CHAPTER 1

INTRODUCTION

The research work presented in this thesis is mainly focused on the synthesis of helical conducting/optically active polymers. These polymers were prepared by using conducting polymers and chiral dopants through “soft template method” and explored for their utility in hydrogels, chiral sensors and chiral chromatography/separator etc. The following sections of this chapter address an introduction to the conducting polymers with a particular focus on helical/chiral conducting polymers.

1.1. Conducting Polymers

Conducting polymers represent a new class of materials with promising properties and applications. This special class of polymers often referred as “Synthetic Metals” possess the unique electronic, electrical, magnetic and optical properties of a metal along with known advantages of conventional polymers like light weight, easy processibility, resistance to corrosion and low cost etc. As a result of these properties, conducting polymers have literally taken charge as conductors with a wide range of applications, either in their innate state or with modification in their morphology such as helical/chiral conducting polymers.

Conducting polymers were first discovered in 1976. In the mid 1970s, the first polymer capable of conducting electricity, polyacetylene, was reportedly prepared by a serendipitous experiment in Shirakawa’s group [1.1]. The subsequent discovery by Alan J. Heeger and Alan G. MacDiarmid that the polymer would undergo an increase in conductivity of 12 orders of magnitude by oxidative doping quickly reverberated around the polymer and electrochemistry communities and an intensive search for other conducting polymers was soon followed [1.2]. In 1976, MacDiarmid, Shirakawa and Heeger, along with a group of young students found that the conductivity of polyacetylene increased by up to 6 orders of magnitude when reacted with iodine (from $10^{-4}$ to $10^{2}$ S/cm); this phenomenon, termed as doping is a result of presence charge carriers in the materials. In addition, it was observed that varying the level of doping in polymers exhibiting wide range of electrical properties; from insulator, or semi-conductor to metal [1.3]. Although polyacetylene is not stable in air, the fact that it could become conducting upon doping led to further experimentation with other known conjugated
polymers. Since 1976, a number of conducting polymers, namely, polypyrrole (PPy), polythiophene (PTh) and polyaniline (PANI) etc have become the focus of many researchers worldwide. The importance of conducting polymers is exemplified by rewarding *Nobel Prize in Chemistry* in the year 2000 to MacDiarmid, Shirakawa and Heeger for the discovery and development of conducting polymers. This was particularly exciting because it created a new field of research and a number of opportunities in the interdisciplinary research in chemistry and condensed-matter physics. As the commonly known polymers in general are saturated and therefore insulators, these were viewed as non-interesting from the point of view of electronic materials.

Conducting polymers are polymers containing an extended $\pi$–conjugated system made up of overlap of singly occupied $p$-orbitals in the backbone of the polymer chain. Although conducting polymers possess a relatively large number of delocalized $\pi$–electrons, a fairly large energy gap exists between the valence band and the conduction band (greater than 1 eV), thus these polymers are considered to be semi-conducting at best. These polymers must be doped (to alter the number of $\pi$–electrons) in order to render the polymers truly conducting.
In conjugated polymers the electronic configuration is fundamentally different, where; the chemical bonding leads to one unpaired electron per carbon atom. Moreover, bonding in which the carbon orbitals are in the sp² configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer. This electronic delocalization provides the highway for charge mobility along the backbone of the polymer chain. Therefore, the electronic structure in conducting polymers is determined by the chain symmetry, i.e., the number and kind of atoms within the repeat unit with the result that such polymers can exhibit semiconducting or even metallic properties. The formation of molecular orbital is shown in Figure 1.1.

Electrically conducting polymers are designated as the fourth generation of polymeric materials. Electronically conducting polymers are extensively conjugated in nature and therefore it is believed that they possess a spatially delocalized band-like electronic structure. These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of the band structure of solid-state semiconductors. It is generally agreed that the mechanism of conductivity in these polymers is based on the motion of charged defects within the conjugated framework. The charge carriers, either positive p-type or negative n-type are the products on oxidizing or reducing the polymer, respectively. The simplest possible form of conducting polymer is the arche type polyacetylene (CH)n. Polyacetylene (PA) itself is too unstable to be of any practical use, though its structure explains basis of all conducting conjugated polymers. Little et al. [1.4] had proposed that properly substituted PA molecule would exhibit superconductivity at room temperature. Hatano et al. [1.5] are the first to report the electrical conductivity of the order of 10² S/cm for trans-PA sample. Conducting polymers such as PANI, PPy and PTh are shown in the following Scheme 1.1 in their non-conducting (undoped) forms.

Scheme 1.1: General structure of PANI, PPy and PTh
In their conducting forms, obtained by oxidation of the undoped forms, the polymers have positive charges located along their chains. Counter-ions from solution are incorporated into the polymer matrix to electrostatically neutralize the charged polymers illustrated in Scheme 1.2.

\[
[M_x]^n + nA^-(sol.) = [M_x]^+ nA^-
\]

Scheme 1.2: Doping in liquid phase

Where, \(x\) is the number of monomer units that share one positive charge and \(A^-\) is the incorporated anion. The resulting polymer is therefore actually a salt of the polymer and the incorporated counter-ions. The incorporated counter-ions have a major influence on the properties and applications of the polymers. This is another unique characteristic of conducting polymers.

1.1.1. Types of Conducting Polymers

Conducting polymers can be classified into different types [1.6] on the basis of conduction mechanism that renders electrical conductivity to these polymers:

❖ **Conducting Polymer Composites**

The conducting fillers such as carbon blacks, graphite flakes, fibers, metal powders and flakes etc have been reinforced into the non-conducting polymeric matrix. The electrical conductivity of the material is decided by the volume fraction of the reinforcements. A transition from insulating to conducting behaviour is generally observed when volume fraction of conductive filler in the mixture reaches a threshold value. The various polymers, which have been used as main matrix, are typically PP, Nylon, and PVC etc [1.7].

❖ **Organometallic Polymeric Conductors**

This type of conducting materials is obtained by adding organometallic groups to polymer molecules. In this type of materials the d-orbital of a chelated metal overlaps orbitals of the organic structure and thereby increases the electron delocalization. The d-orbital may also bridge adjacent layers in crystalline polymers to give conducting property to it. Metallophthalocyanines (Figure 1.2) and their polymers fall in this class of polymeric materials. These polymers have extensively conjugated structures. The bridge transition metal complexes form one of the stable systems exhibiting intrinsic electrical
conductivities, without external oxidative doping. Polyferrocenylene is also an example of this type of polymer. These materials possess strong potential for future applications such as molecular wires, antistatic foils and in fibers etc.

![General structure of polyphthalocyanine](image)

**Figure 1.2: General structure of polyphthalocyanine**

- **Polymeric Charge Transfer Complexes (CTC)**

  There are many charge transfer complexes reported in the literature, e.g., CTC of tetrathiofulvalene (TTF) with bromine or chlorine is a good conductor. The reason for high conductivity in polymeric charge transfer complexes and radical ion salts are still somewhat obscure. It is likely that in polymeric materials, the donor-acceptor interaction promotes orbital overlap, which contributes to alter molecular arrangements and enhanced electron delocalization in TTF:TCNQ [1.8].

- **Inherently Conducting Polymers**

  Research in the field of inherently conducting polymer [1.9] started nearly three decades ago when Shirakawa and his group found drastic changes in the electrical conductivity of polyacetylene films when exposed to iodine vapours. The highest crystalline variety of the polyacetylene showed electrical conductivity of the order of $10^{-5}$ S/cm and was in all possibility the trans-form of polyacetylene. Leading on from this breakthrough, many small conjugated molecules were found to polymerize, producing conjugated polymers, which were either insulating or semiconducting in the oxidized or doped state. The electronic properties of conjugated polymers are found due to the presence of $\pi$-electrons. The conductivity in such polymers arises due to a special type of metallic bonding in which valence electrons are completely delocalized and move almost freely through the crystal lattice. It is therefore necessary for the conjugated polymer backbone to behave as an electrical conductor. This delocalization of electrons may occur
through the interaction of π-bonded electrons in a highly conjugated chain or by a similar interaction of π-electrons with non-bonded electrons of electron rich hetero-atoms (e.g., S, N, etc.) in the backbone. For this, the molecular structure of the backbone should be planar. There should be no torsion at the bonds, which would decrease the delocalization of the electron system.

1.1.2. Synthesis of Conducting Polymers

Conducting polymers are commonly prepared through chemical, electrochemical, sonochemical, interfacial and photo-irradiation polymerization methods using an appropriate monomer. Chemical oxidative polymerization, sonochemical and interfacial polymerization methods are mainly used in the present work. The polymers have been made conducting using dopants like HCl, H₂SO₄ etc.

Doping and De-doping of Conducting Polymers

A common characteristic of all organic conducting polymers is that the conductivity is dependent on the oxidation state of the polymer. A redox process either oxidation or reduction, causes a change in the electronic structure that allows it to conduct electricity. This process is called “doping” which is of two types, viz, p-type and n-type. “p-type doping” refers to a doping process that involves polymer oxidation and results in the formation of charge carriers that are holes, while “n-type doping” refers to a reductive doping process that result in the formation of charge carriers such as electrons. In turn, the term “dedoping” is used for the process that transforms polymers from their conducting state to their insulating state. Oxidation (p-type) doping of conducting polymers results in the polymer backbone being converted from a neutral polymeric chain to a polymeric cation. Subsequently, the overall charge neutrality of the polymer chain is preserved by incorporation of “dopant” counter anions (or cations in the case of reductive doping) into the polymer matrix. Thus, dedoping (reduction) of oxidized polymers generally results in the removal of these dopants counter ions or ingress of cations.

Doping/ dedoping is a reversible process which can be performed manifolds without affecting the structure and functions of parent conducting polymers, leading to switching properties and colour change in the polymer. The switching process can be induced either chemically or electrochemically. In the latter case, the polymer itself acts as the electrode in an electrochemical cell. In the electrochemical process, the level of
oxidation or reduction of the polymer is controlled by the applied potential, and the ion movement involved in charge compensation is usually the anion (or cation for n-type doping) of the supporting electrolyte present in the electrochemical cell. However, in the case of large anionic dopants such as polyelectrolytes, cation movement may predominate in redox processes.

