Chapter 1

Introduction
INTRODUCTION:

The traditional involvement of polymers in electrical application has been as electrical insulators over the years and a variety of their applications have relied on this insulating property. However, with the arrival of conducting polymeric materials in recent past, their potential to perform as active element has been realized [1 - 15].

The conductivity within a given class of materials was generally found to enhance if the size of the molecule was increased, but this was not sufficient enough to warrant a reasonable conductivity. The delocalization of valence electrons (II- electrons) over the molecule was necessary to achieve good conductivity in organic polymers [16 - 18]. Consequently, it was proposed that polyacetylene \(-(CH = CH)_{x}-\) would be conducting [19].

Acetylene, was polymerized by Natta and coworkers [20] for the first time using his newly developed Ziegler Natta catalyst

\[ \text{Ziegler Natta catalyst} \]
\[ x \ (CH = CH) \rightarrow -(CH = CH)_{x} \]

The polyacetylene was obtained as a dark coloured powder completely insoluble in organic solvents. The electrical conductivity of the polyacetylene sample however was first reported to be \(\sim 10^{-5} \text{ S/cm}\) by Hatano et. al. in 1961 [21].
The processing of the polyacetylene of Hatano et. al., which again was powdery and insoluble in organic solvents, was difficult.

Experimentally a breakthrough was achieved when Ito, Shirakawa and Ikeda [22] succeeded in obtaining flexible silver colored polyacetylene film in 1974 with a conductivity of $4.4 \times 10^{-5}$ S/cm at room temperature. They also obtained one copper coloured freestanding polyacetylene film with a conductivity of $1.7 \times 10^{-9}$ S/cm.

It will be interesting to note here the method, which provided highly crystalline polyacetylene film. The Ito et. al. obtained the highly crystalline polyacetylene film using a very similar catalyst like Natta and coworkers [20] but in a much higher concentration than Natta. The method [22] is briefly described here.

The catalyst solution consists of 0.25 mol / liter tetrabutoxytitanium in toluene, to which 1.00 mole / liter triethyl aluminum is added. The mixture is stirred at room temperature for several minutes then cooled to dry ice temperature and degassed under reduced pressure for at least 30 minutes.

In a typical experiment purified acetylene gas under inert conditions is blown over the surface of the catalyst solution. The polyacetylene film immediately forms at the gas - liquid interface and the film thickness can be controlled by duration of the gas - liquid interface.
Three years later, Chiang et. al. were able to show that by doping a material, the conductivity could be increased from the semi conducting to metallic regime [23]. It has been observed by many researchers that when exposed to vapors of chlorine, bromine, iodine and arsenic pentafluoride, the polyacetylene film registered many fold increase in conductivity [24-26]. But because of its insolubility, infusibility and poor environmental stability polyacetylene could not find technological applications. Search for conducting polymers that are stable to ambient environment went on.

Subsequently conducting polymers of polyaniline (PAn) [27], Polypyrroles (PPy) [28], Polyphenylene Vinylene (PPV) [29], Polythiophenes (PT) [30] and many others have reported [15].

PAn, PPy and PT can be prepared either by chemical or electrochemical oxidation. The electrochemical method is generally preferred, as polymeric films deposited on anode surface can be removed to give freestanding films.

**SYNTHESIS OF CONDUCTING POLYMERS:**

Usual methods of polymerization may be employed for preparing conducting polymers. Few of these are discussed here.

**I. Condensation Process:**

This is an important method and many polymers have been synthesized using this.
Important examples are:

i) Synthesis of polyphenylene sulfide [31] from condensation of paradichlorobenzene with Na₂S

\[
x \text{Cl} - \text{C} - \text{Cl} + \text{Na}_2\text{S} \rightarrow \left( \text{S} \right)\text{Cl} + 2 \times \text{NaCl}
\]

ii) Polycondensation of diiodoacetylene with Na₂S [15]

\[
x (\text{I} - \text{C} \equiv \text{C} - \text{I}) + x \text{Na}_2\text{S} \rightarrow \left( \text{C} \equiv \text{C} - \text{S} \right)_x + 2x\text{NaI}
\]

II. Chain Polymerization:

Benzene and naphthalene have been polymerized in arsenic trifluoride solvent using AsF₅ as catalyst [32, 33]

\[
x \text{C} = \text{C} \rightarrow \text{AsF}_5 \rightarrow \left( \text{C} = \text{C} \right)_x
\]
III. Electrochemical Method:

Electrochemical synthesis offers a convenient route to obtain conducting polymers. Thus pyrrole in aqueous acetonitrile solvent containing tetraethyl ammonium tetrafluoroborate was electropolymerised to obtain polypyrrole containing BF$_4^-$ ion (as dopant) as a film on Pt electrode surface [28, 34].

