Chapter-1

Introduction
CHAPTER 1

INTRODUCTION

1.1. Electrically Conducting Polymers

The area of polymer research has triggered a great interest among the wide variety of disciplines of material science. The past two decades have witnessed the tremendous advancement in organic conducting molecules and polymers having comparable electrical, electronic and magnetic properties of metals along with high environmental stability and processibility of the conventional polymers. During this period, a number of conducting polymers were synthesized, which become highly electrically conducting when partially oxidized or reduced, i.e. ‘doped’ [1,2].

A unique feature of all these conducting polymers, otherwise called ‘synthetic metals’, is the π-electron conjugation throughout the polymer backbone, that makes them conductive. Present day material research received much interest in these molecules, because of this π-electron delocalization which gives rise to many interesting properties [1-8]. Along with it, their light weight, processibility and high electrical conductivity suggest their potential applications in many fields such as in rechargeable solid state batteries [9-11], solar cells [12], optical storage [13,14], electrochromic display devices [15-17], light emitting diodes and electro luminescence [18-22], Schottky diodes [23-25], optical signal processing, EMI shielding [26-27], biosensors and ion-sensors [28,32], corrosion inhibition [33], field effect transistors [34], nano-composite materials [35] etc. Recent interests in these materials have been directed towards
chemically controlling their physical and electronic properties via structural variation and investigating their potential applications.

The major significant development which triggered the worldwide research activity in the field of conducting polymers was encountered in 1977 when it was reported by Shirakawa, Heeger and Chiang that polyacetylene film treated with iodine vapors could show electrical conductivity values up to $10^3 \text{ Scm}^{-1}$ [36]. Though Hatano and coworkers first reported the conductivity of the order of $10^{-5} \text{ Scm}^{-1}$ for their polyacetylene sample, much attention was not received because of its intractability and poor environmental stability [37]. In 1970s Ikeda, Ito and Shirakawa of Japan succeeded in the synthesis of free standing polyacetylene films which showed an electrical conductivity of $\sim 5 \times 10^{-5} \text{ Scm}^{-1}$ [38-40].

Subsequently, in 1973 Walatka and co-workers discovered the metallic conductivity in polysulfur nitride $(SN)_x$ [41]. But this material remained as an academic curiosity because of its brittleness and explosive nature. Inspired by the high metallic conductivity of polyacetylene, researches all around the world turned their attention into conducting polymers to discover the fundamental features and their potential applications. Many scientists succeeded in discovering other conducting polymers such as polyparaphenylene, polypyrrol, polythiophene, polyaniline etc. In a significant breakthrough, Ivory et al. suggested that polyparaphenylenes could also be doped to very high electrical conductivity [42]. Various electrochemical methods played a major role in synthesizing more conducting polymers in early 1980's. Polyaromatic systems such as polyphenylenesulphide [43,44], polypyrrol [45], polythiophene [46] and polyaniline [4,47] soon made their appearance in the family of conducting polymers.
Figure 1.1 Chemical structures of some electrically conducting polymers
This thesis covers a well known conducting polymer whose chemical structure can generate, sustain and assist the motion of charge carriers for electrical conduction. For a polymer to be classified under conducting polymer, it should possess some essential features [48].

(i) Presence of extended conjugation which provides a great degree of delocalization of π-electrons in the molecules.

(ii) The degree of conjugation of basic polymer chain, the nature and conjugation length of side groups, the degree of crystallinity, counter ions, chain kinks and cross links may play an important role.

(iii) As pristine conjugated polymers do not contain intrinsic charge carriers, they must be provided extrinsically, typically by a charge transfer process, commonly termed as ‘doping’.

Electrically conducting polymers, though largely amorphous, certain degree of crystallinity is also associated with them. They consist of both delocalized and localized states. The delocalized π-electrons along the polymer backbone are highly polarizable. The ability of electronic delocalization of conjugated polymers, provide them the highway for charge mobility along the polymer chain [2]. The delocalization of π-electrons depends on the extent of disorder, inter-chain interaction etc. The disorder induced localization plays dominant role in the metal-insulator transition and transport properties of conducting polymers. Moreover, the structure of poly conjugated chain, inter-chain interactions, disorder and doping level determine the stability of charge carriers such as solitons, polarons, bipolarons and free carriers in conducting polymers. Hence, a wide range of behavior from metallic to insulating regimes can be observed in the transport properties of such materials [49].
<table>
<thead>
<tr>
<th>ELECTRICAL CONDUCTIVITY (S cm(^{-1}))</th>
<th>Pb at 4k (superconduction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductors</td>
<td>Pt, Au, Ag, Cu</td>
</tr>
<tr>
<td>Si, Ge (Intrinsic)</td>
<td>Hg-Fe, Al</td>
</tr>
<tr>
<td>Si, Ge (Intrinsic) C (Graphite)</td>
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<td>Glass Cotton</td>
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<td>Nylon</td>
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<td>Polyethylene</td>
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<td>Quartz</td>
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Figure-1.2 Electrical conductivity ranges of various materials
1.2. Electrical Conduction

