CHAPTER 1

CONDUCTING POLYMERS
AN INTRODUCTION
1.1 Introduction

For a long time, polymers were considered as nonconductors of electricity and were used as insulating materials. But attempts to make organic materials conducting have already been under way and some success in this direction has been achieved [1]. The charge transfer complex Tetracyanoquinodimethane (TCNQ) - Tetrathiafulvalene (TTF) which has been studied in detail [2] can be regarded as the prototype of conducting organic salts. Recently a compound based on a TCNQ-salt has been used as a solid electrolyte in capacitors [3]. But the lack of reasonable mechanical properties has prevented the widespread applications of these materials. It was a breakthrough, therefore, when Shirakawa found in 1971 that acetylene can be polymerized to give a free standing film with promising mechanical properties [4] and when, somewhat later, MacDiarmid and Heager [5] showed that polyacetylene becomes conducting by exposing it to oxidizing agents like iodine or arsennpentafluoride(AsF₅) and its conductivity can be increased by 13 orders of magnitude to $10^3$ to $10^4$ S/cm. These findings initiated a lot of fundamental investigations, and gave rise to the
development of a new class of materials, which combine the typical properties of plastics with electrical conductivity of metals.

The properties of polymers such as strength, elasticity, plasticity and toughness often compare with those of metals and offer a lot of very important advantages over the latter, normally light weight, greater workability and economy. The important fundamental property which distinguishes metals from polymers is their very high electrical conductivity of the order of $10^{4} - 10^{6} \, \Omega^{-1} \, \text{cm}^{-1}$ [6]. Polymers have generally very high resistivity with conductivity around $10^{-14} \, \Omega^{-1} \, \text{cm}^{-1}$ and this low electrical conductivity has led to widespread use of polymers as electrical insulators [7]. In spite of the low inherent conductivity of polymers, several attempts were made by researches to make them electrically conducting.

Conducting polymers so far developed fall into two distinct groups. The first generation conducting polymers were made by incorporating conductive filler or additives into the normally insulating polymer [8]. Examples are

Rubber + Graphite powder $\rightarrow$ Conductive rubber.

PVC powder + Nickel powder $\rightarrow$ Conductive PVC

Polyster film + Aluminium powder $\rightarrow$ Metallized polyester film etc.
The major practical function of the polymer matrix in these composites is to serve as a 'glue' to hold the conductive elements together in a solid entity. The conductive fillers which are the cause of electrical conduction are evenly dispersed in the polymer matrix. Kusy and Turner [9], and latter Bhattacharya et al. [10] reported the use of 6-10 weight % metallic powder as the conductive fillers, for moderate conductivity. They proposed that the enhanced conductivity at comparatively lower loading of metallic powder is due to the formation of hexagonal ring structure of the metal powder in the polymer matrix. But these composites cannot be regarded as conducting polymers because the polymers present in such composites are non-conducting. These types of polymers are not used as electrical conductor but used mostly in electromagnetic interference shielding applications. The conductivity of these polymers varies as a function of charge incorporated in the polymer, and for charges upto 20% by weight of the polymers, the conductivity ranges between $10^{-6}$ and $10^{-1}$ ohm$^{-1}$ cm$^{-1}$. The concentration of the charges (metallic powders) cannot be increased beyond this limit because then the charged polymers lose the mechanical properties of the host polymer and become less useful [11].
The second generation conducting polymers themselves conduct electric current without the agency of any additives. The delocalized electron cloud and/or non-bonding electrons provide the conduction path in the chain of molecules in these polymers.

The real boom in conducting polymers began only in 1977 when Heeger, Mac Diarmid and Shirakawa [12] at the university of Pennsylvania demonstrated for the first time that polyacetylene which is an insulator exhibits a dramatic increase in electrical conductivity, if it is treated with a strong oxidising or reducing agent. That is, the second generation polymers are either insulators or poor conductors, but on doping they become conducting. The conductivity of such doped polymers depends on the nature of the dopants and level of doping.

Electrical conductivity of the polymers depends on many other factors also.

1) Method of synthesis
2) Method of processing of polymers
3) Degree of crystallinity of polymers and
4) Temperature.

After the polymer is synthesized its purification and processing are very important. Minute concentration of
impurity, particularly an ionic one, has great influence on the conductivity. The degree of crystallinity of the polymer also influences its conductivity appreciably, the conductivity increasing with the degree of crystallinity [13]. Initially the conductivity increases slowly up to 50% crystallinity and then it increases very rapidly.

The chemical stability of a polymer in atmospheric conditions depends on the value of the redox potential. If the reduction potential of a polymer is above the reduction potential of oxygen (-0.146v) the polymer is naturally stable in air. But the same polymer may be attacked by atmosphere if its oxidation potential is higher than that of water (1.23v) [13].

1.2 Historical background of the development of conducting polymers

Natta et al. have reported the polymerization of acetylene by using Ziegler catalyst and obtained polyacetylene in the form of red insoluble powder [14]. This red powder was found to be an insulator. Hatano et al. have also obtained high molecular weight polyacetylene of both crystalline and amorphous types, using various Ziegler-Natta catalysts [15]. This polyacetylene containing long chains of conjugated double bonds has semiconducting
properties. They reported that the polyacetylene was gradually oxidized by air and electrical conductivity decreased by almost five orders, and its colour changed from greenish black to pale orange. It may therefore be assumed that Natta et al. have obtained only the amorphous form of polyacetylene, which may be the CIS-polyacetylene, but the chain structure was complex and far from the expected ideal conjugated carbon chain. Real interest in conducting polymers, arose after the work of Walatka et al. [16] on polysulphur nitride, \((SN)_x\) [17]. Although \((SN)_x\) was first reported by Burt [18], its exciting metallic conductivity was discovered for the first time by Walatka et al. Work on \((SN)_x\) was further stimulated by the observation that it behaves as a superconductor at \(-272.76^\circ C\) [19]. Meanwhile, Shirakawa et al. [20] reported the preparation of a free-standing polyacetylene (PA) film by passing pure dry acetylene gas over the Ziegler-Natta catalyst of titanium tetrabutoxide-triethyl aluminium in toluene at \(-78^\circ C\). They prepared two types of polyacetylene films, one flexible copper coloured and the other silver coloured. The former was confirmed to be Cis-PA and latter to be trans-PA. When these films were exposed to the vapours of bromine and chlorine at room temperature, a dramatic change in their IR spectra occurred without any visible change in the appearance of the films. After the discovery of conducting polyacetylene attempts were made
to synthesize new conducting polymers. In 1979 Diaz and et al. [21] reported a new route for the preparation of conducting polypyrrole by electrochemical synthesis.

The polymerization of pyrrole could be traced back to as early as 1973, when a black amorphous powder was obtained by the oxidation of pyrrole and the polymer was referred to as "pyrrole black" for many years [22]. In the late 1970s and early 1980s, a break-through in poly-pyrrole research occurred when the polymer was prepared in the form of continuous films by anodic oxidation, and was found to have interesting electrochemical properties and a high electronic conductivity [23]. The chronology of the development of some important conducting polymers is given below.

(SN)x synthesized by Burt [18] 1910
Metallic conductivity of (SN)x reported by Walatka et al [17]. 1973
Semiconductivity P.A discovered by Shirakawa et al [20]. 1971
Doping of PA by Shirakawa et al [5]. 1977
Electrochemical synthesis of PPy by Diaz et al [21]. 1979
Conducting PPP by Ivory et al [24]. 1979
Conducting PPS by Rabolt et al [25] 1980
PTh by Tourillon et al. [26] 1982
Conducting Polypara phenylene sulfide by J.E. Forder [27] 1983
Polypyrrole and its derivatives are usually prepared either by electrochemical or chemical polymerization, as depicted in the following equation:

\[
\text{Pyrrole} \quad \overset{\text{Oxidation}}{\rightarrow} \quad \text{Polypyrrole}
\]

The electrochemical polymerization of pyrrole can be performed in either aqueous or organic media [28]. In order to achieve a reasonably fast rate of polymerization, the applied potentials are generally required to be higher than the oxidation potentials of the monomers. However, at high potentials, the polymers undergo undesirable side reactions, such as crosslinking and degradation resulting from over oxidation, leading to substandard quality of the polymers including irreversible loss of electroactivity [28]. The conductivities of chemically prepared polypyrroles are usually lower, than those prepared electrochemically. This is because of the additional resistivity due to the particle-particle transition [29]. The charge transfer salts and the conducting polymers have many features in common for eg., they both exhibit anisotropic, quasi-one dimensional properties [30]. That is, the conductivity is much greater in one direction than in others. In conducting polymers the conductivity is greatest along the chain direction.
1.3 Mechanism of electrical conduction in conducting polymers

The conduction properties of conducting polymers have previously been explained on the basis of the band theory of solids. According to this theory of solids, when a large number of atoms or molecules are brought together to form a polymeric chain or a crystalline solid, an energy band is formed through the interaction of the constituent atomic or molecular orbitals. The band of highest energy that is completely filled by electrons is generally called the valance band. The electrons associated with bands are involved in chemical bonding and are consequently rather localized and are not free to move through the solid. The lowest lying unoccupied levels form a band which is generally called the conduction band. There is a forbidden energy region between the valance band and the conduction band. This energy separation is called the energy gap or band gap, $E_g$. When the energy gap is large the material behaves as an insulator.

Organic polymers are generally insulators because the band gap in them is very large. As a result there are no mobile charge carriers in them to support conduction. The appropriate charge carriers may be generated in an organic polymer by its partial oxidation or partial reduction with
appropriate dopents. The tendency of an organic polymer to get oxidized or reduced is determined by its electronic properties such as the lowest ionization potential and highest electron affinity. Once charge carriers are generated in this way, the system becomes conducting and the effective mobility of these carriers is determined by the corresponding band width. That is, the conduction properties of organic polymers are related to their electronic properties such as band gap, ionization potential, electron affinity and band width.

It was assumed that upon doping, the oxidant removed electrons from the filled valance band and reductants added electrons in to the vacant conduction band. But this model was not useful to explain the conduction mechanism in polyacetylene and other conducting polymers, because from experiments, it was found that the conduction is due to the charge carriers that do not have free spins [31].

To explain the conduction mechanism in conducting polymers, a new model called soliton model was introduced by A.J. Heeger and et al. in 1980 [31]. In this model, charged solitons are believed to be the conducting species for charge transport. Charged solitons are a type of charge defects introduced in a polymer chain on doping with electron acceptors or electron donors. This model was
initially appealing because charged solitons have no spin and the conducting polymers are found to possess spinless transport. The conducting mechanism of polyacetylene agreed with soliton theory because polyacetylene has a degenerate ground state (i.e., two geometric structures corresponding to the same energy). But all other conducting polymers have non-degenerate ground state.

The failure of soliton theory has led to a new theory called polaron and bipolaron theory. According to this concept the polymer chain is ionised on doping and this ionisation process creates a polaron (radical ion) on the chain. At low doping level this polarons are the carriers of electricity. On increasing the doping level the concentration of polaron increases and this results in a probability of interaction with each other, which can be either attractive or repulsive. As a result of this attraction, two polaron may get coupled to form a bipolaron. Bipolarons are doubly charged but spinless. A bipolaron is thermodynamically more stable than two polarons. In the case of polyacetylene, it is believed that due to the degenerate ground state, the bipolarons initially formed disintegrate in to polarons which further decay into spinless charged solitons. Among the conjugated organic polymers, polyacetylene represents a special case because it has a degenerate ground-state, and therefore the
conduction in it is due to soliton and not due to polarons and bipolarons.

The practical realization and the competitiveness of the innumerable applications based on conductivity depend on the stability of the conducting polymers under environmental conditions. Under atmospheric conditions polyacetylene loses its conductivity during 30 days by a factor of 1000 [29], while for polypyrrole a conductivity decrease of only a few per cent is observed over 200 days. A loss of conductivity as found for polyacetylene is intolerable for practical uses. The stability of polypyrrole is comparatively better and may be sufficient for applications which do not demand the conductivity to remain exactly constant. The effectiveness of antistatic devices and shielding equipments for electromagnetic interference, for example, are only weakly influenced by small changes in conductivity [29].