The doping and oxidation of pyrrole occur during the electrochemical polymerization process. These pyrrole units have positive charge, which is balanced by a variety of dopant anions. Undoping of the film can be carried out by treatment with NH$_3$ or other similar chemicals [35].

![Image of polypyrrole structure]

IV. Redox Polymerization:

Polyaniline has been prepared by redox polymerization [35] of aniline with ammonium perdisulphate (NH$_4$)$_2$S$_2$O$_8$ as an oxidant. In a typical preparation, distilled aniline is dissolved in 300 ml of cooled HCl (1.0 M) solution at ~ 0° C. Calculated amount of (NH$_4$)$_2$S$_2$O$_8$ (0.05 M) dissolved in 200 ml of HCl (1M) precooled to ~ 1° C is added to the solution of aniline when dark green precipitate comes out. The
precipitates are washed with HCl (1 M) until the green colour disappears. These polyanilines are shown [36] in Fig. 1.1

Polyaniline exists in four different forms each of which has different electrical conductivities. These polyanilines are shown [36] in Fig. 1.1

Fig. 1.1 Different forms of polyanilines and their conductivity.
DOPING OF POLYMERS:

Doping of polymer enhances the conductivity drastically. It has also been noted that the increase in conductivity of doped polymers depends directly on level of doping. Sometimes a small amount of dopant can cause a substantial change in polymer conductivity and examples are known where the concentration of dopant maybe as high as 50 % [37]. Doping of conducting polymers involves random dispersion or aggregation of dopants and incorporation of dopant molecules in the polymer chain leads to reorganization of polymer [38].

Doping agents are generally reducing or oxidizing agents. Neutral molecules and compounds, which form ions easily, have also been employed as dopants. Neutral dopants are converted into negative or positive ions. Ionic dopants by electron transfer with polymer are either oxidized or reduced.

A simplified scheme [39, 40] of the mode of action of dopant maybe written as:

\[
\begin{align*}
\text{Acceptor} & \\
\text{Polymer} + \text{Dopant} & \rightarrow \text{(Polymer)}^+ + \text{(Dopant)}^- \\
\text{Donor} & \\
\text{Polymer} + \text{Dopant} & \rightarrow \text{(Polymer)}^- + \text{(Dopant)}^+
\end{align*}
\]
The creation of charged defects with no spin (i.e. solitons) has been proposed in doping of polymers as shown above. A donor type dopant gives an electron to the polymer and a negative soliton is formed.

On the other hand, an acceptor type dopant by removing an electron from the polymer will result in a positive soliton.

There are many dopants available, a few of them are:

$I_2$, $Br_2$, $AsF_2$, $FeCl_3$, $H_2SO_4$, $LiClO_4$, $CF_3COOH$, $Na$, $K$, $Ag$.

Generally three methods are widely used for doping of polymers. These are:

I. Gaseous Doping:

Polymers are exposed to the vapours of the dopant under vacuum [40].

II. Electrochemical Doping:

Simultaneous polymerization and doping generally occurs in electrochemical doping [41], although this method of doping may be used for polymers obtained by other methods also. In this method only ionic dopants are used as the electrolyte in polar solvents.
III. Solution Doping:

It involves the use of a solvent in which the dopant is dissolved. The polymer is treated with the dopant solution. The solvents generally used are toluene, acetonitrile, tetrahydrofuran and nitromethane.

It will be interesting to note that self-doping is also possible. This does not need any external doping agent. If the polymer contains an ionisable group, for example, sulfonate moiety, then this may act as a dopant for the polymer [42].

Doping operations are as important as polymerization reactions, since they affect not only the electrical conductivity and stability of organic polymer, but also some of the physical and chemical properties. Some doping operations can be controlled to tailor the conductivity as according to requirements [43].

Mechanism of Doping:

Doping of conducting polymers involves random dispersion of dopants in polymers. It has been found in certain cases that doping results in increase or decrease in bond lengths. The C-C bond length in doped polyacetylene has been reported to increase with donor doping but decrease with acceptor doping.

Creation of charged defects with no spin (called Soliton) has been proposed for conduction in doped polymers [2, 39]. A donor type dopant
gives an electron to the polymer and a negative soliton is formed, while acceptor dopant takes an electron from the polymer resulting in a positive soliton [2, 39]. This is illustrated below (Fig. 1.2) for doped polyacetylene.

![Diagram of soliton formation](image)

**Fig. 1.2** Mechanism of doping through formation of soliton.

At a low concentration of dopant the above chain of sequences occurs. It has been suggested that with increase in doping level, polaron and bipolarons are formed. It may be useful to write here a few lines about polaron [35]. When the electron is removed from the top of the
valence band (by oxidation) of the conjugated polymer, a vacancy (a radical cation) equivalent to a hole is created that does not delocalise completely, and deforming the polymeric structure [35]. This partially delocalised radical cation is called polaron (Fig 1.3).

