2.1 Introduction

Conducting polymers have been extensively studied during the last two decades because of their highly significant contributions in the field of applied as well as basic sciences. The excellent mechanical properties and intriguing electronic properties of this class of polymeric materials make them ideal candidates to be used in many device applications. Until the early sixties the carbon based polymers were extensively used as insulators in the electronic industry. Researches in the beginning of the 1960s at BASF, Germany revealed new structural properties of polymers made by oxidative coupling. This work yielded conducting polymers like polyphenylene and polythiophene exhibiting electrical conductivities up to 0.1 S.cm$^{-1}$. The highly sophisticated microelectronics industry channeled adequate resources for encouraging research and development of novel polymers possessing good physical and electrical properties.

A significant discovery in the development of conducting polymers was the finding in 1973 that the inorganic polymer polysulphur nitride, (SN)$_x$ is as good as a metal with room temperature conductivity of the order of $10^3$ S.cm$^{-1}$ compared to $6 \times 10^5$ S.cm$^{-1}$ for copper and $10^{-14}$ S.cm$^{-1}$ for polyethylene [1]. A major breakthrough in the field of electrically conducting polymers occurred in 1977 with discovery of conducting polyacetylene by Shirakawa et al [2]. Polyacetylene containing conjugated single and double bonds in its structure becomes electrically conducting with a structural
modification consequent to a process called 'doping'. Since this Nobel Prize
winning discovery, much of the work has been centered on synthesis and
characterization of novel polymers with \( \pi \)-conjugated backbone due to their
highly promising optical, electrochemical and conducting properties.

2.1.1 \( \pi \) - conjugated polymers

Last two decades witnessed a resurgence in field of \( \pi \) - conjugated
polymers owing to increased interest from different applied science sectors.
Hectic activities in this field resulted in a large family of \( \pi \) - conjugated
polymers which exhibits a series of promising properties such as tunable
electrical conductivity, photoconductivity, charge storage capacity,
photoluminescence and electroluminescence [3 - 10]. Conjugated polymers are
organic semiconductors that are similar to their inorganic counterparts in their
electronic levels. Both have their electrons organized in bands rather than
discrete levels [3, 4]. Typical band gap between conduction and valence bands
is about 1 to 3 eV. Having such an energy gap suggests that this class of
polymers are normally insulators or at best semiconductors. The electrical
conductivity of \( \pi \) - conjugated polymers can be enhanced to a large extent by
doping it with either an electron donor or an electron acceptor. Introduction of
dopants results in strong electron-phonon interactions leading to the generation
of polarons, bipolarons and solitons in the system [11 - 14].

The charge carriers contributing to conductivity in conjugated
polymers are solitons, polarons and bipolarons. Figure 2.1 shows some of the
popular conducting polymers. The basic structural motif of conjugated
polymer is an alternating sequence of single and double bonds. Trans-
polyacetylene has a degenerate ground state in which there is no preferred
sense of bond alternation. Most of the conjugated polymers possess a non-
degenerate ground state with a preferred sense of bond alternation. Oxidation
polyacetylene generates a cation radical. As there is no preferred sense of bond alternation, the positive charge and the unpaired electron of the cation can move independently along the polymer chain, forming domain walls between two identical parts of bond alternation. In solid state physics a charge associated with a boundary or domain wall is called a soliton [15 - 18]. Figure 2.2 shows soliton formation in polyacetylene.

![Polyacetylene](image1)

**Polyacetylene**

![Polyphenylene](image2)

**Polyphenylene**

![Polythiophene](image3)

**Polythiophene**

![Polypyrrole](image4)

**Polypyrrole**

![Polypyridine](image5)

**Polypyridine**

![Polyaniline](image6)

**Polyaniline**

![Polyphenylene vinylene](image7)

**Polyphenylene vinylene**

Figure 2.1: Structure of some conjugated polymers

![Soliton in Polyacetylene](image8)

Figure 2.2: Soliton in Polyacetylene

In the case of oxidation and reduction of non-degenerate ground state polymers such as polythiophene and polypyrrole, a different mechanism occurs. The initially formed cation radical possesses both spin and charge and can not move independently [19]. A polaron is either a positively charged hole site (radical cation) or a negatively charged electron site (radical anion). It has
a lattice relaxation (distortion) around the charge. Theoretical models demonstrate that two radical ions (polarons) on the same chain interact to produce a dication or dianion called a bipolaron, which accounts for spinless conductivity in these polymers. Figure 2.3 illustrates formation of polarons and bipolarons in polymer chains.

