58]. Schottky Diodes [59.60] and electrochromic devices [61].

1.6. Polymer Blends/Composites

A mixture of materials can be classified as homogeneous or heterogeneous. In the case of polymers. a homogeneous mixture is named as blends and the latter is named as composites. However the term blend is usually reserved for a mixture of two or more polymers. The main aim of making blends/composites is to obtain the combined properties of the components of the mixture. The objectives for making a blend consisting of conductive and insulating polymers is to combine the properties of the component optimally so as to tailor the properties of the blend to achieve appropriate rheological properties together with the right electrical conductivity. Commercially, blends are prepared by mechanical mixing. [46,62]

1.7. Modification of Polymers

In order to change the properties of polymeric materials, the modification of polymers structurally as well as chemically is an important process. By using appropriate techniques they can be modified. Some of them are

- Incorporation of dopants
- Ion implantation
- Ion irradiation

1.7.1. Doping Techniques

Bulk polymers in its pure form are insulators and dopants like camphor sulphonic acid, methane sulphonic acid and hydrochloric acid enhance the electrical conductivity of polymers. Incorporation of dopants modifies the structural properties and the modifications of structural parameters play an important role in improving the conductivity of the polymer. Doping of polymers can be carried out by the following methods

i. Gaseous doping

In this process the doping is carried out by exposing the polymers to the vapours of the dopant under vacuum [63]. The level of dopant concentration is controlled by temperature, vacuum and time of exposure.

ii. Solution doping

This method involves the use of solvents in which the dopants are dissolved and the polymer is treated with the dopant solution [64].

iii. Electrochemical doping

In electrochemical doping [65] simultaneous polymerisation and doping occurs.

iv. Self - doping

Self - doping does not require any external doping agent. The ionizable group in the polymer chain acts as the dopant for the polymer [66].

v. Radiation induced doping

High-energy radiations such as gamma ray, electron beam and neutron radiation are used for doping of polymers [67].

1.7.2. Ion implantation

The use of ion beams to modify the physical and chemical properties of materials is a relatively recent innovation. Doping by ion implantation is a non-equilibrium process in which the dopant atoms are driven into the material by using their excess kinetic energy. In a suitably designed ion accelerator. ion beams of nearly all the elements in the periodic table can be produced. mass analysed and implanted into the target material [68]

1.7.3. Ion Irradiation

Irradiation of materials by high-energy ions is associated with the phenomenon like atomic displacements and structural modifications [69-72]. The effect of ions in the materials depends on the incident ion energy. fluence and ion species. Low energy ions up to few hundred keV are for ion implantation in semiconductors. which modify the surface and interface of materials [73]. The main difference of materials modification by ion implantation and swift heavy ion irradiation is that in ion implantation the incident low energy ions get embedded in the material and cause change whereas in swift heavy ion irradiation the impinging ions do not get embedded in the materials due to their larger range.

Swift heavy ions are being used to probe into the exotic effects of large electronic excitations in different types of materials. eg. metals. semiconductors. superconductors, polymers and organic crystals.

The ion beam irradiation of polymers induces a rapid dissociation of the polymeric structure leading to modification of the polymers [74]. In polymers ion tracks create molecular chain breaking, formation of free radicals and radiolytic processes [75,76]. Also high-energy heavy ions promote cross linkages, formation of carbon clusters and in some cases they generate new chemical bonds.

1.8. Objectives of the Present work

Having discussed the various types of polymers. both in the bulk form and in thin films. their potential applications in making devices. it is imperative at this juncture to spell out the motivation and objectives of this work.

From the fundamental point of view, a clear understanding of the mechanism of conduction in the bulk polymers is highly necessary to tailor the properties. The incorporation of dopants like Camphor sulphonic acid. hydrochloric acid etc. into the backbone of the polymer also enhances the conductivity of the polymer. It is also known that composites are prepared to combine optimally the electrical, mechanical and optical properties of the constituents of the blends. If a clear understanding of the effect of composition on the electrical and optical properties is to be brought out. various weight ratios of the constituents is blended and be studied systematically. Normally devices based on organic semiconductors are required to be fabricated in the thin film form. The properties of these thin films are entirely different with respect to their bulk counter parts. Thin films are to be deposited on suitable substrates and the growth conditions are to be optimised.

Though state of the art technologies namely PECVD and CVD are available for growing thin films. in this thesis. the emphasis is on the employment of inexpensive techniques, which can be home made for growth of thin films. Here ac and rf plasma polymerisation techniques are employed for the preparation of thin films. The advantages are that homogeneous pin hole free and adhesive films can be obtained on glass and quartz substrates. Stress is laid in preparing thin films using rf plasma polymerisation since this technique can bring in conjugation in the structure. This provides the possibility of enhanced conduction and good optical properties. Plasma polymerised thin films are generally insulating in character and if one wants to make device grade films for applications, the conductivity has to be enhanced by appropriate means. One such technique is to introduce dopants like iodine along with the monomer into the plasma chamber.

Techniques like ion beam implantation and swift heavy ion irradiation are also popular techniques to induce changes in the polymer chain and thus enhance the overall properties of the polymer. When thin films are subjected to swift heavy ion irradiation, formation of carbon clusters, cleavage of bonds or breakage of bond during the bombardment of ions, all contribute to the conduction process in the films. Initial studies carried out by Joseph et al [77] in the Magnetics Laboratory indicates that low k films can be synthesised using ac plasma polymerisation technique. Low k films are good intermetallics. The employment of these films as intermetallics necessitate good thermal stability. With this objective in mind various polymer thin films based on polyaniline and polyfurfural will be prepared using rf plasma polymerisation. The irradiation of SHI is undertaken with a view to modifying the various properties of polymer thin films. The influence of fluence on the optical, morphological and electrical properties is also to be studied. This is intended to be carried out on polyaniline and polyfurfural thin films. Polymers in the bulk form will be synthesised by adapting proven techniques. Composites will be synthesised by varying the volume fraction of the constituents in the blends. It is proposed to carry out a systematic study of the composites and to evaluate its various properties. It will be the endeavour of the present study to fit the electrical conductivity/dielectric permittivity data on to known models and thus formulate a plausible conduction mechanism for the electrical conduction in pure polymer and blends.

Polyaniline and polyaniline doped with camphor sulphonic acid are chosen in this study. Phthalocyanine is another candidate selected in this study. Composites of polyaniline doped with camphor sulphonic acid and phthalocyanine are identified to be the blend composites considering their extremities in the conductivity values.

So the objectives of the present work can be spelled out and they are as follows.

- Preparation of bulk Polyaniline with and without dopant by proven chemical routes
- Preparation of tetrameric phthalocyanine via the electrochemical route
- Preparation of conducting polymer composites based on tetrameric cobalt phthalocyanine and polyaniline
- Preparation of polymer thin films based on aniline and furfural by employing RF plasma polymerization technique
- Modification of these polymer thin films by Swift Heavy Ion Irradiation
- Evaluation of their structural Properties
- Investigations on electrical and optical properties
- Morphological studies using Scanning Electron Microscopy
- Determination of the optical band gap of these films
- Photoluminescence studies on pristine and irradiated polymer thin film samples of aniline and furfural and
- Correlation of properties

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Chapter 2

Theory and Experiment

This chapter consists of two parts, in which the first part gives an account of necessary theoretical aspects relevant to this work and the second part deals with a detailed account of the experimental techniques employed for the preparation of polymer samples. The methods adopted for investigating the optical and electrical properties of these polymers are also included in this chapter.

Theory

2.1. Plasma Polymerisation

Plasma polymerisation is one of the many techniques employed for preparation of polymer thin films. It refers to the formation of polymeric materials under the influence of partially ionised gas. That is Plasma. Since it involves the use of an electric glow discharge in vacuum it is also termed as glow discharge polymerisation. Plasma polymerisation can take a variety of forms depending on the monomers and molecular fragments deposited on the surface. With appropriate monomer and operating conditions thin polymer films consisting of hydrocarbons, long polymeric chain consisting of linked carbon atoms and highly cross-linked carbon or hydrogen atoms will be deposited. In order to understand the complex mechanism of plasma polymerisation, one has to be aware of limiting factors concerning polymerisation in vacuum.

A certain volume of any monomer vapour at a fixed temperature and pressure contains much lesser molecules than in the liquid state. Under vacuum conditions the number of these molecules is further reduced. Thus polymerisation in vacuum concerns polymer formation from sparingly dispersed monomers.

The Gibbs free energy change of the polymer formation reaction is given by

$$\Delta G = \Delta H - T\Delta S \qquad (2.1)$$

where ΔH is the heat of reaction, T the temperature and ΔS the entropy factor. When the polymer formation proceeds via the step growth mechanism or the chain growth mechanism, the value of ΔH is unaffected. The entropy factor, ΔS in entire step growth polymerisation is same. But this is dependent on the length of polymer chain during the chain growth. In chain growth polymerisation, the entropy change is always negative and the reaction must be exothermic ($\Delta H \leq 0$) so that spontaneous reaction occurs. If the reaction temperature is raised to a ceiling temperature (T_c), ΔH and ΔS become equal and an equilibrium between the forward (polymerisation) and the reverse reaction (depropagation) is obtained and $\Delta G=0$. From the equilibrium condition

$$T_c = \frac{\Delta H}{T\,\Delta S} \qquad (2.2)$$

At temperatures lower than T_C, negative ΔH offsets the entropy change of propagation, the over all free energy change for propagation is negative and polymerisation proceeds spontaneously. At temperatures higher than T_c the positive entropy term $-T\Delta S$ becomes greater than the ΔH term, ΔG becomes positive and polymer formation cannot proceed spontaneously.

In the gas phase reaction, the ceiling temperature T_c of chain growth polymerisation is much lower than that of liquid phase reaction. The pressure dependence of the ceiling temperature of polymerisation of a monomer is positive which implies that the ceiling temperature of the same monomer in vacuum is much lower. Thus the anticipated T_c is too low to expect appreciable polymer formation by the chain mechanism in vacuum. These factors limit the possibility of polymer formation by the chain growth mechanism in vacuum. The relatively slow process based on the step growth polymerisation of molecules cannot explain the rapid polymer formation in vacuum. Plasma polymerisation taking place in a practical and efficient way under vacuum conditions belongs to a special case.

2.2. Role of Ionisation and Free radicals in Plasma Polymerisation

The ionisation of a molecule by a collision with an electron is the process for creating plasma of a monomer but it is not the primary step in initiating plasma polymerisation. Low energy electrons cannot ionise molecules but can break bonds in organic molecules or create excited species, which initiate chemical reactions. Most ionisation needs energy greater than 10 eV but for dissociation of a molecule it is less than 10 eV. The energies of primary active species and typical bond energies of organic molecules are shown in Table 1.1. and 1.2 respectively.

Table 2.1.

Energy of primary Active Species

Species	Energy (eV)
Electrons	1-30
Ions	0.0025-1
Visible/UV Photons	1-30

Table 2.2.

Typical bond energies of organic molecules

Bond	Bond Strength (eV)
C-C	3.6
C-H	3.5
O-H	4.4
O-C	3.74
N-H	4.04
C=C	6.35
C-F	5.35
C-N	3.17
C=O	7.78

By comparing the energy values of tables it is clear that the electrons in glow discharge plasma have sufficient energy to produce a variety of chemically reactive species (radicals).

The formation of these free radicals is an important process in many glow discharge polymerisation and these free radicals are trapped in the polymer. In ordinary chain growth free radical polymerisation, most of the free radicals are quenched in the termination reaction. Plasma polymerisation proceeds neither by the rapid chain growth mechanism nor by the slow step growth but rather by a rapid step growth. In rapid step growth mechanism, polymerisation and deposition occur simultaneously.

2.3. Electrical Conductivity in Polymers

For many practical applications, it is necessary to be aware of the basic electrical properties of polymers. The electrical conductivity σ can be expressed in terms of number of charge carriers n and the mobility μ as

$$\sigma = ne\mu \qquad (2.3)$$

Here n stands for the electronic charge. Since n and μ are temperature dependent, the conductivity is also temperature dependent. It is expressed as

$$\sigma = \sigma_0 \exp\left(-E_A/kT\right) \qquad (2.4)$$

In the same way the temperature dependence of sheet resistance R_{sh} is

$$R_{sh} = R_0 \exp\left(-E_A/kT\right) \qquad (2.5)$$

However it is not clear that if the rise in temperature influences n or μ. So

$$n = n_0 \exp\left(-E_n/kT\right) \tag{2.6}$$

$$\mu=\mu_o(T) \tag{2.7}$$

Where E_n is thermal activation of carrier generation. It is related to the intrinsic properties of the polymer material, impurities or defects in the material. The temperature dependence of μ can be written as

$$\mu(T)=\mu_o T^{-n} \tag{2.8}$$

$$\mu = \mu_0 \exp\left(-E_\mu/kT\right) \tag{2.9}$$

Where n is a constant. The number of charge carriers and the mobility depend on the applied field. This is reflected as deviations from ohm's law. Electrical conductivity studies explain the type, origin, concentration of energy carriers and the type of conduction mechanism.

2.4. Conduction Mechanisms in Polymers

The transport properties of polymers are investigated using metal-polymer-metal sandwich configuration. Electrical conduction in a metal-polymer-metal configuration can take place via several mechanisms namely Schottky emission, tunnelling, Poole Frenkel, field emission and space charge limited conduction [1]. These are schematically shown in Fig. 2.1 and can be grouped as a) Through conduction band, b) By tunnelling, c) Through impurity bands, d) By Space charge limited process and e) By ionic transport.

Based on the above, the possible conduction mechanisms in polymers are listed below.

1. Conduction process through the conduction band: It includes direct transition of carriers from valence band to the conduction band (1), Schottky emission (2), and the thermal excitation from the trapping levels (3)

2. Tunnelling conduction: It comprises the conduction via insulator barrier gap from metal to the conduction band (4), from trapping level to the conduction band (5), tunnelling directly from the valence band to the conduction band (7) and direct tunnelling between two electrodes.

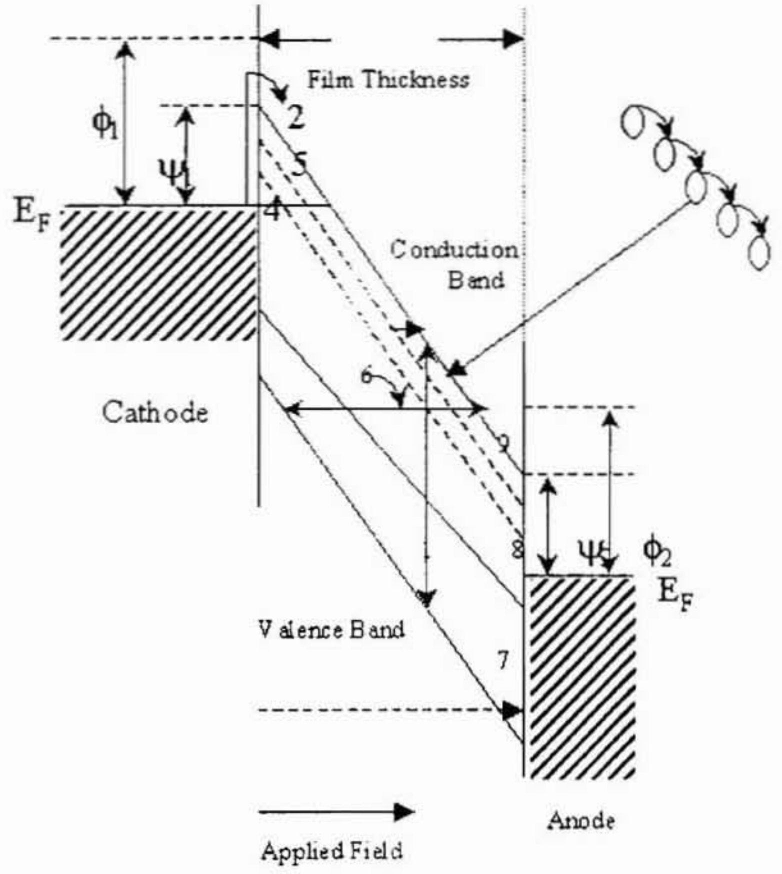


Fig. 2.1. Possible conduction mechanism in metal polymer metal structure

3. Impurity level conduction: Hopping of charge carriers from one impurity level to another in the impurity band (9)

4. Space charge effect: This is due to the barrier of carriers at the metal polymer interface under an external electric field.

5. Ionic conduction can take place under high electric fields by the migration of cation and anion in opposite direction.

However hopping or tunnelling conduction mechanism is the prominent type of conduction mechanism found in conducting polymers. Here we discuss very briefly the hopping and tunnelling conduction mechanisms.

2.4.1. Hopping Conduction

If two molecules are separated by a potential barrier in a sandwich structure, a charge carrier from one electrode to the other can move either by tunnelling or moving over the barrier via an activated state. The later is called hopping of charge carriers. Though polymers are amorphous materials, a short-range order exists in most of these materials. Hence the theory used to explain the electronic band structure in crystalline phase can also be extended to amorphous polymers. If the spatial fluctuations in the interatomic distances are large, the correspondingly large and random fluctuations in the height or depth of the potential wells may lead to the localisation of states below a certain critical and well-defined energy. The hopping conduction process in the localised states can occur only when the carrier mobility is low and the mean free path is comparable with the interatomic distances [2]. In a hopping conduction mechanism, only those carriers with energy of about kT below the fermi level have a significant probability of hopping. The expression for hopping conductivity is given by [3]

$$\sigma = N(E_f)\alpha e^2 a^2 \nu_{ph} \exp\left(-W/_{kT}\right) \qquad (2.10)$$

Where 'N (E_f)' is the density of states, 'α' is a parameter dependent on the extent of overlap of localised states, 'e' is the electronic charge, 'a' the number of electrons per unit volume, 'ν_{ph}' is the phonon frequency and 'W' the activation energy for hopping. The equation indicates that the conductivity temperature dependence is exponential. Mott [3] showed that for strongly localised states, the conductivity at low temperature can be expressed as

$$\sigma \propto \exp\left(-{}^{B}\!/_{T^{1/4}}\right) \qquad (2.11)$$

Where B is a constant related to the hopping mechanism. At high temperatures, deviation from $T^{-1/4}$ occurs which can be understood in terms of interchain hopping. A carrier trapped in a chain after detrapping thermally may flow along the same chain or may hop into an adjacent chain. In polymers the conduction occurs due to two distinct processes: One is by hopping of carriers from trap to trap and the other is hopping of charge carriers from chain to chain.

2.4.2. Tunnelling Conduction

The penetration probability of an electron from one metal electrode to the other through the polymer depends on the applied electric field. In order to calculate the tunnel currents, the effective mass of electron in the conduction band, forces, temperature, dielectric constant and share of potential barrier should be taken into account.

In the metal-polymer-metal configuration, one of the electrodes (metal) is positive biased. For a rectangular potential barrier of height ϕ_t with similar electrodes at high-applied fields, the current density in a tunnelling process is given by [4]

$$J = \frac{2.2e^3V^2}{8\pi h\varphi_t s^2}\exp\left(\frac{-8\pi s}{2.96heV}(2m)^{1/2}\varphi_t^{3/2}\right) \qquad (2.12)$$

Where m is mass of electron and s the interelectrode spacing. This equation is similar to the well-known Fowler Nordheim relation [5], which explains the direct tunnelling. Direct tunnelling involves the transfer of electrons directly from one electrode to the other through their fermi surface levels. According to Fowler-Nordheim, the current density is given by

$$J \propto F^2 \exp\left(-0.689\phi^{3/2} F\right) \tag{2.13}$$

Where F, the applied field is given by V/d. d is the thickness of the film.

These equations dictate that the current density J should be independent of temperature. A plot of Log J vs 1/V yields a straight line, called the Fowler Nordheim plot. The direct tunnelling of electrons from one metal to the other occurs only for samples having thickness less that 100Å.

2.5. Swift Heavy Ion Irradiation

Energetic ion beams play a vital role in the field of materials science. The effect of ion beam on the material depends on the ion energy, fluence and ion species. The interaction of ions with material is a deciding factor in the ion beam material modification. The ions lose energy during their passage through the material, which is either spent in displacing atoms by elastic collisions (nuclear stopping) or exciting the atoms by inelastic collisions (electronic stopping). The energy lost due to nuclear stopping is called nuclear energy loss and the energy lost due to electronic loss is known as electronic energy loss. Apart from these two events, an another mechanism which takes place during slowing down of incident ions is charge exchange process between the ion and the atoms of the solid. This can be expressed as

$$\left(\frac{dE}{dX}\right)_{loss} = \left(\frac{dE}{dX}\right)_{Elect} + \left(\frac{dE}{dX}\right)_{Nucl} + \left(\frac{dE}{dX}\right)_{ch\arg eExchange} \tag{2.14}$$

Where $\left(\frac{dE}{dX}\right)_{Elec}$ is loss due to electron, $\left(\frac{dE}{dX}\right)_{Nucl}$ is loss due to neutron and $\left(\frac{dE}{dX}\right)_{Ch\arg eexchange}$ is loss due to charge exchange. Since charge exchange loss represents a small fraction of the total energy loss, so it can be negligible.

A general way to treat the slowing down of an ion in matter is through stopping power (dE/dX) and defined as the energy (dE) lost by an ion for traversing a distance (dX). Thus the total stopping power can be written as

$$\left(\frac{dE}{dX}\right) = \left(\frac{dE}{dX}\right)_e + \left(\frac{dE}{dX}\right)_n \cong S_e + S_n \tag{2.15}$$

A typical qualitative representation of stopping powers is depicted in Fig. 2.2.

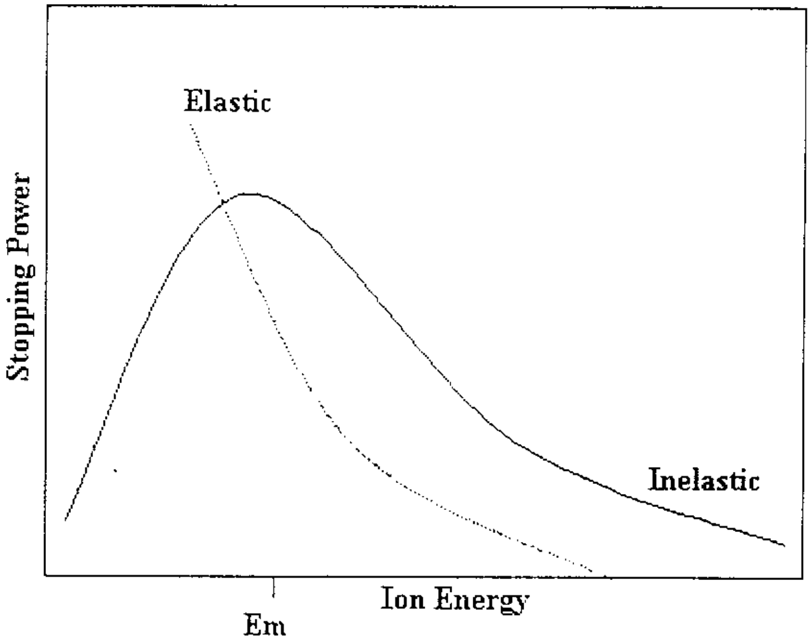


Fig. 2.2. Qualitative representation of elastic and inelastic stopping powers

2.5.1. Electronic Energy Loss

Energetic ions entering inside a solid immediately interacts with many electrons simultaneously. In any one such encounter, the electron experiences an impulse from the attractive Coulomb force as the projectile ion passes its area. Sometimes this impulse may be sufficient either for excitation or for ionisation.

The energy that is transferred to the electron is from the energetic ion. So the velocity of the ion will be decreased as a result of the encounter. At any given time the ion interacts with many electrons, so the net effect is to decrease its velocity continuously until it is stopped. The swift heavy ions can move a few microns to tens of microns in the target because a single encounter of ions with an electron does not deflect its path. So these particles passes a definite range in a given material.

The energy loss per unit path length of the ion is known as Specific Energy Loss. This is also termed as stopping power or linear transfer. In 1913, Bohr first proposed the theory of electronic energy loss (S_e) of energetic ions in solids [6]. He also derived an expression for the S_e. He considered that the target as a collection of harmonic oscillators whose frequency was determined by optical absorption data. Bethe and Bloch [7,8] extended this work for the relativistic ions and solved the problem quantum mechanically in the first Born approximation. The electronic energy loss (S_e) of highly energetic ion in solid is stated as follows

$$S_e = -\left(\frac{dE}{dX}\right)_e = \frac{4\pi e^4 Z_p^2 Z_t N_t}{m_e v^2}\left[\ln\left(\frac{2m_e v^2}{I}\right) - \ln\left(1 - \frac{v^2}{c^2}\right) - \frac{v^2}{c^2}\right] \quad (2.16)$$

Where v and $Z_p e$ are the velocity and charge of the projectile ion, Z_t and N_t are the atomic number and number density of the target atoms, m_e the electron rest mass and e the electronic charge. The parameter I is the average excitation and ionization potential of the target. For non - relativistic projectile ions the term $\ln\left(\frac{2m_e v^2}{I}\right)$ is significant. Equation 2.16 is valid only when the velocity of ions is larger when compared to the velocities of the orbital electrons in the target. From equation 2.16 it is seen that for a non-relativistic ion S_e varies inversely with ion energy. This is because if the velocity of the ion is low, it spends more time in the electron area and transfers greater impulse and impart larger energy to the electron.

2.5.2. Nuclear Energy Loss

Nuclear energy loss is due to elastic binary collision between a projectile ion and target atoms. This is based on the Screened coulomb potential and impulse approximation. The interaction potential, V(r), between two atoms Z_1 and Z_2 can be written in the form of a screened potential using χ as the screening function.

$$V(r) = \frac{Z_1 Z_2 e^2}{r^2} \chi\left(\frac{r}{a}\right) \tag{2.17}$$

Where a is the Thomas - Fermi screening radius for collision and is given by

$$a = \frac{0.885 a_0}{\left(Z_1^{1/2} + Z_2^{1/2}\right)^{2/3}} \tag{2.18}$$

Where a_0 is the Bohr radius and value lie between 0.1Å and 0.2Å for most interactions. Like Thomas - Fermi potential, Lenz-Jensen, Moliere and Bohr potentials are also used to calculate S_n. The expression for the S_n is given as

$$S_n = -\left(\frac{dE}{dX}\right)_n = N_2 \int_0^{T_{max}} T d\sigma_n(E,T) \tag{2.19}$$

Where N_2 is the atomic density of the target, t the energy transferred from incident ion to a target atom. T_{max} is the maximum value of T, and $d\sigma_n$ is the differential cross section.

Using an appropriate screening potential and impulse approximation, the final expression for S_n can be derived. If the screening function is of the form $\chi = a/2r$, then nuclear energy loss is given by

$$S_n = N\frac{\pi^2}{2}Z_1Z_2e^2a\frac{M_1}{M_1+M_2} \qquad (2.20)$$

Though this equation gives the correct order of magnitude for S_n the lacuna is that it deviates considerably in energy dependence.

Experiment

In this section, various experimental techniques employed for sample preparation and analytical tools used for characterisation at various stages are briefly discussed. A brief insight into the fundamental aspects of the analytical tools employed are also briefly dealt with.

2.6. Sample Preparation

2.6.1. Cobalt Phthalocyanine tetramers

Tetramer of cobalt phthalocyanine was prepared, purified and characterised by solution method. In this method, cobalt sulphate, pyromellitic dianhydride, excess urea, ammonium chloride and ammonium molybdate were ground well and heated at 180 °C in nitrobenzene media for 12 hours. The reaction mixture was then cooled, washed with methanol several times to remove nitrobenzene. The crude product was further boiled with 2 N sodium hydroxide containing sodium chloride and filtered. The residue was acidified with hydrochloric acid and washed several times and dried finally to obtain phthalocyanine tetramer. [9,10]

2.6.2. Polyaniline doped with Camphor Sulphonic Acid

Polyaniline is prepared by the direct oxidation of aniline using an appropriate chemical oxidant. For this monomer aniline and aqueous percholoric acid kept at around 4°C and to this ammonium per sulphate was added drop by drop. This mixture was stirred continuously for 2 hours. Further, this product was filtered and washed with water and then with methanol. Subsequently polyaniline doped with percholorate was converted to insulating polyaniline emeraldine base

(PANIEB) using hydrazine hydrate. This PANIEB is doped with camphor sulphonic acid (CSA) by the mixing of camphor sulphonic acid and emeraldine base in the molar ratio of 0.5 CSA to polymer repeat unit in nitrogen atmosphere. This is then purified and dried in a vacuum oven. The entire reaction is as shown in Fig. 2.3. [11,12]. Emphasis was laid in utilising high pure chemicals and solvents for the synthesis.