1.2.1 Band Theory

Various models such as band model, variable range hopping, percolation mechanisms etc. have been suggested to account for the electronic conduction in these materials [50]. According to band theory, a continuous band of states is produced as a result of overlapping of the atomic orbitals of the atoms considered in a solid. Usually, there is a gap between the top of the occupied valance band and bottom of the unoccupied conduction band, termed as "band gap". If electrons are present in the conduction band, it will contribute toward the electrical conduction. If the band gap is greater than 1.5 eV, the electrons can not be excited from the valance band to the conduction band and the material remains as an "insulator". If the band gap is of moderate size (<1.5 eV), some of the electrons can be excited to the conduction band by the application of an electric field leaving holes behind the valance band. These materials behave as "semiconductors". If the band gap is very small, the thermal energy available at room temperature is sufficient enough to excite electrons from the top of the valance band to the bottom of the conduction band and the materials are termed as "intrinsic semiconductors". If the materials are doped by suitable impurities, donor or acceptor bands are created in the band gap and the materials are termed as "extrinsic semiconductors". If the valance band and conduction band overlap each other and thus have no band gap, such materials are termed as "conductors".

The electrical conductivity \( \sigma \) is related to the free carrier concentration \( n \) and the carrier mobility \( \mu \) which is given by-

\[
\sigma = n e \mu
\]

\[\text{------------------------- (1.1)}\]
Figure-1.3 Formation of valance band and conduction band in polymeric materials
Figure 1.4 Relationship of polymers π-electron band structure to vacuum and other energetic parameters.
Figure-1.5  Schematic representation of band structures
where 'e' is the electronic charge on the charge carriers. For intrinsic conductivity, carrier concentration decreases exponentially with increasing band gap. Since conjugated polymers have relatively large band gap and low carrier concentration that results into negligible electrical conductivity.

1.2.2. Hopping and Tunneling Models

Band model satisfactorily explains the electrical conduction in a highly ordered crystalline lattice. In a disordered amorphous system like that in conducting polymers, the mobility of the electrons is impeded by localized electronic states. In such systems, the conduction occurs via discrete jumps from one state to another by variable range hopping or tunneling through the potential energy barrier. Both energetic and spatial distributions of electronic states are affected by the presence of disorder in the latter. If atoms are randomly distributed, the density of electronic energy state tails in to the forbidden zone and the electrons in these tails are localized. There is an intermediate range of electronic energy states at which the mobility is very low. Conduction is possible only if the electrons are excited to higher energy states with greater mobility.

Conduction via localized electrons implies direct jumps across an energy barrier from one site to the next. Thus, an electron may either hop over the top of the barrier or tunnel through the barrier [51].

1.2.3. Percolation Model

Conduction in composite materials depends on the concentration of the conducting phase. Generally, a sharp rise in electrical conductivity is observed at a critical concentration of the conducting phase, the percolation threshold. The percolation model
Figure 1.6  Hopping and tunneling conduction
successfully describes the electrical conduction in composite of conducting with non-conducting polymers. Basically it is a statistical and geometrical approach to explain the shape of the electrical conductivity curve in composite materials and proceeds from a statistical distribution of the conducting particles, which corresponds to a maximum of entropy. It thus denies any interaction between matrix and conducting particles. As the concentration of conducting particles increases, they become closer to each other and at the critical concentration \((\phi_c)\), they are finally sufficiently close together or even touching each other leading to the conduction of charge-carriers.

1.3. Doping In Conducting Polymers

As mentioned earlier, one of the pre-requisite for a conducting polymer to exhibit high electrical conductivity is the \(\pi\)-electron conjugation in which \(\pi\)-electrons overlap along the conjugated chain to form a \(\pi\)-conduction band. A conjugated organic polymer in its pure or undoped state is an insulator with conductivity of the order of \(10^{-10} \text{ S cm}^{-1}\). A high electrical conductivity is achieved only after doping of the polymer with a suitable oxidizing or reducing agent [45,52].