Propagation of polaron through a conjugated polymer chain by shifting of double bonds that gives rise to electrical conduction is shown in Fig. 1.3.

Fig. 1.3 Propogation of polaron through a conjugated polymer chain

It will be now instructive to follow the orbital energy level diagram (Fig. 1.4) for the charge - generation process at the

a. Polymer - donor (dopant) and
b. Polymer- acceptor (dopant) interface.
The highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor are such that the rate constants for recombination $k_2$ are much less than the rate constant $k_1$ for charge generation [1]. The orbital energy level diagram [1] is shown in Fig. 1.4.

**APPLICATIONS:**

Because of their wide range of conductivity from semi conducting (i.e. $10^{-5}$ S/cm) to metallic (i.e. $10^4$ S/cm) coupled with lower price, the organic conducting polymers are being seriously thought as materials that can displace inorganic materials and conventional metals in various applications.
A few such applications are discussed here.

I. Polymeric Batteries:

Conducting polymers were tried to make batteries [6, 7, 15, 36, 44, 45]. The attempt to use these polymers in batteries was not very successful in majority cases. However, those made with polypyrrole or polyaniline as the cathode and lithium-aluminum alloy as anode exhibited more respectable properties to some extent. The electrolytes in these cases were either LiClO₄ or LiBF₄ in propylene carbonate. One serious limitation of this battery is that the energy storage capacity is low and their charging-discharging cycle is relatively low. More recently however, some composites of alkali metal alloy and polyphenylene have been used very effectively in batteries that exhibit much higher energy densities. It has been claimed that polyaniline based battery system has a very high energy density output under acidic conditions. This system can replace lead dioxide as a battery material in lead-acid battery system [46].

The prospect of a polymeric battery is still alive and vigorous research activities are being carried out to develop solid-state batteries.

II. Polymers as Biosensors:

In a biosensor, the sensing element, which responds to the substance being measured, is biological in nature. It has to be connected
to a transducer of some sort so that a visually observable response occurs [36, 12].

By far the most studied and developed biosensor is glucose biosensor. This is based on the fact that the enzyme glucose oxidase catalyses the oxidation of glucose to gluconic acid. The glucose oxidation reaction catalyzed by glucose oxidase (GOD) is

\[
\text{GOD} \\
\text{Glucose} + \text{O}_2 + \rightarrow \text{H}_2\text{O} \text{Gluconic acid} + \text{H}_2\text{O}
\]

In a typical example simultaneous immobilization of glucose oxidase and hydroquinone sulphonate in polypyrrole films has been reported by Kajiya et.al. [47]. Pyrrole is polymerized in presence of glucose oxidase and sodium hydroquinone sulphonate to give a glucose oxidase electrode with immobilized hydroquinone sulphonate in polypyrrole matrix. In such a device, the amount of charge transferred (i.e. current passed) is proportional to the concentration of glucose in the solution. The schematic diagram of a typical biosensor is shown in Fig. 1.5. Since the enzyme is specific, the device can sense glucose in presence of several other components.
Fig. 1.5 A schematic diagram for glucose biosensor.

III. Light Emitting Diodes:

The phenomenon of photoluminescence and electroluminescence in conjugated polymers has drawn attention of researchers worldwide.

Photoluminescence is emission of light on irradiation of the polymer while electroluminescence is emission of light on application of voltage.

The phenomenon of electroluminescence is utilized by light emitting diodes [8, 9, 36, 39, 48, 49]. The PPV film has been demonstrated to be useful as emissive layer in electroluminescence device.
The construction of a typical LED device will be depositing a film of a semi-conducting polymer on indium-tin oxide coated glass surface. The top electrode is deposited on the polymer film. The schematic diagram is shown in Fig. 1.6. It has been indicated that polyaniline can find application as an electro-chromic material in commercial signboards. The colour changes from green to yellow or blue and vice versa on reversal of applied potential [46].

![Schematic diagram of a polymer light emitting diode](image)

**Fig. 1.6** Schematic representation of a polymer light emitting diode

**IV. Miscellaneous Applications:**

Some of the other areas where conducting polymers find application are gas separation membrane [11], photochemical cells [52], optical device [53], mercury storage devices [14], controlled release device for pharmaceuticals [13, 54] and as diverse areas as space, opto-electronics and communication [335, 55-57].
It will be interesting to note that since polyaniline is a highly stable and electroactive material in the presence of acids, it is being considered as a suitable material for corrosion protection of metal surfaces [46].