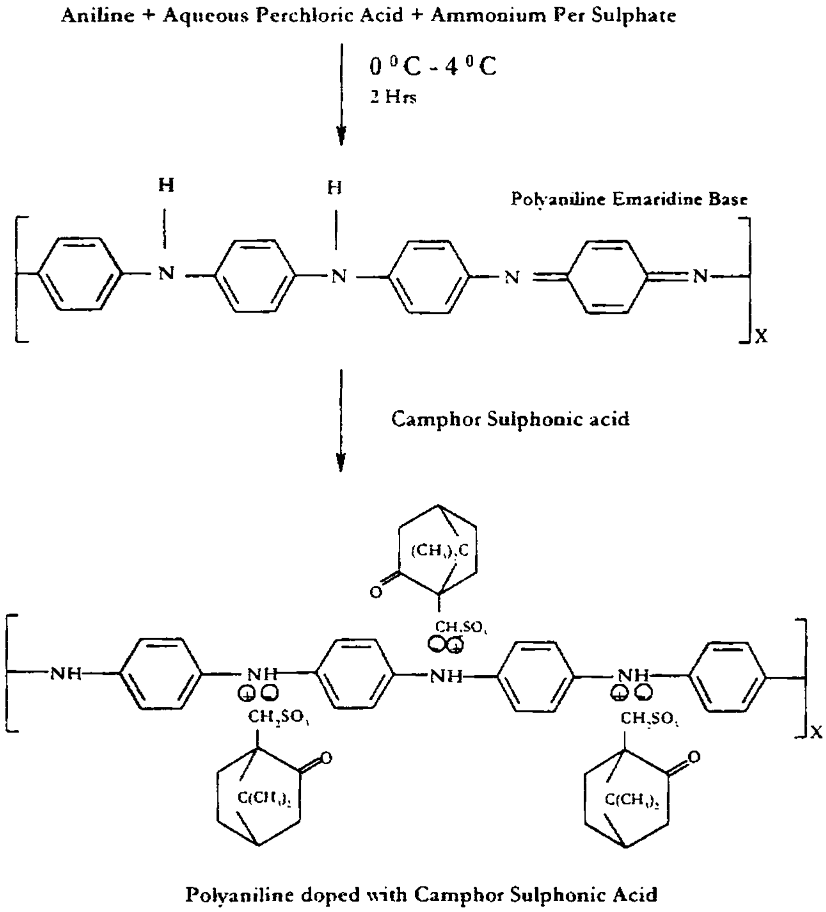


Fig. 2.3. Preparation of polyaniline doped with camphor sulphonic acid

2.6.3. Blends of PANICSA and CoPc

The powdered polyaniline doped with camphor sulphonic acid was blended with tetrameric cobalt phthalocyanine by mixing them homogeneously in an agate mortar. Blends of PANICSA and tetrameric cobalt phthalocyanine corresponding to the following compositions [10%CoPc - 90%PANICSA, 50% CoPc - 50% PANICSA, 90% CoPc - 10% PANICSA] were prepared.

2.6.4. Polyaniline and Polyfurfural Thin Films

Polyaniline and Polyfurfural thin films are prepared using RF plasma polymerisation technique. The experimental set up for the preparation of RF plasma polymerised aniline and furfural is shown in Fig. 2.4. It consists of a long glass tube of length 50cm and of diameter around 8cm with provisions for passing monomer vapour, dopants and for evacuation. Chemically and ultrasonically cleaned glass substrates was placed inside the glass tube exactly under the space separated by the aluminium foil electrodes which are capacitively coupled and wrapped around the glass tube separated by a distance of 5cm. The chamber was evacuated (10^{-2} Torr) and the monomer was admitted into the chamber. Glow discharge was obtained in between the electrodes by applying a high frequency (7-13MHz) and a current in the range of 60-80mA. The processing parameters are optimised and films were prepared under optimum conditions.

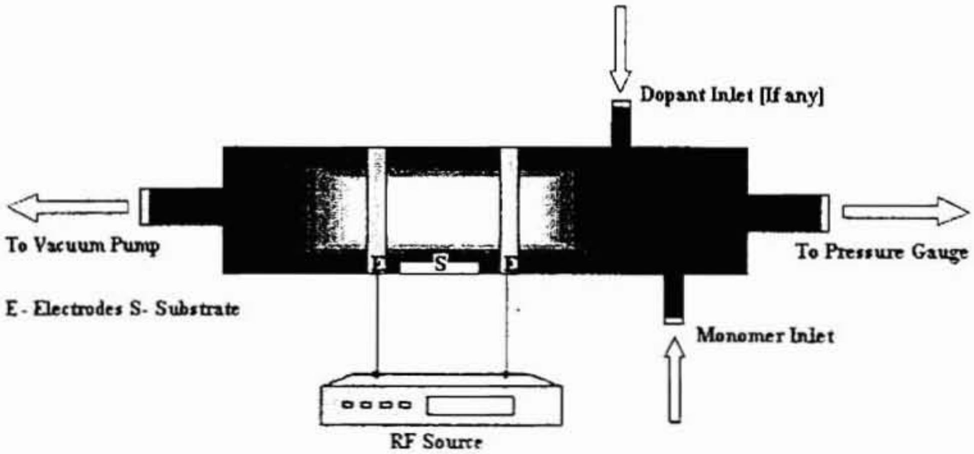


Fig. 2.4. RF plasma polymerisation set up

2.7. Swift Heavy ion Irradiation

RF plasma polymerised thin films of area 1 x 1 cm^2 were exposed to 92 MeV Si ions in the material science irradiation facility of the Nuclear Science Centre, New Delhi. The experimental method and the instrumentation employed for the irradiation are stated in a nutshell in the following sections.

2.7.1. The Pelletron Accelerator

A 15UD pelletron accelerator capable of delivering proton energy upto 32 MeV has been installed at Nuclear Science Centre, New Delhi by the Electrostatic International Inc., USA. This is a tandem Van de Graaff accelerator, in which the charge carrier belt is replaced by a chain of pellets. The digit 15 stands for 15 Million Volts terminal voltage and UD stands for Unit Double. The whole machine is mounted vertically and a schematic of the machine is as shown in Fig. 2.5.

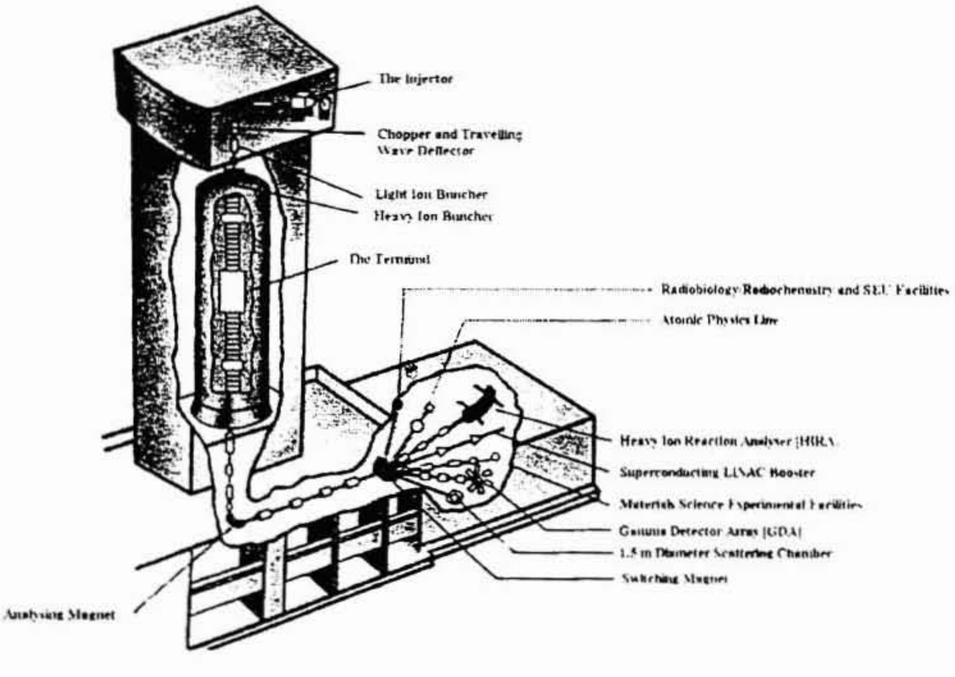


Fig. 2.5. Schematic of 15UD pelletron accelerator at Nuclear Science Centre

The pelletron accelerator has an insulating steel tank of height 26.57m and width 5.5 m. In order to attain insulation (to prevent sparking/discharging) the tank is filled with Sulphur hexafluoride gas at a pressure of 4.0 Torr. A high voltage terminal with 1.52mm as diameter and 3.81mm in length at the middle of the tank can be charged by a high potential varied from 4MV to 16MV using an electrostatic charge transfer device. This terminal is connected to the tank vertically through ceramic titanium tubes know as the accelerating tubes. A potential gradient is maintained with the help of these tubes. Negative ions from the ion source are injected towards the terminal and are stripped off a few electrons through stripper foils. The yield is converted into positive ions. These ions are further accelerated as they proceed to the bottom of the tank at ground potential. As a result the ions from the accelerator gain energy, that is given by,

$$E = V_{\pi}\,(q+1)\ \text{MeV} \qquad (2.21)$$

Where V_{π} is terminal potential and q is the number of positive charges (charge states) on the ions after stripping.

Thus a heavy ion of charge state q will attain a final kinetic energy equal to (q+1) x 16MeV. Thus protons accelerated to a full terminal voltage would have an energy of 32MeV. By using appropriate magnets with respect to the charge states and energies the high energy ions are analysed and are bent at 90^0 with respect to vertical position by using analyser magnet. These redirected ions are directed to the desired experimental area in the beam hall with the help of multi port switching magnet. This switching magnet can redirect the beam to any one of the seven beam lines. The schematic diagram of the 15 UD pelletron machine is as shown in Fig. 2.6. [13]

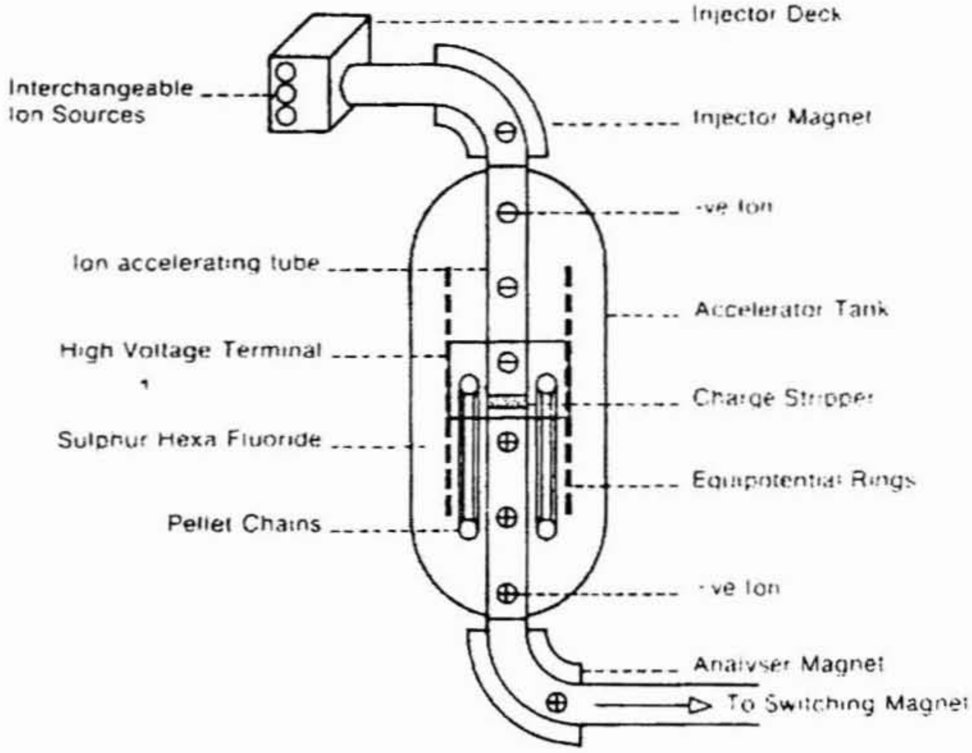


Fig. 2.6. Schematic diagram of the 15 UD pelletron machine

2.7.2. Irradiation Procedure

The irradiation on polymer thin films is carried out at the materials science beam line facility of NSC. This beam line is at 15^0 angle with respect to the direction of the unswitched direct beam. The schematic of the materials science beam line is as shown in Fig. 2.7. [14] The beam line is maintained at ultra low pressure of the order of $1X10^{-9}$ Torr and the irradiation is carried out in high vacuum chamber (HVC). The target ladder is inserted in the HVC from the top. By using magnetic quadrupole and a steerer the beam is focussed on the target. For attaining uniform irradiation the beam is scanned in an area of 1 X 1 cm^2 with the help of a magnetic scanner. The ion fluence is estimated using the ladder current and the current integrator.

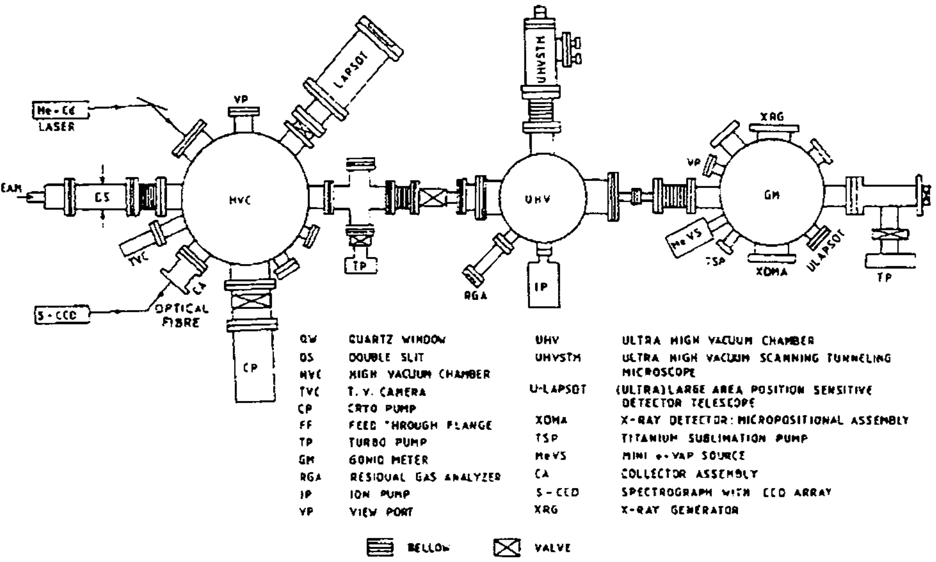


Fig. 2.7. Schematic diagram of the materials science beam line

2.8. Characterisation Techniques

Characterisation at various intermediate stages is a primary requirement to evaluate the properties at various stages. For this, numerous techniques are utilised for the evaluation of structural, optical and electrical properties of the samples. They are described in the subsequent sections.

2.8.1. X - Ray Diffractogram

X ray diffractograms are recorded for comparing the crystallinity of protaned polymer sample with that of the base sample. This is carried out by using Rigaku D Max C. X - ray diffractometer with Cu Kα_1 radiation (λ=1.5415Å). From the plots of intensity versus 2θ, the crystallinity index of the sample is calculated by employing Manjunath et al.'s formula [15] According to this, the resolution of the peak R is given by

$$R = \frac{m_1 + 2m_2 + \ldots\ldots + m_{n-1}}{h_1 + h_2 + \ldots\ldots + h_n} \qquad (2.22)$$

Where m_1, m_2... are the heights of minima between two peaks and h_1, h_2... are the heights of peaks from the base line. From the resolution of the peak (R), the lateral order or the index of the crystallinity (1-R) can be estimated.

2.8.2. Infra Red Spectroscopy

The spectroscopy of the coupled rotational and vibrational excitations is an exquisite probe for structural studies and also for the determination of the internal atomic motions of gas-phase molecules. This is carried out with the aid of vibrational spectroscopy and is conducted with the Fourier transform infrared [FTIR] spectrometer based on a scanning interferometer that modulates a broadband infrared source based on its optical frequency components.

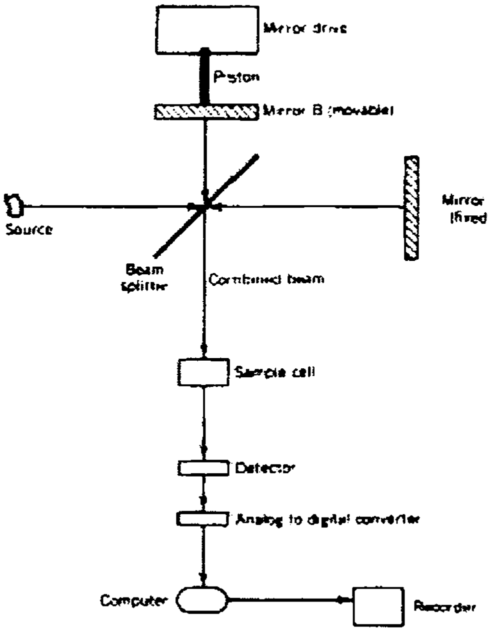


Fig. 2.8. Schematic of an FTIR spectrometer

The ratio of the sample to reference intensity spectra gives the transmission spectrum of the sample. The absorption or transmission peaks of an infrared spectrum correspond to the frequencies of vibration between bonds of the atoms.

Also different materials produce different types of spectra because no two materials have unique combination of atoms. Hence every IR spectrum results in a positive identification of every different kind of materials. This feature makes IR spectroscopy quite useful in material characterization. Schematic of an FTIR spectrometer is as shown in Fig. 2.8.

2.8.3. UV VIS Spectroscopy

Optical measurements comprise an important means of determining the band structures of semiconductors. Photon induced electronic transition between different bands lead to the evaluation of band gap. The photon absorption in many amorphous materials is found to obey the Tauc relation [16], which is of the form

$$\alpha h\nu = B\,(h\nu - E_{Opt})^n \qquad (2.23)$$

Here α is the absorption coefficient, $h\nu$ the photon energy, B a constant and the index n is connected with the distribution of the density of states. The index $n = 1/2$ corresponds to the direct allowed transition energy gap and $n = 2$ represents the indirect allowed transition energy gap.

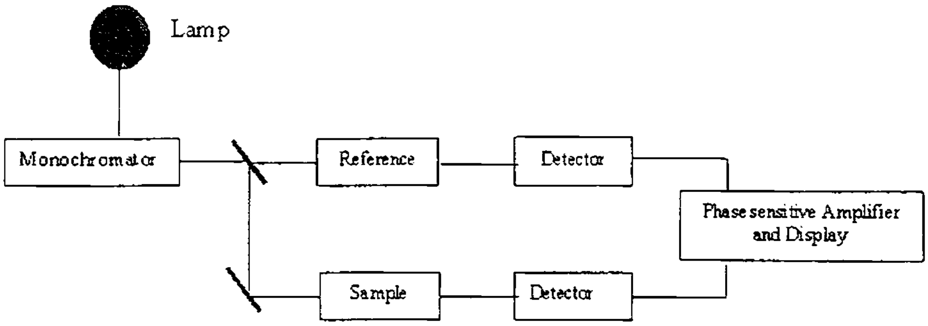


Fig. 2.9. Experimental set up of UV Vis NIR spectrometer

In the present work band gaps of polymer thin films are evaluated from the absorption spectrum recorded using Hitachi U3300 spectrophotometer. The experimental set up of a generic UV VIS NIR spectrometer is as shown in Fig. 2.9.

2.8.4. Scanning Electron Microscope

The Scanning Electron Microscope (SEM) utilises electrons rather than light to form an image. It has many advantages over optical microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at a time. It also produces images of high resolution, which means that closely spaced features can be inspected at a high magnification. SEM can be used to delve into the surface morphology of thin film samples. A schematic diagram of SEM is shown in Fig. 2.10.

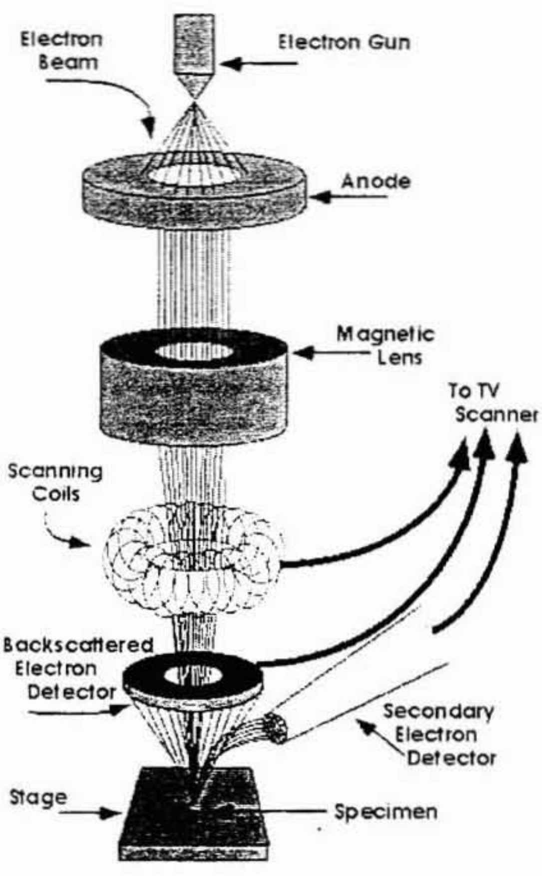


Fig. 2.10. Schematic diagram of SEM

A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses. which focus and direct the beam down towards the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image. All these are carried out under high vacuum.

2.8.5. Dielectric and Conductivity Studies

Among all other electrical properties, dielectric permittivity is the most fundamental electrical property of an insulating material. The dielectric permittivity of a material is defined as the ratio of the permittivity of the material (ε) to that of a vacuum (ε_0) and may be expressed as follows: -

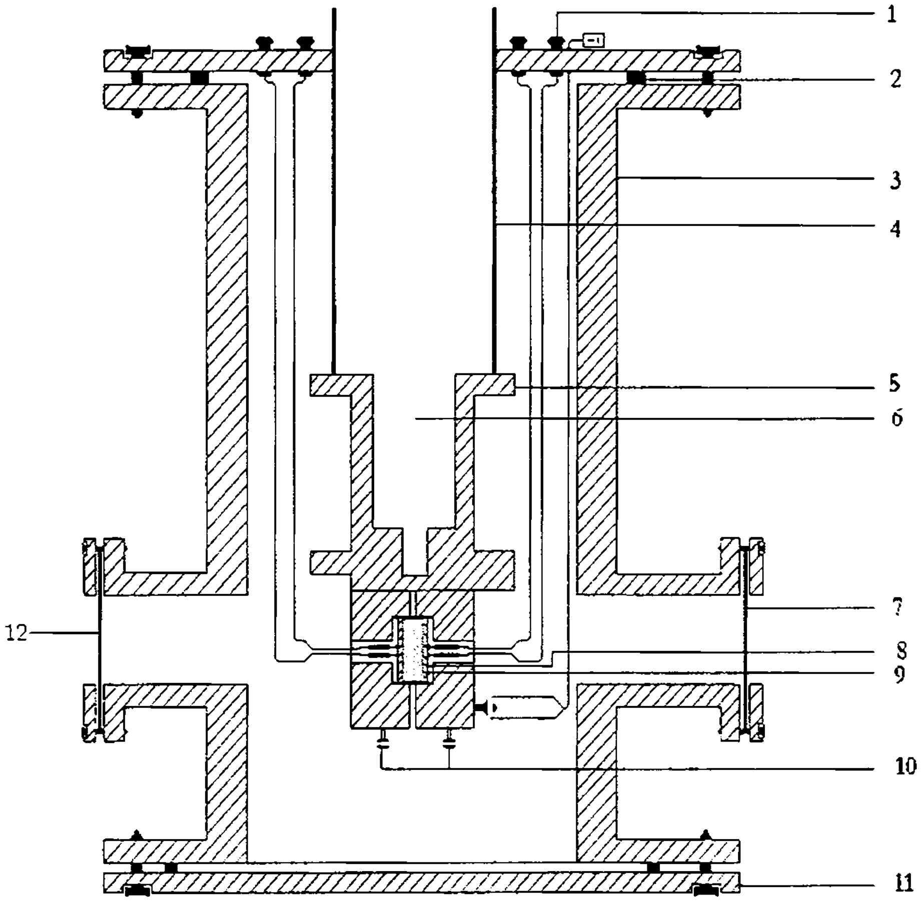
$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \tag{2.24}$$

It changes with frequency, temperature, orientation, pressure and molecular structure of the materials. The dielectric permittivity studies are carried out on polymer samples (Bulk and Thin films) using a home made four probe dielectric cell (Fig. 2.11.) and an impedance analyser.

The capacitance of the sample is calculated by using parallel plate capacitance method and is given by

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{2.25}$$

Where ε_0 is the permittivity of air, ε_r the dielectric permittivity of the material between the parallel plates, A the area of the sample and d is thickness of the sample. By knowing thickness and area of the sample, the dielectric constant is calculated.



1. BNC. 2. Neoprine O ring. 3. MS Chamber. 4. SS Pipe. 5. Sample Holder. 6. Liquid Nitrogen Cavity. 7. Glass Window. 8. Copper Electrodes. 9. Sample. 10. Fixing Screws. 11. MS Flange. 12. To Vacuum Pump

Fig. 2.11. Schematic Diagram of Dielectric Cell

The AC conductivity of the these samples are then evaluated by using the relation

$$\sigma_{ac} = 2\pi f\, \varepsilon_0 \varepsilon_r \tan\delta \qquad (2.26)$$

Here f is the frequency of the applied field and tanδ is the loss factor.

The measurement of permittivity with frequency is automated with the help of package based on graphical program called Lab VIEW.

2.8.6. DC Conductivity

The dc conductivity and subsequently the activation energies are determined by employing a Keithley voltage source and a home made conductivity cell. The details of the set up are shown in Fig. 2.11.

2.8.7. Photoluminescence

Luminescence is the phenomenon in which electronic states are excited by an external energy and the excited energy released in the form of light. When the energy comes from short wavelength light, the phenomenon is called photoluminescence.

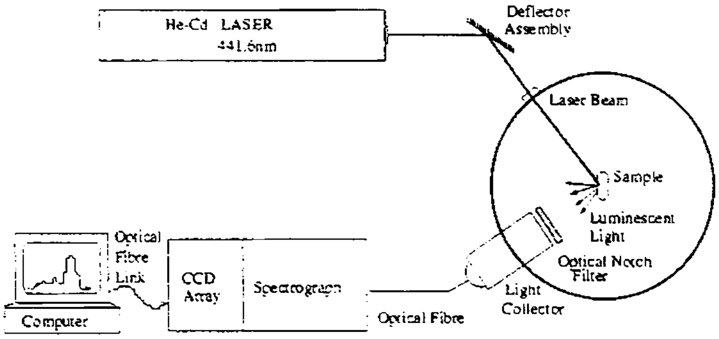


Fig. 2.12. Photoluminescence set up

A light source, sample, light filtering system, and light detector are the main components in photoluminescence experiments. The physics behind it is simple. The light from source hits the sample causing production of electron-hole pairs as well as electron interactions. Some of these interactions cause an emission of light, which is then filtered to its different energies and then recorded by the detector. All of this must occur in the dark. Since we are actually measuring light, data can easily be corrupted.

The plasma polymerised thin films of area 1cm^2 is excited by the He Cd laser and the luminescence light from the sample is collected by the CCD array. The schematic of a photoluminescence set up is as shown in Fig. 2.12.