![Figure 2.3 Polaron and bipolaron](image)

2.1.2 Electrically conducting polymers

As the band gap of typical conjugated polymers ranges from 1 to 3 eV, the electrical conductivity is low and the material can be at best a semiconductor. The electrical conductivity can be considerably enhanced by the introduction of charge into these polymer chains by various methods like oxidation, reduction, acid doping, etc. It was discovered in 1977 that
polyacetylene could be readily oxidized by electron acceptors such as iodine or arsenic pentafluoride or reduced by donors such as lithium [2, 20, 21]. The conductivity of this modified polyacetylene was several orders higher than the original sample. The redox reaction can be carried out in

![Conductivity ladder diagram]

Figure 2.4: The conductivity ladder

vapour phase, in solution or electrochemically. A similar significant finding was reported in 1979 in the case of polyphenylene[22]. Many poly-aromatics and polyheterocyclics are now known to exhibit this enhanced electrical conductivity upon doping. Typical examples are polypyrrole, polythiophene, polyfuran, polyindole, polycarbazole, polyaniline, etc. [23 – 29]. These polymers, because of their high electrical conductivity and ease of preparation, assume great significance in potential technological applications. A comparison of the electrical conductivity of various conducting polymers with that of mercury and metallic copper are given in figure 2.4.
Table 2.1: Conductivity and nature of doping in typical polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Maximum conductivity (S.cm(^{-1}))</th>
<th>Type of doping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene</td>
<td>200 -1000</td>
<td>n, p</td>
</tr>
<tr>
<td>Polyparaphenylene</td>
<td>500</td>
<td>n, p</td>
</tr>
<tr>
<td>Polyparaphenylene vinylene</td>
<td>1 -1000</td>
<td>p</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>40 - 200</td>
<td>p</td>
</tr>
<tr>
<td>Polythiophene</td>
<td>10 - 100</td>
<td>p</td>
</tr>
<tr>
<td>Polyosothianaphthene</td>
<td>1 -50</td>
<td>p</td>
</tr>
<tr>
<td>Polyaniline</td>
<td>10</td>
<td>p</td>
</tr>
</tbody>
</table>

2.1.3 Conduction mechanisms

The concepts of band structure are applicable to conducting polymers also. The conductivity is dependent on the conjugation length of the polymer [30, 31]. The increase in conjugation length increases the carrier mobility, resulting in increased conductivity. The charge carriers have to move along the extended \( \pi \) system of the conjugated backbone (intra-chain conductivity) as well as between the individual molecules (inter-chain conductivity). In conducting polymers like trans-polyacetylene two energetically equivalent resonance structures are possible. Unpaired electrons called solitons are present at the conversion points. This conversion point is actually spread out over several bonds. Solitons introduce a localized electronic state in the middle of the energy gap between the conduction band and valence band of polyacetylene. Conjugated polymers like polypyrrole, polythiophene, etc do not have a degenerate ground state, but different resonance structures can be present and unpaired electrons are formed at conversion points. These electrons polarize the local environment resulting in two electronic states in the
band gap, which then contributes to conductivity. The combination of charge carrier and its distorted environment is called a polaron. Its chemical equivalent is a charged radical.

Figure 2.5 Band structure in an electrically conducting polymer

Although conjugated structures are favourable for conduction due to high charge mobility, low carrier concentration reduces the conductivity. Charge carriers are produced by oxidation or reduction of the polymer and the process is called doping. Oxidation of polymer results in a hole-conducting polymer (p-type), whereas on reduction electron-conducting polymer is formed [4]. The increase in conductivity on doping can be as high as about 13 to 14 orders of magnitude for different dopant combinations [32, 33]. Conductivity caused by n-type doping is less than that produced by p-type doping.
The evolution of polymer band structure with doping is shown in figure 2.6.

![Figure 2.6: Evolution of polymer band structure on doping](image)

2.1.4 Applications of conducting polymers

- **Polymer rechargeable batteries**

  Conducting polymers are used as electrode material for rechargeable batteries [34]. The electrochemical doping process constitutes the basic electrochemistry of battery. The reversibility of electrochemical doping provides a rechargeable battery system.

- **Sensors**

  Conducting polymers are widely used in biological and chemical sensors [35 – 37]. Sensors employing conducting polymers are used in different modes such as pH-based mode, conductometric mode, and potentiometric mode. Heteroaromatic polymers can act as gas and solution sensors. Polypyrrole and polythiophene exhibit conductivity changes upon exposure to both oxidizing and reducing gases. Polyaniline, polythiophene and polypyrrole are the most commonly used conducting polymers used for the fabrication of sensors.
• **Electroluminescent devices**

Polymeric light emitting diodes (PLED) have aroused much interest worldwide since the discovery of electroluminescence in a thin layer of poly p-phenylene vinylene by Friend and co-workers in 1990 [38]. The device is prepared by sandwiching the conducting polymer between an electron-injecting metal (Al or Ca) and hole-injecting material (Indium-Tin-Oxide). Electroluminescence has been reported in many conducting polymers [38 - 41].

• **Antistatic coatings**

Build up of static electricity on an insulator can be prevented by coating it with a thin layer of conducting polymer. Delicate integrated circuits can be protected from static discharge by providing a thin conductive polymer coating.

• **Printed circuit boards**

Conducting polymer coated printed circuit boards are a better alternative to the conventional ones because of their relatively lower cost and better adhesion.