**WHY RESEARCH IN CONDUCTING POLYMERS:**

Since the discovery of the conductivity of TCNQ and its various adducts, the research on polymeric organic conductors has increased. There has been widespread interest in polymeric organic conductors to replace conventional metals and inorganic materials in various applications as have already been indicated in the preceding sections. A wealth of experimental data has been accumulated for these organic conductors. Electrical conductivity of polySchiff’s bases has been a subject of active interest for its many important applications and Russian workers have noted the effect of structure on their electrical conductivity [58]. A large number [1 - 3, 31, 37, 39, 41, 48, 49] of monographs dealing with highly conducting polymers have also appeared. The uses of conducting polymers effectively in rechargeable and solar batteries, having the advantage of lightweight and in opto- electronics, in sensors have been already indicated in the earlier sections. Its applications in information transfer and possibly in space and molecular computing are also advocated [5, 14, 35, 59].

A number of theories have been proposed to explain the properties of these materials, although no single simple mechanism can account for the electrical conductivity in different organic polymeric conductors.
There have been attempts made with different types of quantum mechanical approximations [60-71].

In view of the technological and theoretical importance of organic conducting polymers, it was thought to pursue search in this emerging field. In search of a simple model which is easy to comprehend and can explain the electrical conductivity of organic polymers, Pariser- Parr-Pople (PPP) calculations without configuration interactions [72] was done earlier for some organic polymers in this laboratory [17, 18]. It has generally been accepted that an organic polymer having an extended \( \Pi \)-electron system will be conducting. Of the occupied and unoccupied \( \Pi \)-molecular orbitals, the frontier orbitals i.e. the highest occupied molecular orbital (HOMO) and the lowest unoccupied (LUMO) orbital are the most important ones for a variety of chemical reactions and electronic transitions. The difference (\( \Delta E \)) of the energy between the HOMO and LUMO should provide an idea about the ease of movement of electrons in the polymers. In other words, \( \Delta E \) maybe connected in some way to the electrical conductivity in the systems [17, 18].

This simple approach stated above was more or less effective to explain the conductivity in some organic polymeric compounds [17, 18]. While extending this concept to organic polyesters containing azomethine linkage, as in the present investigation, the inadequacies in this approach became apparent and after deliberations it was decided to calculate [73] the frontier electron density type index (\( S_r \)) given by the equation:

\[
S_r = 2 \sum c_i^2 / k_i
\]
where $k_i$ is the electronic energy of the $i^{th}$ molecular orbital, $c_{ir}$ is the coefficient from the $r^{th}$ center to the $i^{th}$ M.O. and to find some relation between this index and conductivity.

The present study involves PPP calculation on a series of polyesters containing azomethine linkages and attempts to correlate electrical conductivity with energy difference between HOMO and LUMO and also with $S_r$ as stated above.

The thesis consists of the following chapters:

**Chapter 1:**

A brief introduction to the present work is provided here.

**Chapter 2:**

The semi-empirical molecular orbital method Pariser-Parr-Pople (PPP) for $\Pi$-electrons has been described in this chapter.

**Chapter 3:**

A brief account of a few thermal methods like TGA, DTA and DSC is presented in this chapter.
Chapter 4:

Synthesis, characterization (elemental analysis, IR, UV and thermal) and electrical conductivity of polyamides and polyesters derived from Schiff’s bases (obtained from aromatic diamines like p-phenylenediamine / benzidine / diaminodiphenylether and salicylaldehyde) and acid chlorides of terephthalic acid and isophthalic acid are described here. The electrical conductivities of these polymers doped with silver have also been measured. Since the Pariser-Parr-Pople (PPP) calculation is practically impossible for a complete polymer chain, the repeating unit of each polymer has been subjected to PPP calculation. The results of these Pariser-Parr-Pople (PPP) calculations are employed to explain the electrical conductivity of these polymers.

Chapter 5:

The synthesis of another series of polyesters containing azomethine linkages is presented in this chapter. The diamines and the acid chlorides are the same as described in chapter IV, but here, 2-hydroxy-1-naphthaldehyde has been used in place of salicylaldehyde. The polymers are characterized by the methods as those employed for the series described in chapter IV. The electrical conductivities of the polymers are also measured and correlated with the results of PPP calculations. Further, the polymers are doped with silver resulting in the significant enhancement of electrical conductivity.
Chapter 6:

A few transition metal complexes of Schiff's bases (employed for the polyester preparation in the present investigation) have been prepared and characterized using different physicochemical methods. The molecular structures of these complexes have been proposed.

Chapter 7:

An overview of the work carried out is given here.

SUMMARY:

A brief introduction to organic polymeric conductors is presented here. The work carried out in the present investigation has also been indicated here.
REFERENCES:


