CHAPTER 1

INTRODUCTION

1.1 General

The dawn of the electronic age brought with it a tremendous change in the human life style due to the revolutionary discoveries and developments in the field of science and technology. The inorganic semiconductors such as silicon, germanium and gallium arsenide have been widely used in the electronic industry for more than four decades. The invention of transistor by William B. Shockley, Walter H. Brattain and John Bardeen of Bell laboratories during 1960 has contributed immense developments in the field of microelectronics and integrated circuit technology. However, the electrical conduction in the organic crystals like Naphthalene and Anthracene in early 1960’s led to the beginning of organic electronics technology. Organic electronics uses the processable organic, inorganic and hybrid materials to build functional devices on mechanically flexible substrates and consequently it is called as Flexible electronics or Plastic electronics.

Organic based materials are fast replacing traditional inorganic materials due to their numerous advantages. Building a silicon chip requires long and expensive fabrication steps including photolithography and high temperature and high vacuum evaporation steps. The most important characteristics of organic based materials which distinguish them from the traditional inorganic semiconductor materials are - ease of device fabrication, large area applications, compatibility with light weight, mechanically flexible, control of electrical, optical and magnetic properties etc. The main advantages of organic materials includes possibility of handling under ambient conditions, relatively large scale and inexpensive production, electronic tunability, possibility of making composites and blends with other polymers and inorganic materials and tunable mechanical and chemical characteristics (e.g. solubility, strain stress, crosslinking properties).

The scientific community has recognized the factual potential of this field and as a result several Universities, National and International laboratories, Defence organizations all over the world and a large number of companies such as Philips, General Electric, IBM, Motorola, Siemens etc. are actively working in the organic electronics area. The organic electronics
Technology has the potential to produce light emitting diodes, radio frequency identification tags and even integrated circuits compatible and more efficient. Organic light emitting diodes and displays have already taken their places in current markets. Hence, the organic materials are used in, or being developed for, almost all levels of electronics (Salaneck et al, 1990; Yoshino et al, 1997). The building blocks of these organic electronics include polymers, organic-inorganic hybrid materials.

1.2 Polymers

Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units. The repeating units are usually obtained from low molecular weight simple compounds referred to as monomers. The reaction by which monomers are converted into polymers is known as polymerization. The formed polymers can have linear, branched or cross linking structures.

1.2.1 Classification of Polymers

The polymers are classified broadly into two categories viz. Insulating polymers and Conducting Polymers based on the property of electrical conductivity.

**Insulating Polymer**

The polymers which do not show electrical conduction are known as Insulating Polymers. The conductivity of these polymers range from $10^{-10}$ ($\Omega \text{ Cm})^{-1}$ to $10^{-18}$ ($\Omega \text{ Cm})^{-1}$. Polyethylene, Polypropylene, Polyvinyl Chloride etc, are few examples of insulating polymers.

**Conducting Polymer**

The polymers which show electrical conduction are termed as Conducting Polymers. These Polymers possess electronic, magnetic and optical properties of a metal while retaining the mechanical properties and processability of conventional polymers. Polyacetylene, Polyaniline, Polypyrrole, Poly Phenylene Vinylene, Poly Para Phenylene are the most common examples of conducting polymers.
1.3 Conducting Polymers

Until four decades ago all carbon based polymers were rigidly regarded as insulators. The idea that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively used by the electronics industry because of this very property. But, Alan Heeger, Alan MacDiarmid and Hideki Shirakawa have changed this view with their discovery that a polymer, Polyacetylene, can be made conductive almost like a metal. Polyacetylene was already known as a black powder when in 1974 it was prepared as a silvery film by Shirakawa and co-workers from acetylene using a Ziegler-Natta catalyst. In 1977 Shirakawa, MacDiarmid and Heeger discovered that oxidation with chlorine, bromine or iodine vapour made Polyacetylene films $10^9$ times more conductive than they were originally. Treatment with halogen was called ‘doping’ by analogy with the doping of semiconductors. Fig 1.1 shows the electrical conductivities of conducting polymers compared with other metallic, semiconductor, and insulating materials.