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Chapter 3

Electrical Properties of Cobalt Phthalocyanine Tetramers

3.1. Introduction

Phthalocyanines and their polymers are well known for their unique photoconducting and semiconducting properties [1-7]. Though the discovery of these materials is accidental, the phthalocyanine ring is a good ligand and every element in the periodic table including non-metallic elements like silicon and phosphorous form a complex with phthalocyanine ring [1,5,8]. Materials based on phthalocyanines have been of particular significance in many fields concerning energy conversion (photovoltaic & solar cells), electrophotography, photosensitizers, gas sensors, rectifying devices, electrochromism, optical data storage, LB films, liquid crystals, and non linear optics [9,10]. The electrical properties of polymeric phthalocyanine are of interest because of their conjugated structure and stability against light, heat, moisture and air. Hence polymeric phthalocyanines are suitable candidates for use as environmentally stable electrically conductive materials [11-14]. Polymeric metallophthalocyanines of copper (Cu), nickel (Ni) and cobalt (Co) possess large extended conjugated structures and exhibit high conductivity [12,15,16]. Among them, tetrameric cobalt phthalocyanine exhibits greater conductivity than the nickel and copper phthalocyanine tetramers [12]. Hopping or tunneling conduction mechanism is the usual transport of charge carriers found in conducting polymers.

In this chapter, a systematic investigation on the electrical properties of tetrameric cobalt phthalocyanine is carried out. Also their variation with temperature and frequency is discussed. The mechanism of electrical conduction is explained using Mott's variable range hopping model. which is the essence of this chapter.

3.2. Preparation of Cobalt Phthalocyanine Tetramer

Tetramer of cobalt phthalocyanine was prepared, purified and characterised by the solution method [17,18] and is explained in section 2.6.1 of chapter 2. The proposed structure of tetrameric cobalt phthalocyanine is shown in Fig. 3.1.

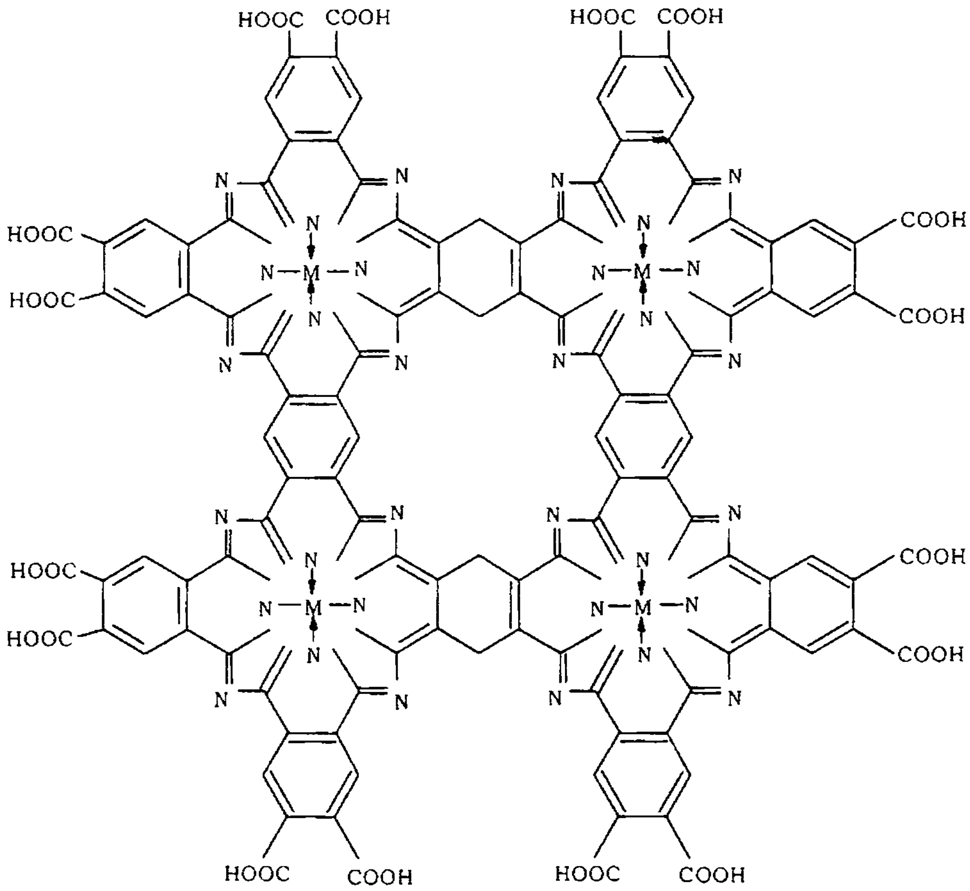

Fig. 3.1. Structure of Metallophthalocyanine Tetramer [M-Cobalt]

3.3. Elemental Analysis

Elemental analysis was carried out in a PERKIN ELMER 2400 Elemental analyser, which uses a combustion method to convert the measured elements [C, H, N] to simple gases. These gases were then estimated by measuring their thermal conductivity. The metal content of the compound was estimated by decomposing a known weight of the material with concentrated sulphuric acid and the estimation of this solution was carried out by atomic absorption spectroscopy.

The elemental analysis carried out on carboxyl-terminated tetramer is shown in Table 3.1. These were calculated based on the structure given in Fig. 3.1. Since the carboxyl-terminated tetramer contains bound water molecules it does not give one to one agreement with the calculated and observed elemental analysis values. The purity of the compound was reconfirmed by the following method [12].

The carboxyl-terminated tetramer (1.0 g) was thoroughly ground to a powder and refluxed in boiling acetic anhydride (20 ml) for 36 hours. The reaction mixture was cooled and filtered. The residue obtained was washed with chloroform and dried in a vacuum oven (1mm Hg) at 373 K for 5 hours. The presence of anhydride was confirmed by characteristic infrared (IR) peaks at 1830 cm^{-1} and 1720 cm^{-1}. The elemental analysis of anhydride terminated tetramer given in Table 3.1 agree fairly well with the calculated values indicating the purity of the product.

Table 3.1.

Elemental analysis of carboxyl terminated cobalt phthalocyanine tetramer and anhydride terminated cobalt phthalocyanine tetramer

Molecular formula of repeating unit		Elemental Analysis (Wt%)			
		C	H	N	Co
Carboxyl terminated tetramer [$C_{120}H_{40}N_{32}O_{32}Co_4.8H_2O$]	Calculated	51.0	2.0	15.88	8.35
	Observed	44.0	1.96	14.90	8.20
Anhydride terminated tetramer [$C_{120}H_{24}N_{32}O_{24}Co_4$]	Calculated	56.89	0.95	17.69	9.30
	Observed	54.86	1.52	17.63	9.20

3.4. Dielectric Permittivity Measurements

The tetrameric cobalt phthalocyanine powder samples were pressed in the form of pellets of diameter 10mm and thickness ranging from 1 mm - 3 mm. The permittivity studies were carried out on these pellet samples using a home made dielectric cell and an HP 4285A LCR meter in the frequency range 100 KHz - 5 MHz from room temperature (300 K) to 383 K under dynamic vacuum (10^{-2} Torr). The cell was standardised using standard teflon samples and the lead and fringe capacitances were estimated. The LCR meter was interfaced via a PC and the dielectric measurements were carried out using a package based on virtual instrumentation (VI) commonly known as LabVIEW. From the measured values of dielectric permittivity and the dielectric loss factor the ac conductivity was calculated.

The dielectric studies of the cobalt phthalocyanine tetramer samples were calculated using the relation

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \qquad (3.1)$$

Where C is the capacitance of the sample, A is the surface area of the sample, ε_0 is the permittivity of air and ε_r is the dielectric permittivity of the sample

The characteristic dependence of dielectric permittivity ε with frequency for different temperatures was plotted and is shown in Fig. 3.2. The dielectric permittivity shows a steady increase with temperature but a decrease with frequency.

Normally, metallophthalocyanine tetramers are highly conjugated and have large planar structure. The π electrons are completely delocalised over the entire molecule. If the applied field is increased the probability of tunneling of electrons between molecules is also increased causing high dielectric permittivity and dielectric loss [14]. The decrease of dielectric permittivity with increase in frequency can be explained using Koop's phenomenological theory [19]. According to this theory the dielectric structure is considered as an inhomogeneous medium of two layers of Maxwell Wagner type [14]. In this model, the dielectric structure is imagined to consist of well conducting grains that are separated by poorly conducting grain boundaries.

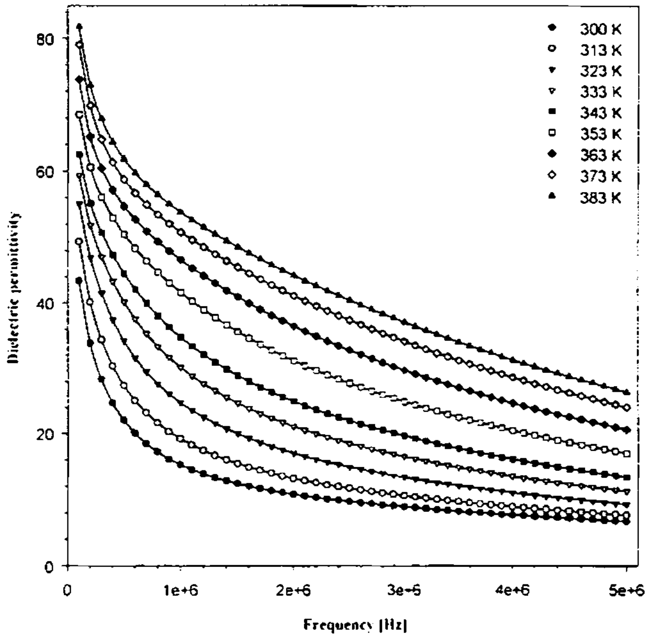

Fig. 3.2. Dielectric permittivity of CoPc tetramer at different temperatures

The variation of tan δ with frequency for different temperatures is shown in Fig. 3.3. In that tan δ shows a loss peak characterised by a relaxation frequency for all temperatures. After the loss factor reaches a maximum it decreases almost linearly at lower temperatures and there is not much variation at higher temperatures. Also from the Fig. 3.3. it is observed that when temperature increases the value of maximum dielectric loss shifts towards higher frequency. Here tan δ depends on both frequency and temperature.

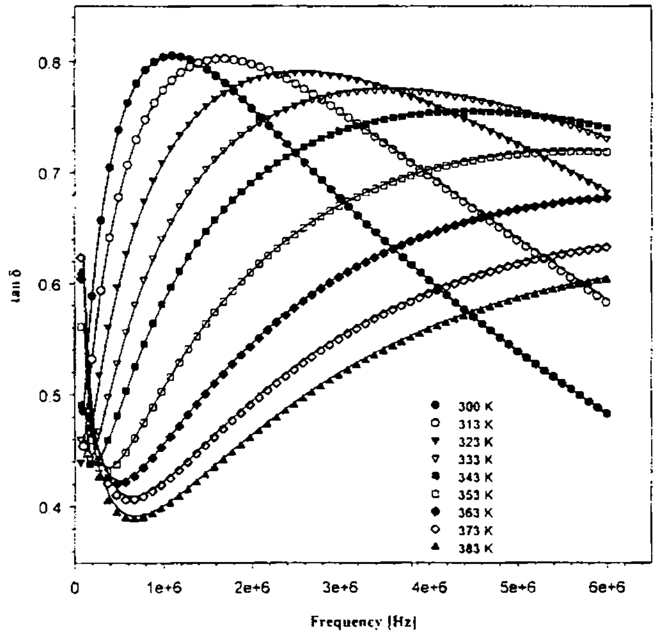

Fig. 3.3. Dielectric loss vs Frequency of CoPc Tetramer at different temperatures

The frequency versus ac conductivity graph was plotted for different temperatures and is depicted in Fig. 3.4. From the Fig. 3.4., it is seen that the value of ac conductivity does not show much variation at lower frequencies both at room temperature and at higher temperatures. That is, there is no appreciable variation of ac conductivity with temperature at lower frequencies. (≈100 KHz) Above 100 KHz it shows a rapid increase with frequency. This is in accordance with the theory of ac conduction in amorphous materials, which predicts that for polaron transport or other hopping modes, the ac conductivity will increase monotonically with increased frequency of the applied field [20]. The ac conductivity, dielectric permittivity and dielectric loss can be related by the following equation

$$\sigma_{ac} = 2\pi\varepsilon_0\varepsilon_r f \tan\delta \qquad (3.2)$$

Where ε_0 is the permittivity of air, ε_r is the dielectric permittivity of the sample, f is the frequency and tanδ is the dielectric loss.

The variation pattern of ac conductivity with frequency for different temperatures is shown in Fig. 3.4. and indicates that the ac conductivity increases with temperature as the frequency increases. This is because as the temperature increases the mobility of charge carriers also increases. When frequency increases the dielectric permittivity decreases (Fig. 3.2.), tan δ is also found to increase with increase of frequency. However, the rate of decrease of dielectric permittivity with frequency is lower than the rate of increase of loss factor with frequency and hence there is a net increase of ac conductivity with increase of both frequency as well as temperature.

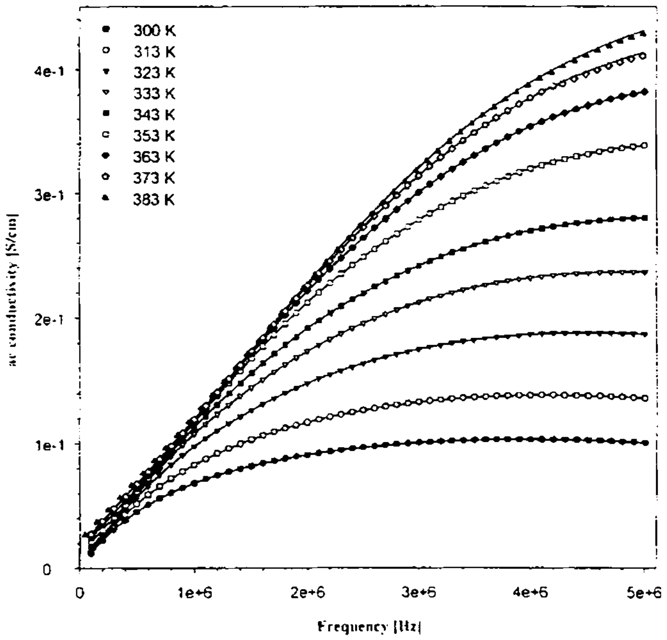

Fig. 3.4. ac conductivity of CoPc tetramer with frequency at different temperatures

3.5. DC Conductivity Measurements

Electrical conductivity measurements was carried out on the pellets of tetrameric cobalt phthalocyanine using Keithley 487 Picoammeter and a conductivity cell under high vacuum (10^{-5} Torr) in the temperature range 90 K – 300 K by employing a two probe technique.

phthalocyanine because of the extended conjugated structure the energy values are much lower as seen by our measurements. The dc conductivity values obtained for the tetramer is $\approx 10^{-3}$ S/cm, which is much higher than that of monomeric phthalocyanine (10^{-10} S/cm). It is found that the ac conductivity is higher than that of dc conductivity. If the charge transport is due to hopping, the ac conductivity will be higher than the dc conductivity [22]. This proves that hopping type of charge transport occurs in the tetrameric cobalt phthalocyanine. In the case of dc conduction, charge carriers have to cross the entire sample and if the hopping sites are randomly distributed, the current path will inevitably include some long distance hops, which have a very small hopping probability. At high frequencies, hopping mainly occurs between close neighbours, because the field is reversed before the long distance hop.

3.6. Conduction Mechanism

In order to understand the conduction mechanism in these conjugated systems a Mott's variable range hopping model is used [23]. According to this model, in a disordered material when the charge carriers are localised due to random electric fields, instead of band conduction, charge transport takes place via phonon assisted hopping between localised states. Since the localised states have quantized energies extending over a certain range, activation energy is required for each hop.

The mechanism is based upon the idea that carriers tend to hop larger distances to sites, which lie energetically closer than to their neighbours.

According to the Mott's Variable range hopping model, the dc conductivity in three dimensions can be expressed as

$$\sigma_{dc} = \sigma_o \exp\left[-\left({}^{T_o}\!/_{T}\right)^{1/4}\right] \qquad (3.4)$$

Where T is the temperature. T_0 is the Mott's Characteristic temperature and is given by

$$T_0 = \frac{\lambda \alpha^3}{KN(E_F)} \qquad (3.5)$$

Where $\lambda \approx 18.1$ is a dimensionless constant [24], α is the inverse rate of fall of the wave function [25], K is the Boltzmann Constant and N (E_F) is the density of states at the Fermi energy.

The Range of hopping R [26] and the energy for hopping W in three-dimensional variable range hopping are expressed as

$$R = \left[\frac{9}{8}\pi \alpha KTN(E_F)\right]^{\frac{1}{4}} \qquad (3.6)$$

and $$W = K\left(T_0 T^3\right)^{\frac{1}{4}} \qquad (3.7)$$

Log σ vs $T^{-1/4}$ gives best fit as seen in Fig. 3.7. Log σ vs $T^{-1/2}$ is shown in Fig. 3.6. and is not a perfect fit compared with Logσ vs $T^{-1/4}$. The value of Mott's Characteristic temperature T_0 has been calculated from the graph log σ vs $T^{-1/4}$ [Fig. 3.7.] and is found to be 9.68×10^6 K.

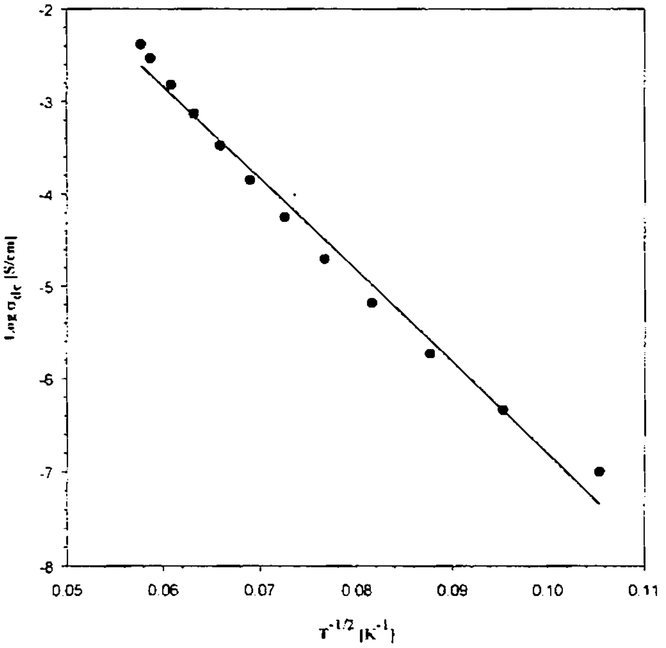

Fig. 3.6. Plot of log σ_{dc} as a function of $T^{-1/2}$

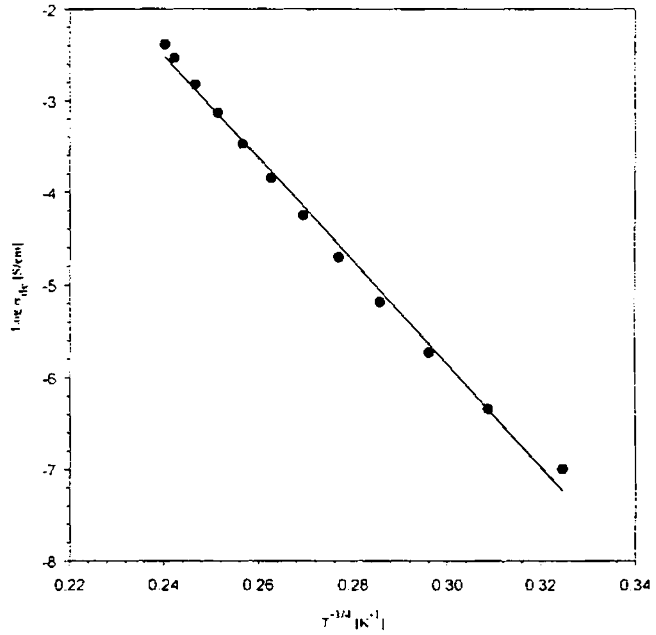

Fig. 3.7. Plot of log σ_{dc} as a function of $T^{-1/4}$

From equations 3.5,3.6 and 3.7 the value of N (E_F), R and W were calculated at 100K and the values cited (Table 3.2) are estimated after assuming a reasonable value for α = 1 Å. Table 3.2 depicts the Mott temperature and its parameters for tetrameric cobalt phthalocyanine. Low values obtained for the mobility indicates that the electronic states are localised, in accordance with the hopping mechanism.

Table 3.2.

Mott temperature, Density of states at the Fermi energy, Range of hopping and energy for hopping of tetrameric cobalt phthalocyanine

Sample	Mott temperature T_0 (K)	N (E_F) $cm^{-3}eV^{-1}$	R_{hop} (Å) (100K)	W_{hop} (eV) (100K)
Tetrameric cobalt phthalocyanine	$9.68 X 10^6$	$2.17 X 10^{22}$	3.20	0.15

The temperature dependence of dc conductivity has been studied and is found that it follows the 3D variable range hopping. From the above discussions it is seen that the best fit to the dc conductivity can be achieved with a $T^{1/4}$ behaviour and the values of T_0, N (E_F), R and W can be found by assuming that the conduction is three dimensional and follows the variable range hopping model. In order to enhance the conductivity of phthalocyanine, they can be modified either by thermal or chemical treatment [27,28].

3.7. Conclusion

The variation of dielectric permittivity of tetrameric cobalt phthalocyanine with temperature and frequency has been studied and it is found that the dielectric permittivity values increases from 43 to 81 at 100 KHz in the temperature range of 300 K to 383 K. The dielectric permittivity decreases with frequency up till 5MHz and almost remains constant thereafter. The activation energy for electrical conductivity is found to be 0.12 eV and the conduction behaviour is found to fit the 3 dimensional variable range hopping model with the values of 9.687×10^{6} K, 2.168×10^{22} $cm^{-3}eV^{-1}$, 3.20 Å and 0.15 eV for Mott temperature T_0, density of states at the Fermi energy N (E_F), range of hopping R and hopping energy W at 100K respectively.

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Chapter 4

Investigations on the Electrical and Structural Properties of Polyaniline Doped With Camphor Sulphonic Acid

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4.1. Introduction

Ever since the discovery of polyacetylene, the field of conducting polymers became an attractive research topic for chemists, physicists and electrical engineers alike [1]. In recent years much of the attention is devoted to the study of the semiconducting properties of these polymers. Among the various conducting polymers, polyaniline, polypyrrole and polythiophene need special mention owing to their potential applications [2-7] and interesting properties. In that, polyaniline is unique because the electrical properties vary with respect to their oxidation states of the main chain and protonation of the imine nitrogen atoms.

The wide range of electrical, electrochemical and optical properties of polyaniline along with its excellent stability makes it a useful electronic material for various applications. Some of the potential devices based on polyaniline are organic light emitting diodes [8], low power rechargeable plastic batteries, gas sensors, super capacitors, photovoltaic cells [9], liquid crystal displays [10,11] and Schottky devices [12–14]. Bulk polyaniline in its pure form is an insulator and dopants like camphor sulphonic acid, methane sulphonic acid and hydro choloric acid enhance the electrical conductivity of polyaniline [15]. The enhancement of the conductivity in these materials is either by the generation of extended states in doped molecules or by charged defects with electronic structures [16].

Incorporation of dopants also modifies the structural properties of polyaniline. This modification plays an important role in improving the conductivity of the polymer.

Pure polyaniline and polyaniline doped with camphor sulphonic acid is synthesised in the bulk. The electrical, structural and morphological properties are evaluated. The results are explained based on the crystallinity and morphology of the samples. This chapter deals with the analysis of these results.

4.2. Sample Preparation

Polyaniline is prepared by the direct oxidation of aniline using an appropriate chemical oxidant [17, 18]. The method employed for preparing PANICSA is cited in section 2.6.2 of chapter 2.

4.3. X - Ray Diffractogram

XRD scans for polyaniline emeraldine base (PANIEB) and polyaniline doped with camphor sulphonic acid (PANICSA) were recorded using a Rigaku D Max C, X - ray diffractometer with Cu Kα radiation (λ=1.5415Å). The samples were scanned at the rate of 1^0 per minute in the reflection mode over a range of 2θ from 5^0-35^0.

The X Ray diffractograms obtained for PANIEB and PANICSA are depicted in Fig. 4.1. It has been reported that the crystallinity of the polyaniline sample depends on the conditions set during the synthesis of the polymer [19]. The XRD pattern of polyaniline emeraldine base powder shows distinct peaks at $2\theta \approx$ 9.80°, 10.75°, 12.10°, and 20.60°. The peak at 2θ = 20.60° indicates that the PANIEB is amorphous. The reported value for this amorphous peak is at 2θ = 19.50° [20].

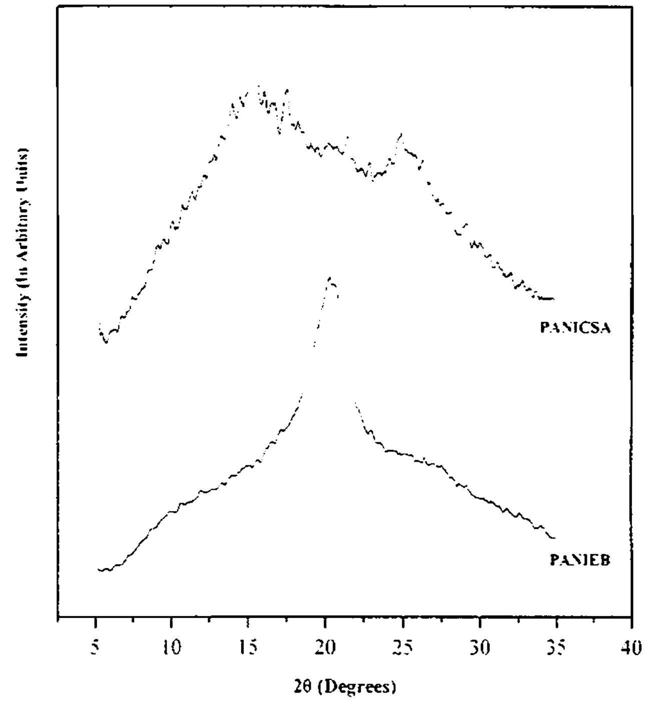

Fig. 4.1. XRD Scans of Powdered PANIEB and PANICSA

However, in the case of polyaniline doped with camphor sulphonic acid, broad and weak diffraction appeared at 2θ ≈ 13.90°, 15.40°, 17.55°, 21.38°, 22.84°, and 24.88°. In the case of PANIEB the amorphous peak is at 2θ = 20.60°. But the corresponding peaks for PANICSA were observed at 15.40°, 17.55°, and 21.38°. This is an indication that doping induces certain amount of crystallinity in the samples. However, the appearance of an appreciably sharp crystalline peak at 2θ = 15.40° for CSA doped PANI with a weak crystalline peak at 2θ = 24.88° may also be due to the change in the crystalline form of the sample. From the X ray diffractogram, (Intensity versus 2θ) the crystallinity index of the sample was calculated by employing a formula put forwarded by Manjunath et al.'s [20]. According to this, the resolution of the peak R is given by

$$R = \frac{m_1 + 2m_2 + ... + m_{n-1}}{h_1 + h_2 + ... + h_n} \quad (4.1)$$

where m_1, m_2... are the heights of minima between two peaks and h_1, h_2... are the heights of peaks from the base line.

From the resolution of the peak (R), the lateral order or the index of the crystallinity (1-R) was calculated. The percentage of crystallinity for PANICSA has been estimated by employing the relation (4.1) and it has been found to be 56%.

4.4. Morphology

In order to confirm the crystallinity of polyaniline doped with camphor sulphonic acid, the SEM of polyaniline emeraldine base and polyaniline doped with camphor sulphonic acid has been carried out by using JEOL Scanning Electron Microscope and is shown in Fig. 4.2. (a) and (b). In PANIEB, the particles are seen agglomerated with out much interparticle spacing.