Doping of conjugated polymers increases the carrier concentration in the polymer and thus generates very high electrical conductivity [42]. This is achieved by oxidation or reduction with electron acceptors or donors respectively e.g. the polymer is oxidized by the removal of the electron by the acceptor, there by producing a radical cation or hole in the chain. If the hole can overcome the Coulombic binding energy to the acceptor anion with thermal energy or at high dopant concentrations, it moves through the polymer chain and contribute to the electrical conductivity.
The behavior of the conductivity with both acceptor and donor dopants is suggestive of the conventional substitutional 'p' and 'n' type doping of a semi-conductors. In conducting polymers, doping is not substitutional, the doping species reside alongside the polymer chains and there is a charge transfer process between the polymer chains and dopant molecules. This doping process is different from the doping of inorganic semiconductors, where the dopants are added in parts per million. In conducting polymers, the dopant concentrations are exceptionally high as doping involves the random dispersion of dopants in molar concentrations and that in some cases the dopants constitute about 50% of the final weight of the conducting polymer composition [53]. Thus, the conducting polymeric systems are often visualized as charge-transfer complexes.

The dopant ions such as BF$_4^-$, ClO$_4^-$, I$_3^-$ (p-type) can oxidize the polymer chain to create the positive charges on the conjugated polymer backbone, i.e. p-type doping. The dopant ions such as Na$^+$, Li$^+$, Rb$^+$ etc. (n-type) can reduce the polymer to create negative charges on the polymer backbone, i.e. n-type doping [49]. To a great extent carrier concentration depends on the doping level, structure of conducting polymer chain, inter-chain interactions, disorder etc. The distribution of dopant ions may not be uniform due to the complex morphology of the polymer matrix. Hence, both the structure and doping induced disorders may play major roles in the charge transport [54].

1.3.1. Chemical Doping

The initial discovery of the ability to dope conjugated polymers involved charge-transfer redox chemistry, oxidation (p-type doping) or reduction (n-type doping). This can be illustrated with the following examples [2].
p-type doping:

\[(\pi\text{-polymer})_n^{+3/2} \text{ny} (I_2) \rightarrow [(\pi\text{-polymer})^{y+} (yI_3)^{y-}]_n \quad \text{----(1.2)}\]

n-type doping:

\[(\pi\text{-polymer})_n^{+} \text{ny Na}^+\text{Naphthalide}^- \rightarrow [(yNa^+)(\pi\text{-polymer})^{y-}]_n \quad + \text{Naphthalene} \quad \text{----(1.3)}\]

1.3.2. Electrochemical Doping

Complete doping to the highest possible dopant concentration yields reasonably high quality materials. However, attempts to obtain intermediate doping levels often result in inhomogeneous doping. Electrochemical doping was invented to solve this problem where the electrodes supply the redox charges to conducting polymer, while ions diffuse into (or out of the polymer in case of undoping) the polymer electrode from the nearby electrolyte for electroneutrality. The doping level is determined by the voltage between the conducting polymer electrode and the counter-electrode at electrochemical equilibrium or by the amount of electronic charge passed during the process. A particular doping level is precisely achieved by setting the electrochemical cell at the corresponding applied voltage and waiting as long as necessary for the system to come to an electrochemical equilibrium as indicated by the current through the cell going to zero. Electrochemical doping can be illustrated by the following examples-

p-type doping:

\[(\pi\text{-polymer}) + x Li^+BF_4^- \rightarrow (\pi\text{-polymer})^{x^+} (xBF_4^-) + x Li^+ \quad \text{----(1.4)}\]
**n-type doping:**

\[(\pi\text{-polymer}) + x \text{Li}^+\text{BF}_4^- \rightarrow (\pi\text{-polymer})^x(\text{Li}^+)^x + x \text{BF}_4^- \]  \(1.5\)

This technique is used for doping of polymers obtained by other methods as well as for redoping or further doping. In this process, only ionic types of dopants are used as electrolyte dissolved in polar solvents [2].