Conducting polymers are usually classified as cation salts of highly conjugated polymers. (Dinesh et al 2004). The cation salts are obtained by electrochemical oxidation and electrochemical polymerization or chemical oxidation (removal of an electron). It is also possible to obtain anion salts of some highly conjugated polymers (which also are conducting, but much less stable than the cation counterparts) by either electrochemical reduction or by treatment with a reagent such as solutions of Sodium naphthalide.

![Conjugated polymers](image)

*Fig 1.1 Electrical conductivities of conjugated polymers compared with other common materials.*
The key property of a conducting polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized sigma bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized "Pi" bond which is weaker. However, conjugation is not enough to make the polymer material conductive. In addition, charge carriers in the form of extra electrons or holes have to be injected into the material by doping. A hole is a position where an electron is missing. When such a hole is filled by an electron jumping in from a neighboring position, a new hole is created and so on, allowing charge to migrate a long distance.

1.3.1 Classification of Conducting Polymers

The electrically conducting polymer can be classified into three groups on the basis of their structural units which are as shown in Fig. 1.2 (Dinesh et al 2004).

- The first group includes hydrocarbon polymers, e.g. Polyacetylene.
- The second group includes polyaromatics involving only carbon atoms, e.g. Poly para phenylene and Poly phenylene vinylene.
- Third group includes polymers containing heteroatoms in the backbone, such as Polysulphurnitride (SNx), Polyaniline and polymers containing organic heterocyclic units eg. Polypyrrole, Polythiophene.

![Fig 1.2 Conducting polymers](image)
1.3.2 Synthesis of Conducting Polymers

In the past two decades, synthesis and characterization of conducting polymers have become two of the most important areas of research in polymer and materials science. In this context, major attention has been focused on synthesis of conducting polymers having:

- Good processability
- Ease of synthesis
- More defined and three dimensional structure
- Stability in both conducting and non conducting states
- Solubility in water and
- Unique properties

As conducting polymers are organic materials, there is a certain amount of flexibility in their synthesis, which allows one to tailor their properties. This flexibility will be a key factor in successful commercialization of conducting polymers.

1.3.3 Characterization of Conducting Polymers

The physico-chemical characteristics of synthesized conducting polymers are determined using various advanced characterization techniques as listed below:

- UV-Visible Spectroscopy: To understand electrochromic window and non-linear optical material.
- IR Spectroscopy: To determine chain orientation and structure of polymers and to elucidate mechanism of polymerization.
- Nuclear Magnetic Resonance: For structure confirmation, chain orientation and molecular motion.
- Scanning Electron Microscope: To investigate the morphology of conducting polymers.
- Thermo Gravimetric Analysis and Differential Scanning Calorimetry: For understanding glass and melting transitions and decomposition temperature.
- Raman Analysis: For vibrational assignments.
1. Dependence of conductivity on temperature, electric field and magnetic susceptibility to understand the conductivity mechanism.

2. Electroluminescence: For potential use in light emitting diodes.

3. X-Ray Diffraction analysis: For understanding of crystal structure.

4. Rutherford Backscattering: For element depth profiles, in order to gain insight into the conductivity mechanism.

1.3.4 Applications utilizing the polymers inherent conductivity

Upon realization that polymers could be made electrically conductive, the applications were immediately grasped.

- Conducting polymers are proving extremely useful in electromagnetic shielding and antistatic applications.
- Conducting polymers are set to emerge in devices used to store energy in the form of super capacitors and photovoltaic applications.
- Conducting polymers are involved in developing new rechargeable battery technologies.
- Polymer photovoltaics using conducting polymers are also being developed.
- The PLED was first demonstrated by Richard Friend and co workers of Cambridge University in 1990. The PLED products are being used in display technology.
- Another interesting application that uses the dynamic properties of conducting polymers is electrochromic devices.
- More futuristic applications for conducting polymers that are receiving considerable attention include electromechanical actuators (artificial muscles).
- Conducting polymers provides beneficial protection to many metals in a corrosive environment.