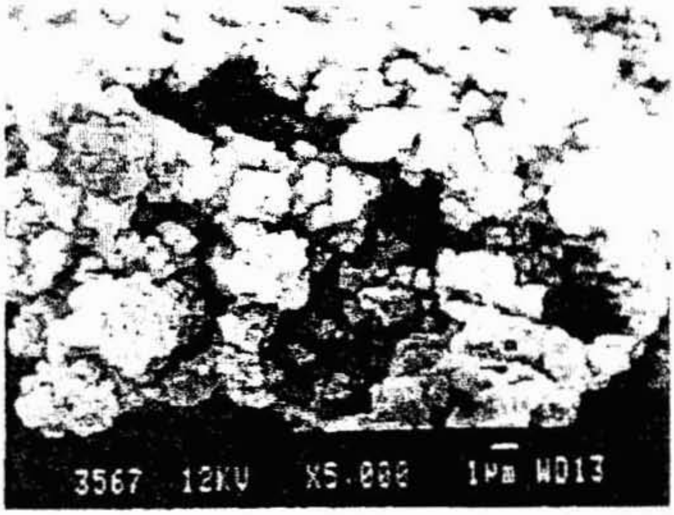

Fig. 4.2. A. Scanning electron micrographs of PANIEB

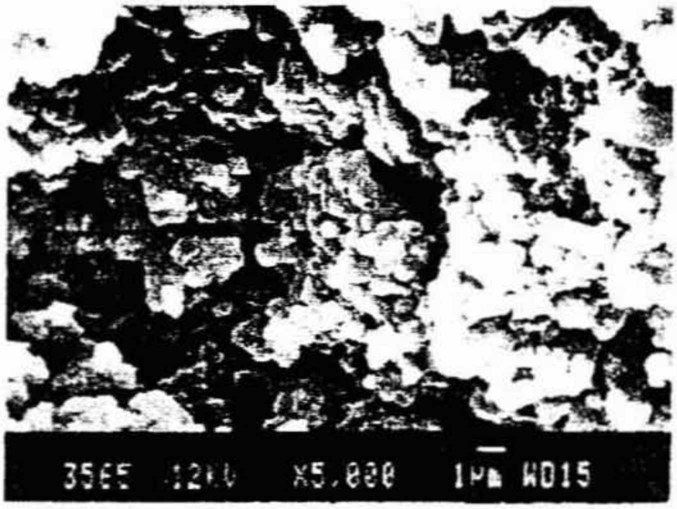

Fig. 4.2. B. Scanning electron micrographs of PANICSA

The grain size is ~ 0.6 μm. However, in PANICSA the particles can be seen distinctively. The grain size is ~ 0.8 μm. From SEM and XRD studies, it can be concluded that polyaniline doped with Camphor sulphonic acid is more crystalline than that of polyaniline emeraldine base.

4.5. FTIR Studies

Fig. 4.3. shows the FTIR spectrum polyaniline emeraldine base and polyaniline doped with camphor sulphonic acid.

In the PANICSA Spectrum the peaks at 1475 cm^{-1}, 1558 cm^{-1} indicate that the aromatic ring is retained in the polymer. Also it exhibits two distinct peaks at 2926 cm^{-1} and 2960 cm^{-1}. These peaks are assigned to the C-H stretching. The peak at 3432 cm^{-1} shows the stretching of NH Group. The peak at 1286 cm^{-1} corresponds to the C-H in plane of deformation [21]. Also the peaks at 792 cm^{-1}, 1042 cm^{-1} correspond to the sulphonic acid group. The existence of a peak at 1738 cm^{-1} shows that the ketone group [22] is in tact.

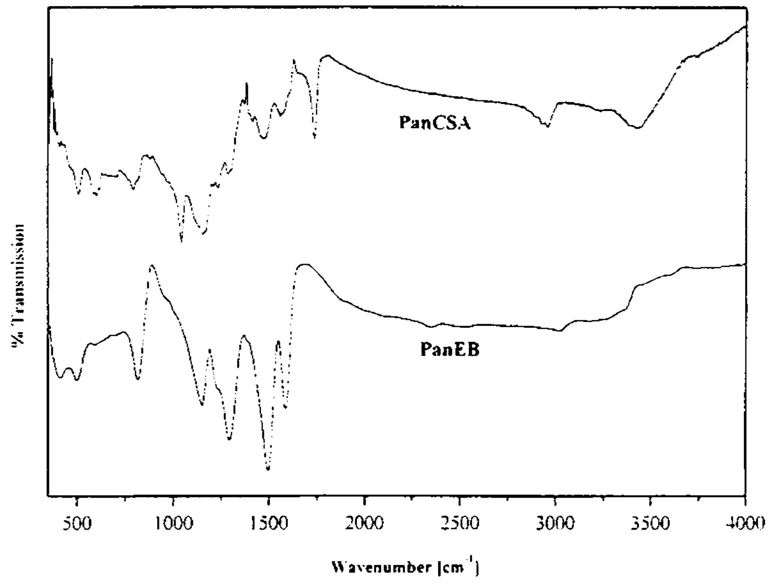

Fig. 4.3. FTIR Spectra of PANIEB & PANICSA

However, in the FTIR Spectrum of PANIEB, there are no peaks corresponding to sulphonic acid group and ketone group. Hence it is concluded that the monomer aniline is getting polymerised and the sulphonic acid group is attached to NH group. Based on FTIR spectra and further analysis a plausible structure of PANICSA is suggested and is as shown in Fig. 4.4.

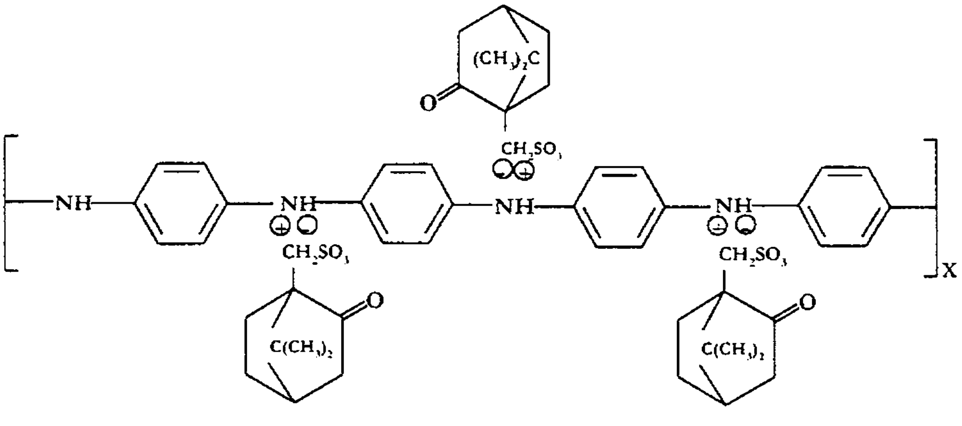

Fig. 4.4. Structure of PANICSA

4.6. Dielectric and AC conductivity Studies

The powdered polyaniline doped with camphor sulphonic acid samples were pressed in the form of pellets with a diameter 10 mm. Dielectric permittivity studies were carried out on these samples by using a home made four probe dielectric cell and an HP 4285A LCR meter in the frequency range 100KHz to 2MHz in the temperature range 300K to 373K under the dynamic vacuum (10^{-2} Torr).

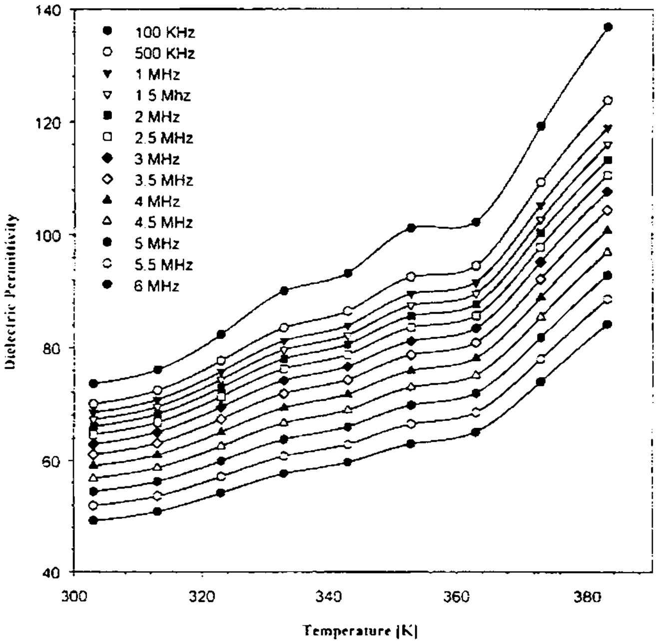

Fig. 4.5. Variation of Dielectric permittivity with Temperature

The variation of dielectric permittivity with temperature and frequency is shown in Fig. 4.5. and Fig. 4.6. The value of dielectric permittivity varies form 73 - 136. When temperature increases, the dielectric permittivity also increases and it decreases with frequency. From Figs. 4.5. and 4.6. it is seen that in the lower temperature regime the change in dielectric permittivity is small but it rises there after. Also the increase is rapid at higher temperatures.

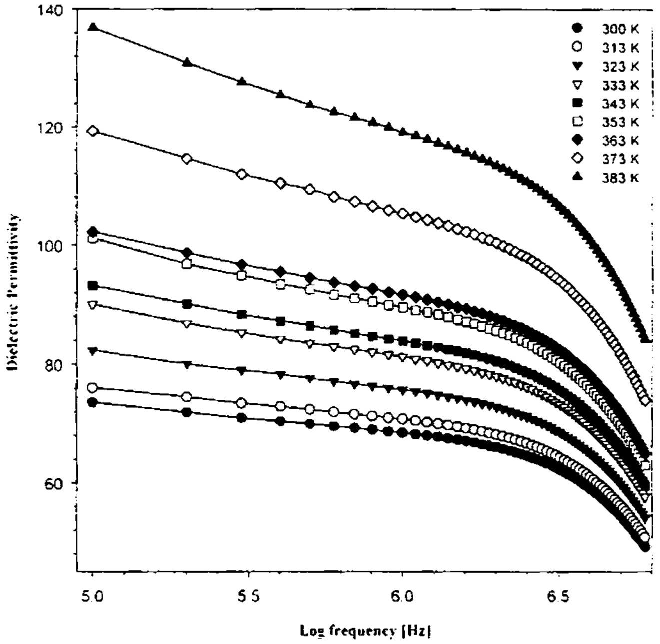

Fig. 4.6. Variation of Dielectric permittivity with Frequency

The increment of dielectric permittivity is rapid above 360K. The increase of dielectric permittivity with temperature could be related to the well-known phenomenon that the polarisation increases with temperature, which was found to be valid in a wide range of materials [23]. This is due to the effect of interfacial polarisation caused by space charges and microscopic filed distortion [24]. If the applied field is increased the probability of tunneling of electrons between molecules is also increased which cause high dielectric permittivity and dielectric loss.

The variation of ac conductivity with frequency for different temperatures is shown in Fig. 4.7. When frequency increases the ac conductivity also increases with temperature. The variation of σ_{ac} is small at lower temperatures and shows rapid change at higher temperatures. σ_{ac} can be written with the help of the following equation [25].

$$\sigma_{ac} \alpha \omega^{n} \tag{4.2}$$

where ω is the angular frequency and n is the index which is characteristic of the type of conduction mechanism/relaxation mechanism dominant in amorphous materials. The value of n evaluated from Fig. 4.7. is around 0.045 both at lower and higher temperatures.

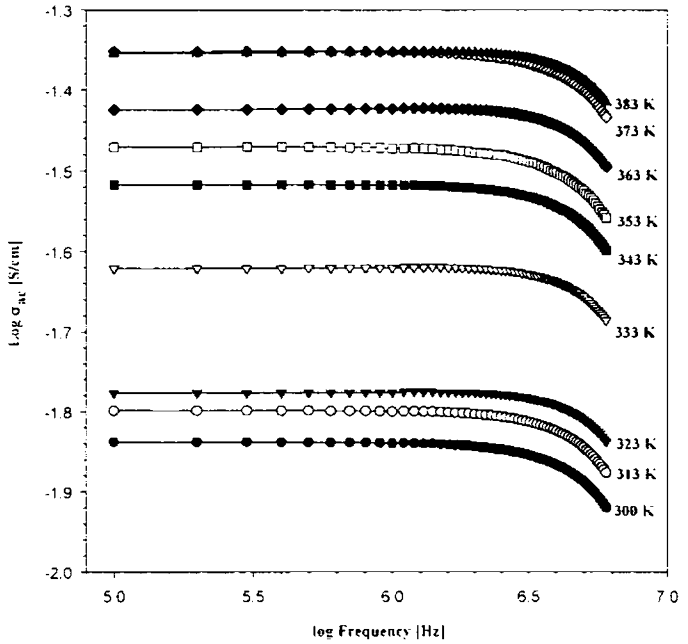

Fig. 4.7. ac Conductivity of PANICSA as a function of frequency

Fig. 4.8. shows the characteristics dependence of the ac conductivity with temperature at different frequencies. The activation energy calculated from these plots is 0.069 eV. The activation energy required for hopping process for materials with higher dielectric permittivity is assumed to be quite low. Also because of this low activation energy, a weak temperature dependence of electrical conductivity is expected to appear around room temperature [26].

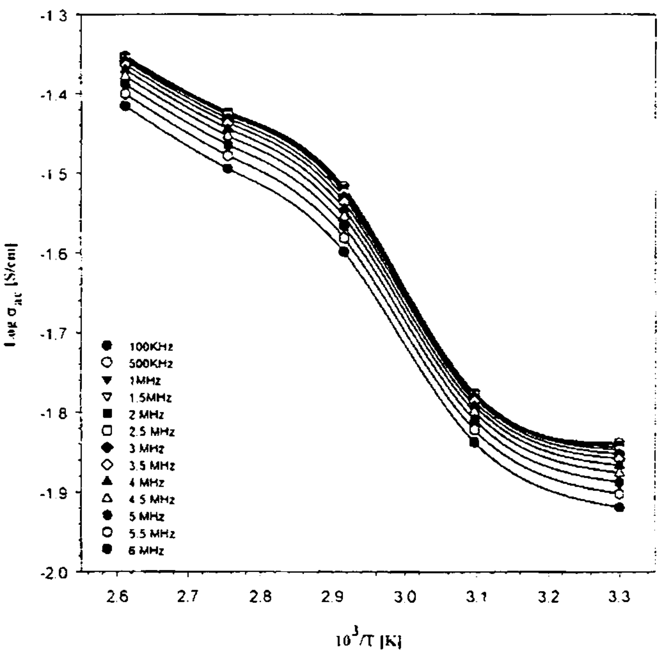

Fig. 4.8. AC Conductivity of PANICSA as a function of temperatures

4.7. DC Conductivity Studies

The current voltage measurements were carried out on these samples and the characteristics are studied. The sample shows ohmic behaviour without any breakdown. The variation of dc conductivity with temperature is plotted and is shown in Fig. 4.9. The conductivity value of PANICSA calculated at room temperature is around 27 S/cm. The temperature dependent of DC conductivity indicates that the observed metallic DC conductivity is due to only a small fraction of delocalised carriers which are primarily localised in metallic islands and that the achievable conductivity for such systems when the entire charge carriers density participates surpasses that of copper [6]. It has also been shown that the relaxation of an electric field in a charge carrier system is attributable to the charge hopping of mobile carriers, which can lead to both short-range σ_{ac} and long-range σ_{dc}. The activation energy is calculated by employing the following relation

$$\sigma_{dc} = \sigma_o Exp\left(-\frac{E_A}{K_B T}\right) \qquad (4.3)$$

Where σ_0 is constant. E_A is the activation energy and K_B is the Boltzmann Constant. The activation energy calculated is around 0.015 eV. The disagreement between the activation energy value of σ_{ac} and σ_{dc} suggests that the hopping conduction mechanism plays an important role for the conduction process [27].

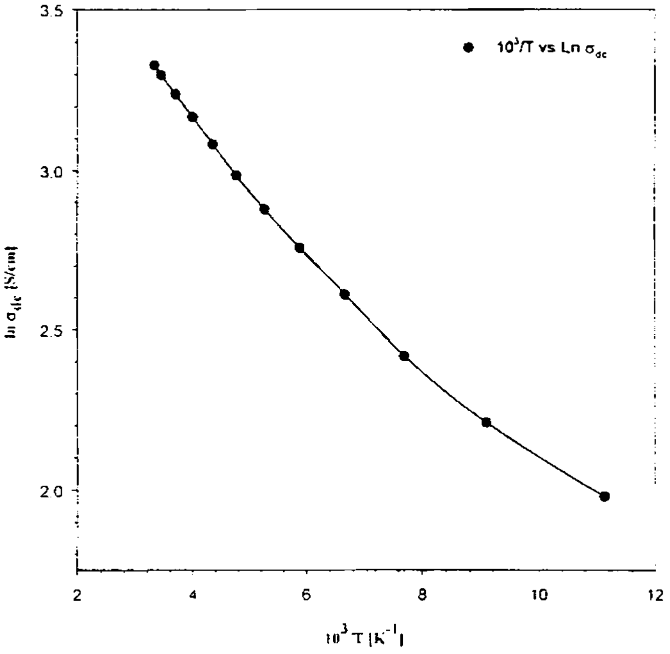

Fig. 4.9. DC Conductivity of PANICSA as a function of temperature

4.8. Conclusion

From the FTIR spectrum and further analysis it can be concluded that the sulphonic acid group is attached to the polyaniline chain without altering the aromatic ring. The retention of the aromatic ring in the polymer structure is responsible for the high thermal stability to the material. X Ray diffraction studies indicate that the doping of polyaniline with camphor sulphonic acid modifies the structure. The percentage of crystallinity was calculated and found to be increasing. This is in conformity with the findings of electron micrography studies. The dielectric studies on PANICSA proved that the cross-linked polymers posses good dielectric behaviour at higher temperatures. It is known that the dependence of conductivity on frequency and the low activation energies of the carriers are indicative of a hopping conduction mechanism. It can be seen that doped PANICSA is semiconducting.

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Chapter 5

Studies on Polyaniline - Tetrameric Cobalt Phthalocyanine Composites

5.1. Introduction

Organic and metallo organic polymers gained importance because of their electrical, electronic, non-linear optical, electrochemical and photochemical applications [1-4]. In order to make use of these polymer compounds for specific applications they are modified either by co-polymerisation or by making blends with other polymers [5]. The production of blends using organic and metallo organic polymers is an attempt to obtain new polymeric materials by combining properties of the components of the blend [6,7]. The use of blends/composites in various electric and electronic devices attracted attention because of their conductive properties, chemical stability and low price. Among the many conducting polymers, polyaniline seems to be one of the best candidates for preparing conducting polymer composites since it is stable both thermally and environmentally [8-11]. The blends of polyaniline doped with sulphonic acid [12], phosphoric acid in different polymers such as polymethyl methacrylate [13], cellulose [14] and polyurethane [15] have been investigated. Electrical properties of polyaniline blended with other polymers are relatively different from the pure polyaniline. Along with the incorporation of insulating polymers into conducting polymers, introducing polymeric/oligomeric phthalocyanine into polyaniline matrixes are also investigated [7, 16]. A conductive composite using polyaniline and polymeric phthalocyanine can be used as a rechargeable batteries [16].

In this chapter optical, electrical and morphological studies on blends of polyaniline - oligomeric cobalt phthalocyanine are discussed. The dielectric and conductivity measurements of polyaniline at different proportions with oligomeric cobalt phthalocyanine are carried out for different temperatures and the conduction mechanism in these composites is explained based on the Mott's variable range hopping model.

5.2. Preparation of PANICSA - CoPc Composites

Powdered polyaniline doped with camphor sulphonic acid (PANICSA) was blended with tetrameric cobalt phthalocyanine (CoPc) by mixing them homogeneously in an agate mortar for several hours. The method of preparation of both the polymers is explained in section 2.6.3 of chapter 2.

5.3. FTIR Studies

The FTIR Spectrum of tetrameric cobalt phthalocyanine and PANICSA/CoPC composites are as shown in Fig. 5.1. and 5.2. respectively.

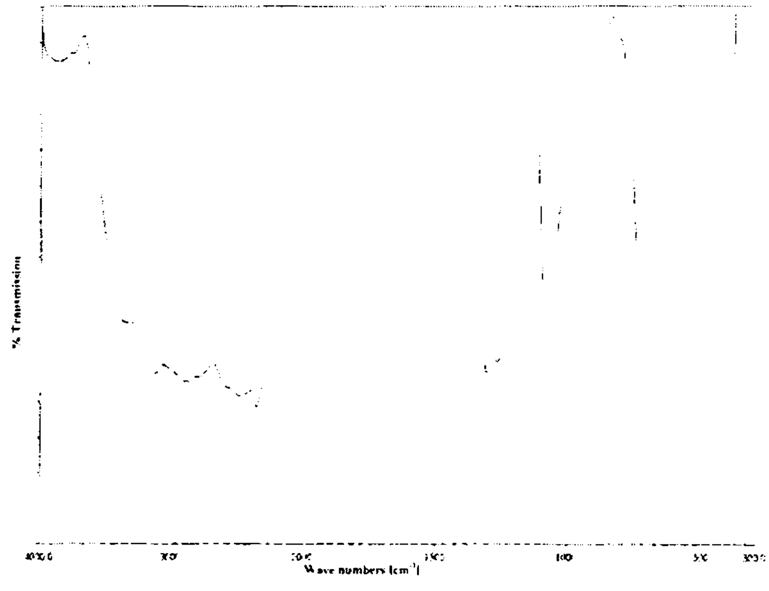
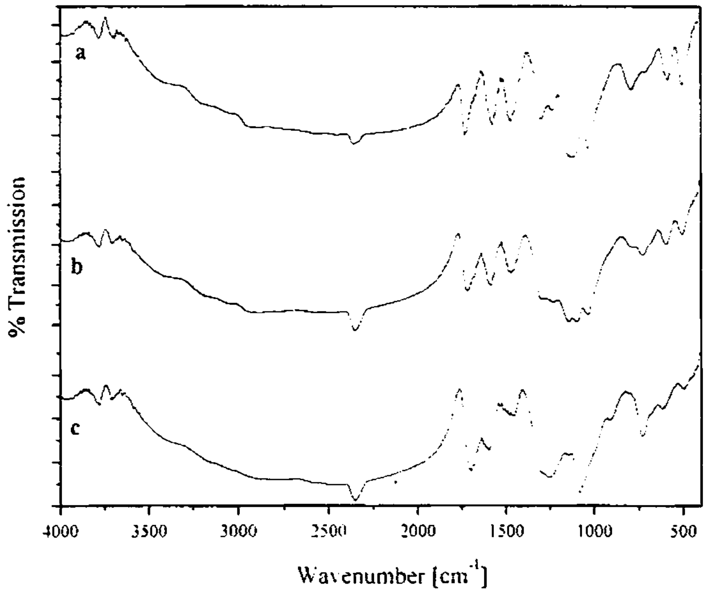


Fig. 5.1. FTIR Spectrum of tetrameric cobalt phthalocyanine

In Fig. 5.1, the peak at 721cm^{-1} is attributed to non-polar deformation vibrations of the CH bonds of benzene ring [17]. The peaks at 1460cm^{-1}, 1307cm^{-1}

are indicative of skeletal stretching vibrations of C-C in benzene ring and the characteristic peak for C=N skeletal stretching vibration is also noted at 1517cm^{-1} [18]. Metal ligand vibration band is observed at 904cm^{-1} for tetrameric cobalt phthalocyanine indicating the stability of the metal phthalocyanine, which is due to the strong bonding between the metal ion and four surrounding nitrogen atoms [19]. The CO stretching and OH deformation confirm the presence of COOH, which is characterised by the band 1696cm^{-1}. Moskalev and Kirin found an intense band at 1006cm^{-1}-1008cm^{-1} and Stymne observed at 1539cm^{-1} for NH vibration in metal free phthalocyanine [20,21]. The absence of these peaks in Fig. 5.1. suggests that the sample doesn't have any metal free phthalocyanine.

IR spectra of polyaniline with tetrameric cobalt phthalocyanine blends show peaks at 715-733cm^{-1}, 904-1038cm^{-1}, 1081-1100cm^{-1} and 1695-1728 cm^{-1}, which are attributed to phthalocyanine skeleton [22-24]. In addition to that the bands at 1460-1479cm^{-1}, 1578-1597cm^{-1}, 1234-1299cm^{-1} and 1129-1142cm^{-1} are corresponds to the polyaniline [25].



a. PANICSA 90 CoPc 10: b. PANICSA 50 CoPc 50: c. PANICSA 10 CoPc 90

Fig. 5.2. FTIR Spectra of Conducting polymer composites

In that the bands at 1234-1299cm^{-1} and 1129-1142cm^{-1} show that the incorporated polyaniline in composites is camphor sulphonic acid doped polyaniline. Apart from these the peaks at 1695-1728cm^{-1} in the blends correspond to –COOH group. These data prove that the respective cobalt phthalocyanine tetramer is incorporated into polyaniline matrix.

5.4. Dielectric Studies

5.4.1. Dielectric Permittivity

A typical set of graphs depicting the dielectric behaviour of the conducting polymer composites of polyaniline with tetrameric cobalt phthalocyanine over frequency range 100KHz-5MHz at different temperatures were carried out and is shown in Figs. 5.3. – 5.8.