• **Molecular electronics (ME)**

ME is an interdisciplinary field evolving from physics, chemistry, biology, electronics and information technology. Among organic materials conducting polymers have attracted most attention for possible application in ME devices because of their unique properties and versatility [42 - 46]. The conductivity of these polymers can be tuned from insulating regime to superconducting regime by the degree and nature of doping. These polymers offer the advantages of light weight, flexibility, corrosion-resistivity, high chemical inertness and ease of processing. The progress in the field of ME is dependent on the synthetic routes and molecular tailoring. Conducting
polymers can be prepared both by chemical and electrochemical methods. By varying the nature of the groups, specific interactions with external physical and chemical phenomena can be developed in these materials leading to molecular devices such as transducers, memories and logic operators.

Conducting polymers like polyaniline, polypyrrole, polyacetylene and poly 3-alkyl thiophene are used in Schottky diodes [47 - 50]. Many conjugated polymers are used for the fabrication of organic thin film field effect transistors [51 - 57].

- Microwave engineering

The response of conducting polymers to microwave frequencies has been extensively studied because of their use in reflector antenna coating, electromagnetic interference shielding, frequency selective surfaces, radar absorbing materials, etc.

2.2 Polymerization Techniques

Conducting polymers are prepared by a variety of polymerization methods such as chain growth (addition), step growth (condensation), electrochemical, ring opening and plasma polymerization.

2.2.1 Step-growth polymerization

In step-growth polymerization, a polymer is formed by the step-wise repetition of the same reaction. If the monomer is represented by $M$ and the growing molecules by $M_1$, then step growth polymerization can be represented by

$$M_1 + M = M_2 + H_2O,$$

$$M_2 + M = M_3 + H_2O,$$

$$M_m + M_n = M_{m+n} + H_2O$$

It is seen that the reaction at each step is identical to the first reaction.
2.2.2 Chain-growth polymerization

In chain-growth polymerization, a long chain molecule is formed by a series of consecutive steps that is completed in a very short time. In this case, products are only final polymers. Unlike the case of step growth polymerization, intermediate size molecules cannot be isolated. Consequently, entire polymer formation can be essentially considered a one step process, as long as the concept of chemical reaction that relies on the identification of reactants and products is concerned.

If the chain carrying species is indicated by $M^*$ and the monomer by $M$, the chain growth mechanism can be shown by

\[
M^* + M = M_2^*
\]

\[
M_2^* + M = M_3^*
\]

\[
M_n^* + M = M_{n+1}^*
\]

\[
M_m^* \Rightarrow M_m
\]

The first three reactions represent the propagation reaction and the last reaction in which the chain carrying species is lost is the termination reaction. In the step growth polymerization, each growth step is a chemical reaction between two molecules whereas in chain growth polymerization, each individual growth step is a chemical reaction between a chain carrying species and a molecule.

A typical example of the chain growth polymerization is the addition polymerization. Depending on the nature of the reactive species, the addition polymerization can be classified as free radical polymerization, cationic polymerization and anionic polymerization.
2.2.3 Radiation polymerization

Polymerization initiated by ionizing radiation such as γ rays from $^{60}$Co or high-energy beams is somewhat similar to plasma polymerization. For elucidating the mechanism of plasma polymerization, an understanding of radiation polymerization is helpful.

The significant difference between radiation polymerization and the polymerizations discussed so far is that no initiator is employed in radiation polymerization. The chain carrying species are created by ionization of a monomer molecule. Radiation induced polymerization differs from the polymerization by an initiator in that (i) free radical and ionic polymerization co-exist, (ii) ion radicals contribute to the initiator reaction and (iii) ionic sites have no counter ions.

2.2.4 Plasma polymerization

Plasma polymerization (glow discharge chemical vapour deposition) technique to prepare thin polymer films has been rapidly developing in the field of organic materials as well as in that of conventional inorganic ones [58 - 62]. Polymerization of molecules, inorganic or organic, saturated or unsaturated occurs in various plasma environments such as plasma jets, electron beams, ion beams, corona discharges, laser induced plasmas and non-equilibrium glow discharges. Plasma polymerization is a thin film process where thin films deposit directly on the surfaces of the substrate. In this process growth of low molecular weight molecules (monomer) into high molecular weight molecules (polymer) occurs with the assistance of plasma energy, which involves activated electrons, ions and radicals. In plasma polymerization, plasma acts as an energy source to initiate polymerization reactions. Ion-molecule and radical-molecule mechanisms are mainly
responsible for the dissociation of neutral species and subsequent polymerization. Introduction of inert gases as carriers enhances these reactions. Polymers formed by this technique are highly cross-linked and bear little resemblance to polymers prepared by conventional polymerization.

- **Mechanisms of plasma polymerization**

  In view of the multitude of reactive species and parametrical factors affecting the nature of glow discharge, the polymerization mechanisms and the polymerization routes are highly complex. Numerous models have been proposed for the large variety of organic and inorganic substances in the presence or absence of other species, carriers and catalysts which involve ionic, radical or both mechanisms in polymerization. The explanation of the reaction mechanisms are usually based on qualitative observations and measurements of the overall deposition rates rather than the direct identification of the active species present. The neutral species entering the plasma reactor are transformed into reactive species as electric energy is given to the neutral species by the electrons. These active particles comprising of ions, free radicals, excited atoms and molecules and radical ions together with the neutral species may be involved in one of the following reaction schemes:

  (i) They interact in the gas phase ionically or via radical mechanism at high rates to form polymers, usually powders before reaching a surface.