**1.3.3. Radiation Doping**

The semi-conducting polymer chain in locally oxidized and nearby chain is reduced by photo-absorption and charge separation i.e. electron-hole pair creation and separation into free charge-carriers.

\[hv \quad (\pi\text{-polymer})_m + (\pi\text{-polymer})_n \rightarrow [(\pi\text{-polymer})_m]^x + [(\pi\text{-polymer})_n]^x \]  \(1.6\)

where \(x\) is the number of electron-hole pairs. In case of photo-excitation, the photoconductivity is transient and lasts only until the excitations are either trapped or decay back to the ground state. In contrast, the induced electrical conductivity is permanent in case of chemical or electrochemical doping until the charge-carriers are purposely removed by undoping [2]. High energy radiations such as \(\gamma\)-rays, electron beams and neutron radiations are used for doping of polymers by neutral dopants. For example, \(\gamma\)-ray irradiation in the presence of \(\text{SF}_6\) gas or neutron radiation in the presence of \(\text{I}_2\) has been used to dope polythiophene [54].

**1.3.4. Doping by Acid-Base Chemistry**

In this doping process, the number of electrons associated with the polymer backbone does not change. The energy levels are
rearranged during doping. Polyaniline was the first example of the doping of an organic polymer to highly conducting regime by this process. Protonation by acid-base chemistry leads to an internal redox reaction and converts the semi-conducting emeraldine base into highly conducting emeraldine salt. The chemical structure of the emeraldine base form of polyaniline is somewhat similar to an alternating block copolymer. Upon protonation of the emeraldine base to the emeraldine salt, the proton-induced spin unpairing mechanism leads to a structural change with one unpaired spin per repeat unit but with no change in the number of electrons.

1.3.5. Undoping

In conducting polymers, the doping process can be reversed i.e. conducting polymers can be rendered insulating by neutralization back to the uncharged state which is referred to as undoping or dedoping or compensation or electrical neutralization etc. Exposure of oxidatively doped polymers to electron donors or conversely of reductively doped polymers to electron acceptors effect dedoping [43,46,46,55,56]. This forms the basis of the application of conducting polymers in rechargeable batteries/electrodes.

1.4. Charge Carriers or Defects in Conducting Polymers

Generally, conducting polymers are largely amorphous in nature with a very small degree of crystallinity. Besides the conjugational defects mentioned earlier, these polymers like other solid polymers contain different kinds of structural kink irregularities such as cross links, branch- points, conformational defects etc. Formations of these defects including conjugational defects are essential as this would determine the chemical and physical properties of a given polymer. Introduction of particular
1. An unstable diradical with spin and without charge.

2. A stable polaron ‘p-type’ with spin and charge.

3. A stable bipolaron ‘p-type’ with charge and without spin.

4. A stable polaron ‘n-type’ with spin and charge.

5. A stable bipolaron ‘n-type’ with charge and without spin.

Figure-1.7 Formation of polarons and bipolarons in polyparaphenylene on reaction with oxidizing and reducing agents
defects such as solitons, polarons and bipolarons are the only means to attain high electrical conductivity in conducting polymers.

As mentioned earlier, charges added to polymer chains do not behave as low mass particles, as in the case of conventional inorganic semiconductors. They are intrinsically localized as a result of relaxation of the polymer chain round the charge to form defects that may be of solitons, polarons or bipolarons type [55]. Most of the electronic properties of these materials are determined by the behavior of the defect states. The theoretical understanding of them has been achieved in recent years [56-60].

During the polymerization e.g. in case of polyacetylene, it is possible that the bond alternation of the atoms constituting the polymer backbone may be disrupted leading to the creation of domain walls or the so called solitons in such systems [60, 61]. Solitons can either exist in neutral or charged states. Neutral solitons are electrically neutral, but possess a spin. Charged solitons are spinless but are electrically charged. The concentration of the charged solitons can be increased by doping with a suitable dopant.

Another type of defects, is called polarons, which can be visualized as electrons trapped in a polarized lattice of given material. They are electrically charged and have spin. The polarons are radical ions associated with lattice distortion and localized electronic state in the gap. These are the typical charge carriers often found in polymers such as polyaniline, polythiophene, cis-polyacetylene etc. whose ground state become energetically inequivalent when separated by polarons. Population of polarons in a conducting polymer varies with the temperature and the extent of doping [62]. When concentrations of the polarons are high enough, it is possible that two polarons may approach each other and result in
Figure-1.8 Schematic representation formation of polarons and bipolarons with increasing dopant concentration (x) and its impact on electrical conductivity and spin concentration of the conducting polymer.
the formation of a bipolaron. It is defined as a pair of like charges (di-ion) associated with a strong local lattice distortion. Bipolarons are doubly charged but spinless [63,64]. These defects occupy distinct energy levels, in the band gap of a given polymer.