1.1.3. Influence of Dopants on Properties

Conducting polymers, once studied solely for their high conductivities are now extensively used in more dynamic applications where rapid switching from doped to neutral form is desirable. Charge injection (doping) in these materials leads to a wide variety of interesting and important phenomena which now defines the conducting polymer field. This reversible intercalation of ions in the polymer matrix triggers significant changes in the material’s optical, ionic, electrical and morphological properties. These properties can be tuned by varying dopant size and nature from small molecules to high molecular weight polymers as well as by using different preparation techniques. Table 1.1, summarizes several properties of conducting polymers that change according to their charge states. As sketched in Figure 1.3, doping can be accomplished in several ways depending on the nature of polymer and its intended application.

![Figure 1.3: Different methods of doping in conjugated polymers](image-url)
### Table 1.1: Qualitative properties of conducting polymers in two extreme redox states

<table>
<thead>
<tr>
<th>Property</th>
<th>Neutral Form</th>
<th>p-doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometry</td>
<td>Without ions</td>
<td>With ions</td>
</tr>
<tr>
<td>Content of solvent</td>
<td>Small</td>
<td>Higher</td>
</tr>
<tr>
<td>Volume</td>
<td>Small</td>
<td>Higher</td>
</tr>
<tr>
<td>Color: cathodically or anodically coloring</td>
<td>Transparent or bright dark</td>
<td>Dark or transparent</td>
</tr>
<tr>
<td>IR optical properties</td>
<td>Highly transmissive</td>
<td>Highly absorptive</td>
</tr>
<tr>
<td>Electronic conductivity</td>
<td>Semiconducting</td>
<td>Metallic</td>
</tr>
<tr>
<td>Ionic conductivity</td>
<td>Smaller</td>
<td>High</td>
</tr>
<tr>
<td>Diffusion of molecule</td>
<td>Dependent on structure</td>
<td>--</td>
</tr>
<tr>
<td>Surface tension</td>
<td>Hydrophobic</td>
<td>Hydrophilic</td>
</tr>
</tbody>
</table>

The initial discovery of the ability to dope conjugated polymers involves chemical doping by charge transfer redox chemistry. In case of PA, oxidation (p-doping) was accomplished by exposing the polymer to iodine vapours whereas reduction (n-doping) involved treatment with sodium naphthalenide (Figure 1.4 A). In this case, complete doping results in high quality materials with metal like conductivities. Another unique chemical doping procedure is PANI protonation by acid-base chemistry. This leads to an internal redox reaction converting the semiconducting form of PANI (emeraldine base) to a metal (emeraldine salt). Although chemical doping is an efficient process, controlling the level of dopant ions is rather difficult. Attempts to reach intermediate doping levels resulted in inhomogeneous doping. As an alternative, electrochemical doping allows for fine tuning of the doping level by simply adjusting the potential between the working and counter electrodes (Figure 1.4 B). The working electrode supplies the redox charge to the conducting polymer, while ions diffuse in or out of the electro-active film to compensate the electronic charge. Thus, any doping level can be achieved by setting the electrochemical cell to a desired potential and sweeping for the system to attain an equilibrium state. This type of doping is permanent, meaning that the charge carriers remain in the film unless a neutralization potential is purposely applied. Some high performance optical materials require a different type of doping based on localized...
oxidation via photo-absorption (Figure 1.4 C). Upon photo-excitation from the ground state to the lowest energy excited state, recombination back to the ground state can be radiative (luminescence) (PPV, PPP) or non-radiative (PTh, PA). Photo-conductivity lasts only until the excitations are either trapped or decay back to the ground state and the material becomes neutral.

Another way to dope a conducting polymer is the electrical injection of electrons and holes into HOMO and LUMO, respectively. However, the polymer is not doped in the sense of chemical or electrochemical doping because there are no counter ions present in the film. By charge-injection (Figure 1.4 D) at the metal-semiconductor interface, the polymer (semiconductor) can be used as an active layer in field effect transistors and thin film diodes. Dual-carrier injection in a polymer film sandwiched between two metal
electrodes provides the basis for light emitting diodes. As seen in Figure 1.3 and Table 1.1, charge injection in conducting polymers opens up a remarkably wide range of possible applications for this newer class of materials.

1.2. Polyaniline

Polyaniline (PANI) has received much attention because of its electronic, thermo-electronic and optical properties as well as its good environmental stability and ease of synthesis. PANI is also unique among organic conducting polymers in that its electrical properties are controlled by both its oxidation state and degree of protonation. Consequently, PANI is widely used for various applications such as rechargeable batteries, transistors, super-capacitors, electro-chromic displays, actuators, sensors and anti-corrosion coatings etc.

1.2.1. Synthesis of Polyaniline

PANIs are commonly synthesized by chemical or electrochemical oxidative polymerization of anilines in acidic solution. However, other polymerization techniques such as enzymatic, plasma, ultrasonic irradiation, photo-chemically initiated and polymerization using electron acceptors have now been developed. The properties of PANI such as morphology, crystallinity, conductivity, molecular weight, electrochemical behavior and processibility strongly depend upon the method and conditions of preparation.

1.2.1.1 Chemical Polymerization

PANI can be synthesized by the oxidation of aniline using various chemical oxidants in acidic solution. Chemical polymerization has the advantage of being a simple process capable of producing bulk quantities of PANI on a batch basis.

The main parameters affecting the polymerization and the properties of final products are: (1) nature of solvent (2) nature of acid (3) nature of oxidant and (4) temperature etc. Although optimal conductivities are obtained when ammonium persulphate is used as oxidant, other chemical oxidant such as ceric sulphate, potassium dichromate, potassium iodate, hydrogen peroxide and ferric chloride have also been employed. For battery applications, Fe(ClO₄)₃ and Cu(BF₄)₂ are preferably used as oxidizing agents because the PANI produced contain ClO₄⁻ or BF₄⁻ anions, which are
usually used in lithium batteries. Chemically synthesized PANI with Cu(BF₄)₂ is fibrous, while a granular shape is obtained when PANI prepared using APS.

Protonic acids used in polymerization have been varied from strong inorganic acids, e.g., hydrochloric acid, hydrobromic acid, perchloric acid, sulfuric acid and nitric acid to large anion organic acids such as camphursulphonic acid (HCSA), dodecylbenzenesulfonic acid (DBSA) and p-toluenesulfonic acid (p-TSA).

Chemical synthesis of PANI has generally been carried out in aqueous solution at low temperature since this leads to PANI with high molecular weight and less defect sites such as undesirable branching due to ortho-coupling. At extremely low temperature (-30 and -40 °C), conjugated polymer with high molecular weight of upto 400,000 have been obtained. However, the reaction time required is more than 2 days and the polydispersity is relatively high (PD> 2.5). Consequently, the most widely used temperature range for chemical polymerization of aniline monomers has been reported as 0-5 °C.

Mechanism of Chemical Polymerization

The reaction mechanism now generally accepted for the synthesis of PANI with APS as oxidizing agent is shown in Scheme 1.3. The first step involves formation of the radical cation of aniline. Subsequently, re-aromatization of the cation p-aminodiphenylamine (PADPA) occurs which is then oxidized to diradical dication. Although “head to tail” (e.g., N-para) coupling is predominant, some coupling in the ortho-position also occurs leading to the defect in conjugation in the resultant polymer. Chain propagation occurs in the third step, the diradical dication couples with the monomeric radical cation of aniline forming a trimer and the chain propagates further via coupling of polymer fragment-radical with aniline radical cation. The resultant polymer is pernigraniline salt. In the last step, when entire oxidant is consumed, the remaining aniline reduces the pernigraniline to form the final product, the green emeraldine salt. Prolonged reaction times lead to degradation of the polymer especially with an excess of oxidant as the pernigraniline form undergoes hydrolysis at the imine double bond more readily than the emeraldine form [1.10-1.14].

1.2.1.2 Electrochemical Polymerization

Electrochemical synthesis of PANI has some advantages including greater control over the oxidation potential and the fact that the products do not need to be exhaustively
purified from excess monomer, oxidant and acid due to the deposition of polymer on the working electrode. The properties of electrochemically deposited films are greatly influenced by the polymerization conditions employed such as monomer concentration, counter-ion or supporting electrolyte, solvent, pH of the electrolyte, synthesis temperature, deposition time, electrochemical technique (e.g., potentiostatic, potentiodynamic or galvanostatic) and working electrode substrate.

**Mechanism of Electropolymerization**

Generally accepted mechanism of electrochemical oxidation described as an electrochemical-chemical-electrochemical (ECE) [1.15-1.17] process is similar as shown in Scheme 1.3.

![Scheme 1.3: Polyaniline growth mechanism](image)

The polymerization is initiated by an electrochemical (E) process and is propagated by the repetition of a chemical (C) process followed by an electrochemical (E) process. Oxidation of aniline (step-1) to form its radical cation on the electrode surface is independent of the pH of the synthesis medium and is the rate determining step of the process. There are three different resonance forms of the oxidized aniline radical. These
forms with the radical on the N- and on the para-position of the aromatic ring are the most likely to react in a coupling reaction (step-2) to give a dimer by elimination of two protons, so called “head-to-tail” or “para-coupling”. This dimer then undergoes rearomatization to the neutral state giving p-aminophenylamine (PADPA) intermediate.

Although coupling between ortho-aniline radical cation is less likely to be involved due to electrostatic repulsion between the adjacent charged amine group, ortho-coupling may proceed to a limited extent. This results in the formation of undesirable products. In propagation of the chain (step-3), the radical cation of the dimer/oligomer is oxidized at the potential required to oxidise the aniline and then couples with a para-aniline radical cation to increase the polymer chain length. The conducting emeraldine salt (PANI.HA) deposited on the working electrode is obtained from the simultaneous doping of the polymer by protonation (step-4) during chain propagation. As the intermediate species and polymers are in the cationic form, neutralization of charge is achieved by incorporation of counter anion (A⁻) from the electrolyte [1.18-1.20].