  (ii) The active species tend to move to the surface where they are adsorbed or rebound into the gas phase. Each sorption represents a deposition step. The adsorbed particles subsequently interact and engage in ionic or radical polymerization on the surface and form a thin film.

- **Basic reactions in a glow discharge**

  The primary processes in the generation of ions involve electron impact and photo-ionization. Similarly free radicals may be generated by electron
impact. Ionization process also takes place via collisions of metastable species and molecules or atoms. These processes are referred to as Penning ionization and treated in terms of metastable-normal and metastable - metastable collisions resulting in ionization. Some of the basic reactions are given below:

Primary ion production by electron impact and photo-ionization:

\[ e^- + A \rightarrow A^+ + 2e^- \]
\[ h\nu + A \rightarrow A^+ + e^- \]

The following basic reactions control deposition of films in a glow discharge.

Excitation (rotational, vibrational, electronic):

\[ e^- + A_2 \rightarrow A^* + A \]

Dissociative attachment:

\[ e^- + A_2 \rightarrow A^- + A^+ + e^- \]

Ionization:

\[ e^- + A_2 \rightarrow A_2^+ + 2e^- \]

Dissociative ionization:

\[ e^- + A_2 \rightarrow A^+ + A + 2e^- \]

Inelastic collisions between heavy particles-

Penning dissociation:

\[ M^* + A_2 \rightarrow 2A + M \]

Penning ionization:

\[ M^* + A_2 \rightarrow A_2^+ + M + e^- \]

Charge transfer:

\[ M^+ + A_2 \rightarrow A_2^+ + M \]

Collisional detachment:

\[ M^+ + A_2^- \rightarrow A_2 + M + e^- \]
Atom recombination:

\[ 2A + M \rightarrow A_2 + M \]  
(M – monomer)

In the presence of free radicals and ions, both are capable of inducing polymerization and both ionic and free radical mechanisms may operate depending on the conditions. Free radicals react at rates 10-100 times faster than ions.

- Merits of plasma polymerization technique

Polymers formed by plasma polymerization demonstrate unique chemical and physical properties. Many films can be deposited in plasma at low temperatures, whereas conventional vapour deposition would require prohibitively high temperatures. Plasma polymers are amorphous, hard, tough and insoluble in organic solvents. They are resistant to high temperatures. These unique properties result mainly from the chemical structure of the plasma polymer chains, which are highly crosslinked and branched. The polymer chains are not illustrated from the concept of a repeating unit. Such singularity of polymer chains is the result of the particular initiation reaction triggered by plasma energy, which is higher than that of conventional energy sources such as heat or ultra violet rays. Other advantages include better adhesion to the substrate, reduction of pinholes, smoothness of surfaces and improved chemical and wear resistance. This resulted in the worldwide application of this technology for thin film fabrication.

- Applications of plasma polymerized films

Pinhole-free polymer films prepared from glow discharge plasmas of organic vapours have wide ranging applications. The film structure and the composition depend primarily on the monomer, but are also affected by deposition parameters such as the power applied to the discharge, monomer
flow rate, system pressure and substrate temperature. Films suited for specific applications can be prepared by controlling these parameters.

Plasma polymers prepared from $C_2H_2$ - nitrogen discharges show low degree of cross linking with hydrophilicity and are used for reverse osmosis applications [63]. High quality conducting polymers have been prepared by plasma polymerization techniques. Flawless films prepared by this method are widely used in electronic device industry. Conducting polythiophene films were prepared by Sadhir et. al. [64]. The conductivity of polymerized films can be modified by co-polymerization [65]. Plasma polymerization has shown to be compatible with microelectronic fabrication process and has been used for the deposition of photoresistors [66, 67]. Plasma polymerized methyl methacrylate films are used for photonic applications [68]. Plasma deposited organic films are widely used as protective coatings for metals and other refractive surfaces.

**Experimental setup for plasma polymerization**

Four elements are essential for any plasma polymerization setup. They are (i) electric power source for the initiation and maintenance of glow discharge, (ii) the reaction chamber, (iii) the vacuum system and (iv) the control system and the monomer gas flow.

**Electric power source:** The electric power source employed in plasma polymerization can be operated by both direct and alternating currents with frequencies ranging from 50 Hz to the microwave region. Depending on the power source used the methods are labeled as DC plasma polymerization, AC plasma polymerization, RF plasma polymerization and microwave plasma polymerization. Commercially available units employ a frequency of 13.56 MHz. The electric energy from the power source is transmitted into the
reaction chamber with inductive or capacitive coupling. The type of coupling system is restricted by the frequency and shape of the reaction chamber.

**Reaction chamber:** Various types of reaction chambers are in use for plasma polymer coating. Basically there are two types – a tubular type chamber and a bell jar type chamber. Tubular chamber is compact and convenient for laboratory use whereas bell jar designs are used for commercial applications.