1.4 Literature Survey

Several researchers have been carried out systematic studies on conducting polymers. Synthesis of Polyacetylene was reported by Natta et al 1958, Polyaniline by Leitheb 1862. Films of Polypyrrole and Polythiophene were prepared in 1979 and 1982 (Kuo et al 1998). Discovery of Conducting Polymers led to several electronic applications. Yifan Xu and Paul
Berger (2003) have studied High electric-field effects on short-channelPolythiophene polymer field-effect transistors. High quality Aluminum electrolytic capacitors have been made using doped Polypyrrole as solid electrolyte (Kudoh et al 1991). Borrough et al (1990) demonstrated the light emitting property of Poly (P-Phenylenevinylene). It is difficult to make blue LED’s of inorganic materials, but, the first blue LED based on a conjugated polymer was reported by Ohmori et al (1991). Conducting Polymer like Polyaniline, Polythiophene, Polypyrrole have been previously quite frequently applied in Biosensor design and investigations. Conducting Polymer NanoWire based BioFET has been reported by Adam et al (2000).

A report of the specific detection of a few hundred molecule of genetic material using a fluorescent Polythiophene is made (Ebtisans et al 2000). Many conjugated polymers have been found to show the Photovoltaic effect, including Polyacetylenes, (Tani et al 1980; Tsukamoto et al 1982; Sasabe et al 1988), Polythiophene and its derivatives (Glenis et al 1984; Glenis et al 1986; Horowitz et al 1986), and Poly Phenylene Vinylene and its derivatives (Karg et al 1993; Marks et al 1994; Yu, et al 1994). Polymer p-i-n junction photovoltaic cells are described by Jun Gao et al (1998). Conducting polymers, particularly the soluble derivatives, are attractive alternative charge dissipators for e-beam lithography. (Angelopoulos et al 2001). First conducting polymer to be evaluated in this type of application is Polyaniline (Angelopoulos et al 1989).

Among Conducting Polymers Polyaniline is extensively studied by researchers because of its good environmental stability and ease of preparation. Its electrical properties are in a range that is attractive for semiconductor devices. Polyaniline can be easily doped by non-redox doping method. There are plenty of reports available on different acid as well as ester dopants used for polyaniline. The standard route of synthesis of doped polyaniline is the one with Hydrochloric acid as dopant ions as reported by many authors Prokes et al (1999). The other mineral acids commonly used include Sulfuric acid Andreatta et al (1988), High molecular weight long-chain organic sulfonic acids include Camphor sulfonic acid (Sariciifti et al 1993), p-Toluene sulfonic acid (Gazotti et al 1996), Dodecylbenzenesulfonic acid (Cao et al 1992), Polystyrenesulfonic acid (Haba et al 1999).

It has been reported that the composite system by blending Polyanilne with a commodity polymer improves its mechanical properties (Kobayashi et al 1984; Malmonge et al 1995;

Microwave absorption properties of a conductive thermoplastic blend based on polyaniline was studied by Cristiane et al (2004). Studies on electrical characteristic of Doped Polyaniline under the UV exposure were done by Valsangiacom et al (2004). Studies of electrical properties of Polyaniline Irradiated by X-rays have been carried out by Artem et al (2005). Studies on Optical Properties of Polyanililne/Cds Nanocrystals composite film has been carried out by Ghiordanescu et al (2001). Capacitors Based on Conducting Polyaniline Films are fabricated by Aghlara (2003).

Temperature dependence of electrical conductivity in Polyaniline composites and Blends has been studied by (Reghu et al. 1992; Reghu Menon et al 1993; Yoon et al 1995; Wan-Jin Lee et al. 2000). Polyaniline materials with metal oxalate complexes of Cr, Fe, Mn, Co and Al were synthesized by chemical oxidative polymerization and polymer materials were characterized by spectral studies, X-ray diffraction and by Conductivity measurements (Murugesan and Subramanian 2002).

The influence of anion on properties and electrochemical behavior of polyaniline was investigated by Trivedi (1999). Hwang et al (1995) have studied use of Pani-FeOCl composite for electrode fabrication in rechargeable battery. Huguenin et al (2000) also studied Pani-V2O5 composites for electrode fabrication in rechargeable battery. The use of hetero polyanions as dopants for Polyaniline in electrochemical studies has been studied by Barth et al (1999). When Pani is encapsulated into nanoporous aluminosilicate doped with Cu$^{2+}$ or Fe$^{3+}$, molecular wires are formed (Luca and Thomson 2000). Lewis inorganic acids such as SnCl4 (kulszewicz-Bajer et al 1999) and FeCl3 (Genoud et al 2000) are the recently investigated dopants. Fusalba and Belanger (1999) have reported a novel inorganic-organic material of Pani with MoS3 dopant. Polyaniline-fly ash composites were synthesized,
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1.5 Polyaniline (PANI)

Polyaniline (PANI) is one of the oldest conductive polymers known. It was first prepared by Letheby in 1862 by oxidation of aniline in Sulphuric acid (Kumar and Sharma 1998). Poly aniline has been investigated extensively for over 100 years and has attracted special interest as a conducting material for several important reasons; the monomer is inexpensive, the polymerization reaction is straightforward and proceeds with high yield and PANI has excellent stability (Heeger and Angew 2001). A first fairly detailed description of this product which was earlier known as ‘aniline black’ was provided by Green and Woodhead. The later discoveries on Polyaniline dealt with its electrical conductivity and other properties like electro-chemical redox activity, reversible doping/dedoping, electrochromism etc. (Diaz and Logan 1980). Further attention has been focused on PANI due to two prime reasons: (i) It can be synthesized easily both by electrochemical and chemical oxidation processes and (ii) it shows a particular sensitivity to the proton activity of its environment (Holze 2001).

1.5.1 Structure of Poly aniline

Green and Woodhead were the first to depict PANI as a chain of aniline molecules coupled head-to-tail at the para position of the aromatic ring (Green and Woodhead 1910, 1912). They have proposed a linear octameric structure for PANI. Polyaniline, a typical phenylene based polymer, has a chemically flexible –NH– group in the polymer chain flanked by phenyl rings on either sides. The diversity in physicochemical properties of PANI is traced to the –NH– group. The difference in the composition of amine and imine segments of PANI generates several oxidation states of this material ranging from completely reduced leucoemeraldine to completely oxidized pernigraniline states as shown in Fig 1.3. The different forms of PANI can be readily converted to one another by simple redox methods. Out of several possible oxidation states, the 50 % oxidized emeraldine salt state shows electrical conductivity (Rao et al 2001). Polyaniline and its derivatives attract considerable interest because of their electroactivity, low density, good electrical conductivity and environmental stability. But
because they are intractable, there is a need to modify them in order to make them as processable as conventional organic polymers.

![Chemical Structures](image)

**Fig 1.3 Various possible oxidation states of Polyaniline**

### 1.5.2 Synthesis of Polyaniline

There are two methods for the synthesis of PANI. The first one is the direct oxidation of aniline by chemical oxidation and the second one is through electro oxidation on an inert electrode.