1.5. Degradation and Stability of Conducting Polymers

Polymers also undergo chemical reactions, provided that the reactants are made available at the reaction site, leading to deterioration of useful polymer properties which is termed as 'degradation'. The same is applicable in case of conducting polymers also. There are many external causes of degradation such as light, heat, mechanical stress, oxygen, moisture, atmospheric pollutant etc. along with the factors effective at the time of processing. Also, the intrinsic factors such as reactive sites, e.g. super-oxides, defects, chemically reactive groups may degrade the polymer properties with or without the combinations of external factors [65]. The inter- and intra-chain reactions between the reactive sites can alter the chemical structure of conductive polymers, affecting their dopability and hence the electroactivity [66,67]. Intrinsic degradation of doped conjugated polymers would be affected by the reactivity of the dopant and the reactivity of polymer backbone.

The oxidative degradation proceeds via chemical reactions of peroxy radicals. In presence of atmospheric oxygen, the polymers that contain bonds with low dissociation energies, such as O-O, C-N, C-Cl and C-C are susceptible to oxygen attack at elevated temperatures. Usually, thermal stability of the polymers is less than usually expected because of the accidental inclusion of weak linkages in the main chain.
The conjugated bonds present in conducting polymers, undergo $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions, leading to formation of free radicals on exposure to sun light. The UV radiations containing enough energy to cause C-C, C-N and C-O homolytic bond fission. Thus produced free radicals can react with atmospheric oxygen leading to oxidation accompanied by depletion of chain length of the polymer.

The chemical reactions of environmental degradants and those trapped during synthesis, such as moisture, oxygen, other environmental gases etc. may also have some degradative effect on the polymer properties which may involve electrical neutralization of the polymer backbone through a process generally called compensation. During chemical compensation an oxidized polymer (p-type doped) reacts with a reducing agent like NH$_3$ accompanied by a loss of electrical conductivity [68-70].

Conducting polymers are being used as electrode materials in non-rechargeable (primary) and rechargeable (secondary) batteries. These materials are highly sensitive to electrode reactions and have low catalytic activity towards side reactions, sufficient mechanical strength, fabricability, low cost etc. The electrode materials must also possess high stability towards degradation during the passage of current or the storage. Degradation of electrode materials leads to instability in electrode potential with time. A good shelf life, i.e. capable of retaining its charged state is a prequalification for a commercial battery. The durability studies of polymeric electrodes may be done galvanostatically or potentiostatically to evaluate their life in battery applications [66].

The ability of a polymer to retain its useful properties is defined as stability and the preventive measures undertaken to
inhibit degradation process is termed as 'polymer stabilization'. Various methods are employed to stabilize conducting polymers such as (i) by incorporating antioxidants such as benzoquinone (ii) by ion implantation or by predoping the material with strong electron acceptor prior to oxygen exposure (iii) by encasing the polymer in a system with reduced oxygen and moisture permeability (iv) by synthesizing new polymers with less susceptibility to intrinsic degradation to oxygen and to moisture even at elevated temperature etc. [71,72].

1.6 Objectives

One of the major problems with the conducting polymers is the non-processibility by solvent or melt techniques. Most of them are insoluble in common solvents and undergo degradation before reaching the melting point. Also they have very poor mechanical strength and are environmentally unstable. Very recently many researchers have succeeded in overcoming these problems [73] and are generating polymer composite and blends [74,75] which can show better stability and mechanical strength.

This thesis is devoted to the studies of a well-known conducting polymer, polyaniline, which is one of the environmentally stable polymers. Here, the monomer is easily available and much cheaper than the monomers of any other conducting polymer. Moreover, the synthesis of the polymer by chemical method is much easier and efficient.

The thesis describes various studies on the polymers derived from aniline and substituted anilines aimed at a greater understanding of electric, electronic and thermal properties of the materials and the problems impeding their applications.
Chapter-2 gives a brief description on the physics and chemistry of polyanilines. It gives a summary of the various methods of synthesis spectral electrical and thermal properties. A brief discussion on the work so far done is presented.

Chapter-3 deals with the details experimental works carried out such as materials used, synthesis of the various co-polymers and different methods employed to study their properties.

Chapter-4 deals with comparative studies on polyaniline and the copolymers of aniline with $o$-, $m$- and $p$-nitroanilines respectively.

Chapter-5 is devoted to comparative studies of polyaniline and the copolymers of $p$-methoxyaniline with aniline and $o$-toluidine.

Chapter-6 deals with comparative studies on copolymers derived from aniline with $o$-toluidine and $p$-toluidine.
References

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