**Vacuum system:** The reaction chamber must be maintained at a low pressure to obtain a stable glow discharge state. In most cases a combination of diffusion and rotary pumps is employed to reduce the pressure. A constant pressure must be maintained during the plasma polymerization process, since the operating pressure is one of the factors controlling the polymerization reactions.

**Control system and monomer gas flow:** The flow rate of the monomer gas is one of the factors that determine the appearance and the chemical composition of plasma polymers. Changes in the monomer flow rate during the polymerization process should be avoided. The monomer flow is carefully controlled using a needle valve or a mass flow controller.

- **RF plasma polymerization system**

  At frequencies above 1MHz, direct contact between electrodes and plasma is no longer necessary. The energy can be fed to the plasma indirectly by capacitive or inductive coupling (Figure 2.7, 2.8). In the case of capacitive coupling the electrodes enclose the plasma tube. The tube lies on the axis of a coil for inductive coupling. For plasma deposition RF generators with fixed frequency and adjustable power are preferred.
2.3 Synthesis of conducting polymers

The polymers selected and prepared for the present study are polyaniline (PANI), polypyrrole (PPy), poly N-methyl pyrrole (MPy), polythiophene (PTh). Acid-doped forms of PANI are also prepared. Composites of PANI with poly vinyl chloride (PVC) and PPy with PVC are synthesized for their thermal characterization.

The polymer samples are prepared by chemical synthesis as well as radio frequency (RF) plasma polymerization. Powder samples are prepared by the chemical route whereas polymer thin films are coated on glass substrate by RF plasma polymerization technique.
2.3.1 Chemical synthesis

- Polyaniline (PANI)

Chemical oxidative polymerization of aniline is carried out using ammonium persulphate as initiator in the presence of 1M hydrochloric acid at 0 – 5°C. The reaction is allowed to continue for four hours. Polyaniline thus formed is vacuum-dried. It is dedoped by treating it with ammonium hydroxide for twentyfour hours, and then doped with different dopants – 1M hydrochloric acid, 1M sulphuric acid and 1M camphor sulphonic acid. The powder samples are pelletized to form pellets of 1 cm diameter with a thickness of less than 1 mm.

To combine the electrical conductivity with the desirable physical properties of a polymer, conducting polymers can be introduced into a host polymer matrix. The resulting structure is an interpenetrating network. In this study chemical oxidative polymerization of aniline is carried out using ammonium persulphate as initiator in the presence of 1M HCl and emulsion grade polyvinyl chloride. The polymerization reaction is carried out for four hours at room temperature. It is then filtered, washed and dried. PANI/PVC composites are prepared in 3:1, 2:1 and 1:1 compositions. The powder samples are pressed into pellets of thickness less than 1mm.

- Polypyrrole (PPy)

PPy is chemically prepared by the polymerization of pyrrole with ferric chloride in the presence of methanol. The reaction is carried out for twenty minutes at 0 - 5°. It is then filtered, washed and dried in vacuum for sixteen hours. Pellets of less than 1mm thickness are prepared from the powder samples.
PPy/PVC composite is prepared by the polymerization of pyrrole with ferric chloride in the presence of methanol and emulsion grade polyvinyl chloride. The reaction is carried out for twenty minutes at 0 – 5°C. It is then filtered, washed and dried under vacuum for sixteen hours at room temperature. PPy/PVC compositions 3:1, 2:1 and 1:1 are prepared using the above procedure. The powder samples are pelletised.

2.3.2 Preparation of Plasma Polymerized Films

Capacitively coupled RF plasma polymerization unit is used for the preparation of polymer films in this study. The tubular chamber is of about 40 cm in length and 6 cm in diameter. The monomer container is connected to this tube through a needle valve. An inlet is also provided for admitting iodine vapour into the reaction chamber, so that in situ iodine doping may be performed. Aluminium foil rings are used to couple RF power to the reaction chamber. The chamber is attached to a rotary pump through a stop cock. The RF generator uses four RCA tetrodes. It is a tuned-plate tuned-grid RF oscillator designed to generate RF power at 7 MHz. The power can be adjusted over a limited range.

- Preparation of polyaniline films

The polymer thin films are prepared on optically flat glass slides of dimensions 75 x 25 x 1.4 mm. The glass plates are first cleaned in running water and are immersed in chromic acid for about 1 to 2 hours in order to remove alkaline impurities. The slides are then washed in distilled water and are cleaned ultrasonically. The microscopic impurities are stripped off by ultrasonic agitation in water. The glass slides are then dried and placed in the deposition chamber. The chamber is evacuated to a pressure of approximately 0.4 m bar keeping the monomer needle valve closed. The RF power is switched on and a glow appears in between the electrodes. About 1 ml of the
Monomer aniline is taken in a small glass container and the monomer vapour is supplied to the reaction chamber through a needle valve. The needle valve is fully opened and the monomer vapour is admitted into the chamber. The valve is closed after half a minute. The RF power is switched on. The distance between the aluminium rings is adjusted to get uniform glow. Now the needle valve is carefully adjusted to regulate the monomer flow. After a deposition time of about 15 to 25 minutes, a thin film of the polymer gets coated on to the glass plate.

PANI films are also prepared with in situ iodine doping. Films are coated under different pressure conditions of the reaction chamber. Films of different thickness are prepared by allowing different reaction time.

For the measurement of the dc conductivity of the PANI films, aluminium electrode is coated on glass substrate. PANI film is allowed to form on this lower electrode by placing this in the plasma reactor. The upper electrode is coated on this film with proper masking so as to form metal-polymer-metal structure of effective area 0.25 cm$^2$. A similar structure is prepared with iodine doped PANI film.

- **Preparation of polypyrrole films**

  About 1ml of analytical grade pyrrole monomer (Lancaster) is taken in the monomer container and is attached to the plasma reaction chamber through a needle valve. Films of different thickness are coated on ultrasonically cleaned glass substrate as in the case of PANI. Deposition time of 30 – 50 minutes is allowed.

  Al-PPy-Al structure is prepared with and without iodine doping as in the case of PANI.
- **Preparation of poly N-methyl pyrrole films**

  2 ml of N-methyl pyrrole monomer (Merck) is taken in the monomer container. Films of different thickness are coated on glass substrate by changing the deposition time. Iodine doped films are also prepared.

- **Preparation of polythiophene films**

  Plasma polymerization of thiophene monomer (Merck) is carried out as described in the above cases. Relatively higher deposition time (45 minutes to 1 hour) has to be allowed to obtain films of suitable thickness. In situ iodine doping is carried out to obtain doped films. Al-PTh-Al structure is prepared for conductivity studies.

- **FTIR spectra of plasma polymerized films**

  While the chemical synthesis of polymerization followed in the present study is a standard, well established and product specific route, the plasma polymerization technique is a more complex route of polymerization as already pointed in section 2.2.4. Hence the FTIR spectra of all the plasma polymerized samples are recorded to check whether the ring structure is completely lost under the plasma deposition conditions used in this study.

  A comparison of the IR spectra of chemically prepared and plasma polymerized PPy shows that most of the peaks of chemically prepared PPy are present in the plasma polymerized sample also. A small shift is observed in many of the absorptions. The presence of ring vibrations points to the retention of the ring structure to some extent. In chemically prepared PPy, characteristic peaks of the pyrrole functional groups can be seen. The broad peaks at approximately 3450 cm\(^{-1}\) is typical of N-H stretch and the peak at approximately 1620 cm\(^{-1}\) corresponds to C=C and C=N in-plane vibrations in the pyrrole structure. The peak at approximately 1310 cm\(^{-1}\) is attributed to the
Figure 2.9 IR spectrum of plasma deposited PPy

Figure 2.10 IR spectrum of chemically prepared PPy
secondary amine C-N stretching. The peaks at 790 cm\(^{-1}\) and 920 cm\(^{-1}\) are a combination of a number of absorptions corresponding to \(\text{NH}_2\) wag, symmetric
\[N-C\] stretching or its deformation. In the FTIR spectrum of plasma polymerized pyrrole, different absorptions corresponding to alkenes resulting from broken rings also appear as peaks between 500 and 1000 cm\(^{-1}\). When pyrrole rings are broken, branching and cross linking reactions tend to occur predominantly. Thus primary secondary or even tertiary amines may appear in the plasma polymerized sample. This tends to make absorptions in this region complicated.

The absorption in the IR region for plasma polymerized film of N-methyl pyrrole compares well with the spectrum of PPy film. The C-H stretching of methyl group is seen around 2930 cm\(^{-1}\).

![Figure 2.13 IR spectrum of chemically prepared PANI](image)

In the case of plasma polymerized PANI the peak at 3356 cm\(^{-1}\) is assigned to the N-H asymmetric stretch of PANI. The absorptions at 1590 cm\(^{-1}\) and 1500 cm\(^{-1}\) belong to the C=C stretching. Peaks at 1240 cm\(^{-1}\), 750 cm\(^{-1}\) and 689 cm\(^{-1}\) correspond to the C=N stretch and C-H out of plane deformations. The peaks corresponding to ring stretching are fairly strong,
which is indicative of the retention of the ring structure. The spectrum chemically prepared PANI is given for comparison.

In the IR spectrum of PTh, the peaks in the range of 2800 – 3100 cm\(^{-1}\) is due to aliphatic and aromatic C-H stretching vibrations. The range

![Figure 2.14 IR spectrum of plasma deposited PTh.](image)

600 – 1500 cm\(^{-1}\) is the fingerprint region of PTh. The peak at 830 cm\(^{-1}\) represents the aromatic C-H out of plane deformation mode whereas the other absorptions in this region are attributed to the ring stretching modes, aromatic C-H in-plane and out of plane deformations. The peak at 705 cm\(^{-1}\) is due to the aromatic C-H out of plane bending vibrations. The absorption at the 2320 cm\(^{-1}\) is the region where contributions from C=C stretching or S-H stretching appear. The broad peak at approximately 2925 cm\(^{-1}\) represents the stretching mode of methyl and methylene groups and aliphatic structures. The peak around 3275 cm\(^{-1}\) indicates the presence of some acetylene structures of plasma polymerized thiophene.
**Electrical conductivity measurements**

Chemically prepared polymer samples in the powder form is pelletised to form pellets of about 1cm diameter with thickness less than 1mm. Silver paste is coated on either side so as to serve as terminals for applying a DC bias voltage. V-I measurements are carried out keeping the pellets in conductivity cell using Keithley Source Measure Unit (SMU), Model: 236. Dependence of conductivity on temperature in the case of PANI and PPy is investigated by keeping the samples in a cryostat [C T I Cryogenics, Helix Tech Corporation and Cryo Industries America Inc. Atkinson Model: 22].