Polymerization in Aqueous Solution

The electrochemical polymerization of aniline is usually carried out in aqueous acidic solution to maximize aniline monomer solubility and electroactive and conductive PANI emeraldine salt films only form when the pH is less than 3. Unusual chemical bonds, N-N bonds characteristic of “head-to-tail” coupling are observed for PANI electrodeposited at pH> 3. The unusual bonds interrupt the conjugation length of the polymer backbone leading to low conductivity of the polymer product. Acid (HA) solution generally used include inorganic acid such as HCl, HF, H₂SO₄, HNO₃ and HClO₄ as well as large organic sulphonic acids such as camphursulphonic acid (HCSA), p-toluensulphonic acid (p-TSA) and dodecylbenzenesulphonic acid (DBSA) which also provide a sufficiently low pH. From these acids, the dopant anions (A⁻) incorporated into the polymer chains during polymerization.

The dopant anion incorporated affects the rate of deposition, the morphology, conductivity and electrochemical behaviour of the polyaniline film. For example, sulphate anion promotes higher polymerization rates than to chloride or perchlorate ions. The conductivity of polyaniline emeraldine salt (PANI.HA) films electrodeposited from aqueous inorganic acids decreases in the order HClO₄>HCl>HBF₄>H₂SO₄. Moreover, films deposited slowly are denser and less porous than rapidly deposited films.
Polymerization in Non-Aqueous Solution

Electrochemical polymerization in non-aqueous electrolytes has also been investigated. The main objective of using non-aqueous solution is to avoid degradation and undesirable side reaction during polymerization in aqueous electrolytes. In addition, there is no need to remove water from deposited films before using in non-aqueous system such as batteries. Several types of non-aqueous solvents have been used for electroactive PANI films. Miras et al. have reported the electro-polymerization of aniline in a protophobic solvent with a large donor number such as acetonitrile containing LiClO$_4$ as supporting electrolyte without adding any acid. The formation of electroactive and conductive PANI can occur in such a solvent because the proton from oxidation of aniline is retained around the reaction layers and can protonate the polymer chain during growth. In contrast, electro-inactive films were obtained from protophilic solvents such as propylene carbonate, DMSO and THF.

However, with the organic solvents such as acetonitrile, propylene carbonate and ethylene carbonate polymerization of aniline using the very strong acid like trifluoroacetic acid (CF$_3$COOH) resulted in electroactive and conductive polyaniline and also enhances the polymerization efficiency. The polymerization of aniline in 1,2-dimethoxyethane (DME) containing LiClO$_4$ and CF$_3$COOH yielded an electrically inactive material. Osaka et al. reported that the mole ratio of CF$_3$COOH to aniline influences the electroactivity and morphology of the resultant PANI films. If the ratio of [CF$_3$COOH] to [aniline] is less than one, then electroactive films are obtained. Increasing the acidity of polymerization solution improved the electro-activity and charge discharge performance of the polymer. Osaka et al. also found that the dielectric constant of the solvents plays an important role in the deposition of electroactive PANI, because protons dissociated from CF$_3$COOH in high dielectric constant solvents are necessary to generate protonated aniline radicals in the initial step of polymerization.

Another approach is the use of an organic solvent such as acetonitrile and propylene carbonate (PC) containing anilinium tetrafluoroborate (ATFB) as supporting electrolyte and precursor for PANI. The Walden product (W, product of the viscosity and conductivity) of the polymerization solutions indicated that the degree of dissolution of AFB in MeCN is smaller than in PC, which influences the charge-discharge properties of the PANI.
Pekmez and Yildiz have prepared PANI by electro-polymerization of aniline in the presence of anhydrous cuprous ions in acetonitrile containing tetrabutylammonium perchlorate as supporting electrolyte. During electro-polymerization by potential cycling, in situ electro-oxidation of Cu$^+$ to Cu$^{2+}$ ions during the positive scans and in-situ electro-reduction of molecular H$_2$ to H$^+$ ions take place simultaneously. Aniline can also be oxidized by electro-generated Cu$^{2+}$ ions producing a much higher concentrations of aniline cation radicals which enhance the polymerization efficiency.

Electrochemical polymerization of PANI in ionic liquid was first investigated by Tang and Osteryoung in 1991. A mixture of aluminium chloride with 1-methyl-3-ethyl-imidazolium chloride in different molar ratios was used as solvent and electrolyte for electro-polymerization of aniline. Electroactive PANI was produced in all conditions. The oxidation potential of aniline in acidic medium was lower than in neutral and basic medium.

In summary, we can say that there are two important factors in order to obtain conductive and electroactive PANI from electro-polymerization in non-aqueous systems: sufficient concentration of protons and good ionic conductivity of the electrolyte. PANI grown from the non-aqueous media have the same molecular structures as those deposited from aqueous acid with mainly “head-to-tail” of para-coupling of aniline monomers. This suggests that the mechanism of electrochemical polymerization of aniline in aqueous and organic solvents is the same.

1.2.2. Doping Mechanism in Polyaniline

Before the details of conduction in PANI are discussed, three frequently used physical terms for describing conduction in solid have to be understood; namely soliton, polaron and bipolaron as shown in Figure 1.5 [1.21]. Soliton, sometimes called as conjugational defect, is an unpaired electron created in the polymer backbone during the synthesis of conductive polymer, in very low concentration. Conjugational defect is a misfit in the bond alternation so that two single bonds will touch. Soliton can be generated in pairs, as soliton and antisoliton. Three methods being used to generate additional solitons are chemical doping, photogeneration and charge injection. An electron will be accepted by the dopant anion to form a carbocation (positive charge) and a free radical during the chemical doping (oxidation) of the polymer chain, known to organic chemists as radical cation or polaron to physicists. Both the soliton and polaron
can be neutral or charged (positively or negatively) as shown in Figure 1.5. The conductivities of PANI can be transformed from insulating to conducting through doping. Both n-type (electron donating, such as Na, K, Li, Ca) and p-type (electron accepting, such as I₂, BF₄⁻, Cl⁻) dopants have been utilized to induce an insulator-to-conductor transition in electronic polymers. The common dopants for PANI are hydrochloric acid, sulphuric acids and sulfonic acids. For the degenerate ground state polymers, the charges added to the backbone at low doping levels are stored in charged soliton and polaron states for degenerate polymers and as charged polarons or bipolarons for non-degenerate systems. Such a situation is also encountered in PANI, which does not have two degenerate ground states, i.e., the ground state is non-degenerate due to the non-availability of two energetically equal Kekule structures.

Figure 1.5: Defects in conjugated polymer chains: a “physico-chemical dictionary” (Adapted from reference [1.33])
In the doping process, the heteroatoms like nitrogen will be protonated and become a bipolar form (Figure 1.6). The conventional distortion of molecular lattice can create a localized electronic state, thereby lattice distortion is self-consistently stabilized. Thus, the charge coupled to the surrounding (induced) lattice distortion to lower the total electronic energy is known as polaron (i.e., an ordinary radical ion) with a unit charge and spin = $\frac{1}{2}$. A bipolaron consist of two coupled polarons with charge = $2e^-$ and spin = 0.

![Diagram of polaron and bipolaron lattice](image)

**Figure 1.6: Polaron and bipolaron lattice** (a) emeraldine salt in bipolaron form (b) dissociation of the bipolarons into two polarons (c) rearrangement of the charges into a ‘polaron lattice’ (Adapted from reference [1.22, 1.23])

The polaron and bipolaron have a unique property called “spin-charge inversion”: whenever soliton bears charge, it has no spin and vice-versa (Figure 1.7). Charged solitons are spinless while neutral solitons carry a magnetic moment [1.23]. Bipolarons are not created directly but must form by the coupling of pre-existing polarons or possibly by addition of charge to pre-existing polarons (Figure 1.8) [1.8, 1.24-1.25]. At the molecular level, a polymer is an ordered sequence of monomer units. The degree of unsaturation and conjugation influence charge transport via the orbital overlap within a molecular chain. The charge transport becomes obscured by the intervention of chain folds and other structural defects.
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Introduction

Figure 1.7: Spin-charge inversion of a conjugational defect

Figure 1.8: Protonation process leading to the formation of polaron and bipolaron in doped PANI (a) emeraldine salt in bipolar form (b) dissociation of the bipolarons into polarons (c) rearrangement of the charges into a “polaron lattice”. (Adapted from references [1.24-1.25])
The connectivity of the transport network is also influenced by the structure of the dopant molecule. The dopant not only generates a charge carrier by reorganizing the structure (chemical modification) it also provides intermolecular links and sets up a micro-field pattern affecting charge transport. Any disturbance of the periodicity of the potential along the polymer chain induces a localized energy state. Localization also arises in the neighbourhood of the ionized dopant molecule due to the coulomb field. The conductivity of various conducting polymer tends to be relatively insensitive to the identity of the doping agent. The most important requirement for a dopant is sufficient oxidizing or reducing power to ionize the polymer. For example, though I\textsubscript{2} is a relatively weak electron acceptor, it induces conductivity in polyacetylene (500 S/cm), which is comparable to that achieved on doping with AsF\textsubscript{5}, a strong electron acceptor (1100 S/cm) [1.26].

It is well known that polyaniline with conjugated π-electron backbones can be oxidized or reduced more easily and more reversibly than conventional polymers. Charge-transfer agents (dopants) affect this oxidation or reduction and in doing so convert an insulating polymer to a conducting polymer with near metallic conductivity in many cases. Since PANI behave like amorphous solids and the simple band theory fails to explain the conduction of electricity in polymers, we have to assume the validity of the band theory of solids for polymers to the nearest approximation to explain the conduction in polymers [1.27].

Further, we have to look at the basis of doping effects on the PANI in order to understand the conduction mechanism in PANI. During the synthesis of PANI, the polymer backbone can have inherited a certain concentration of conjugational defects. On doping the PANI with oxidizing agent like DBSA (p-doping), protonation is realized in which DBSA accept the electrons, conferring positive charges on the PANI chain and the positive charges of the cationic PANI chains are balanced by the anionic part of the acids [1.28]. When electron is removed from the top of the valence band (by oxidation) of PANI, conjugational defects are generated from the distorted PANI’s backbone lattice as PANI is a one-dimensional material, resulting in a vacancy (a radical cation or called positive polaron) equivalent to a hole is created [1.27, 1.29]. A polaron gives rise to two levels (polaron bands) in the band gap due to the formation of polaron lattice defect state. The dopant, DBSA itself on the other hand, would be incorporated into the PANI and sits as counter-ions somewhere between the polymer chains. If the concentration of defects on the PANI backbone is high enough, the wave functions of the individual defects will
overlap and the Peierls distortion will be suppressed not only locally but also globally, leading to the disappearance of energy gap and PANI chain will becomes metallic [1.21].

Nevertheless, before the wave functions of the polarons overlap are suggested, the electrostatic interaction between the charge of the polarons and that of the counter-ions has to be taken into account. The remaining unpaired electron on the PANI chain contributes to the propagation of polaron through a conjugated polymer chain by shifting of double bonds alternation that give rise to electrical conductivity (Figure 1.9) [1.27]. Such polaron is not delocalize completely, but is delocalized only within a few monomeric units deforming the polymeric structure. The energy associated with this polaron represents a destabilized bonding orbital. It has a higher energy than the valence band, (to the nearest band theory approximation) and lies in the band gap. If another electron is subsequently removed from the already oxidized polymer, another polaron or a bipolaron will be created. Low doping level gives rise to polarons and with increase in the doping level more and more polarons interact to form bipolarons [1.27, 1.30]. The energy levels in polymers as a result of doping are indicated in Figure 1.10. Moreover, the midgap states could acts as hopping centers and the electrical transport mechanism could well be variable-range hopping (VRH) for PANI, as has been proposed in amorphous semiconductors [1.23, 1.26].

![Unpaired Electron](image)

**Figure 1.9: Propagation of polaron through a conjugated polymer chain by shifting of double bonds (Adapted from reference [1.27])**

In general, doping will not be homogeneous and even a sample doped moderately will consist of lightly and heavily doped regions. Owing to the local anisotropy of the samples caused by the polymer chains (one-dimensionality), the percolation behavior (formation of connected paths of highly doped regions) is very difficult to predict and the observed conductivity will very often be a combination of variable-range hopping in
lightly doped regions and tunneling between more heavily doped domains in the PANI and its composites.

![Energy band diagrams and defect levels for polaron and bipolaron in undoped, lightly doped and heavily doped conducting polymers (Adapted from reference [1.27])](image)

Figure 1.10: Energy band diagrams and defect levels for polaron and bipolaron in undoped, lightly doped and heavily doped conducting polymers (Adapted from reference [1.27])

In a VRH model [1.23], the conduction of charge carriers could be explained by the hopping mechanism (Figure 1.11). Hopping is like a man crossing a river by jumping from stone to stone, where the stones are spread out at random, as illustrated in Figure 1.11 (a). It is obvious that the more stones available, the higher the conductivity, $\sigma_{dc}$ because that can jump effortlessly from stone to a nearer stones compared to hopping from stone to a far apart stone.

To discuss the temperature dependence of hopping conductivity, it is more reasonable to look at the band structure represented in Figure 1.11 (b). There are localized states in the energy gap ($E_g$), distributed randomly in space as well as in energy. The Fermi energy level (FE) is about at the center of the $E_g$ with the states below FE is occupied and the states above empty (except for thermal excitations). Electrons will hop (tunnel) from occupied to empty states.

Most of the hops will have to be upward in energy. There are many phonons available at high temperature, which can assist in upward hopping. As these phonons freeze, the electron has to look further and further to find an energetically accessible state. As a result, the average hopping distance will decrease as the temperature decreases – hence the name “variable range hopping”. Since the tunnelling probability decreases exponentially with the distance, the conductivity also decreases. It is well known that
doping process produces a generous supply of potential carriers, but to contribute to conductivity they must be mobile. It is also found that the hopping conduction of conducting polymer (including PANI) may be hampered by three elements contributing to the carrier mobility [1.26], namely single chain or intramolecular transport, interchain transport and interparticle contacts. These three elements comprise a complicated resistive network, which determines the effective mobility of the carriers. The polarons and bipolarons are mobile and under the influence of electric field, can move along the polymer chain, from one chain to another and from one granule to another. At higher temperature, softening process will eventually alter the macroscopic and microscopic properties of PANI [1.27-1.31].

![Figure 1.1](image-url)

**Figure 1.11:** (a) Hopping transport: a man crossing the river by jumping from stone to stone and (b) electronic level scheme of disordered PANI to demonstrate the hopping conductivity (CB = conduction band, VB valence band, FE = Fermi energy, \( W \) = energetic distance between states, \( R \) = local distance between states, \( E_g \) = energy gap) [1.26]

### 1.3. Applications of Conducting Polymers

As emphasized throughout this chapter, conducting polymers exhibit novel properties not typically available in other materials. Upon realization that polymers could be made electrically conducting, the possibility that lightweight conductors capable of
replacing metals in many applications was immediately grasped. However, this promise has not been realized to date. The development of highly conducting polymers with adequate mechanical properties and stability has yet to be achieved. However, materials with lower conductivities (100-200 S/cm) that can be produced routinely are proving extremely useful in electromagnetic shielding applications. Another area that utilizes the semiconducting nature of conducting polymers is antistatic applications. Electrostatic discharge (ESD) is particularly damaging for electronic components, where a high voltage surge can destroy components. Consequently, all electronic components are shipped inside antistatic materials. It is often desirable that the packaging material be transparent so that the contents can be viewed. The challenge for antistatic coatings (metals and polymers) is to provide both the desired level of surface conductivity and the transparency required (as well as adhesion, scratch resistance, etc).

A number of companies seek to overcome the limitations of existing materials by using conducting polymers for ESD application. The main materials currently in use are ionic conductors, carbon-black-filled plastics and vacuum metallized plastics. Ionic conductors operate by absorbing moisture from the atmosphere to form a conductive surface (10^-11 - 10^-12 S/cm). They are highly transparent coatings but are also highly sensitive to moisture and become ineffective when humidity is low. The ionic conductors are also easily removed by washing so that reuse of the container is difficult. Carbon-black-loaded polymers give lower surface resistivities (10^-3 - 10^-5 S/cm), which is suitable for electromagnetic interference shielding but is too low for ESD usage. Recently, conducting polymers have been considered for micro-electronics applications. Philips Electronics is involved in the development of “plastic chip” technology using conducting polymers. In this application, a simple processor chip is fabricated using PANI electrodes and a polythiénylenevinylene semiconductor layer. The layers are spin coated onto a polyimide substrate. Patterning of the polyaniline electrodes is achieved by exposing the polymer to UV light through a suitable mask. A photosensitizer molecule incorporated into the polyaniline absorbs the UV light and induces a photochemical reaction that leads to an increase in conductivity of 10 orders of magnitude. The end result is patterned tracks of conducting polyaniline in a non-conducting matrix. The performance of all-plastic circuits is poor compared with silicon-based electronics. However, the devices are designed for applications where low cost and mechanical flexibility are desired and therefore this technology has several advantages. One example being pursued is the
“smart label” to replace the ubiquitous barcode placed on virtually all packaged products. In recent times, Mitsubishi Rayon in Japan has been producing a water-soluble sulfonated methoxyaniline polymer for use in e-beam lithography. Similarly, IBM has introduced a family of water-soluble PANI (Pan Aquas) that are effective at eliminating resist layer charging when used as 200 nm thick layers. The same polymers were also shown to be effective in reducing charging of non-conducting specimens during scanning electron microscopy. The advantage of using conducting polymers (compared with more traditional sputtered metal coatings) is that the polymer can be easily dissolved so that specimens can be non-destructively analyzed. Other applications for conducting polymers in micro-electronics fabrication include the use of PANI coatings for electrode-less deposition of copper connectors, while future applications may include interconnects and even devices such as diodes and transistors.

There are mainly two groups of applications for organic conducting polymers which are briefly described as follows:

- **Application Based on Conductivity of Conjugated Polymers**

  These applications just use the conductivity of the polymers. The polymers are used because of either their lightweight, biological compatibility for ease of manufacturing or cost. Electrostatic materials, conducting adhesives, electromagnetic shielding, printed circuit boards, artificial nerves, antistatic clothing, piezo-ceramics, active electronics (diodes, transistors), and aircraft structures [1.32-1.39].

  **Electrostatic Materials:** By coating an insulator with a very thin layer of conducting polymer, it is possible to prevent the accumulation of static charge. This is particularly important where such a discharge is undesirable. Such a discharge can be dangerous in an environment with flammable gases and liquids and also in the explosives industry. Bayer uses PTh as an antistatic layer in film products.

  **Conducting Adhesives:** By placing monomer between two conducting surfaces and allowing it to polymerize, it is possible to stick them together. This is a conductive adhesive and is used to stick conducting objects together and allow an electric current to pass through them.

  **Electromagnetic Shielding:** Many electrical devices, particularly computers, generate electromagnetic radiation, often radio and microwave frequencies. This can cause
malfunctions in nearby electrical devices. By coating the inside of the plastic casing with a conductive surface this radiation can be absorbed.

**Electrochemical Switching, Energy Storage and Conversion:** The next most obvious applications of conducting polymers utilize their conductivity and electroactivity. Conducting polymers such as PPy are readily oxidized and reduced according to the reaction in Figure 1.12 for cases where the counter-ion is able to freely leave the Conducting Electroactive Polymers (CEP) matrix and where it is immobilized within the CEP matrix. Anion movement predominates in cases where small mobile dopant, e.g., Cl$^-$ is used. If large anion dopants such as polyelectrolytes are employed, cation movement will predominate. The fact that conducting polymers can be charged and discharged has aroused much interest among those involved in developing new rechargeable battery technologies. The conducting polymers are usually combined in a cell, with lithium as the other electrode and a usable voltage of approximately 3 V is obtained. The achievable energy densities are several times that of the nickel-cadmium and lead-acid batteries. These solid-state batteries were introduced commercially in the early 1990s by Bridgestone (Japan), Allied Signal (USA) and Volta (Germany), but the products were discontinued due to low sales. The low sales have been attributed to the release of other competing battery technologies, such as lithium-ion batteries. A breakthrough in battery design was announced by Johns Hopkins University researchers in 1996. Whereas, previous battery designs used a conducting polymer as one electrode only (cathode) and the new design incorporated a polymer cathode, anode and electrolyte. The design gives good battery performance and has the advantages of high flexibility and light weight. Such improvements may give new impetus to polymer battery commercialization.

![Figure 1.12: Electrodynamic character of PPy](image-url)
Recent research has suggested that conducting polymers are set to emerge in devices used to store energy in the form of super capacitors and photovoltaic systems. Conducting polymers are being researched for “redox super-capacitors.” In these devices, the redox chemistry of the polymer is used. However, the design of the device is such that the conducting polymer is applied as a thin coating on a high-surface-area substrate. This design allows for very rapid charging and discharging of the polymer so that capacitor-like performance is obtained. All solid-state redox super-capacitors using PTh and PPy with a solid polymer electrolyte have been reported as having storage capacities of 18 F/g.

**Polymer Photovoltaics:** Polymer photovoltaics using conducting polymers are also being developed. In a typical arrangement, the photosensitive polymer such as polyphenylene vinylene (PPV) and its derivatives is sandwiched between two electrodes as shown in Figure 1.13. One electrode is a transparent material, typically indium-tin-oxide (ITO)-coated glass, and the other electrode is a low-work-function metal such as aluminum or calcium. Light is absorbed by the polymer, creating excitons (electron-hole pairs) that dissociate at an appropriate interface to give charge separation and, hence, current flow.

![Figure 1.13: Design of polymer photovoltaic device](image)

Efficiencies of polymer-based photovoltaics are very low compared with silicon semiconductor materials. However, polymer photovoltaics have the potential to be manufactured very cheaply and can be applied to very large areas, such as rooftops and exterior walls of buildings. Efficiencies are being improved further by chemical modification of the polymer and better design of the photovoltaic device. One approach to
polymer modification is to attach “light harvesting” groups to the polymer chains so as to increase the amount of light absorbed.

**Display Technologies:** Process used for the photovoltaic device can be reversed to produce a light emitting diode (LED). When an electric field is applied to both the electrodes as shown in Figure 1.14, electrons are injected into the conduction band of the polymer layer from the cathode (usually a low-work-function metal such as aluminium or calcium). At the ITO anode, electrons are removed from the valence band of the polymer to produce vacancies, or holes. The free electrons and holes move in opposite directions under the influence of the electric field and, when they combine, a photon of light is emitted. The colour of the light emitted depends on the band gap between the valence and conduction bands in the polymer.

![Figure 1.14: Design of a polymer light emitting diode](image)

An appropriate derivative of PPV polymer has produced PLEDs that emit the three colors red, blue and green. The PLED was first demonstrated by Richard Friend and co-workers at Cambridge University in 1990. The early devices had an efficiency ~ 0.01%, but this has now been improved to 4% or better, which provides sufficient light to be seen in daylight. Removal of excess heat also stabilizes the polymer against degradation. PLEDs offer one of the most exciting prospects for conducting polymer commercialization, because they offer several advantages over existing technologies for flat panel displays. Several breakthroughs in the synthesis and processing of electroluminescent polyphenylene vinylene (PPV) by the Cambridge University group have spearheaded the commercial development of flat screen displays. The first products were backlit displays for automobile instrument panels and mobile phones. The displays
were being manufactured by Philips in partnership with Cambridge Display Technologies, a company spun off from the original research at Cambridge University. Uniax Corporation, in USA, has also entered into a partnership with Philips to commercialize conducting polymer displays based on the research work of Nobel Laureate Professor Alan Heeger’s group at the University of California, Santa Barbara.

**Printed Circuit Boards:** Many electrical appliances have printed circuit boards. These are copper coated epoxy-resins. The copper is selectively etched to produce conducting lines used to connect various devices. These devices are placed in holes cut into the resin. In order to get a good connection the holes need to be lined with a conductor. If the board is etched with potassium permanganate solution a thin layer of manganese dioxide is produced only on the surface of the resin. This will then initiate polymerization of a suitable monomer to produce a layer of conducting polymer.

**Cellular Communication:** The versatility in the synthesis of some CEPs especially PPy now enables a range of bioactive surfaces to be created. Studies involving growth and control of biological cell cultures on conducting polymers are already in place. Using this approach, it has been shown that electrical stimuli can be used to address living cells in culture and hence stimulate and regulate growth. The growth and differentiation of PC12 cells can be assisted by electronically controlled release of a nerve-growth-factor protein. Langer’s group has shown that neurite outgrowth on PPy is facilitated by passage of current through the structure.

**Aircraft Structures:** Modern planes and space crafts are often made with lightweight composites. This makes them vulnerable to damage from lightning bolts. By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft.

- **Applications Based on Electroactivity of Conjugated Polymers**

  This group utilizes the electroactivity character of the materials. Molecular electronics, electrical displays, chemical, biochemical and thermal sensors, rechargeable batteries and solid electrolytes, drug release systems, optical computers, ion exchange membranes, electromechanical actuators, 'smart' structures and switches [1.40-1.42].

**Rechargeable Batteries:** Batteries were one of the first areas where conducting polymers promised to have a commercial impact. Conducting polymer based batteries were
investigated by leading companies like BASF/VARTA and Allied Signal. A number of conducting polymers such as polyacetylene, polyaniline and other polyheterocycles have been used as electrode materials for rechargeable batteries.

**Chemical Sensors:** The combination of tunable chemical properties with the electronic properties of conducting polymers has also had a tremendous impact on the development of new sensors. Sensing surfaces have been designed that are capable of interacting with simple anions, metal ions, small organic molecules or proteins. The electrical signals measured can be current flow, change in capacitance or change in resistance. The area of biosensors has proven particularly interesting in this regard because conducting polymer systems have been shown to be capable of in-situ control of antibody-antigen interactions, making them reversible under selective conditions. The most successful commercial sensing systems that utilize conducting polymers are the so-called electronic noses. Conducting polymer based sensors can be operated either to measure the concentration of a target vapour species quantitatively, or to analyse a complex mixture of vapour qualitatively. For single vapours, the detection limits can be in the low ppm region. Exposure to a mixture of vapours results in a unique pattern of responses that is usually deciphered using standard chemo-metric techniques. The pattern can be used like a fingerprint to identify certain products or to establish the quality of foodstuffs, wines, perfumes, etc. The electronic nose has similar components to the natural nose. The electronic nose has found its most widespread application in the food industry. Using resistometric and other detection systems, on-going research is aimed at improving selectivity and sensitivity both in the vapour phase and in solution. Particular emphasis has been placed on chemical functionality of the polymer to increase the selectivity of the sensor to the desired species in a complex mixture. The sensitivity at present is limited primarily by the method of sensor fabrication; the detection limit is lowered by producing ultrathin and coherent layers of the conducting polymer. Screen printing and ink-jet printing techniques provide some interesting opportunities in this regard.

**Physical Sensors:** Conducting polymers have also been used as sensors for the physical environment, particularly for strain or stress. PPy strain gauges have been constructed from both neat films and from coated stretch fabrics such as Lycra®. Strain gauge materials are characterized by their gauge factor (change in resistance w.r.t. change in length), dynamic range, linearity and hysteresis. The application of PPy to stretch fabrics to yield strain gauge materials having a dynamic range up to 100% has opened up several
new exciting applications. An almost linear strain gauge response with low hysteresis can be obtained from PPy-coated Lycra® from 20 to 60% strain. These materials have particular application in the field of biomechanics where the strain gauge fabrics can be incorporated into regular sports clothing. Figure 1.15 shows an example of a patented knee sleeve using PPy/Lycra® combined with a feedback device that emits an audible signal when the knee angle reaches a preset degree.

Figure 1.15: Fabric strain gauge for determining knee flexion

**Electrochromic Devices:** Another interesting application that uses the dynamic properties of conducting polymers is electrochromic devices. For example, PTh and PANI undergo distinct colour changes when an electrical potential is applied. Thin films of PTh can be switched from red (oxidized) to blue (reduced) and polyaniline transcends a spectrum of colours as different potentials are applied to it. This has possible applications in advertising displays and smart windows. This bi-stable material can also be used as a memory storage device for information storage.

**Electromechanical Actuators:** More futuristic applications for conducting polymers that are receiving considerable attention include electromechanical actuators (artificial muscles). Electromechanical actuators are materials that can change their physical dimensions when stimulated by an electrical signal. In case of conducting polymers, the volume change occurs as a result of ion movement into and out of the polymer during redox cycling. The change in volume can be up to 3% (although much higher-volume changes have recently been reported on very small devices). The performance of conducting polymer actuators compares favorably with natural muscle (10% stroke and
0.3 MPa stress) and with piezoelectric polymers (0.1% stroke and 6 MPa). The piezoelectric polymers are driven by high electric fields usually requiring 100-200 V, whereas the conducting polymers require only 1-5 V to operate. Some of the disadvantages of CEP actuators include a slow response time and limited lifetime, although recent results have shown strain rates of 3%/s (natural muscle can respond at 10%/sec) giving 1% strain for more than 100,000 cycles. An important development in conducting polymer actuators was the recent demonstration of a solid state actuating device that will hasten the commercial application. Figure 1.16 shows the bending operation of an actuator consisting of three layers: gold, CEP, membrane, where the membrane is porous and contains the electrolyte that acts as both an ion source and ion sink.

The use of electromechanical actuators based on CEPs is currently being pursued in a number of applications. For example, IPRI is currently focussing on a concept introduced by De Rossi to produce a rehabilitation glove in collaboration with North Shore Hospital Service (Sydney, Australia) as shown in Figure 1.16.

![Figure 1.17: Rehabilitation glove showing sensor strips on each finger](image)

The actuators will be integrated throughout the wearable glove structure to provide assisted movement during rehabilitation. IPRI is also currently involved in the development of actuators for an electronic Braille screen in collaboration with Quantum Technology (Sydney, Australia). A convenient user interface is the single biggest barrier to blind people’s accessing information in the Internet age. The future of Braille lies in a low-cost, refreshable surface, or screen, where the individual Braille dots are raised and
lowered electronically by low-voltage/low power actuator systems, allowing changing messages or decision options to be displayed.