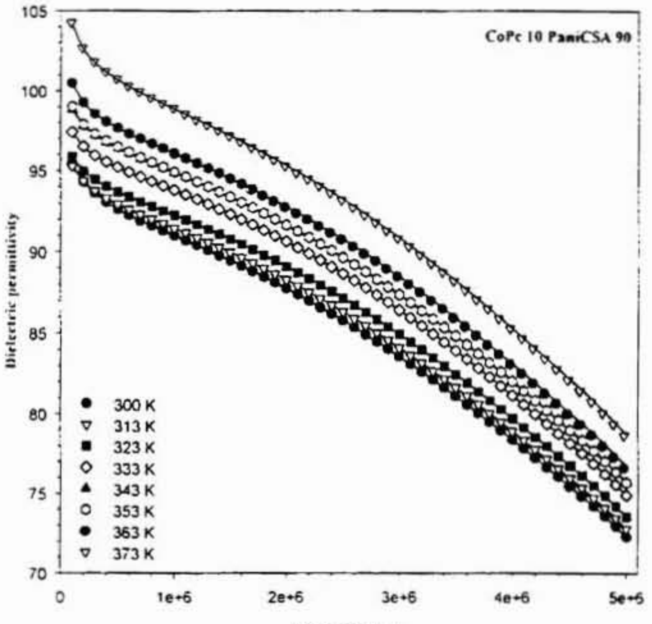


Fig. 5.3. Variation of dielectric permittivity of CoPc10 PANICSA90 at different temperatures

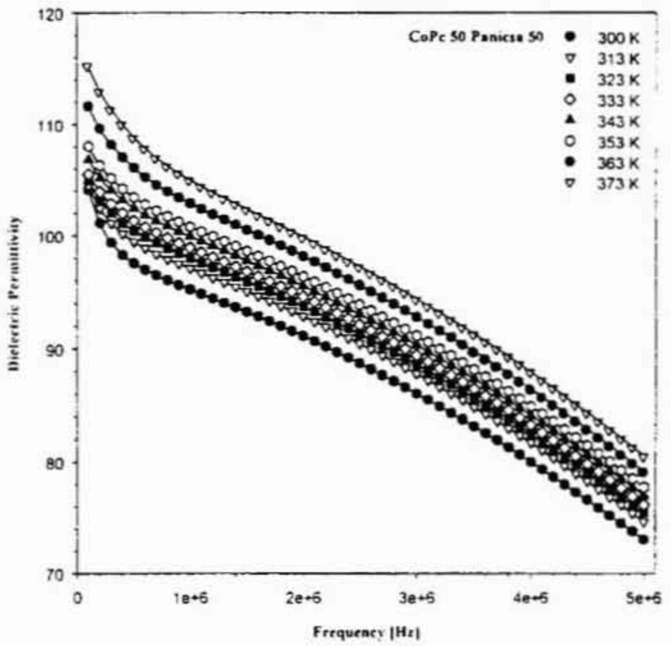


Fig. 5.4. Variation of dielectric permittivity of CoPc50 PANICSA50 at different temperatures

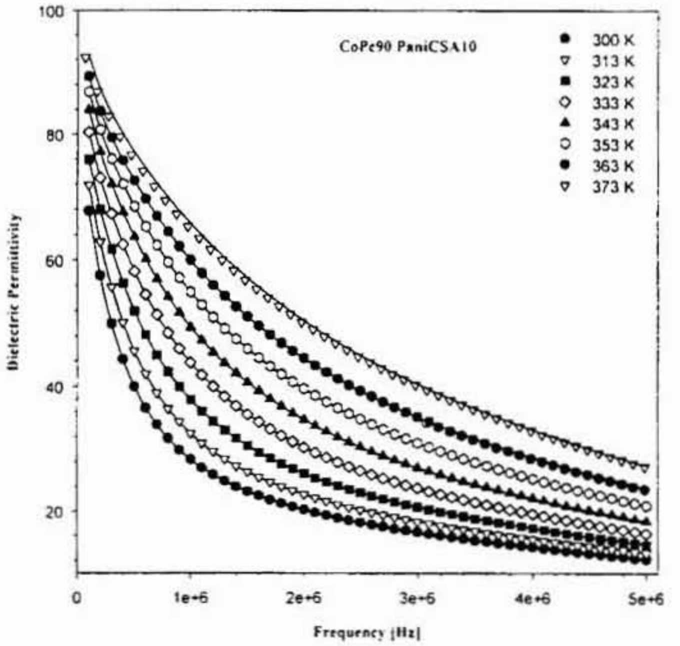


Fig. 5.5. Plot of frequency vs dielectric permittivity for CoPc90 PANICSA10

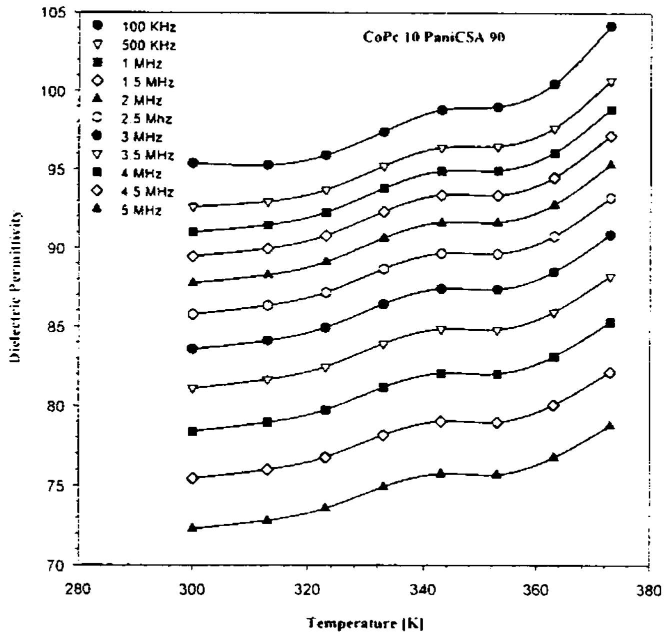


Fig. 5.6. Variation of dielectric permittivity of CoPc10 PANICSA90 at different frequencies

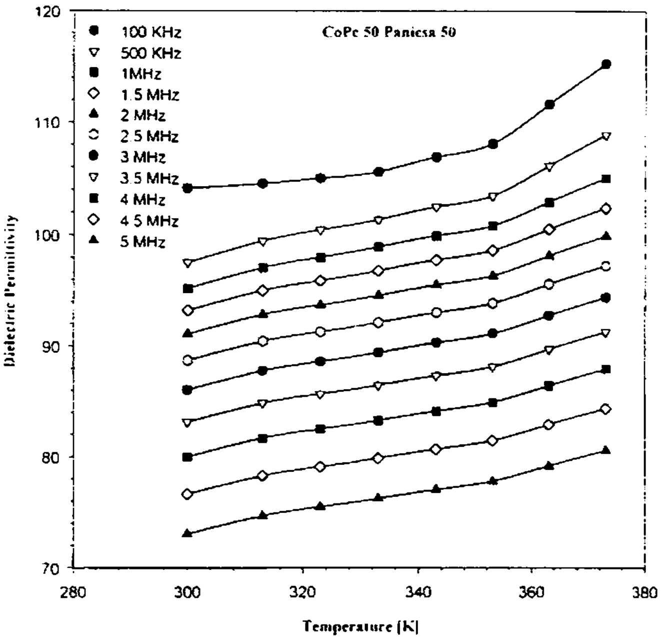


Fig. 5.7. Temperature vs dielectric permittivity of CoPc50 PANICSA50

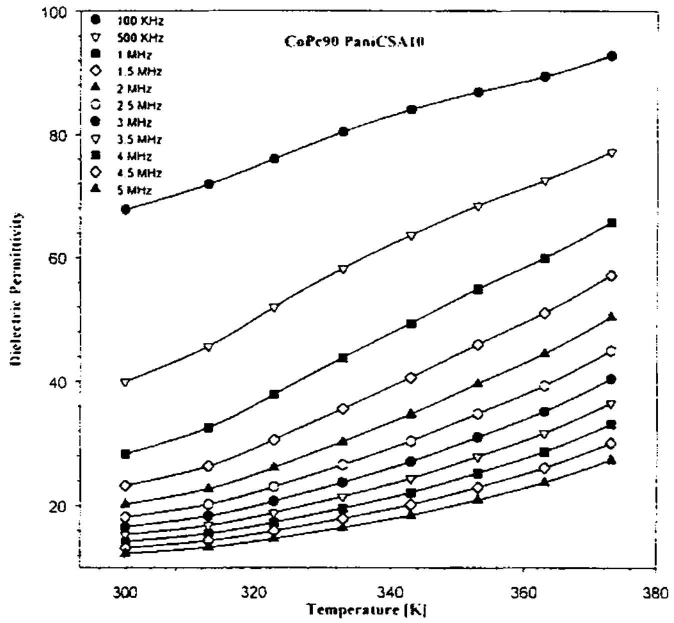


Fig. 5.8. Variation of dielectric permittivity of CoPc90 PANICSA10at different frequencies

The pattern of variation of dielectric permittivity for all compositions is almost similar and the values at 373K for 1MHz are tabulated and are shown in Table 5.1.

Table 5.1.

Value of Dielectric permittivity of cobalt phthalocyanine, polyaniline doped with camphor sulphonic acid and their composites

Sample	Dielectric Permittivity [373K, 1MHz]
CoPc	50.78
CoPc90 PANICSA10	65.71
CoPc50 PANICSA50	104.99
CoPc10 PANICSA90	98.86
PANICSA	105.26

The value of dielectric permittivity at 1MHz of oligomeric cobalt phthalocyanine at 373K is 50.78 and it increases with increase of polyaniline concentration, till both PANICSA and CoPc are at equal proportions and after that it decreases. However the value of dielectric permittivity of CoPc10 PANICSA90 approaches towards the PANICSA value. This shows that the tetrameric cobalt phthalocyanine doesn't influence the dielectric permittivity of composites.

The dielectric permittivity increases with increase of temperature and at each temperature it decreases monotonically with increasing frequency. This may be due to the tendency of induced dipoles in macromolecules to orient themselves in the direction of the applied field when the frequency of alternation is low. However at high frequencies the induced dipoles will hardly be able to orient themselves in the direction of the applied field and hence the dielectric permittivity decreases [26]. Frequency dependence of the dielectric permittivity in these composites is more pronounced at lower frequencies. This is because the interfacial polarisation plays an important role in these composites at lower frequencies. This polarisation will arise only when the phases with different conductivities are present [27]. Conducting polymers and its composites show high dielectric permittivity due to the large effective size of metallic islands in these compounds and easy charge transfer through well-ordered chains in disordered regions.

5.4.2. Dielectric Loss

The dielectric loss vs frequency curves for composites are presented in Figs. 5.9. – 5.11. The loss factor decreases with increase of frequency and increases with temperature. This is usually associated with ion drift, dipole polarisation or interfacial polarisation [28]. The increase of dielectric loss with decreasing frequency is very rapid at low frequencies. Also the study of miscibility in blends/ composites by dielectric relaxation involves the assessment of one or more loss peaks. In binary blends one or multiple loss peaks will occur [29]. These blends does not exhibit peaks except in the case of CoPc90% PANICSA10% composition. In the case of CoPc90% PANICSA10% mixture there appears a peak in the dielectric loss curve at higher frequencies. Also the loss peak is shifted towards the higher frequency as the temperature increases. This shift in the loss peak is in accordance with the Debye theory of orientation.

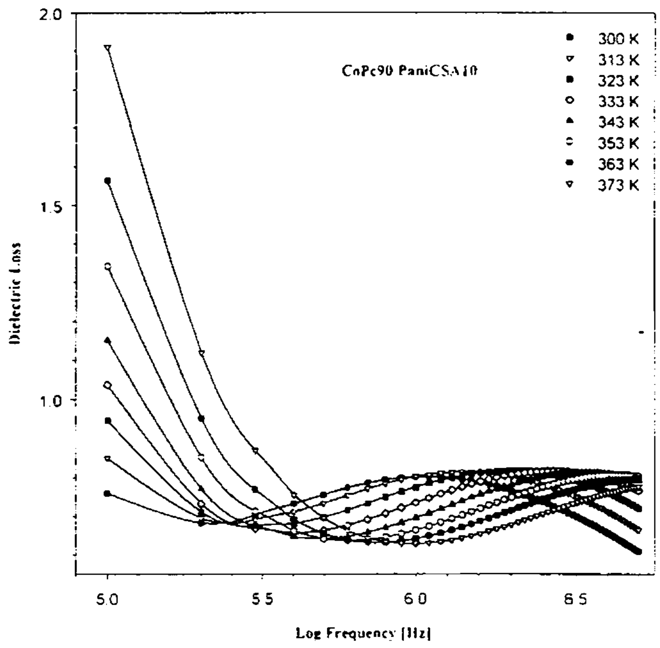


Fig. 5.9. Variation of dielectric loss of CoPc90 PANICSA10 at different temperatures

This indicates that CoPc90% PANICSA10% mixture behaves more like CoPc. The appearance of a peak only in this composition is because of the extended conjugated structure of CoPc tetramer, which causes delocalisation of the charge and hence the peak shift towards higher frequency. As polyaniline content increases in the mixture, the mixture exhibits the characteristic of polyaniline itself because of very high conductivity of polyaniline there by leading to loss peak at lower frequency. This dielectric loss behaviour is in accordance with the dielectric permittivity behaviour observed for the same blends.

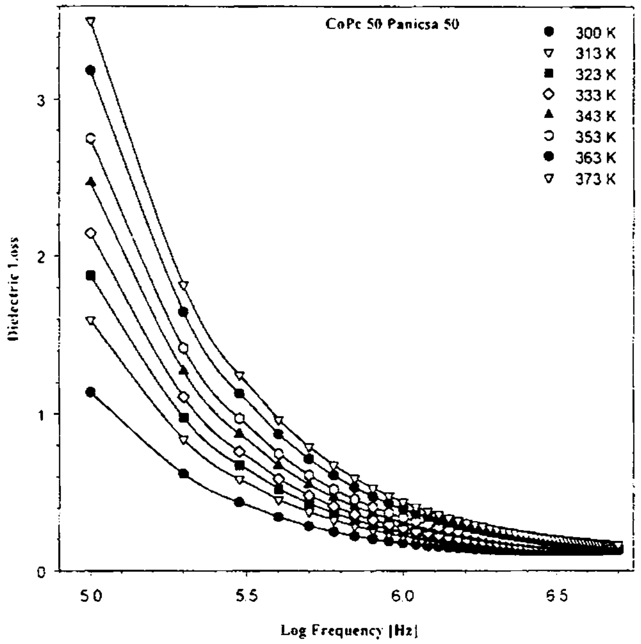


Fig. 5.10. Plot of frequency vs Dielectric loss for CoPc50 PANICSA50

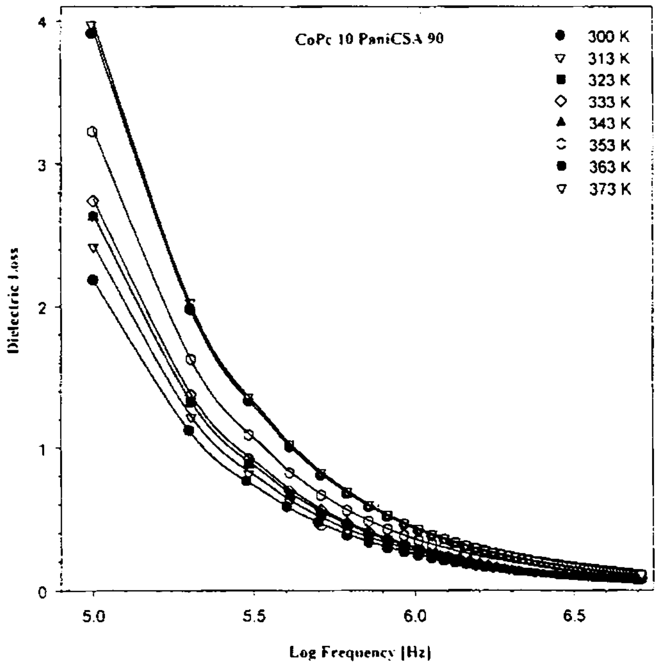


Fig. 5.11. Dielectric loss vs frequency curves for CoPc10 PANICSA90

5.5. AC Conductivity

AC conductivity of the composite samples is calculated from the measured dielectric permittivity and dielectric loss. Variation of AC conductivity of conducting polymer composites with frequency for different temperatures is shown in Figs. 5.12. – 5.14.

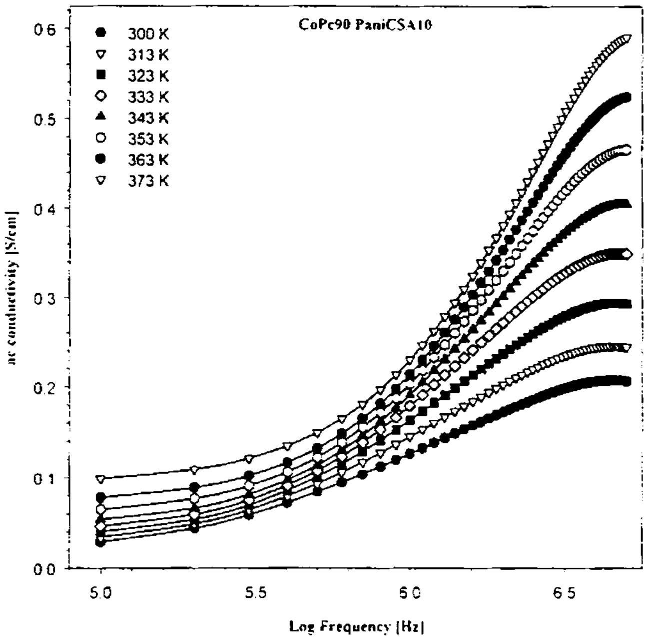


Fig. 5.12. Variation of AC conductivity of CoPc90 PANICSA10 with frequency at different temperatures

From the curves it is seen that in samples with high concentration of CoPc frequency dependence is predominant where as in the sample with high concentration of PANICSA show less frequency dependence. This is because the incorporation of phthalocyanine materials in conducting polymers improves the charge storage capacity of the blends. The ac conductivity obeyed the empirical relation of the form [30]

$$\sigma_{AC}(\omega) = A\omega^{s} \qquad (5.1)$$

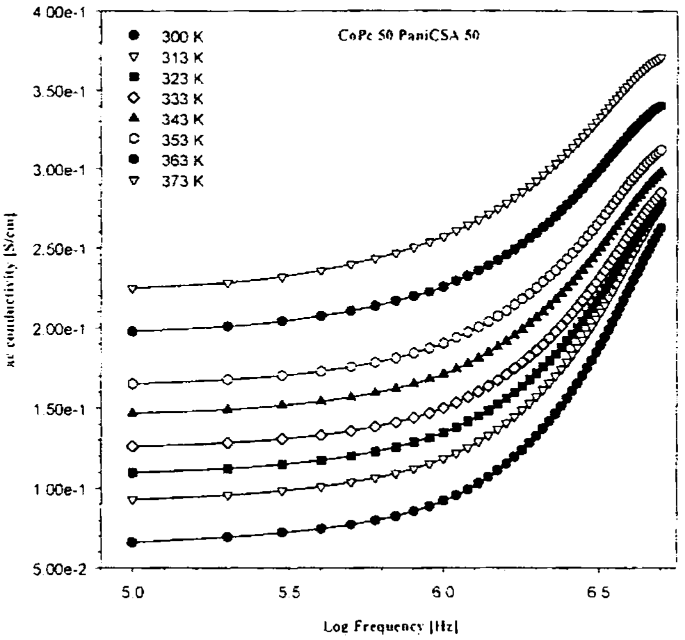


Fig. 5.13. Variation of AC conductivity of CoPc50 PANICSA50 with frequency

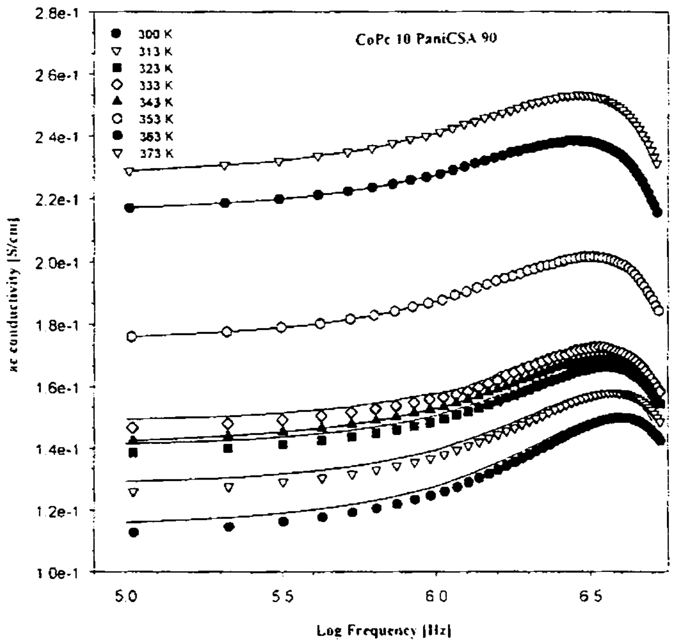


Fig. 5.14. Variation of AC conductivity of CoPc10 PANICSA90

The variation of exponent s with temperature gives information about the conduction mechanism involved. The value of s is less than 1 for all samples. An increase in AC conductivity with frequency and weak temperature dependence indicates that there may be charge carriers, which are transported by hopping through the defect sites along the polymer chain [31].

5.6. DC Conductivity

To investigate the charge transport mechanism in composites, the temperature dependence of the electrical conductivity is studied in the temperature range 70K to 300K for all compositions. The temperature dependence of dc conductivity for different volume fractions of polyaniline doped with camphor sulphonic acid is shown in Fig. 5.15.

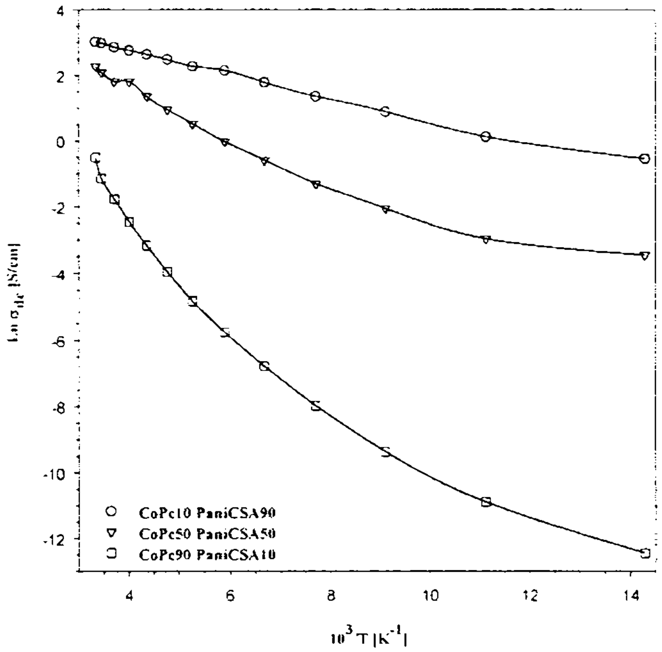


Fig. 5.15. Temperature dependence of dc conductivity of composites

In semiconductors, if the main conduction mechanism is due to the carriers excited beyond the mobility edge into non - localised or extended states, the dc conductivity is expressed as [30]

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \qquad (5.2)$$

Where σ_0 is the proportionality constant, E_a the activation energy, k the Boltzmann constant and T is the temperature.

The conductivity increases with increase of temperature for all compositions and it increases with increase of volume fraction of polyaniline doped with camphor sulphonic acid (PANICSA). The activation energy values are evaluated from the graph (Fig. 5.15.) and it is found that this decreases with increase of volume fraction of polyaniline doped with camphor sulphonic acid. The low values of activation energy implies that the conduction is due to the excitation of carriers into mobility edge and/or to the localised states at the band edges which is inadequate to explain the conduction mechanism.

The conductivity data is analysed with the help of Mott's Variable range hopping. In polymers with non - degenerate ground states, the charge transport is due to polarons and bipolarons [32,33]. This mechanism is consistent with the existence of high - density states in the band gap. Charge carrier localisation may give rise to the formation of polarons and the charge transport may be considered due to the variable range hopping. According to Mott's Theory the conductivity is expressed as

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^N\right] \qquad (5.3)$$

In this equation, if N=1/2 or 1/4 corresponds to the variable range hopping conduction in one dimension or in three dimension respectively. Where T_0 is the Mott's characteristic temperature and is explained in chapter 3. Log σ vs $T^{-1/2}$, Log σ vs $T^{-1/4}$ are plotted for composites and are shown in Figs 5.16. – 5.18.

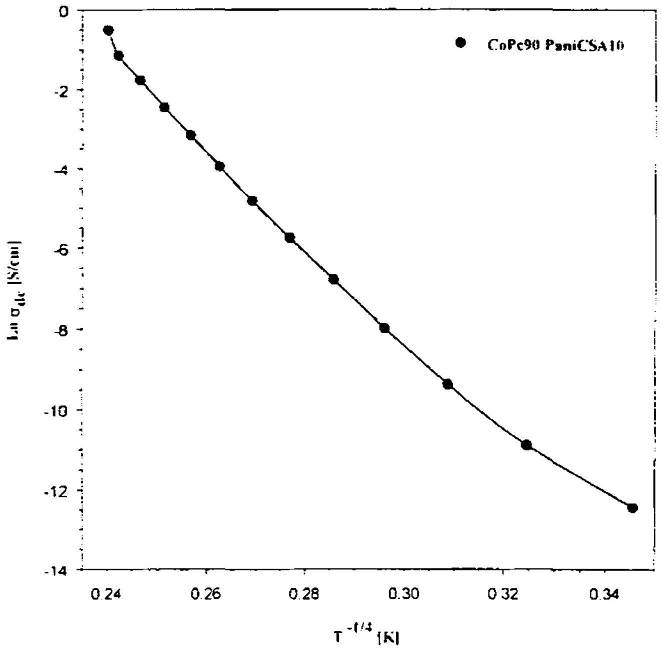


Fig. 5.16. lnσ_{dc} vs $T^{-1/4}$ for CoPc90 PANICSA10

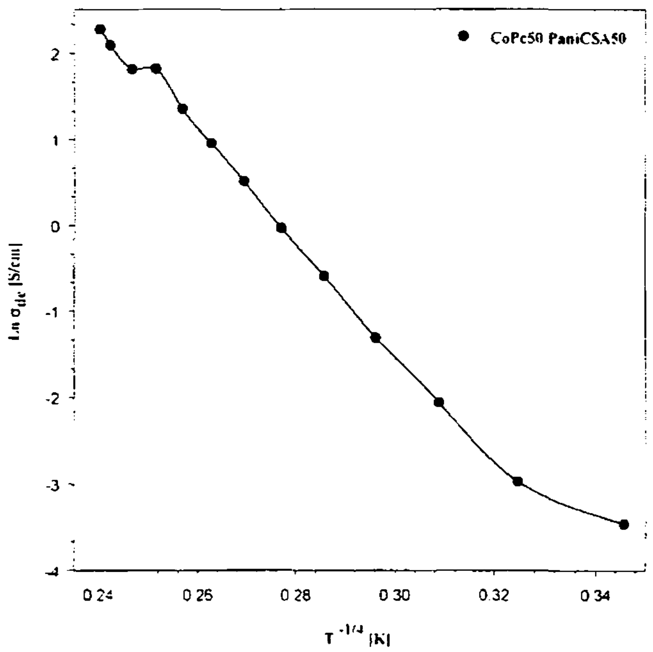


Fig. 5.17. lnσ_{dc} vs $T^{-1/4}$ CoPc50 PANICSA50

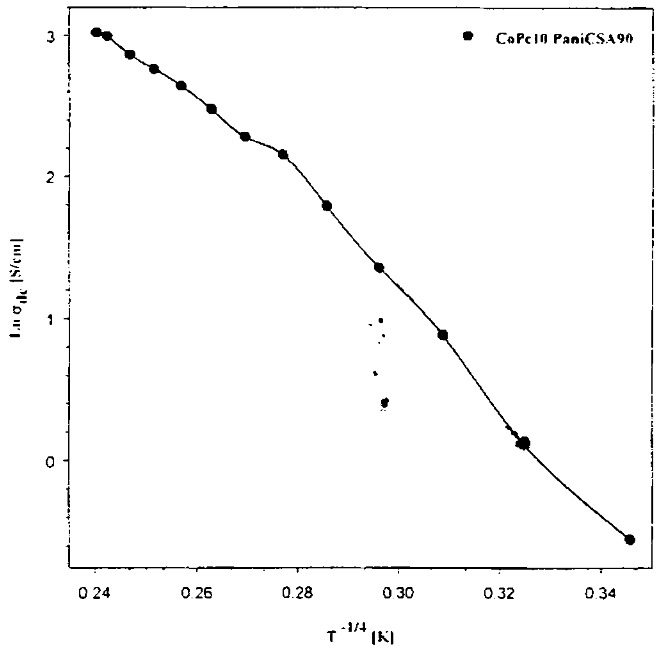


Fig. 5.18. $\ln\sigma_{dc}$ vs $T^{-1/4}$ CoPc10 PANICSA90

From the plots Mott's characteristic temperature is evaluated. Based on the obtained T_0 and using appropriate relation Motts parameters for composites are calculated and are tabulated in Table 5.2.

Table 5.2.

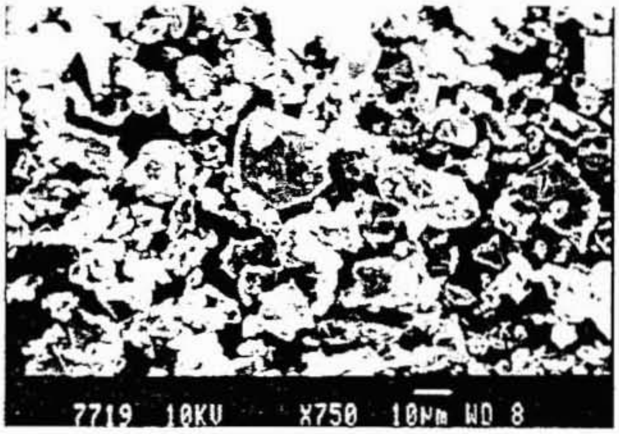
Mott's parameters for composites

Sample	Mott Temperature	N (E_F) $cm^{-3}eV^{-1}$	R_{hop} (Å) 100K	W_{hop} (eV) 100K	E_a (eV)
CoPc 90 PANICSA 10	1.7187 x 10^8	1.2225 x 10^{21}	1.5626	0.3119	0.095
CoPc 50 PANICSA 50	1.1929 x 10^7	1.7614 x 10^{22}	3.044	0.16	0.049
CoPc 10 PANICSA 90	1.376 x 10^6	1.527 x 10^{23}	5.22	0.052	0.029

From Table 5.2. it is seen that depending on the volume fraction of polyaniline. density of states at the Fermi energy. range of hopping. energy for hopping of composites are changed. Not only the Mott's parameters the conduction mechanism also changes. The available literature indicates that the conduction mechanism of unblended polyaniline is one dimensional variable range hopping. But tetrameric cobalt phthalocyanine follows the three - dimensional hopping conduction. From our observations. it is clearly seen that tetrameric cobalt phthalocyanine and polyaniline composites follows the three - dimensional hopping conduction.