- **Chemically prepared PANI**

  The variation of conductivity with temperature in the case of samples doped with 1M HCl and 1M camphor sulphonylic acid, in the range 140 to 300 K is investigated keeping the pellet in a cryostat.

- **Chemically prepared PPy**

  As in the case of PANI, variation of conductivity with temperature is investigated in the case of chemically prepared PPy by placing the PPy pellet in the cryostat.

- **Plasma polymerized aniline film**

  Al-PANI-Al sandwich structure is prepared and V – I measurements are carried out using the Keithley Model 236 SMU, placing the sample in a conductivity cell. The measurements are taken for a film of thickness 630 nm in the voltage range of 0 - 20 volts. Conductivity of the sample is computed from the V – I plot.

  Measurements are repeated for iodine-doped film of thickness 1230 nm in the voltage range 0 – 20 V.
• Plasma polymerized pyrrole film

  V - I measurements for plasma polymerized pyrrole films in the undoped and doped forms are taken as in the case of PANI film.

• Plasma polymerized N-methyl pyrrole film

  Room temperature conductivity of N-methyl pyrrole in the undoped and doped forms is obtained from the V - I measurements.

• Plasma polymerized thiophene film

  V - I measurements on undoped iodine-doped thiophene films are carried out as outlined in the case of PANI.

2.4.1 Results and discussion

The variation of electrical conductivity of 1M HCl doped PANI, 1M camphor sulphonie acid PANI and PPy (as-prepared) with temperature are shown in figures 2.15 - 2.17. For a large variety of disordered materials the conductivity is described by the Mott's law for variable range hopping [69, 70]. The plots indicate variable range hopping conduction mechanisms in these specimens. As the thermal energy decreases with temperature, there are fewer nearby states with accessible energies, resulting in increase in the mean range of hopping. The expression for conductivity is given by  \( \sigma = \sigma_0 \exp \left( - \frac{T_0}{T} \right)^n \); where \( \sigma_0 \) and \( T_0 \) are constants. \( n = 1/2 \) for 1-D hopping mechanism whereas \( n = 1/4 \) corresponds to a 3-D variable range hopping conduction. In the present study the variation of conductivity of these samples with temperature can be fitted into a relation with \( n = 1/4 \). This suggests that the major contribution to the conductivity is by 3-D variable range hopping in the samples under investigation.
Figure 2.15 Variation of conductivity with temperature for HCl-doped PANI

Figure 2.16 Variation of conductivity with temperature for CSA-doped PANI
Figure 2.17 Variation of conductivity with temperature for PPy

Figure 2.18 V-I plot for plasma polymerised PANI (undoped)
Iodine doped PANI

\[ \sigma = 2.66 \times 10^{-10} \text{S m}^{-1} \]

Figure 2.19 V - I plot for plasma polymerized PANI (iodine-doped)

Undoped PPy

\[ \sigma = 1.83 \times 10^{-11} \text{S m}^{-1} \]

Figure 2.20 V - I plot for plasma polymerised PPy (undoped)
Iodine doped PPy
\[ \sigma = 4.78 \times 10^{-8} \text{Sm}^{-1} \]

Figure 2.21 V - I plot for plasma polymerised PPy (iodine-doped)

Undoped MPy
\[ \sigma = 1.74 \times 10^{-12} \text{Sm}^{-1} \]

Figure 2.22 V - I plot for plasma polymerised MPy (undoped)
Figure 2.23 V - I plot for plasma polymerised MPy (iodine-doped)

Figure 2.24 V - I plot for plasma polymerised PTh (undoped)
Table 2.2 Conductivity of plasma polymerized films

<table>
<thead>
<tr>
<th>Polymer film</th>
<th>Conductivity (Sm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Undoped</td>
</tr>
<tr>
<td>PANI</td>
<td>$2.5 \times 10^{-12}$</td>
</tr>
<tr>
<td>PPy</td>
<td>$1.83 \times 10^{-11}$</td>
</tr>
<tr>
<td>MPy</td>
<td>$1.74 \times 10^{-12}$</td>
</tr>
<tr>
<td>PTh</td>
<td>$2.10 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

All the polymer samples show ohmic behaviour in the applied voltage range (Fig: 2.18 – 2.25). The values of conductivity for the different polymer samples are given in table 2.2. The conductivity shows an increase of two to three orders with iodine doping. Plasma polymerized films show a high degree of cross linking and side reactions. There is no local order in such films.
Iodine, being an electron acceptor contributes to the conductivity of the films to some extent.

2.5 Band gap measurements

Absorption of energy in the uv-visible region of the electromagnetic spectrum provides information about the electronic transitions in a solid. The electrons are excited from a filled band to empty band by the absorption of photons. This results in a sharp increase in the absorption coefficient and the onset of this rapid change in absorption coefficient is called the fundamental absorption edge. The corresponding energy is referred to as the optical energy-gap or the band gap energy. There are two kinds of optical transitions at the fundamental absorption edge of crystalline and amorphous solids - direct transition and indirect transition. For a direct transition from the valence band to the conduction band, the wave vector of the electron must be conserved. Only vertical transitions are allowed between the valence and conduction band. The bottom of conduction band and top of valence band lies at $k=0$ as shown in figure 2.26 so that electrons near the top of valence band can make direct transition to the states near the bottom of conduction band.

If the bottom of conduction band and top of valence band lies at the same $k$ value, then absorption process do not require change in $k$ and hence direct transition is possible. However, if the bottom of conduction band and top of valence band has different $k$, then the absorption process requires a change in $k$. In order to conserve momentum in such indirect transitions, participation of a phonon is required in the optical absorption process.
Tauc, Bardeen, and Davis and Mott independently derived the following equation relating the absorption coefficient $\alpha$ with the photon energy $h\nu$ [71 - 73].

$$\alpha h\nu = B (h\nu - E_g)^n;$$ where $B$ is a constant reflecting the degree of randomness of the structure of the amorphous solid, $E_g$ is the optical band gap of the absorption process. For direct allowed transitions $n = 1/2$ and for indirect ones $n = 2$.

The product of absorption coefficient and thickness of the film can be directly read from the uv-visible-NIR spectrophotometer. Knowing the thickness of the films the absorption coefficient of the samples can be
obtained. Direct and indirect transition energy gaps can be obtained from the plots of $(\alpha h\nu)^2$ versus $h\nu$, and $(\alpha h\nu)^{1/2}$ versus $h\nu$ respectively.

Absorbance of all the polymer samples are recorded using the uv-visible-NIR spectrophotometer (Varian Cary 5000).

The plots showing the variation of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ with photon energy for the different polymer films are shown in figures 2.27 – 2.42.

![Figure 2.27. Variation of $(\alpha h\nu)^2$ with $h\nu$ for undoped PANI](image-url)
Figure 2.28. Variation of $(\alpha \nu)^{1/2}$ with $\nu$ for undoped PANI.

Figure 2.29. Variation of $(\alpha \nu)^2$ with $\nu$ for I-doped PANI.
Figure 2.30. Variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for I-doped PANI.

Figure 2.31. Variation of $(\alpha h\nu)^{2}$ with $h\nu$ for undoped PPy.
Figure 2.32. Variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for undoped PPy.

Figure 2.33. Variation of $(\alpha h\nu)^2$ with $h\nu$ for I-doped PPy.
Figure 2.34. Variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for I-doped PPy.

Figure 2.35. Variation of $(\alpha h\nu)^2$ with $h\nu$ for undoped MPy.
Figure 2.36. Variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for undoped MPy.

Figure 2.37. Variation of $(\alpha h\nu)^2$ with $h\nu$ for I-doped MPy.
Figure 2.38. Variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for I-doped MPy.

Figure 2.39. Variation of $(\alpha h\nu)^2$ with $h\nu$ for undoped PTh.
Figure 2.40. Variation of $(\alpha h \nu)^{1/2}$ with $h \nu$ for undoped PTh.

Figure 2.41. Variation of $(\alpha h \nu)^2$ with $h \nu$ for I-doped PTh.
Table 2.3 Direct and indirect transition gaps of the plasma polymerized films

<table>
<thead>
<tr>
<th>Polymer film</th>
<th>Band gap (eV)</th>
<th>Undoped</th>
<th>Iodine doped</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Direct</td>
<td>Indirect</td>
</tr>
<tr>
<td>PANI</td>
<td>2.73</td>
<td>2.33</td>
<td>2.53</td>
</tr>
<tr>
<td>PPy</td>
<td>2.73</td>
<td>2.05</td>
<td>2.55</td>
</tr>
<tr>
<td>MPy</td>
<td>2.83</td>
<td>2.26</td>
<td>2.7</td>
</tr>
<tr>
<td>PTh</td>
<td>2.8</td>
<td>2.1</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Direct and indirect transition gaps of the different films obtained from these plots are shown in table 2.3. It is observed that for all samples there is a reduction in direct and indirect band gaps on p-type doping with
iodine. This reduction, although not appreciable, is in agreement with theoretical predictions.

Conclusions

Chemically prepared polyaniline and polypyrrole powder samples show a variable range hopping conduction mechanism as illustrated in the respective plots. All the plasma polymer films under study show an ohmic behavior. There is no deviation from this behavior in the voltage and thickness ranges used.

Direct and indirect transition energy gaps are of comparable magnitudes for all the polymer films prepared by RF plasma polymerization [74]. On p-doping with iodine all samples show a reduction in the band gap.

References
73. E A Davis, N F Mott, Phil. Mag. 22 ((1970) 903.