**Chemical Synthesis**

PANI—emeraldine salt can be easily obtained as dark green powder by polymerization of aniline in aqueous media using oxidizing agents such as ammonium per sulfate, potassium iodate, hydrogen peroxide, potassium dichromate etc. The main advantage of chemical synthesis is its ease and capability to produce large volume of Polyaniline in good yield. The reaction is carried out in acid medium and pH is maintained between 0 and 2. The concentration of the monomer employed varies between 0.01 and 1 M. Oxidative chemical polymerization is generally carried out at low temperatures (−15 to 5 °C) in order to obtain PANI with high molecular weight.
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**Electrochemical Synthesis**

The electrochemical synthesis of a conducting polymer is an electro-organic process, rather than an organic electrochemical one, because emphasis is on the electrochemistry and electrochemical process, rather than organic synthesis. Electrochemical synthesis is normally carried out in a single compartment cell. The cell consists of the electrodes, electrolyte and power supply. A standard three electrode configuration, which comprises of a working electrode, a reference electrode and a counter electrode, is commonly used in synthesizing the Polymer.

1.5.3 **Electrical Property**

The Electrical conductivity of the Polyaniline reported by different investigators is found to be in the range of $10^8$ to 400 S cm$^{-1}$ (James 1999). This conductivity will increase as better processing methods are developed reducing structural defects. The conductivity can be tuned to specific end uses for a variety of applications. Polyaniline is reasonably stable under ambient conditions and, with the proper selection of dopants, retains its conductivity over long periods of time (~ five years). Polyaniline easily switches from the conductive form (emeraldine salt) to the insulative form (emeraldine base) as a function of pH. Under acidic conditions the polymer acid dopes and becomes conductive. When exposed to higher pH levels the polymer switches to the insulative form. This facile switching can be cycled many times.

1.5.4 **Polyaniline Blends**

Polymer blends can be simply defined as the mixture of two or more polymers or copolymers. Blends of two polymers are usually prepared to achieve desired properties, which cannot be given by the individual polymers. Electrically conductive Polyaniline based blends with commodity polymers can be produced by using common solution and melt processing techniques. Examples of commodity polymers are polyethylene, polypropylene, polystyrene, PVC, phenol-formaldehyde resins, and different types of thermoplastic elastomers.
1.5.5 Polyaniline Composites

Composites of conducting polymers with insulating polymers and other materials are often used to impart synergistic effects such as mechanical strength, environmental stability, and processability to the materials. The word ‘composite’ consists of the Latin prefix ‘com’ meaning ‘together’ and ‘posit’ meaning ‘to put or place’, which means ‘put together or made up of separate parts’. Polyaniline composites can be made by dispersing particles such as Fullerene, graphite fibers, metals and metal oxides in polymer matrices.

1.5.6 Applications using Polyaniline

- Packaging Industry: Injection moulded antistatic products, Antistatic films.
- Electronics: Antistatic packaging of components, Printed circuit boards.
- Fenestration: Electrochromic "smart" windows, Electrochromic automobile rear vision systems.
- Textile Industry: Conductive fabrics
- Automotive Industry: Antistatic charge dissipation, Paint primers, Electrochromic rear vision systems.
- Construction: Antistatic floors, Antistatic work surfaces.
- Mining: Conductive pipes for explosives, Antistatic packaging.

1.6 Aim and Scope

The extensive work has been reported in literature about the doping with protonic acid in PANI to improve its electrical conductivity. Although Pani is studied extensively by the researchers, the studies on Composites of Metal halides with Polyaniline are sparse. The polymer metal composite opens a new field for the development of advance material in different applications of the modern world.

In view of these, the main objectives of the present investigations are;

- to synthesize the Polyaniline and
- to synthesize the composites of PANI with Magnesium and Zinc Chloride
- to characterize the polymer for their electrical and structural properties
1.7 The Dissertation

The subject matter of the dissertation has been divided into five chapters. A brief introduction of the conducting polymer, the relevance of the study, a detailed survey of literature providing a glimpse of the work done in this area by various investigators all over the world and the aim and scope of the present study are outlined in this chapter. In chapter 2, the description of experimental methods which describes the synthesis of polymers and poly aniline composites with the metal halides are presented. Chapter 3 gives details of the characterization techniques used in the present work. Chapter 4 includes the results and discussion obtained by characterization of the polymer and its composites. Conclusions and a discussion of possible future work with polyaniline metal halide composites are indicated in Chapter 5.