5.7. Morphology

Fig. 5.19. represents the electron micrographs of polyaniline - tetrameric cobalt phthalocyanine composites. From Fig.5.19. it is seen that the distribution of the polymer depends on the volume fraction of the polymers in composites. This is clearly seen in our conductivity measurements. That is Depending on the volume fraction of the polymer the conductivity value is changed.



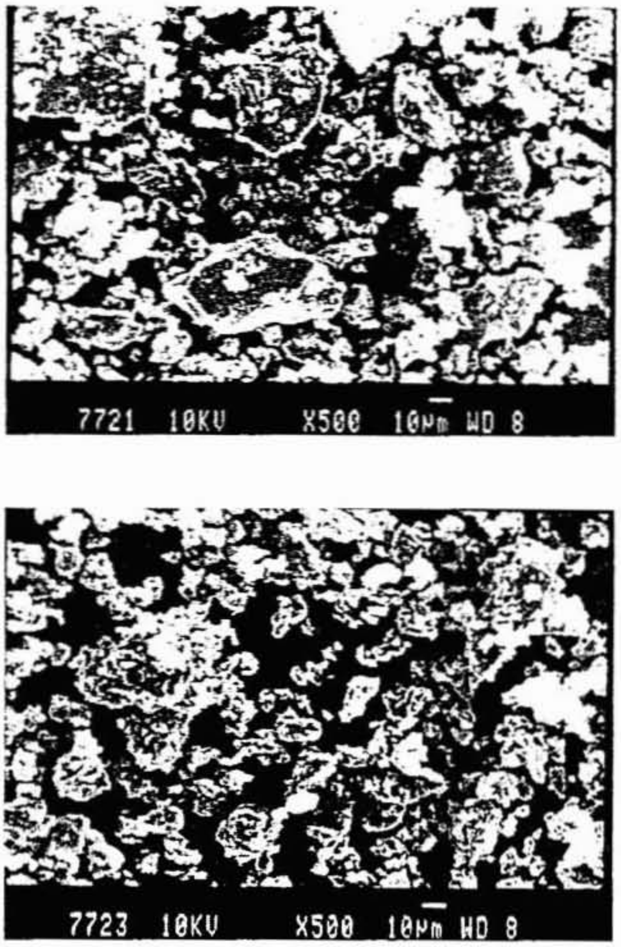


Fig. 5.19. Surface morphology of conducting polymer composites

5.8. Conclusion

Blends of polyaniline and tetrameric cobalt phthalocyanine are prepared. The incorporation of tetrameric cobalt phthalocyanine into polyaniline matrix is confirmed with the help of FTIR spectrum. The dielectric studies of these blends are carried out in the frequency range 100KHz – 5MHz and the corresponding dielectric loss are compared. From I-V studies it is clear that variable range hopping conduction is the dominant conduction mechanism in the blends and it obeys the 3D type mechanism. The conduction mechanism is explained with the help of Mott's theory and the conduction parameters are determined. Distributions of polymer components in conducting polymer composites are confirmed with the scanning electron micrographs.

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Chapter 6

Investigations on Pristine and Swift Heavy Ion Irradiated Plasma Polymerised Aniline Thin Films

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6.1. Introduction

Organic polymers having extended π electron conjugation assume significance because of their special electrical properties, morphology and crystallinity compared with other polymers [1]. The synthesis of conducting polymers, which are environmentally, stable, processable, and with good mechanical properties leads to the possibility of new applications. [2,3] Also conducting polymers were investigated extensively for understanding the underlying physics of the conduction process and for possible applications. Some of the potential devices based on these polymers are organic light emitting diodes, sensors, low power rechargeable batteries, super capacitors, photo voltaic cells and low dielectric materials in ICs [4-8]. Polyaniline occupies an important position among conducting polymers [9,10] as it is inexpensive, environmentally stable and exhibit high conductivity. RF Plasma polymerization is one of the novel techniques for preparing polymer thin films. Thin films prepared by employing this technique are pin - hole free, uniform in thickness cross - linked and thermally stable. Structural, optical and electrical properties can be modified when it is doped with appropriate dopants [11-13]. Apart from adding dopants, irradiation of polymer thin films with swift heavy ions also modifies their various properties [14-16]. These swift heavy ions on bombardment results in the breaking of covalent bonds, promotion of cross linkages, formation of carbon clusters, liberation of volatile species and in some cases formation of new chemical bonds [17,18]. They also can induce changes in the electrical conductivity and optical band gap [19,20].

In this chapter the investigations carried out on RF plasma polymerised aniline thin films are described. The changes in structural, optical, morphological and electrical properties of pristine polyaniline are compared with the irradiated polyaniline.

6.2. Experimental Techniques

Polyaniline thin films were coated under optimum conditions. These coated thin films were shifted to a metal coating unit for coating the counter electrode. The aluminium electrode was coated by evaporating high purity aluminium wire under high vacuum. (8×10^{-5} Torr) These films were in the sandwich form of cross sectional area 2.5×10^{-5} m^2. The thickness of the film was measured by a homemade setup employing Tolansky's interferometric method [21].

Polyaniline thin films of area 1×1 cm^2 were exposed to 92 MeV Si ions in the material science irradiation facility of the Nuclear Science Centre, New Delhi. The ion beam current was ~ 3pna (particle nano ampere). The irradiation was carried out at room temperature and under high vacuum. The irradiation fluence was in the range of 10^{11}-10^{13} ions/cm^2, which depends on the time of irradiation and the incident ion current.

6.3. Structural Studies

The FTIR spectra of aniline, polyaniline and irradiated polyaniline are as shown in Fig. 6.1.A and B. The band assignments of the FTIR spectrum of polyaniline are given in Table 6.1. The peaks at 1656cm^{-1} and 1423cm^{-1} correspond to the retention of aromatic ring of polyaniline. The peak at 3207cm^{-1} shows the vibration of NH group [22]. The peaks at 2883cm^{-1} and 2834cm^{-1} are indicative of the CH stretch in polyaniline. The peak at 1059cm^{-1} is due to CH in plane deformation and CN stretching is observed at 971cm^{-1}. Substituted benzene ring is also detected from the peaks 783cm^{-1} and 676 cm^{-1}.

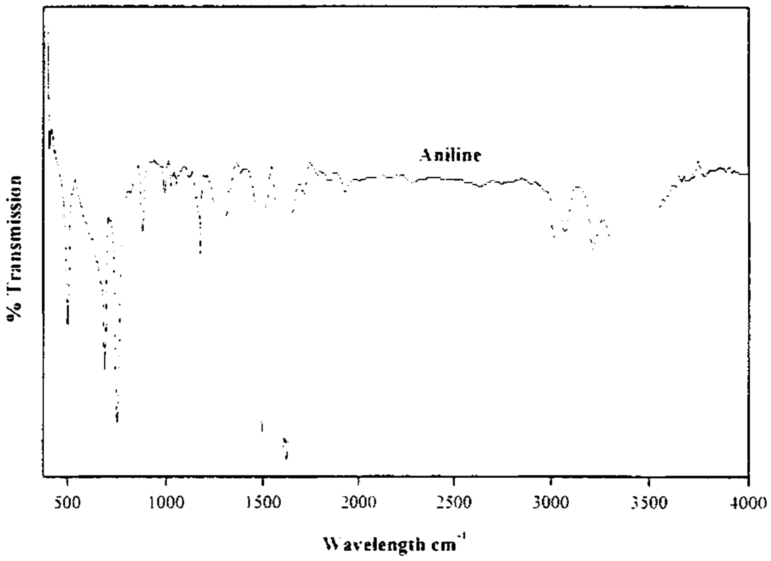

Fig. 6.1. A. FTIR Spectrum of Monomer aniline

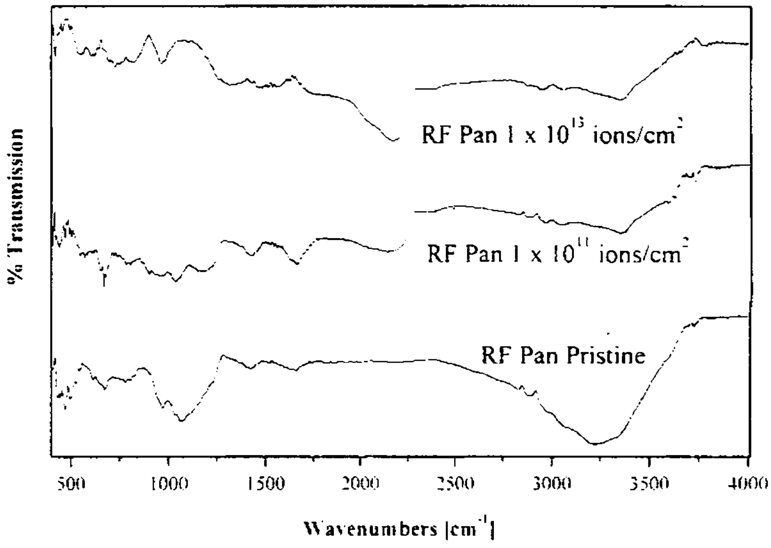

Fig. 6.1. B. FTIR Spectra of Polyaniline Pristine and irradiated polyaniline at different fluences

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Table 6.1.

FTIR assignments of Polyaniline Pristine and irradiated polyaniline at different fluences

Assignment	RF Polyaniline		
	Pristine	Irradiated	
		1×10^{11} ions/cm^2	1×10^{13} ions/cm^2
N-H Vibration	3207	3353	3340
C-H Stretch C-H Stretch	2883 2834	3058 2875	3058 2873
$C \equiv C$	-	2132	2183
Ring Stretch Ring Stretch Ring Stretch	1656 1423	1664 1436	1565 1548 1444
CH in plane deformation	1059	1037	
C-N Stretch C-N Stretch	971	973	975 1326
CH Out of plane deformation	783	804	825

From the FTIR spectrum of polyaniline it is clear that the plasma-polymerised aniline is highly disordered. Based on the above discussion and from available literature it is inferred that the hydrogen abstraction is a possibility during plasma polymerisation. From FTIR analysis a plausible structure for plasma polymerised aniline is proposed and is shown in Fig. 6.2.

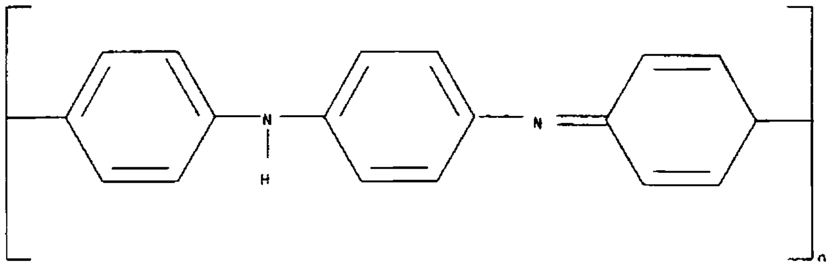


Fig. 6.2. Tentative structure of RF plasma polymerised aniline

From the FTIR spectrum, peaks assigned to the irradiated polyaniline are tabulated in Table 6.1. FTIR spectrum of polyaniline irradiated with swift heavy ions also shows broad peaks. From the spectrum, it can be seen that there is intense shift in NH stretching and CH stretching bands with respect to the polyaniline pristine. This indicates that the swift heavy ion irradiation disturbs the polymer chain. Also there is no intense shift in peaks corresponding to the aromatic ring, which is an indirect evidence to the fact that the swift heavy ion irradiation doesn't affect the aromatic ring. Apart from these fundamental spectral bands, the bands at 2132 cm^{-1} and 2183 cm^{-1} are observed [23] for films bombarded with fluence of 1 X 10^{11} ions/cm^{2} and 1 X 10^{13} ions/cm^{2} respectively. This peak corresponds to the $C \equiv C$ group. The intensity of the peak increases with increase of fluence. Based on this a tentative structure for the irradiated polyaniline thin film is proposed and is shown in Fig. 6.3.

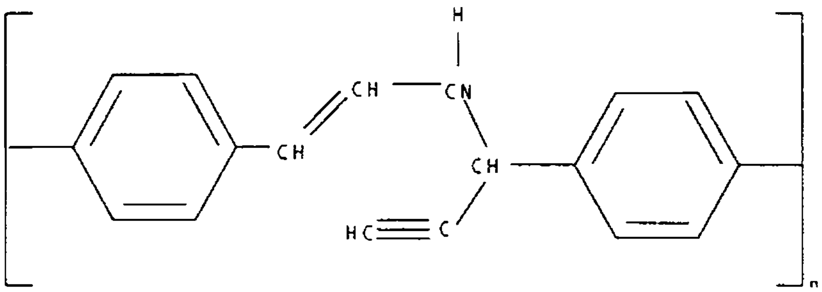


Fig. 6.3. Tentative structure of SHI irradiated RF plasma polymerised aniline

6.4. Optical Studies

The photon absorption in many amorphous materials is found to obey the Tauc relation [24], which is of the form

$$\alpha h\nu = B\,(h\nu - E_{Opt})^{n} \qquad (6.1)$$

Here α is the absorption coefficient, $h\nu$ the photon energy, B a constant and the index n is connected with the distribution of the density of states. The index $n = 1/2$ corresponds to the direct allowed transition energy gap and $n = 2$ represents the indirect allowed transition energy gap.

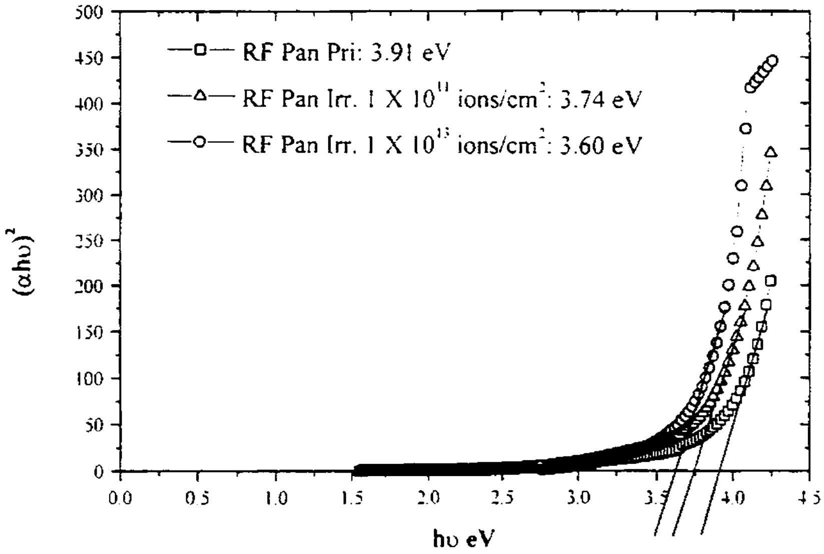


Fig. 6.4.A. UV VIS spectra of polyaniline pristine and irradiated polyaniline at different fluences

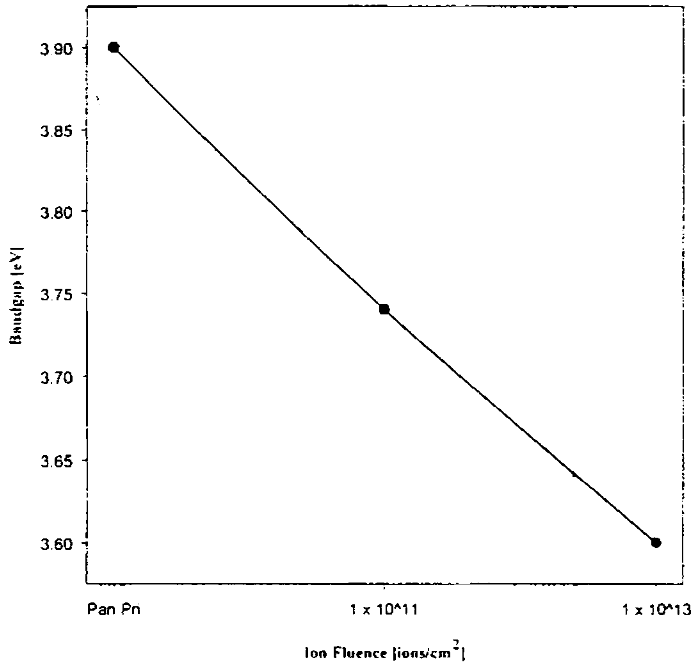


Fig. 6.4.B. Ion fluence vs Bandgap

UV Vis absorption studies are carried out on pristine and irradiated polyaniline thin films using Hitachi U3300 spectrophotometer. The absorbance is plotted against the photon energy for polyaniline pristine and the irradiated polyaniline thin films and is depicted in Fig. 6.4.A. The intercept of this plot on the photon energy axis gives the bandgap of the samples. From Fig. 6.4.B it is clear that there is a decrease in the optical bandgap of irradiated thin films. The bandgap decreases with increase of ion fluence. It can be seen that while pristine polyaniline exhibits a band gap of 3.91 eV. Polyaniline irradiated with fluence of 1 x 10^{13} ions/cm^2 exhibits a band gap of 3.60 eV. The bombardment of swift heavy ions on these thin film samples results in rearrangement and bond shifting which leads to ring opening in which $C \equiv C$ terminals are formed. In this process the resulting product have extended conjugated structures thus reducing the band gap.

6.5. Electrical Studies

Capacitance and dielectric loss were measured by employing HP 4192A impedance analyser and a dielectric cell in the frequency range of 100 Hz to 1 MHz in the temperature range 300-373K. Dielectric permittivity was calculated from the known values of capacitance, thickness and the area of the sample. Further, from the measured values of dielectric constant, dielectric loss and frequency, ac conductivity was calculated by using an empirical relation $\sigma_{ac}=2\pi\varepsilon_0\varepsilon_r\tan\delta$. All these measurements were made under dynamic vacuum.

6.5.1. Capacitance and Dielectric Loss as a Function of Frequency and Temperature

The capacitance of the plasma polymerised aniline as a function of frequency at five different temperatures is shown in Fig. 6.5.

From Fig. 6.5. it is found that the capacitance is frequency dependent. A circuit model proposed by Goswami and Goswami [25] explains this type of behaviour. According to the model the capacitor system is assumed to comprise a frequency independent capacitive element C' in parallel with a discrete temperature resistive element R, both in series with a constant low value resistance r. Basis on this model, the measured series capacitance C_s is given by

$$C_s = C^1 + \frac{1}{\omega^2 R^2 C^1} \tag{6.2}$$

Dielectric loss is given by

$$\tan\delta = \frac{(1 + r/R)}{\omega R C^1} + \omega r C^1 \tag{6.3}$$

Where ω is angular frequency. The temperature dependence of the model is represented by a thermally activated process and is given by

$$R = R_0 \exp\left(-{}^{E_a}\!/_{KT}\right) \qquad (6.4)$$

Where R_0 is a constant and E_a is activation energy. Equation (6.2) predicts that C_s decreases with increasing ω_s and at higher frequencies C_s remains constant for all temperatures. Equation (6.2) also envisages that, because of the decreasing value of R, C_s will increase with increase of temperature for any frequency. This effect is shown in Fig. 6.5 and 6.6.

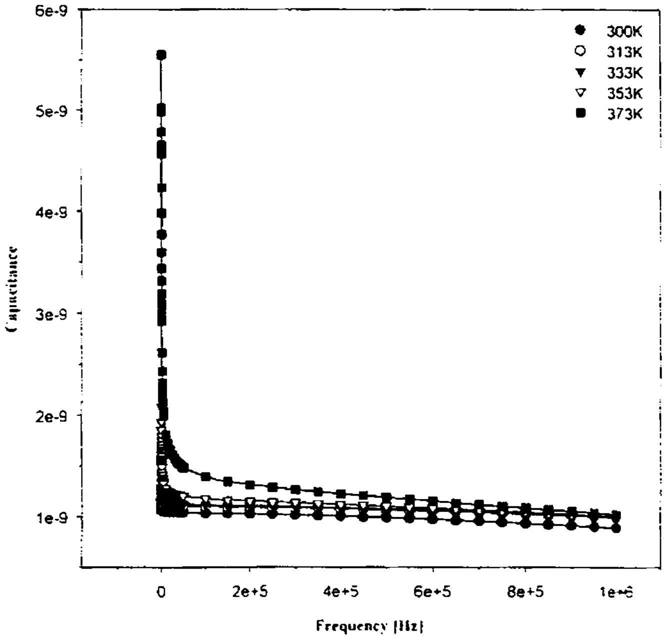


Fig. 6.5. Capacitance of plasma polymerised aniline thin film as a function of frequency at different temperatures

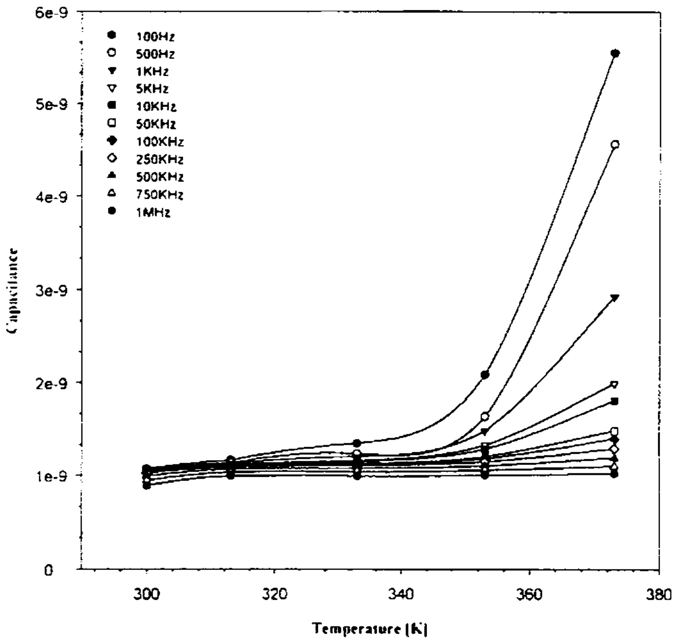


Fig. 6.6. Dependence of capacitance of polyaniline thin film as a function of temperature at different frequencies

The variation of loss with frequency for different temperatures is shown in Fig. 6.7. As per equation (6.3) $\tan\delta$ decreases with increase of frequency till the loss minimum is reached and after that $\tan\delta$ increases with increase of frequency. From Fig. 6.7. it is seen that at 373K there occurs a peak at 350Hz. It is reported that [26] similar kind of such peaks are expected at other temperatures and there occurs a peak shift. This could not be observed in our case since they might be beyond our ac measurement range. This increase of dielectric loss with decreasing frequency is usually associated with ion drift, dipole polarisation or interfacial polarisation [26]. Variation of $\tan\delta$ with temperature is shown in Fig 6.8 and is consistent with equation (6.3). In equation (6.3) the ω^{-1} term becomes dominant because of the decreasing value of R with temperature.

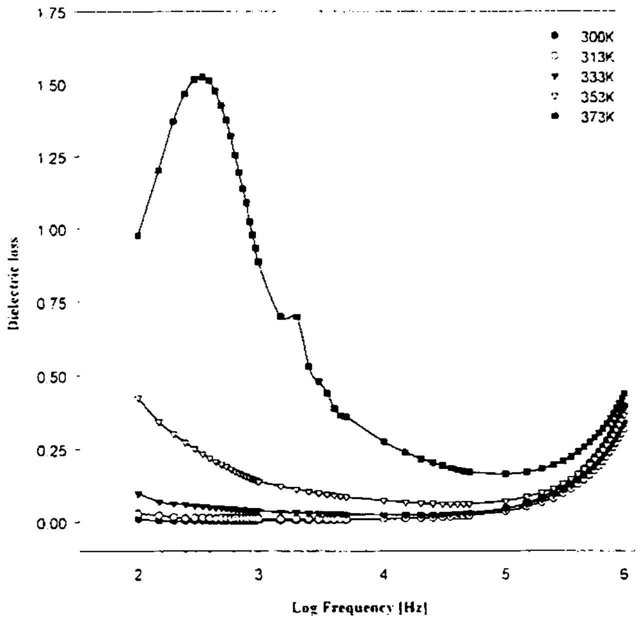


Fig. 6.7. Dielectric loss of polyaniline thin film as a function of frequency at different temperatures

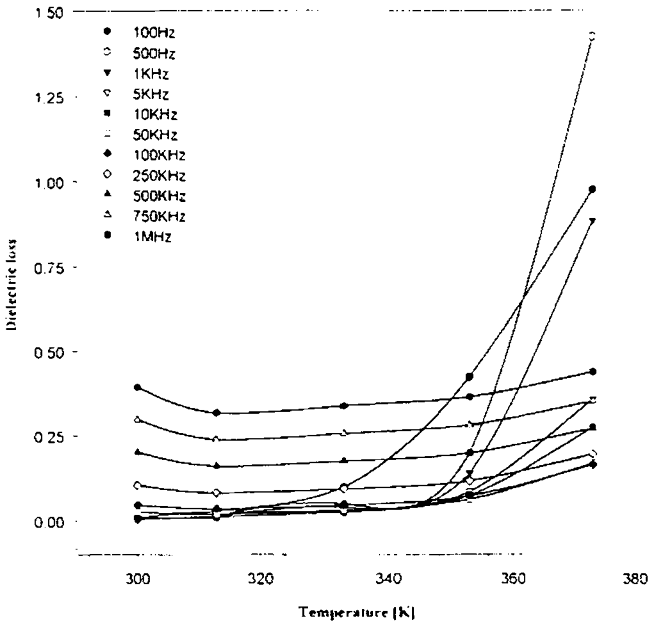


Fig. 6.8. Dielectric loss of polyaniline thin film as a function of temperature at different frequencies

6.5.2. Dielectric permittivity as a Function of Frequency and Temperature

The dielectric studies of plasma polymerised polyaniline thin film samples are calculated using the relation

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \qquad (6.5)$$

Where C is the capacitance of the sample. A is the surface area of the sample, ε_0 is the permittivity of air and ε_r is the dielectric permittivity of the sample.

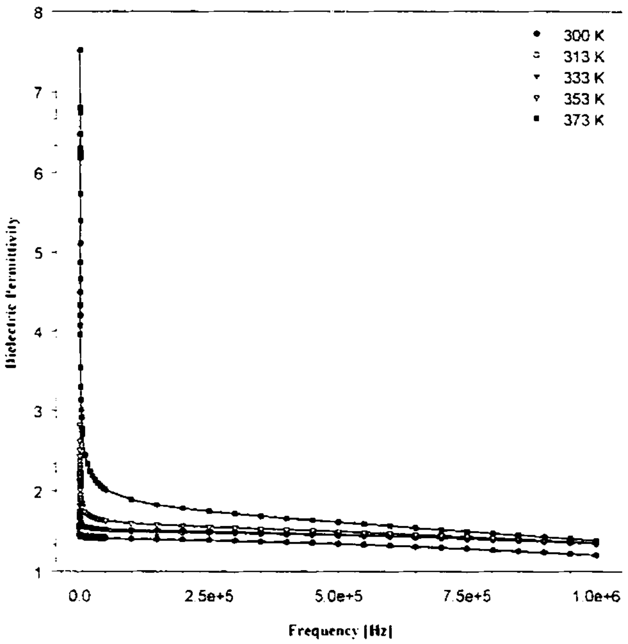


Fig. 6.9. Dielectric permittivity of polyaniline thin film as a function of frequency at different temperatures

The dielectric measurement was carried out in the frequency range of 100Hz to 1MHz. The variations of dielectric permittivity with frequency for different temperatures were plotted and are shown in Fig. 6.9. The dielectric permittivity lies in the range 7.52 and 1.38 for the entire frequency range for which the experiment was carried out (300K - 373K). The dielectric permittivity value lies between 1.45 and 1.20 at room temperature for the entire frequency range, which is considerably low. The characteristic dependence of the dielectric permittivity can be explained with the help of interfacial polarisation mechanism. Usually, interfacial polarisation is the type of polarisation found in the sandwich configuration. The space charge accumulations at the structural interfaces of an inhomogeneous dielectric material cause the interfacial polarisation and this was explained by Maxwell and Wagner in terms of a two-layer dielectric model.