**Drug Release Systems:** Conducting polymer films and coatings are also ideal hosts for the controlled release of chemical substances, including therapeutic drugs, pesticides, fungicides, and many others. The oxidation or reduction of the polymer involves the movement of ionic species into and out of the polymer material. By incorporating the target species as the dopant in the conducting polymer, the redox chemistry of the polymer can be used to release the target species at the desired time. In other applications, the release can also be automatically stimulated by a change in the environment. For example, it is known that the galvanic coupling of conducting polymer coatings (such as PANI) to metals like steel and aluminium causes a reduction of the polymer from the emeraldine salt state to the LB, and this process involves the release of the dopant ion into the surrounding electrolyte. It has been speculated that the dopant could be designed such that it acts as a corrosion inhibitor for the metal and so the polymer can release the inhibitor at the point when corrosive conditions first form. Both anionic and cationic species can be incorporated into the polymer and released at the desired time. Anionic species are the usual dopant ions incorporated with PPy, PANI and PTh polymers but it is also possible to trap cations.

**Catalyst:** Conducting polymers show redox property; therefore these are expected to behave as redox catalyst. Several reports have been found in the literature on modification of conducting polymers and their use as catalyst for small organic molecules. Conducting polymers in their various oxidation states interconvert each other, which permits to construct redox cycle for catalytic reactions. The catalytic activity has been revealed to be controlled by doping. Coordination of transition metals to the nitrogen atoms (in case of PANI and PPy) affords the complexes, in which transition metals are considered to interact through a conjugated chain. The characteristics of conjugated polymers are reflected on the complexes, which are expected to provide novel catalytic system.

**Corrosion Protection:** Controlled release of corrosion inhibitors may be involved in new-generation corrosion protection coatings based on conducting polymers. Considerable evidence indicates that conducting polymers provide beneficial protection to many metals in a corrosive environment. Many studies since the mid 1980s have shown that a coating of PANI, PPy or PTh can inhibit the corrosion rate of mild steel, stainless steel,
aluminium and copper. The conducting polymer can be applied either as a neat coating or as a dispersion in another polymer binder. In most studies, a barrier topcoat is also applied over the top of the conducting polymer “primer.” Figure 1.17 illustrates the corrosion resistance of mild steel coated with PANI primer/epoxy topcoat after 3 years immersion in saltwater. Although large blisters have formed (after approximately 2 years), there is little sign of rust. Corrosion inhibiting paints that use polyaniline as the active ingredient are available from the German company Omecron Chemie. Other companies, such as DSM in the Netherlands, are believed to be interested in developing corrosion-resistant formulations based on PPy.

Figure 1.17: Pictorial view of corrosion resistance of steel coated with PANI primer and an epoxy

There are numerous other applications reported in fuel cells, heavy metal removal from aqueous solutions, film industry and more importantly chiral conducting polymers.

1.4. Helical/Chiral Conducting Polymers

1.4.1. Helical Polymers

The helix is the central structural motif in biological macromolecules, such as DNA and proteins and it is also the ubiquitous object in nature from microscopic to macroscopic points of view. Most importantly, the helical conformation is inherently chiral, and right- and left-handed helices are exactly mirror images of each other; therefore, they cannot be superimposed. Accordingly, if one of the helices could be selectively synthesized, induced, or constructed for molecules, supramolecules, oligomers or polymers, they should be optically active without any additional configurationally
chiral components. Inspired by sophisticated biological helices that are of key importance for their elaborate functions in living systems involving molecular recognition, replication and catalytic activity, chemists have been challenged to develop artificial helical polymers, supramolecules and oligomers with a controlled handedness, not only to mimic biological helices and functions but also for their potential applications in materials science, such as ferroelectric liquid crystals (LCs) and nonlinear optical materials, sensing specific molecules, the separation of enantiomers, and asymmetric catalysis [1.43]. The history of helical polymers extends back to the 1950s, when Pauling and Watson and Crick discovered the right-handed R-helix for proteins and the right-handed double stranded helix for DNA in 1951 and 1953, respectively. Natta in 1955 found that the highly isotactic polypropylene synthesized by the Ziegler-Natta catalyst possessed a helical conformation in the crystalline state. Although the isotactic helical polypropylene exists in an equal mixture of right- and left-handed helices in the solid state and the polypropylene cannot maintain its helical conformation, thus instantly changing to a random conformation once dissolved in solvents, this was a significant milestone in the field of synthetic helical polymers, through which a number of isotactic vinyl polymers have been prepared and their helical structures in the crystalline state have been revealed [1.44-1.50].

Hence, helical polymer should be chiral in nature. So, to understand the basic principle behind helical polymer, it is necessary to elaborate chirality and chiral polymer.

1.4.2. Necessity of Chirality for Helicity

A chiral molecule is a type of molecule that has a non-superposable mirror image. The feature that is most often the cause of chirality in molecules is the presence of an asymmetric carbon atom. The term chiral in general is used to describe an object that is not superposable on its mirror image. Achiral (not chiral) objects are objects that are identical to their mirror image. Human hands are perhaps the most universally recognized example of chirality:

In chemistry, chirality usually refers to molecules. Two mirror images of a chiral molecule are called enantiomers or optical isomers. Pairs of enantiomers are often designated as "right-" and "left-handed". Enantiomers have identical chemical and physical properties in non-chiral environment. For example, they have identical melting points, boiling points, solubility and electronic absorption spectra. However, enantiomers
interact with plane polarized light in opposite ways. An enantiomer can be named by the direction in which it rotates the plane of polarized light. If it rotates the light clockwise (as seen by a viewer towards whom the light is traveling), that enantiomer is labeled (+) and its mirror-image is labeled (−). The (+) and (−) isomers have also been termed d- and l-, respectively (for dextrorotatory and levorotatory). This phenomenon is called optical activity. A chiral compound composed of equimolar amounts of two enantiomers is called a racemate and is optically inactive.

Individual enantiomers often exhibit different properties in chiral environments such as biological systems, which contain many chiral compounds such as proteins, carbohydrates and nucleic acids. This means that the biological activity of an enantiomer may differ markedly from that of its mirror image. One form can have a desirable therapeutic effect while the other may be useless or even toxic. Due to this, the use of enantiomerically pure compounds in pharmaceuticals and agricultural chemicals has grown greatly in importance in recent years. There is a growing concern against marketing of racemates [1.51-1.54].

Chirality is known as an important feature of molecules for the formation of helical architectures at different length scales. The chiral entities can be polymerized into high-molecular-weight polymer chains (i.e., chiral polymers). Owing to the stereo-regularity of chiral entities in the chiral polymers, helical conformation could be formed.

A variety of superstructures, in particular, helical architectures can be fabricated by self-assembling chiral polymers. Nevertheless, the phase behavior of the self-assembled morphologies resulting from chiral polymers is much more complicated because of the long relaxing time and the complex energetic consideration for the intramolecular and intermolecular interactions of polymer chains. For a chiral polymer, two different kinds of states are considered. One is non-racemic chiral and the other one is racemic chiral. For a non-racemic chiral polymer, corresponding enantiomers having different mirror images of the chiral entities are present in asymmetrical proportions, including chiral entities located in a polymer backbone (i.e., main chain) or in a side group (i.e., side chain). The chirality is one of the origins for the formation of helical architectures and the handedness control of a self-assembled helical architecture is, in principle, determined by chirality [1.55-1.57].

1.4.3. Chiral Conducting Polymers
CHAPTER I

Introduction

Following the first report of chiral PPy by Baughman et al., in 1985 there has been considerable interest in optically active conducting polymers due to their potential applications in the areas like asymmetric synthesis, chiral separations and chiral sensors etc. The two type of chirality mostly found in chiral conducting polymers are central chirality and helical chirality. Central chirality typically arises when a carbon atom in a molecule has four different groups attached to it in a tetrahedral arrangement. Polymers such as PANI whose backbones can have a helical structure can adopt either a left or right handed twist giving rise to helical chirality. A helix with a right handed screw sense is symbolized by P (plus) and a left handed helix by M (minus).

Optically active conducting polymers have been prepared by polymerization of (i) monomers bearing chiral substituents, (ii) achiral monomers in the presence of a chiral dopant anion, or (iii) achiral monomers in the presence of a chiral template. The induction of chirality in pre-formed achiral conducting polymers such as emeraldine base may also occur via acid-base or electrostatic interactions with chiral acids.

1.4.3.1 Chiral Polypyrrole

Chiral PPy was first prepared by Baughman and co-workers in 1985 via the electro-polymerization [1.58] of pyrrole monomers bearing chiral substituents (R*) covalently attached to the pyrrole N centres. Salmon and Bidan et al. [1.59, 1.60] similarly electro-polymerised the related N-substituted chiral pyrroles. Stable PPy films were deposited on ITO-glass electrodes, permitting the recording of their circular dichroism (CD) spectra. However, no CD bands associated with the polymer $\pi-\pi^*$ or bipolaron absorption bands were observed in the visible region, indicating that the presence of the chiral N-substituents did not induce chirality in the polypyrrole chains. The alternative electro-polymerisation of pyrrole monomers bearing chiral substituents at the 3-position of the pyrrole ring has provided a useful route to optically active PPy in their fully oxidised, conducting form. This was first demonstrated in 1990 by Delabouglsise and Garnier [1.61], who prepared the amino acid-substituted polypyrroles (Figure 1.1) (a) (R = CH$_2$OH, CHMe$_2$, Ph) by electro-polymerizing the corresponding pyrrole monomers. As with other 3- and N-substituted PPy, these novel polymers exhibited lower conductivities (ca. 1 S/cm) compared to unsubstituted PPy, presumably due to twisting of the polymer chains by the bulky substituents. Circular dichroism studies of the films showed that the substituted PPy to be optically active, each exhibiting
a strong CD band at ca. 470 nm associated with the bipolaron band at 465 nm observed in the corresponding UV-Visible spectrum. Chiral discrimination by a chiral PPy was demonstrated soon after by Moutet et al. [1.62] with polymer (b), synthesized by the electro-polymerization of pyrrole monomer bearing a β-D-glucose derivative at the N-centre. The specific rotation [αD] of the pale yellow reduced form of the polymer was 45001, consistent with macromolecular asymmetry in the PPy chains induced by the chiral substituent.

Figure 1.18: Amino acid-substituted PPy

Cyclic voltammetric studies of (b) in the presence of (+)- and (-)-camphor sulfonate (CSA⁻) ions revealed strong enantioselective recognition between the two dopant anions. Significantly higher oxidation–reduction currents were observed with (-)-CSA⁻ present in the electrolyte. Further striking evidence of chiral discrimination appeared in the electrochemical polymerisation of the chiral pyrrole monomer on a vitreous carbon electrode, where polymerisation was facile in CH₃CN containing (-)-CSA⁻, but completely inhibited by (+)-CSA⁻. Recently, Pleus and co-workers [1.63, 1.64] prepared films of the chiral polypyrroles (c) and (d) bearing (-)-ethyl L-lactate as the
chiral inducing group located at either the pyrrole ring 3-position or the ring N centre. No circular dichroism studies were carried out, but cyclic voltammograms recorded in the presence of (+)- or (-)-CSA⁻ ions showed the polymers to be enantioselective. For example, preferential doping of (c) by (-)-CSA⁻ occurred, as indicated by the substantially higher charge passed when cycling the potential in the presence of this enantiomer rather than (+)-CSA⁻. Exploiting their enantioselective properties, the polypyrroles (c) and (d) were subsequently successfully employed as chiral electrodes for the stereoselective reduction of prochiral ketones.

In a related study by Costello et al. [1.65], a series of chiral ester substituted polypyrroles were prepared via chemical polymerisation (FeCl₃ in water/CH₃CN) of the pyrrole monomers (e) [R= (R)- and (S)-menthol, -Boc-alaninol and -phenylethanol]. When fabricated into sensors, the polymers exhibited chiral discrimination between enantiomeric molecules such as (R)- and (S)-menthol. Chiral polypyrroles of the type (f) and (g) bearing N-bonded chiral ester substituents have also been synthesised via electropolymerisation of the corresponding monomers in acetonitrile solvent containing tetra-butylammonium perchlorate [1.66]. When these chiral PPy were instead electro-chemically grown in the presence of (+)- or (-)-CSA⁻, the S/N ratios determined via XPS for the isolated polymer products revealed significant chiral discrimination in uptake of the enantiomeric (+)- and (-)-CSA⁻ dopant ions during polymerisation. In addition, the electrical conductivity of the PPy (f) prepared in the presence of (+)-CSA⁻ was twice that of the analogous polymer grown in the presence of the (-)-CSA⁻ enantiomer [1.67].

1.4.3.2 Chiral Polythiophene

Preparation of chiral PTh have generally involve the polymerization of thiophene monomers containing chiral substituents covalently bound at the 3-position or disubstituted at 3- and 4-positions. The strong optical activity of the polymers measured by circular dichroism was attributed in early reports to the adoption of one-handed helical conformation by the polymer chains under the influence of the chiral side chain. However, an elegant series of papers by Meijer et al. [1.68, 1.69] suggest that the chiral induction is associated with the aggregation of polymer chains to give supra-molecular helical structures and this hypothesis is supported by the fact that optical activity is only observed when the polymer is in a “poor” solvent or when cast as a film. The only
exception appears in the presence of a “good” solvent, i.e., chloroform, THF and iso-octane exhibits bisignate cotton effect in the near-UV region.

These chiral poly(alkylthiophenes) also exhibit thermo-chromism and solvato-chromism. Thus upon heating or adding of a “good solvent”, a marked blue shift is observed for the $\pi-\pi^*$ absorption band. Improved regularity of poly(3-alkylthiophene)s results in enhanced electrical conductivity and optical properties due to longer conjugation length. A comparison of the chiroptical properties of regio-regular and regio-irregular revealed that the regio-regularity in the side chain substitution pattern is very important to obtain high optical activity. This is due to the high degree of interaction order in the regio-regular form but the chirality of the supramolecular aggregates in a “poor” solvent can be switched “on” and “off” through a doping and dedoping process by adding copper (II) trifluoromethane sulphonate and triethylenetetramine, respectively [1.70-1.72].

### 1.4.3.3 Chiral Polyaniline

Optically active polyanilines (PANI) were first reported in 1994, when emeraldine salts of the type PANI-HCSA (HCSA = (+)- or (-)-camphorsulfonic acid) were prepared by two alternative routes: (i) the electro-polymerization of aniline in the presence of enantiomeric HCSA acids and (ii) the acid doping of pre-formed emeraldine base. A variety of approaches to chiral PANI have since been developed, almost invariably involving incorporation of chiral dopant ions onto growing or pre-formed PANI chains. Interestingly, this versatile route to chiral polymers has generally proved unsuccessful for PPy and PTh. This may be due to the absence of strong H-bonding sites (such as polyaniline’s NH centres) on unsubstituted pyrrole and thiophene rings with which to bind to complementary sites on chiral dopant anions [1.73-1.75]. Chirality in the polymer backbone was confirmed by the presence of circular dichroism bands in the visible region, where the chiral CSA$^-$ dopant ion does not exhibit circular dichroism band in the visible region, whereas the chiral CSA$^-$ dopant ion does not exhibit the circular dichroism bands in this region.

Doping of the chiral dopant anions into the polymer structure during either electro-polymerization or during doping of EB in organic solvents has been suggested to cause the polyaniline chains to adopt a one handed helical confirmation. Alternatively, the optical activity observed in the ES products may arise from the formation of chiral
supramolecular aggregates in which the polyaniline chains are nearly planar. Supporting
the latter suggestion is the observation that optical activity in the visible region was
observed for PANI(+)-HCSA produced by doping EB with (+)-HCSA in a “good”
 solvent such as m-cresol [1.76].

PANI(+)-HCSA and PANI(-)-HCSA films produce mirror imaged circular
dichroism spectra [1.62]. Interestingly, electrochemically and chemically prepared
PANI(+)-HCSA films show markedly different features in their UV-Visible and circular
dichroism spectra. This is attributed to different conformations for their polyaniline
chains, namely “extended coil” and “compact coil” [1.77].

Alternative routes to optically active polyaniline doped with one hand of HCSA
have been reported using in-situ chemical polymerization [1.78] or the strong electron
acceptor DDQ in an organic solvent [1.79]. The CD spectra of the PANI-(+)-HCSA films
prepared in both cases are quite different from those previously reported for PANI-(+)-
HCSA films prepared by electro-deposition in water [1.80]. These observations again
indicate that the conformation of PANI-(+)-HCSA ES depend on the synthetic route.

Chiral PANI colloids and nano-composites have also been synthesized [1.81-1.85].
Routes include chemical, electrochemical and enzymatic polymerization of aniline in the
presence of chiral HCSA as dopant and with polyacrylic acid as a template or polystyrene
sulphonate (PSS) as a steric stabilizer. Interestingly, a positive CD band at 420 nm is
observed for chiral PANI.HCSA enzymatically synthesized whether the chiral dopant is
either (+)-HCSA or (-)-HCSA. This suggests that the hand of polymer product is
determined by the enzyme rather than the hand of the dopant anion present.

Chiral poly(2-methoxyaniline).HCSA ES and POMA-(+)-HCSA/(-)-HCSA can
also be prepared by either the electropolymerization of 2-methoxyaniline in the presence
of one enantiomer of HCSA or via doping preformed ES of POMA with one hand of
HCSA. The bisignate CD bands of POMA(+)-HCSA/(-)-HCSA films exhibit mirror
imaged CD spectra in the visible region, suggesting the adoption of opposite helical hands
for the POMA chain in the two polymers [1.86,1.87].

The alternative use of chiral ammonium ions for the chiral induction has been
successfully used recently to prepare active poly(2-methoxy-5-sulphonic acid). Chiral
induction is believed to involve acid base interaction between free acidic SO$_3$H groups on
the polymer chain and chiral amines amino alcohols.

1.5. Applications of Chiral Conducting Polymers

The chirality of pharmaceutical and electronic products is a very important issue. A recent analysis has revealed that the active ingredients in nine of the top ten drugs marketed worldwide are chiral. However, only six of these are currently sold as single enantiomers while others are marketed as racemates. The optical activity and potential stereo-selectivity of chiral conducting polymers might have useful applications in this area, including their use enantioselective chromatographic phases or membranes for chiral separations and as chiral modified electrodes for asymmetric electrosynthesis or as a chiral sensor. The advent of chiral conducting polymers has opened up new approaches to achieve these goals, as given below:

1.5.1. Chiral Sensors

In pioneering studies, Kaner and co-workers [1.88-1.90] have shown from UV-Visible spectral changes and flow-injection quartz crystal microbalance studies that chiral polyaniline emeraldine base films derived via alkaline dedoping of chemically synthesized PANI-(+)HCSA and PANI-(+)HCSA emeraldine salts exhibit chiral discrimination between the enantiomeric amino acids D- and L-phenylalanine. Recently, chiral emeraldine base films derived from electrochemically generated PANI-(+)HCSA and PANI(-)HCSA films have been reported to show similar enantioselectivity towards L- and D-phenylalanine [1.91]. The strong enantio-selectivity of other chiral conducting polymers such as polypyrrole and polythiophenes suggests that they may also have potential as chiral sensors. Costello and co-workers have developed chiral vapour phase sensors based on chiral poly-(3-substituted-pyrrole)s. The polymers were fabricated into chiral sensors by coating the chiral monomer onto poly-(vinylidene)difluoride (PVDF) membrane and polymerizing within the membrane structure using ferric chloride oxidant, and then mounting the membrane between silver contacts. The sensors exhibited significant chiral discrimination properties, showing differential changes in electrical resistance and mass when exposed to different enantiomers in the vapour phase, such as (R)- and (S)-menthol, 2-butanol, limonene and carvone. These results suggested that the chiral side group on the pyrrole repeat units plays the main role in the selective adsorption
characteristics of the polymers. A sensor based on polypyrrole doped with (S)-mandelate anions has also been reported to distinguish between (R)- and (S)-mandelate [1.92].

1.5.2. Separation of Enantiomers

❖ Chiral Stationary Phases

The chiral discrimination studies indicate that optically active conducting polymers have promising potential as novel chiral stationary phases for the chromatographic separation of enantiomeric chemicals. For example, Kaner and co-workers [1.93] have exploited the enantio-selectivity of chiral emeraldine base for the chromatographic separation of racemic amino acids into their D- and L-forms. Separation of the enantiomeric amino acids D- and L-tryptophan using chiral conducting PPy membranes has also been reported by Ogata [1.94]. The enantioselective membranes were prepared by electro-deposition of PPy in the presence of the chiral dopants poly-(L-glutamic acid) or dextran sulphate onto a platinum-coated quartz crystals with the same amount of chiral PANI emeraldine base after injecting D- and L-phenylalanine, respectively. Recently, optically active PTh incorporating as ring substituents chiral selectors such as (R)-(+) and (S)-(+)N-(3,5-dinitrobenzoyl)-phenylglycine used in Pirkle-type stationary phases have been synthesized [1.95]. These may have potential utility in HPLC based enantioselective analysis of chiral chemicals.

❖ Molecularly Imprinting Polymers

Molecularly imprinted polymers (MIPs) have attracted considerable recent interest as materials for the recognition and separation of enantiomeric chemicals. Nagaoka and co-workers [1.82] were the first to exploit this approach with conducting organic polymers, employing over oxidised PPy films imprinted with L-glutamate for the enantioselective uptake of L- and D-glutamic acid. An advantage of these PPy over MIPs based on conventional polymers is that the complementary chiral cavity is easily created with simultaneous expulsion of the anionic template species via an electrochemical over oxidation/dedoping process. Using cyclic voltammetry, electrochemical quartz microbalance studies and fluorescence spectroscopy, they established that L-glutamate was inserted about ten times more efficiently into the templated PPy than D-glutamate. The opposite enantio-selectivity was exhibited for an analogous PPy based MIP templated with D-glutamic acid. The sensor also exhibited good selectivity between several other L- and D-amino acids. Nagoaka and co-workers similarly prepared PPy
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based molecularly imprinted with L-lactate for use in chiral separations. An electro-modulated column packed with carbon fibres modified with the latter imprinted PPy exhibited high enantio-selectivity for the uptake of L-amino acids over D-amino acids. In related studies they produced over oxidised PPy colloids (particle diameters 50-100 nm) imprinted with L-lactate that showed similar chiral discrimination towards L- and D-amino acids. Recently, other researchers have described PPy based MIPs imprinted with L- and D-tyrosine or L- and D-aspartic acid which exhibited amino acid enantio-selectivities as high as 27. Imprinting (+)- or (-)-camphorsulfonate anions into PPy nanowires of ca. 100 nm diameter has also been found to provide MIPs capable of distinguishing between the D- and L-enantiomers of the amino acid phenylalanine [1.96-1.98].

1.5.3. Electrochemical Asymmetric Synthesis

Electrochemical asymmetric synthesis has a number of potential advantages over conventional chemical and enzymatic methods. In particular, the tedious (and often expensive) attachment and subsequent removal of chiral auxiliaries employed in chemical asymmetric synthesis is not required. Operation should also be possible in a wider range of solvents than with enzyme-based systems. With the advent of chiral electrodes based on conducting polymers, the largely neglected but potentially exciting area of electrochemical asymmetric synthesis has begun to attract increasing interest. Similar studies by Pleus and co-workers have revealed that chiral PPy films may be employed as chiral electrodes for the enantioselective electro-reduction of prochiral ketones such as acetophenone, 4-methylbenzophenone and 2,5-dimethylbenzophenone to their corresponding chiral alcohols, (R = H or Me, R₀ = Me or Ph). The electro-reductions of the ketones were carried out in DMF/0.50 M LiBr at -2.2 V (vs. Ag/AgNO₃) in the presence of phenol as the proton donor. The nature of the chiral substituents covalently bound to polypyrroles influenced the optical purity of the chiral alcohol products produced, with enantio-selectivities of nearly 20% being achieved.

1.5.4. Chiral Catalysts

Several studies have been reported in which composite chiral electrodes composed of a conducting organic polymer together with a chiral moiety and an appropriate metal catalyst have been employed in asymmetric hydrogenations. For example, coordination (through its bipyridine unit) of the chiral thiophene ligand to transition metal centres such
as Rh(I), Ir(I), Ru(II) and Co(II) forms complexes that act as novel catalysts for the asymmetric hydrogenation of prochiral ketones to the corresponding alcohol. However, only low enantiomeric selectivity was observed (4-21% enantiomeric excess) [1.99]. Attempted electro-polymerisation to the corresponding ligand containing PTh units, to create macromolecular chirality in the hydrogenation catalyst, was not successful. More recently, electrodes coated with a poly-(N-substituted PPy) film incorporating L-(+)-lactic acid and palladium metal have been found to stereo-specifically hydrogenate methylbenzoylformate and butylbenzoylformate to give (R)-(−)-methylmandelate and (R)-(−)-butylmandelate, respectively.

1.5.5. Miscellaneous Applications

Several sensor systems using π-conjugated, water-soluble PTh have been developed to detect biological macromolecules in water. A positively charged achiral polythiophene binds to a negatively charged DNA, and the complex showed induced Cotton effects in the PTh chromophore regions due to the induction of a helical ordering through electrostatic interactions with DNA as a chiral template in water [1.97]. This concept of an induction of helicity on achiral PTh has been extended to sensing the helicity and conformational transition of a polysaccharide schizophyllan (SPG) [1.97] as well as the chirality of various nucleotides such as adenosine triphosphate (ATP) [1.97] by means of absorption and CD spectroscopic methods. The SPG complex showed the high quantum yield of circularly polarized luminescence not only in the solution state but also in the precipitated powder [1.98]. The chirality induced by the complexation with SPG, was further immobilized through a sol-gel reaction with tetraethoxysilane [1.99]. A negatively charged, luminescent achiral polythiophene assembles with a positively charged, synthetic peptide with a random coil conformation in an aqueous solution, resulting in a supramolecular helix-bundle [1.100]. Interestingly, by mixing the two polymers in water, a preferred-handed helical conformation and a predominant R-helix are simultaneously induced in both polymers upon complexation via electrostatic interactions, as evidenced by the appearance of ICD in the π-conjugated chromophore region of accompanied by a significant enhancement of the Cotton effect due to an R-helix formation. When optically active zwitter-ionic PThs were used instead, their helically assembled structures and chiral properties can be detected by CD and emission spectra, leading to a novel sensory system for peptide helix bundles [1.101] and DNA hybridization [1.102, 1.103].
A helical conformation with a preferred helical sense can be produced or induced in nonracemic solvents during the helix-senseselective polymerization of bulky monomers or in dynamically racemic helical polyisocyanates and polysilanes, respectively, although chiral bias seems to be too weak to control the overall handedness of the helical polymers. Interestingly, when a chiral nematic phase was used as a polymerization solvent, Akagi and co-workers have found that helically twisted polyacetylene fibrils with either a clockwise or counter clockwise direction can be prepared by the polymerization of acetylene in chiral nematic LC phases \[1.104\]. (R)- or (S)-binaphthyl derivatives having a mesogenic unit combined with the nematic LC and induce a chiral nematic phase, in which the polymerization of acetylene with a homogeneous Ziegler-Natta catalyst proceeded to give hierarchically assembled helical fibrils consisting of multi-domains with a spiral morphology, as observed by SEM; each domain is composed of a helically twisted fibril with a one-handed screw-sense. Besides the helical polyacetylene fibrils, related helical fibrils composed of other \(\pi\)-conjugated polymers with controlled spiral morphology have also been prepared by polymerization of the corresponding monomers in the chiral nematic phase used as an asymmetric induction field \[1.105\].

A versatile approach for chiroptical inversion switching and chiroptical memory with rewritable (RW) and write once read-memory (WORM) modes has been developed by Fujiki et al., by taking advantage of the characteristic feature of temperature and molecular weight-dependent helicity inversion of certain helical polysilanes in the solid state \[1.106\]. A cast film of a low molecular weight \((M_w) 1.3 \times 10^4\) and \((M_w/M_n) 1.16\) on a quartz substrate reversibly switches between almost mirror-image CDs with the transition temperature \((T_c)\) at approximately 47 °C upon heating followed by slow cooling; this change can be repeated by the multiple heating-cooling cycles, indicating the chiroptical inversion switch. On the other hand, when the film was rapidly quenched from above \(T_c\), the Cotton effect sign hardly switched, and as a consequence, the helicity at high temperature is retained. This chiral memory effect can be further erased by heating to above the \(T_c\), so that the chiroptical inversion switching and chiroptical memory with RW modes are possible using a low molecular weight by controlling the cooling conditions in the solid film. Interestingly, when a higher molecular weight \((M_w) 2.5 \times 10^4\) and \((M_w/M_n) 1.16\) was used instead, the helix-helix transition took place only upon heating. This irreversible change in the CD signals suggests a possible non erasable
memory usable as the WORM mode. Molecular springs with a switchable helical pitch (helical springs) triggered by external stimuli may undergo mechanical spring like motions that will provide intriguing potentials for constructing molecular nano-machines capable of expressing their motions to perform a mechanical operation on a macroscopic scale. Percec et al. have brought about the realization of such a system using self-organizable dendronized helical cis-PPA.

1.6. Aim

Keeping, the importance of helical conducting polymers in view, the primary focus of our research work is to develop helical/chiral conducting polymers with improved properties either by template or non-template method. It is aimed that the use of chiral dopants with requisite electrostatic forces and hydrogen bonding will induce chirality or helicity in the polymer. The monitoring of doping level and morphology of the finally prepared chiral polymer is of prime interest due to the futuristic applications of helical materials. We have used different chiral dopants to improve the overall properties of chiral conducting polymers with better conductivity and crystallinity. Moreover, the significance of the work lies in the fact that the desired properties are achieved with retention of conformation at nano-scale. To achieve this target, a systematic plan is chalked out below to carry out this research programme.

1.7. Plan of Work

This work consists of mainly synthesis and application of helical/chiral conducting polymers which are essentially chiral PANI synthesized from soft-template method and accomplished through the following steps:

a) Conducting PANI, i.e., nanofibers of PANI have been synthesized by using interfacial and sonochemical methods.

b) In-situ induction of helicity in PANI nanofibers was made by the use of different chiral dopants.

c) Effects of secondary doping have been studied with naturally occurring amino acids.

d) Different morphologies of chiral PANI have been reported from naturally occurring amino acids.

e) Different chiral structures were further used for technological applications.
1.8. References


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