In microelectronic circuits, RC time delay can be reduced by using this type of low dielectric permittivity materials as an intermetallic dielectrics [27]. The time delay depends on two factors one is due to resistance of the interconnections and the other is the capacitance of the dielectric media. RC delay can be calculated by the formulae [8],

$$RC = 2pk\varepsilon_0\left[\frac{4L^2}{P^2} + \frac{L^2}{T^2}\right] \tag{6.6}$$

Where ρ is the resistivity, L the length of the interconnection, T the metal thickness. k the dielectric constant. ε_0 the permittivity of air and P=W (metal Width) + S (Space between metals). The dielectric permittivity of the RF plasma polymerised aniline thin film is 1.20. According to equation (6.6) it is found that the dielectric permittivity of polyaniline k=1.20 will reduce RC delay by about 70%.

6.5.3. AC Conductivity as a Function of Frequency and Temperature

The variation of ac conductivity σ_{ac} as a function of frequency for different temperatures of RF plasma polymerised aniline thin film is shown in Fig. 6.10. From Fig. 6.10 it is seen that the conductivity increases with increase in temperature and frequency. The conductivity increases rapidly at higher frequencies.

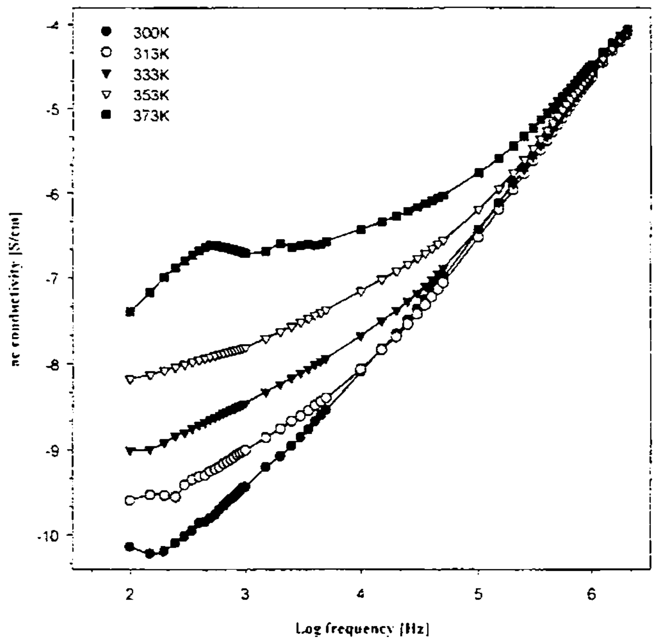


Fig. 6.10. Ac conductivity of polyaniline thin film as a function of frequency at different temperatures

This can be interpreted by involving the following empirical relation [28]

$$\sigma(\omega) \alpha \omega^n \qquad (6.7)$$

where ω is the angular frequency and n is the index used to understand the type of conduction mechanism in amorphous materials.

The values of n determined from Fig. 6.10 lie between 0.5 and 1.1 for lower frequencies. The value of n in this frequency range is in accordance with the theory of hopping conduction in amorphous materials [29].

The value of n gives the type of the dominant conduction mechanism in amorphous materials. This power law is an approximation of the Austin and Mott model, which describes the ac conductivity. Phonon assisted hopping of charge carriers through tunnelling from a localised site to another one is the basic physics behind the power law relation predicted by the Austin and Mott [30]. Also Mott and Austin explained the dependence of ac conductivity at lower temperatures by the relation [30]

$$\sigma_{ac} = A\left(\frac{e^2}{\alpha^5}\right)\{N(E_F)\}^2 kT\omega\{\ln(\nu_{ph}/\omega)\}^4 \qquad (6.8)$$

This relation can be modified as follows by differentiating with respect to ω

$$\frac{d\ln\sigma_{ac}(\omega)}{d\ln\omega} = 1 - \frac{4}{\ln\left(\nu_{ph}/\omega\right)} \qquad (6.9)$$

The value of n also determined by the phonon frequency and it depends on the ac frequency [30].

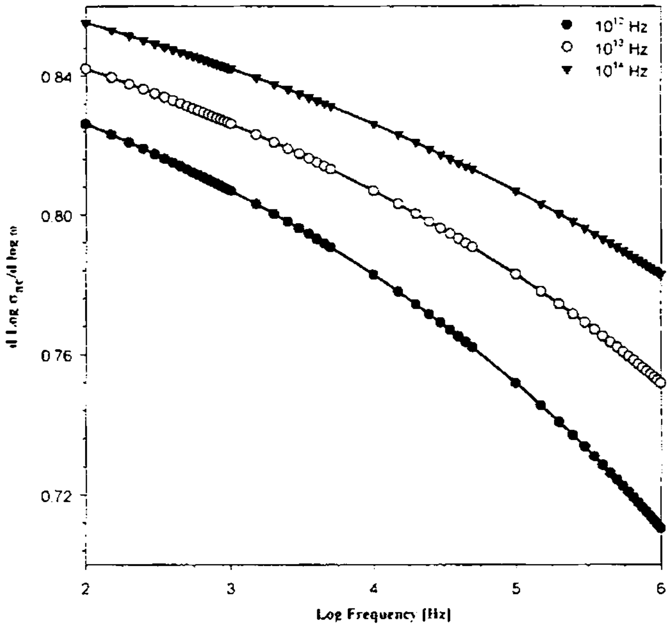


Fig. 6.11. dLog σ_{ac}/dlog ω as a function of the frequency for 3 typical phonon frequencies

Fig. 6.11 is the plot between $d\log\sigma_{ac}/d\log\omega$ and log frequency for three typical values of the parameter ν_{ph}: 10^{12},10^{13},10^{14} Hz. From the Fig. 6.11, it is seen that, depending on the phonon frequency the value of $d\log\sigma_{ac}/d\log\omega$ lies between 0.71 - 0.88 for the entire frequency range. The predicted values of n lie within the values of n obtained from our experiments, provided that a single hopping ac conductivity mechanism operates in the plasma polymerised aniline thin films. Based on this it may be concluded that the conductivity is due to hopping. Also it is necessary to compare the experimental and the predicted values for finding out whether it is single or multiple hopping conductivity [30].

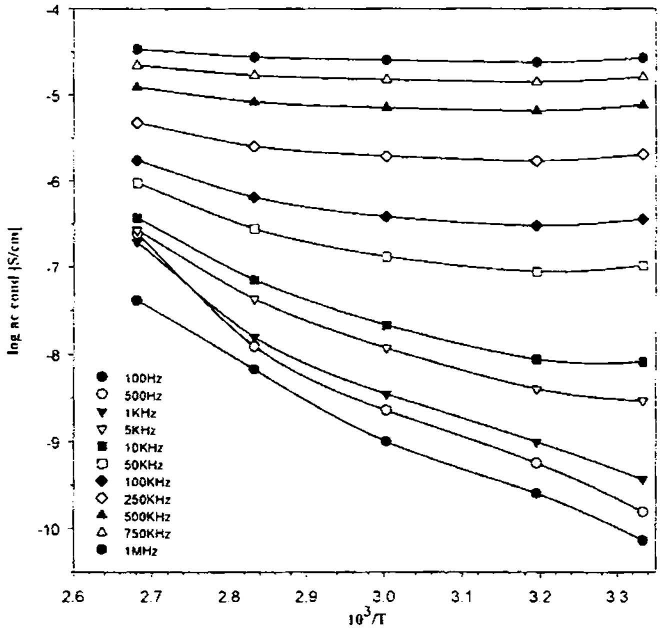


Fig. 6.12. Ac conductivity of polyaniline thin film as a function of temperature at different frequencies

The variation of ac conductivity with temperature as a function of different frequencies is shown in Fig. 6.12. Activation energies were calculated and are found to be in the range 0.356 eV - 0.1435eV, which is considerably low. From Fig. 6.12 it seen that the ac conductivity of the RF plasma polymerised polyaniline thin films is frequency dependent and it has very low activation energy. The low activation energies of these films indicate that hopping conduction mechanism occurs in RF plasma polymerised aniline thin films.

6.5.4. Effect of Swift Heavy Ions on Dielectric Permittivity

The dielectric measurements were performed on the irradiated polyaniline thin films and pristine polyaniline films and are shown in Fig. 6.13. The dielectric permittivity for pristine films decreases with increase of frequency. The value of dielectric permittivity for the irradiated thin films is less than one. This violates the classical mechanical rule. It is also observed that the dielectric permittivity decreases with increase of ion fluence. This decrease in the dielectric permittivity can be explained on the basis of the decrease in the number of sites, which are available for polarization and flow of space charge carriers, which could be correlated to the production of defects created in the thin films due to the irradiation.

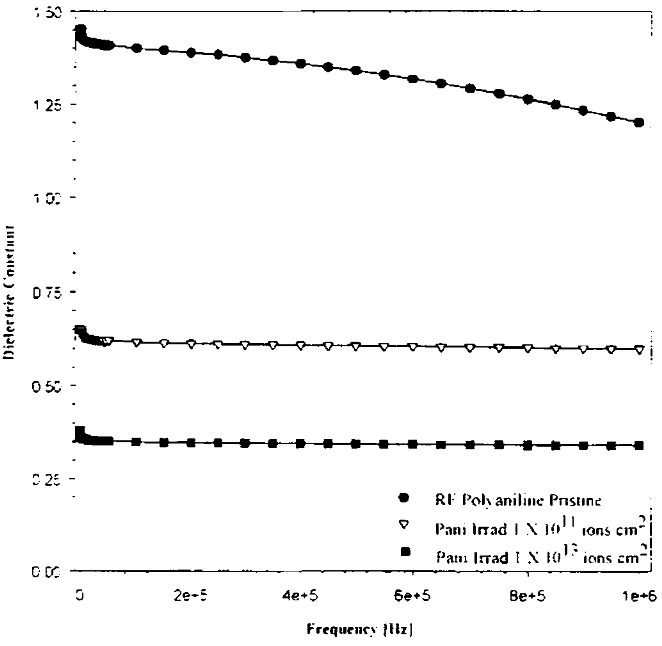
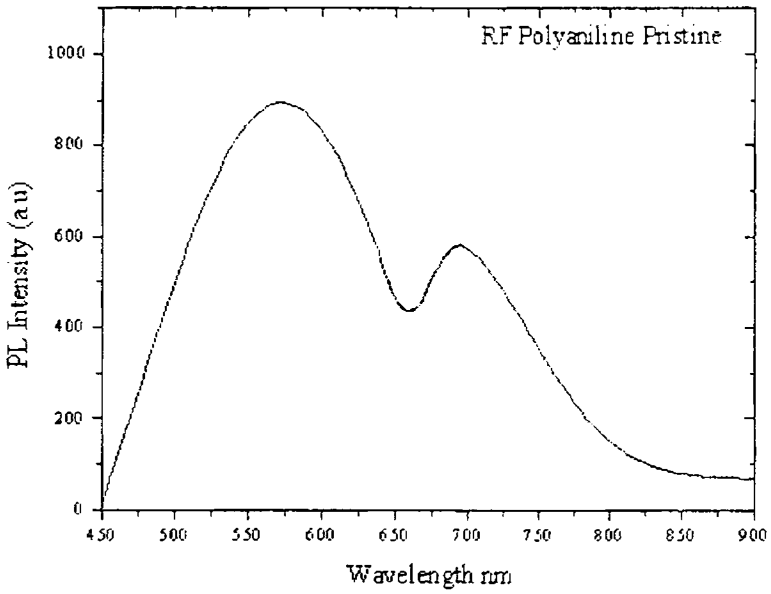


Fig. 6.13. Variation of Dielectric permittivity with ion Fluences

It may be noted here that irradiated samples exhibit ultra low dielectric permittivity (k<1). There is no immediate explanation for this observation and further investigations are necessary to ascertain the origin of ultra low permittivity in swift heavy ion irradiated thin films. In literature reports on ultra low are scanty. [31]

6.6. Photoluminescence Studies

Photoluminescence spectra were recorded for plasma polymerised aniline samples before and after irradiation and is shown in Fig. 6.14. The pristine sample exhibits the peaks at 575nm and 680nm. After irradiation the nature of PL spectrum remains similar but the peak intensity varied with the ion fluence. The peak intensities are compared for different ion fluences. From Fig. 6.14. it is clearly seen that the intensity of the incident beam decreases and the shoulder peak intensity increases with increase of ion fluences.



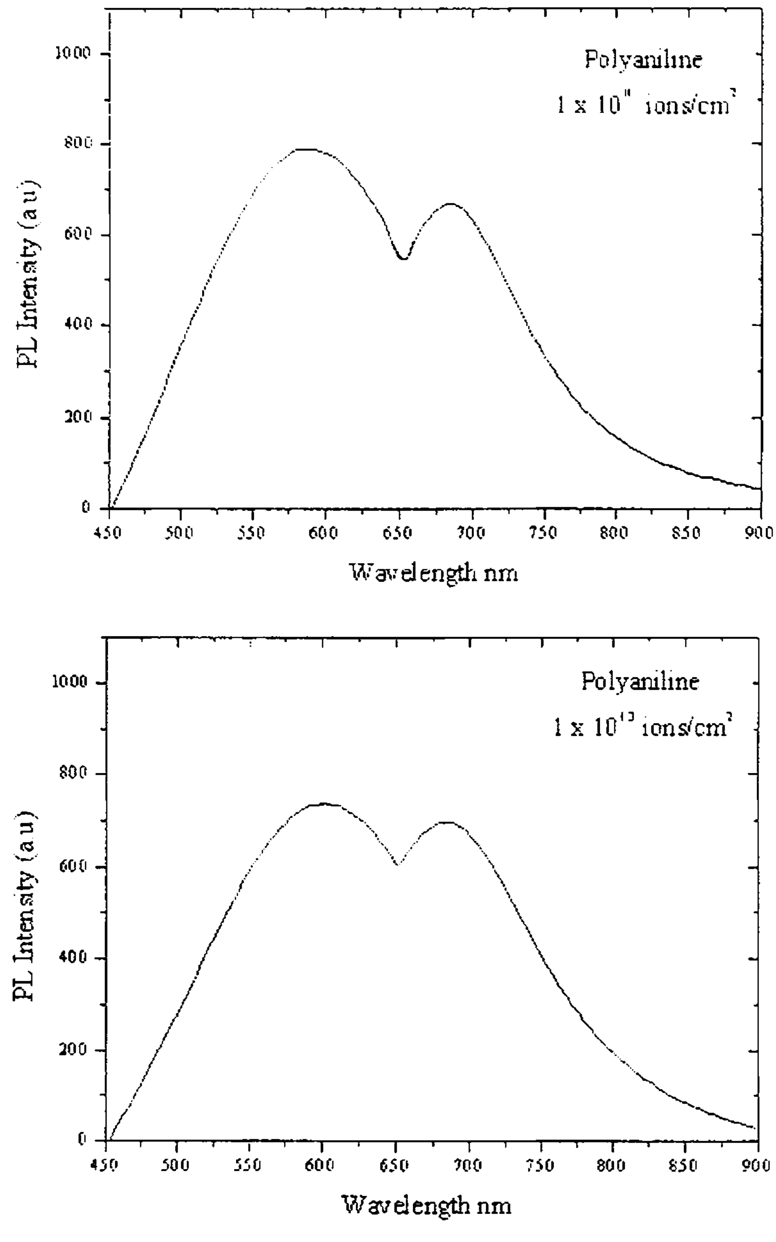


Fig. 6.14. Photoluminescence spectrum of polyaniline pristine and irradiated thin films

In general the effect of irradiation can be viewed in two ways.

1. The restructuring of the surface chemical species because of the energy deposited through electronic loss during the process of irradiation
2. Formation of radiation induced defects leading to non-radiative recombination centres.

FTIR spectra indicate that the pristine polyaniline retains the benzene ring and the ring is not opened up. But after irradiation, the ring is opened up because of high-energy ions, which induce structural changes. The increase of intensity of a shoulder peak may be attributed to the rearrangement of bonds as well as the increase of conjugation in the polymer. The incident peak intensity decreases with ion fluence. This could be due to opening of benzene rings. This is in conformity with FTIR results.

6.7. Surface Studies

Surface morphology studies are carried out on plasma polymerised pristine and the irradiated aniline thin films.

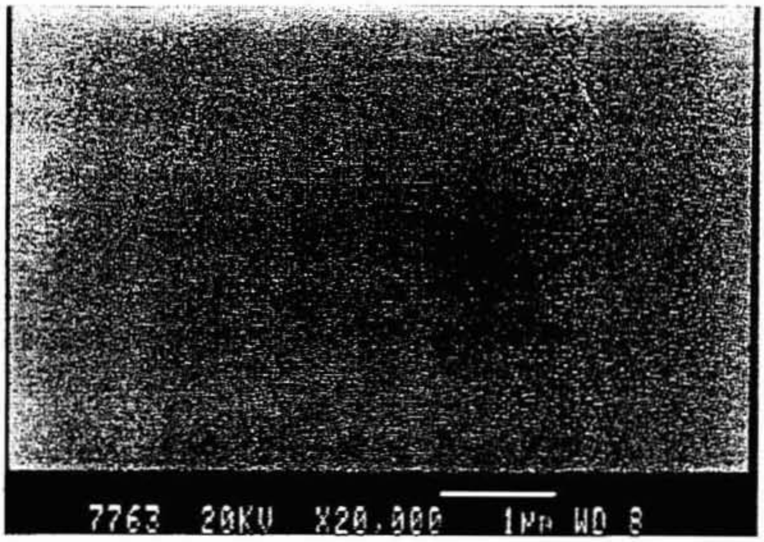


Fig. 6.15. Electron micrographs of plasma polymerised aniline thin films

Fig. 6.15 depicts the micrographs of the plasma polymerised aniline thin film surface. From the micrographs it can be seen that the film surface is very smooth and non porous. The micrographs of irradiated polyaniline films are also shown in Fig. 6.16. It must be mentioned here that upon irradiation the film is found to be broken with a separation of 4μm on the lateral side and ~8μm on the longitudinal side.

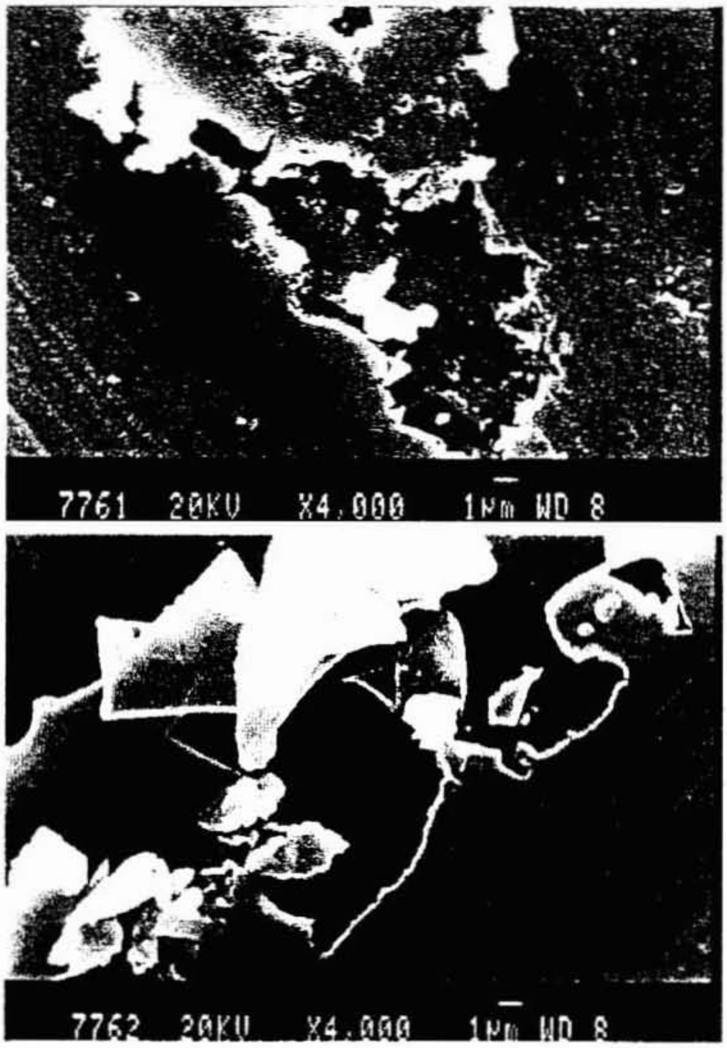


Fig. 6.16. Electron Micrographs of irradiated plasma polymerised aniline thin films

6.8. Conclusion

RF plasma polymerised aniline is irradiated with swift heavy ions and the effect of SHI on the structural and optical bandgap is studied. FTIR spectral results are compared with the standard data and based on the analysis a tentative structure for the pristine polyaniline and the irradiated polyaniline are proposed. The change in optical band gaps for irradiated samples are evaluated and it is found that the optical band gap reduces with increase of fluence. Electrical and morphological studies are carried out on the irradiated thin films and the results are compared with the pristine thin films.

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Chapter 7

Studies on Pristine and SHI Irradiated Plasma Polymerised Furfural Thin Films

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7.1. Introduction

Furan is a five membered ring organic material. By introducing functional group to the furan significant changes in their properties can be obtained [1]. Furfural is an aldehyde derivative of furan. Unlike binary mixtures the interaction strength of furfural is strong [2]. This is because of the presence of hydrogen bond interactions between the carbonyl group of furfural and the -OH group of the alcohol. But the strength of furfural decreases with increase of chain length [3]. Polyfurfural resin thin film device prepared by thermally induced polymerisation shows a photovoltaic behaviour [4]. The structure and properties of Polyfurfural prepared by using ac plasma polymerisation are reported [5] and shows a significant change as compared with their derivatives. Like ac plasma polymerisation [6]. RF plasma polymerisation is also a handy technique for preparing polymer thin films from their monomer vapour.

In this chapter the investigations carried out on RF plasma polymerised furfural thin films is described. The changes in structural. optical. morphological and electrical properties of the irradiated polyfurfural are explained with respect to the pristine polyfurfural thin films.

7.2. Structural Studies

FTIR spectra of plasma polymerised furfural and swift heavy ion irradiated polyfurfural are recorded (Fig. 7.2) using BRUKER EQUINOX 55 FTIR spectrometer and the band assignments are given in Table 7.2. These band assignments are compared with the available monomer furfural values, which are tabulated in Table 7.1.

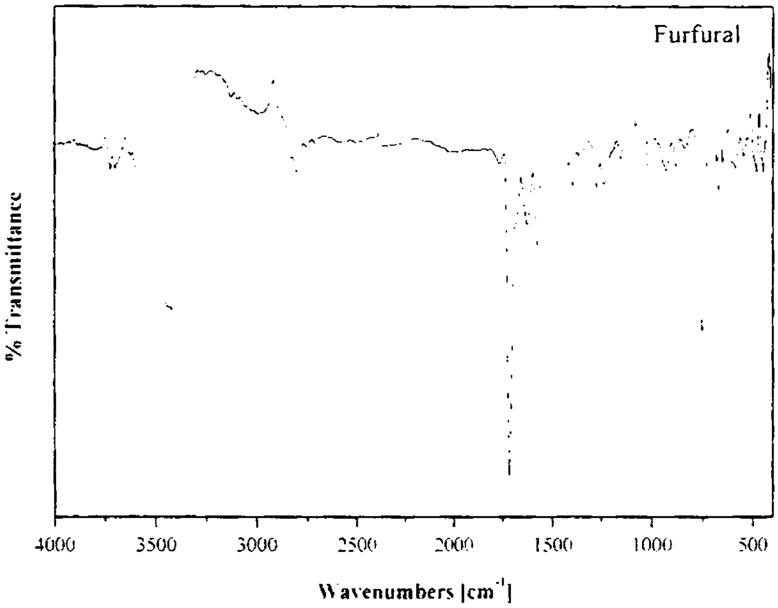

Fig. 7.1. FTIR spectrum of monomer furfural

Table 7.1.

Band Assignments for Monomer Furfural

Monomer Furfural Wavenumber cm^{-1}	Assignment
1720	C=O stretch
1460	C=C
1390	C-O
1160	C-O-C
1040	C-O-C
885	Ring Stretch
766	C-H out of plane

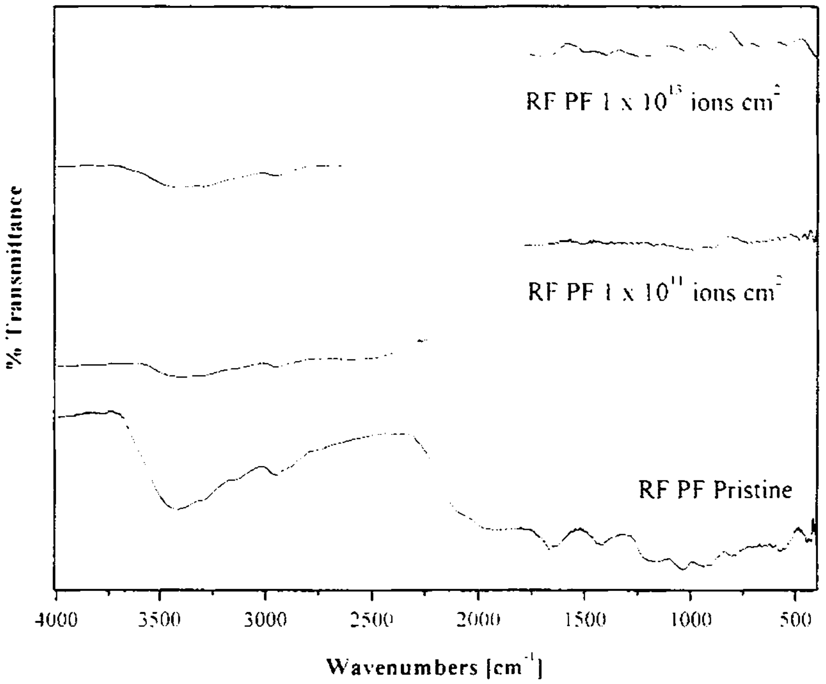

Fig. 7.2. FTIR spectra of polyfurfural pristine and irradiated thin films

Table 7.2.

FTIR assignments for Polyfurfural Pristine and irradiated polyfurfural

Assignment	Polyfurfural		
	Pristine	Irradiated	
		1 x 10^{11} ions/cm^2	1 x 10^{13} ions/cm^2
CH stretch	2938	2958	2940
C=O stretch	1666	-	-
C=C stretch	1411	1396	1400
C-O-C asymmetric stretch	1159	-	-
C-O-C symmetric stretch	1033	-	-

Ring Characteristics	933	-	-
Ring Characteristics	808	-	-
CH deformation	-	901	890
CH deformation	-	753	728

From Tables 7.1 and 7.2 it is seen that most of the characteristic peaks of furfural is present in the polyfurfural and the five membered ring is retained after polymerisation [7] process too. Due to hydrogen abstraction [8] and based on the FTIR analysis a plausible structure is proposed and is shown in Fig. 7.3.

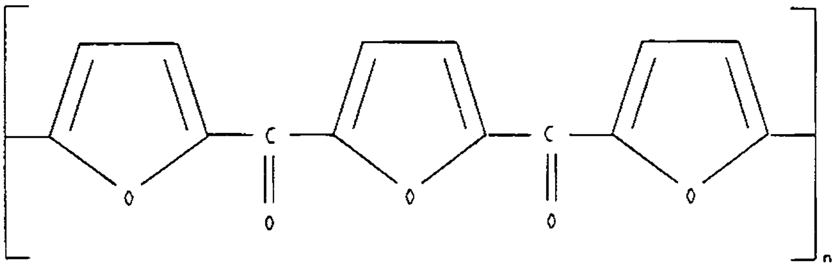

Fig. 7.3. Possible structure of plasma polymerised furfural

FTIR spectrum of SHI irradiated polyfurfural thin films are shown in Fig. 7.2. and the band assignments are shown in Table 7.2. From the spectrum it is observed that the ion bombardment results in the clevage of the ring of furfural and leading to a carbonised structure with the elimination of carbon dioxide. The intensity and position of the key bands also changes due to ion irradiation. The FTIR spectrum of the irradiated thin films is very broad and without much significant features. This observation also points to the formation of carbonised structure.

7.3. Optical Studies

In order to find out the optical band gap of pristine and SHI irradiated polyfurfural UV Vis absorption studies are carried out using Hitachi U3300 spectrophotometer. The spectral variation in absorbance obeys the Tauc relation [9]. The absorbance is plotted against the photon energy and the band gaps are evaluated for the pristine and SHI irradiated thin film samples. It can be seen that while the pristine plasma polymerised furfural sample exhibited a bandgap of 3.08 eV, the bandgap of SHI irradiated samples decreased considerably to 2.61 eV. It is important to note that the bandgap decreases as the fluence of ion increases. This may be due to the opening of the ring structure leading to conjugation of the carbonised due to the impact of heavy ions.

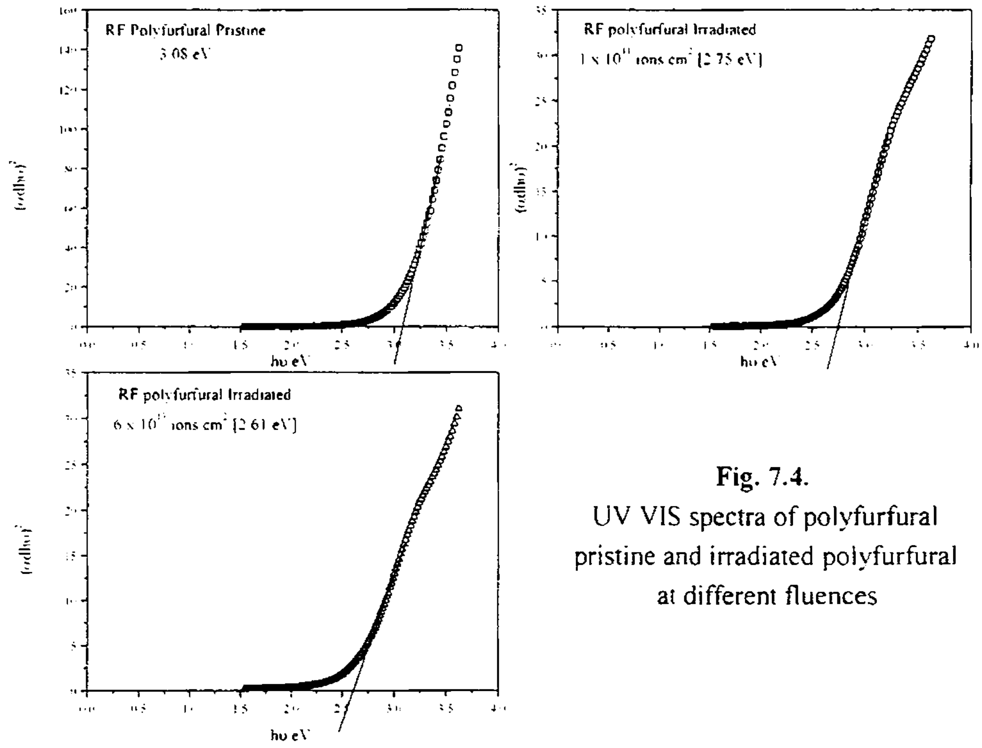

Fig. 7.4.
UV VIS spectra of polyfurfural pristine and irradiated polyfurfural at different fluences

7.4. Photoluminescence Studies

Photoluminescence studies on pristine and irradiated polyfurfural were conducted. He Cd laser of wavelength 442nm is used for excitation. Fig. 7.5 shows the photoluminescence response of the polyfurfural samples. Polyfurfural pristine and irradiated samples exhibited a broad photoluminescence peak centred on 605nm. It is interesting to note that the peak intensity of the photoluminescence spectrum decreases with increase of ion fluence. This is because of the change in structure. It is clear from the Fig. 7.5. that there is a decrease in the luminescence intensity. This is primarily caused by absorption of the light in the irradiated polyfurfural thin film also. The fact that we can still observe luminescence on the irradiated thin film demonstrates that the SHI irradiation alter the optical activity of the material.

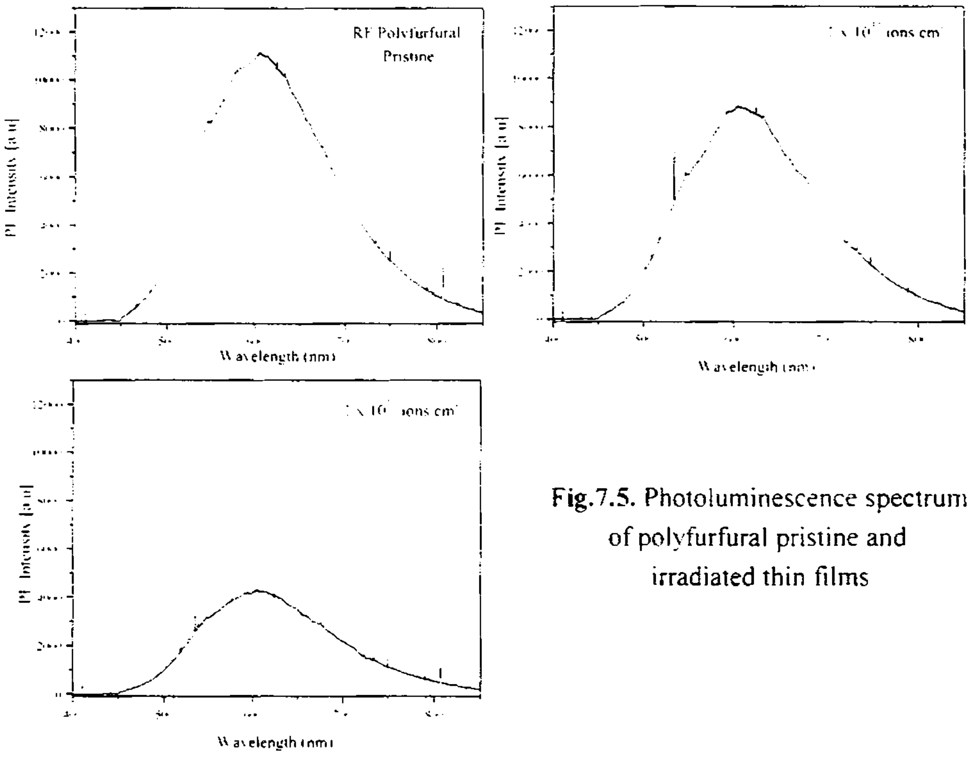

Fig.7.5. Photoluminescence spectrum of polyfurfural pristine and irradiated thin films

7.5. Dielectric Studies

Dielectric permittivity studies were carried out on RF plasma polymerised furfural in the frequency range of 100Hz to 1MHz at different temperatures. The variation of dielectric permittivity with frequency for different temperatures is as shown in Fig.7.6. and 7.7. The variation pattern for all temperatures is almost the same. Dielectric permittivity values of the RF based polyfurfural lies between 10 and 1.4 for the entire temperature and frequency range measured. At room temperature the value lies between 1.9 and 1.4, which is considerably low. Also it is seen that at low frequencies the value of dielectric constant is high and it decreases with increase of frequency but it increases as temperature increases. This type of behaviour can be attributed to the interfacial polarisation, which is usually found in the metal/polymer/metal structure. This type of behaviour can be explained with the help of Maxwell Wagner theory of polarisation [9]. According to Maxwell and Wagner, the space charges in metal/polymer/metal structure are accumulated at the structural interfaces of an inhomogeneous dielectric material, which as appears to the interfacial polarisation. Like in RF plasma polymerised aniline thin films, polyfurfural thin films also exhibited low k characteristics.

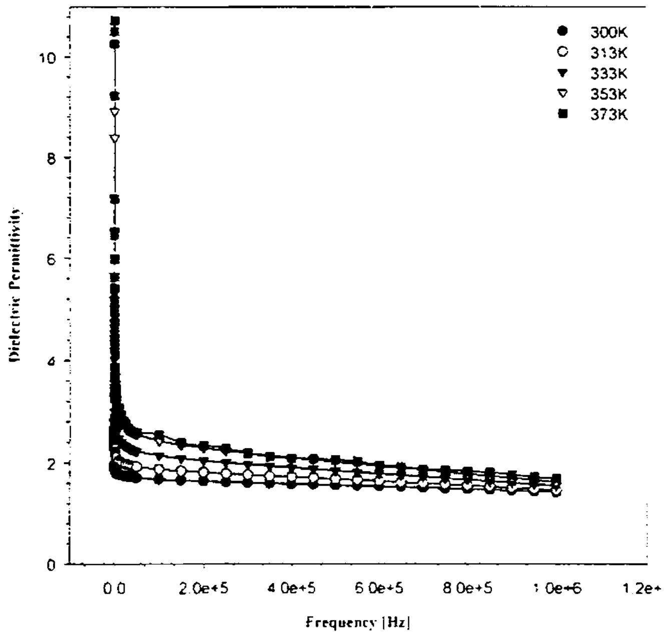

Fig. 7.6. Variation of dielectric permittivity with temperature

Dielectric measurements on irradiated polyfurfural samples are carried out and compared with the pristine samples. The variation of dielectric permittivity with frequency at room temperature for pristine and irradiated thin films are as shown in Fig 7.8.

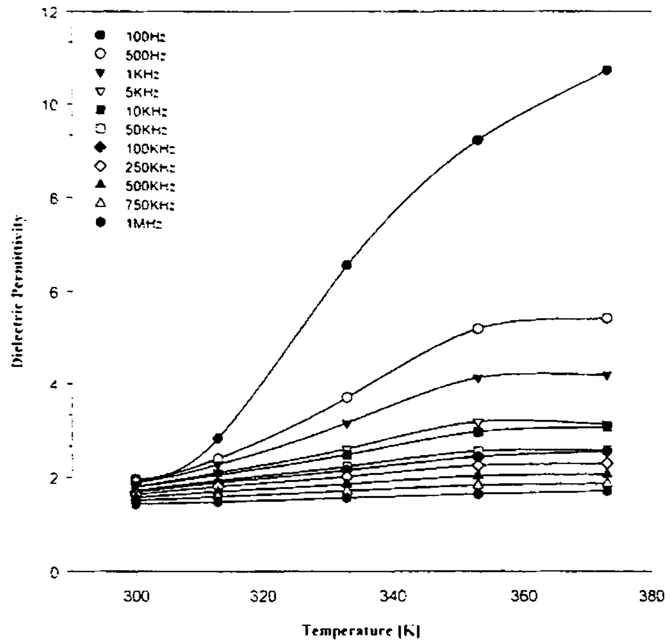

Fig. 7.7. Variation of dielectric permittivity with frequency

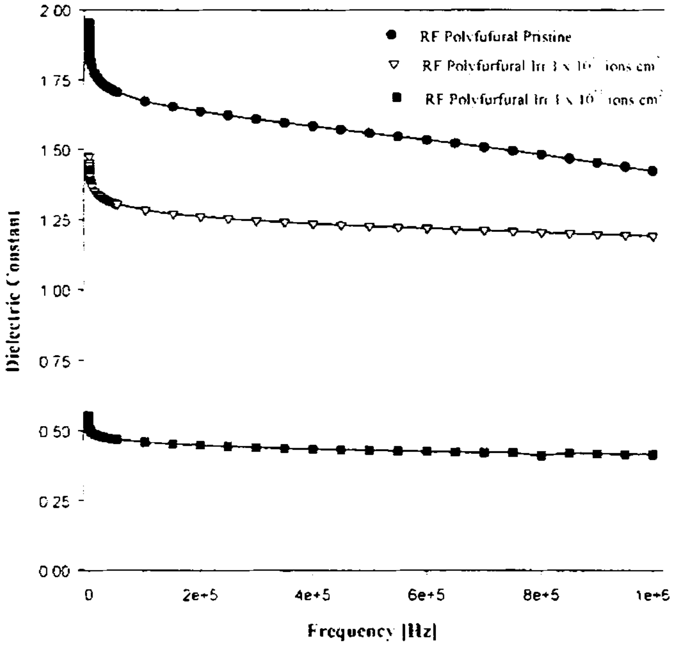

Fig. 7.8. Dielectric permittivity vs Frequency at room temperature for pristine and irradiated polyfurfural thin films

From Fig. 7.8. it is seen that when frequency increases the dielectric permittivity decreases and it is almost constant at higher frequency. As the fluence increases, the dielectric permittivity decreased. This may be explained as follows. In the case of ion irradiation in polymer thin films, the damage is caused by elastic and inelastic collisions. It is reported that if elastic energy loss is high, a highly disordered region is formed. This is known as an explosion spike. As the fluence increases, heavy sample damage with high density of extended defects occurs. These regions overlap and an amorphous layer is found. This decreases the density of the polymer which leads to further reduction in dielectric permittivity [10].

7.6. Ac conductivity studies

AC conductivity of polyfurfural is calculated from the observed dielectric constant, dielectric loss for a given frequencies at different temperatures. The variation of ac conductivity with frequency in the temperature range of 300K-373K is shown in Fig. 7.9. and 7.10. The value of ac conductivity increases with increase of both temperature and frequency. The value of n for polyfurfural is calculated using the relation

$$\sigma(\omega) \propto \omega^{n} \qquad (7.1)$$

and is found to lie between 0.3 to 1.0 for frequencies below 100KHz. This value of n at lower frequencies is in accordance with the theory of hopping conduction in amorphous materials [11].

Thermal activation energy is determined from the plots of ac conductivity vs temperature at different frequencies and is found to be lie between 0.033 and 0.335 through out the entire ranges of temperature and frequency under evaluation. The frequency dependence of ac conductivity and very low activation energies suggests that the hopping type of conduction mechanism is dominant in plasma - polymerised furfural.

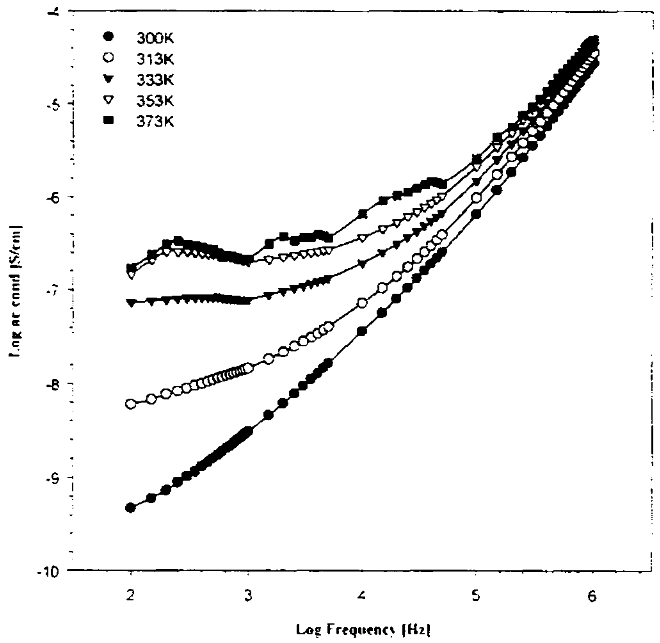

Fig. 7.9. Log σ_{ac} vs Log Frequency

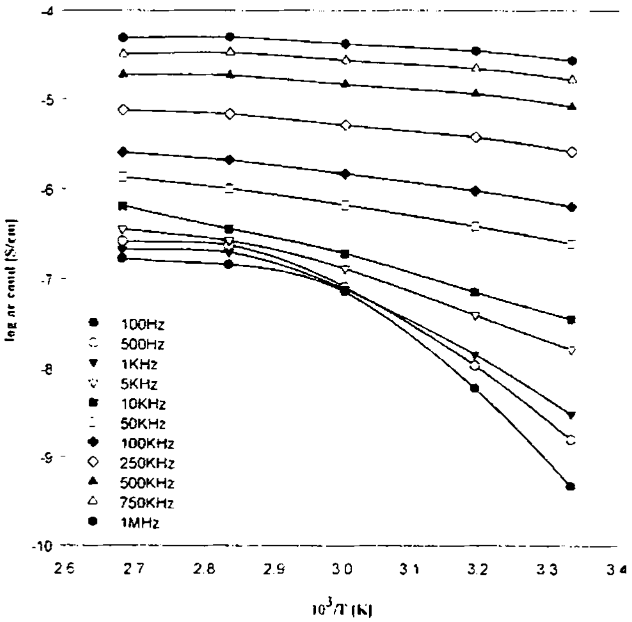

Fig. 7.10. 10^3/T vs Log ac conductivity

7.7. Surface Studies

The surface morphology of RF plasma polymerised furfural thin films is investigated by Scanning Electron Microscope. Fig. 7.11. shows the surface of a polyfurfural thin film.

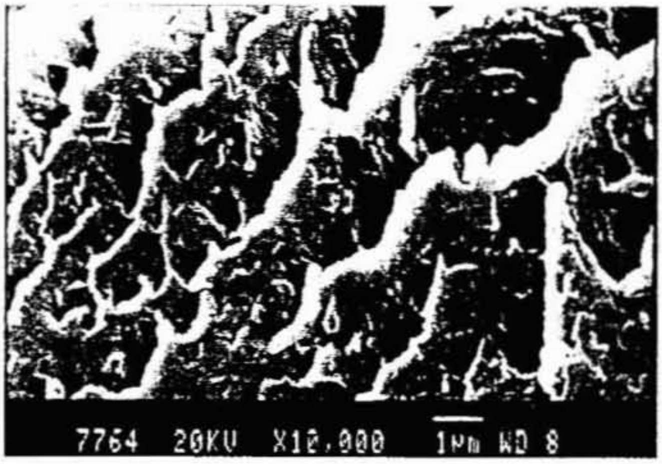

Fig. 7.11. Surface structure of polyfurfural thin films

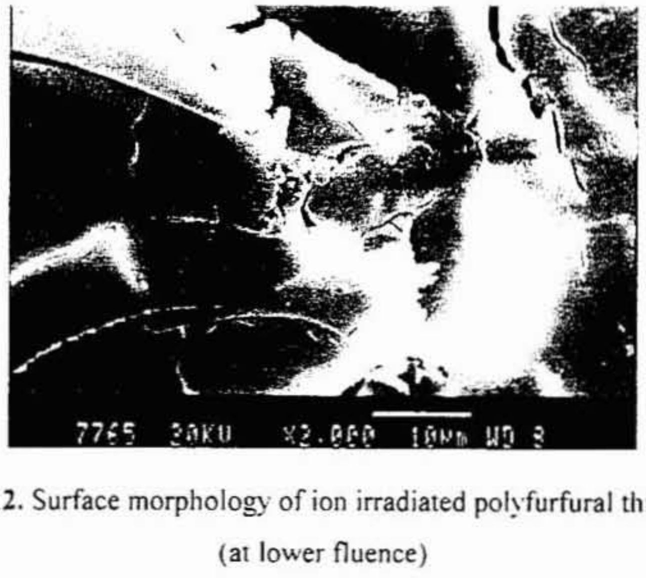

Fig. 7.12. Surface morphology of ion irradiated polyfurfural thin films (at lower fluence)

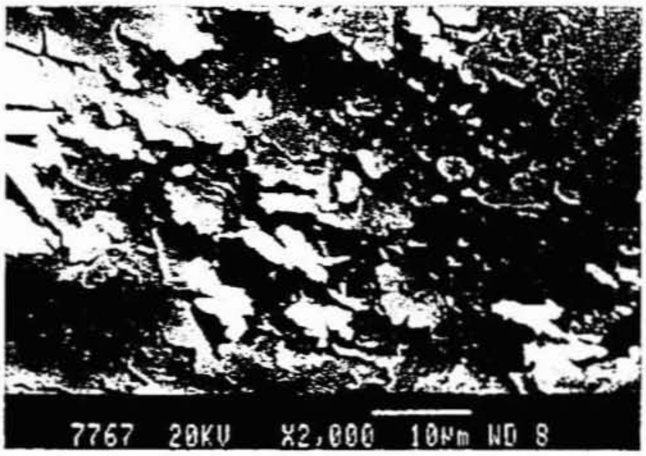

Fig. 7.13. Surface morphology of ion irradiated polyfurfural thin films (at higher fluence)

Rf plasma polymerised furfural thin films exhibit a smooth surface as revealed by the micrographs (Fig. 7.12 and Fig 7.13). From the micrographs it is noticeable that the ion bombardment has damaged the film surface and cracks are found on the surface.

7.8. Conclusion

Polyfurfural based on RF plasma polymerisation is successfully prepared and the ion bombardment on these films is carried out at different fluences. Based on the findings of FTIR analysis a plausible structure for the pristine and the SHI irradiated polyfurfural is suggested. There are clear evidences in the FTIR spectrum for the formation of carbonisation, however, tools like NMR are necessary to confirm these and also for the elucidation of the structure without ambiguity. Determination of optical bandgaps for the pure and irradiated thin films suggests that the bandgap decreases with increase of ion fluence.

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Chapter 8

Summary and Conclusion

The discovery of conducting polymer was accidental. but the later developments in this field were all trendsetters for the future. The development of high-density batteries, Light Emitting Diodes. EMI shields. Schottky diodes. liquid crystal displays and sensors were all spin-offs of research in this area of polymer physics. This area is ever expanding and this has led to the birth of molecular electronics which will soon replace conventional semiconductors based on Silicon or GaAs compound semiconductors. Such is the appeal of this branch of electronics based on polymers, that millions and millions of money is being spent on research on developing new devices and in understanding the underlying physics and chemistry of these materials.

Any material whether organic or inorganic has to be in the thin film form and hence most of the studies oriented towards applications are investigated in this state. However. it is customary and natural to delve into the various properties of these organic materials in its bulk form. since. only a clear understanding of its properties at the bulk level will only lead to further progress in the thin film form.

This emphasises the importance of research on conducting polymers in the bulk and thin film form. It has been known that composites can be prepared to combine the useful properties of its constituents and so composites of these polymers are often investigated with this motive. Once these composites are synthesised and thoroughly investigated. techniques exist to prepare them in the thin film forms.

This thesis also dealt with a similar approach in the sense that a detailed investigation was conducted on bulk samples namely cobalt phthalocyanine tetramers. polyaniline doped with camphor sulphonic acid. their composites in various proportions and finally thin film samples of selected polymers.

Understanding the electrical conduction mechanism is of utmost importance as far as the applications are concerned. With this objective in mind. a detailed investigation was carried out.

Synthesis of polymers in the bulk form and in the thin film was undertaken in the laboratory itself. This was necessitated because of the fact that the history of the prepared samples are available for immediate references.

Different polymers were synthesized and characterised. for example. bulk polymers belonging to the family of polyaniline were thoroughly characterised for purity and composition. Doping of these polymers modify the electrical properties and alter the structure and induce changes in the optical properties. They were doped with dopants such as hydrochloricacid. camphor sulphonic acid etc.

Cobalt phthalocyanine tetramers was synthesised by employing a simple chemical technique. Composites were made using Cobalt phthalocyanine tetramers and polyaniline doped with camphor sulphonic acid. These composites were investigated thoroughly to explain the electrical properties of these materials.

A detailed investigation into the electrical properties of Cobalt phthalocyanine tetramers and the analysis of the results based on a model has lead to the proposal of an appropriate conduction mechanism in these materials. It has been found that Cobalt phthalocyanine tetramers obey Mott's variable range hopping model and it is (3D variable range hopping). Permittivity measurements conducted on these samples reveal that the dielectric constant lies in the range 43-81for a wide range of frequencies.

Pure Polyaniline and polyaniline doped with camphor sulphonic acid were synthesised by direct oxidation of aniline. XRD studies indicate that the crystallinity is enhanced on doping. This has further supporting evidences from morphology studies.

Studies carried out on composite samples indicate that by appropriate combinations of polyaniline doped with camphor sulphonic acid + Cobalt phthalocyanine tetramers the properties can be tailored. However it must be monitored here that the properties are not governed by the law of mixtures but determined by a variety of factors namely grain size, interpenetration of constituent layers, vacancies created etc. Here in the composites too, the conduction could be due to hopping of charges and the plausible mechanism of conduction is the 3D variable range hopping. Parameters like density of states, density of states at the Fermi energy, range of hopping and hopping energy were estimated and could be fitted into on existing models based on hopping.

Any material if it has to be transformed into a device it has to be built in the thin film form. Hence studies on the thin film form of polymers assume significance. In most of the cases, the electrical and optical properties of these films are different from their counterpart cousins in the bulk form. There is also an intimate relationship with the structural property of the film, with the optical and electrical properties.

State of the art techniques such as PECVD, vacuum coating, spin coating exists for the preparation of thin films. Inexpensive and simple techniques like plasma polymerisation are also handy in preparing thin films directly from the monomers. One such technique is RF plasma polymerisation and good quality thin films were prepared using this technique. Using RF plasma polymerisation technique polymer thin films based on aniline and furfural could be synthesised. The evaluation of various properties namely electrical/optical indicate that low k film can be synthesised. This is an important finding in the sense that thin films based on RF polyaniline/RF Polyfurfural can be potential intermetallics in the IC circuitry. Simple empirical calculations show that the employment of these films with low dielectric permittivity (k=1.20) will reduce RC delay by about 70%.

Modification of optical properties of thin films is generally achieved by incorporating dopants. One such technique is to introduce iodine into the backbone of the polymer. This modifies the optical bandgap of these films considerably. Other methods like irradiation of thin films by swift heavy ions. also produces noticeable changes in the films and the possibility of bond breakage, cleavage of bond angles, carbon cluster formation and production of nano channels exists. This motivated us to carry out swift heavy ions on selected samples of polyaniline and polyfurfural. The outcome of these results are extremely encouraging. Silicon ions were employed to irradiate these thin film samples at an energy of 92MeV. The optical and structural properties of pristine and irradiated samples were evaluated and compared. Irradiation of thin film samples with SHI for various fluences indicate that the structure of these irradiated samples are modified and bandgaps are reduced. A tentative structure for both polyaniline and polyfurfural pristine/irradiated has been proposed. The observed change in optical bandgaps in polyaniline/polyfurfural has been attributed to the C≡C bond and carbonised structure respectively. Pristine and irradiated polyaniline/polyfurfural exhibit photoluminescence and its intensity decrease with increase in ion fluence. However in both these films no peak shift is noticed.

Scope for further research/work

One of the notable outcome of this work is the synthesis of low k thin film based on RF plasma polymerisation. Permittivity values at room temperature lie in the range 1.20 - 1.45 over a wide frequency range (100KHz - 1Mhz). This is promising and scope exists to initiate a systematic study on these films so that they can be employed as good intermetallics in IC circuitry. However, it must be mentioned here that for applications, thermal stability of the film is an important criteria. Thermal stability studies could not been carried out. So scope exists to produce thermally stable low k thin films based on other polymers using plasma polymerisation technique.

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Polyaniline doped with camphor sulphonic acid (bulk) exhibit good electrical characteristics. The bulk targets of polyaniline doped with camphor sulphonic acid can be vacuum evaporated and thin films can be coated on various substrates. A systematic study on the growth of these thin films and evaluation of various properties and comparison and correlation of properties between the bulk and thin films could as well be another topic for research. This could lead to fabrication of devices based on cobalt phthalocyanine tetramers and polyaniline doped with camphor sulphonic acid.

In a similar manner, composites can be prepared by employing cobalt phthalocyanine tetramers and polyaniline doped with camphor sulphonic acid in the bulk and by appropriate techniques thin films can be grown. Such a study will bring out the usefulness of these materials for specific applications. The structures proposed in this thesis are all based on FTIR data and intuition and often tentative in nature. These materials could be studied using NMR technique. A clear and definitive structure can be proposed only with the help of data collected using NMR.

Swift heavy ion irradiation has been found an effective tool to modify the optical/structural properties. The physics of modification still remains elusive and an elaborate work needs to be carried out in this regard. The employment of higher energy and various fluences will definitely help to study these aspects.

Since pristine and irradiated thin films show photoluminescence scope exists to fabricate photoluminescence devices based on RF polyaniline and polyfurfural. If the conductivity and optical band gap of these films can be tailored. plasma polymerised aniline and furfural are good candidates for photovoltaic devices. A definitive structure for polyfurfural and polyaniline thin films could not be proposed. If the conductivity of these films can be increased by a few orders of magnitude and the mechanism of conduction is understand properly. these films stand a great chance of becoming potential candidates for applications like light emitting diodes. Schottky diodes. liquid crystal displays and sensors.

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