1.4 Chemical synthesis of conducting polymers

Synthesis consists an important part of research on conducting polymers. A brief description of the general procedure for the preparation of conducting polymers is given below.
1.4.1 Polyacetylene

Free standing films of polyacetylene were obtained when acetylene gas was allowed to pass over Ziegler-Natta type catalyst solution in toluene at \(-78^\circ\text{C}\) [32]. The polyacetylene films were formed on the surface of the catalyst solution. The cis/trans ratio of polyacetylene obtained depends on the nature of the catalyst and the polymerization conditions. However, cobalt and nickel containing catalysts, particularly nickel acetylacetonate, offer the best trans-content in the polyacetylene. Polyacetylene was also prepared in arsenic trifluoride solvent using arsenic pentafluoride as the catalyst. The polyacetylene obtained by this process was claimed to be soluble in acetone and tetrahydrofuran (THF) [33].

Shirakawa et al. reported the preparation of freestanding polyacetylene film by passing pure dry acetylene gas over Ziegler-Natta catalyst of titanium tetrabutoxide triethyl ammonium in toluene at \(-78^\circ\text{C}\) [34]. They prepared two types of polyacetylene films, one flexible copper coloured and the other silver coloured. The former is Cis-PA and the latter is trans-PA. The conductivity of Cis PA was found to be \(\sigma = 1.7 \times 10^{-9}\) S/cm and that of trans polyacetylene \(4.4 \times 10^{-5}\) S/cm.
1.4.2 Polyparaphenylene sulphide (PPS)

Polyparaphenylene sulphide, as commercial polymer, is synthesized by reacting p-dichlorobenzene with anhydrous sodium sulphide at 260°C, under normal pressure or at 140°C under 19 atm pressure. A small amount of reducing agents, such as hydrazine [35] or sodium sulphide is added to the polymerizing solution. The crucial step in the synthesis is the dehydration of sodium sulphide.

1.4.3 Polyparaphenylene (PPP)

Like PPS, polyparaphenylene is prepared by the step polymerization process involving the reaction of 1,4 dibromobenzene with magnesium in the presence of nickel chloride bipyridyl catalyst. The use of catalyst promoter was reported to produce 92 to 100% yield.

1.4.4 Polypyrrole

The theme of this thesis is the preparation of polypyrroles containing different counter anions and investigation of their properties, and hence a detailed account of their synthesis is given in chapter 2.
1.5 Electrochemical synthesis

Conducting heterocyclic polymers such as polypyrrole, polythiophene, polyfuran and their derivatives are usually obtained from their monomers by electrochemical polymerization and simultaneous doping with a dopant [28]. The technique of electrochemical polymerization essentially makes use of an electrochemical cell consisting of one or two compartments made of glass or teflon. The cell consists of an anode, a cathode and a reference electrode which is generally the standard calomel electrode (SCE). The anode is generally a metallic foil such as platinum, nickel, or a semi-conducting film such as indium tin oxide (ITO). The cathode is usually a platinum wire. The electrochemical reaction is generally carried out in a non-aqueous medium and the solvents generally used are acetonitrile, benzonitrile or tetrahydrofuran. The simultaneous doping of the polymer is done by carrying out the electrochemical reaction in the presence of both a chosen and a supporting electrolyte which could either be a quaternary ammonium salt of the type $R_y N^+X^-$ (where $R$ = alkyl, aryl radical and $X^-$ = Cl$^-$, Br$^-$, I$^-$, ClO$_4^-$, BF$_4^-$, PF$_6^-$) or a metal salt of the type $MX$ (M = Ln$^-$, Na$^+$, Ag$^+$ and $X$ = BF$_4^-$, ClO$_4^-$, PF$_6^-$, AsF$_6^-$).
The electro-chemical polymerization offers a number of advantages: (1) homogeneous polymer films of controllable thickness are obtained (2) films are formed directly at the electrode surface (3) reaction is carried out at room temperature, and (4) doping of the polymer can be achieved with the desired ion simultaneously.

1.6 Doping methods

The term "doping" as applied to inorganic semiconductors does not really apply to the organic semiconductor field because the processes are fundamentally different. Nonetheless, the term is widely applied to polyacetylene and other organics.

Doping of the polymers may be done by the following methods.

1) Gaseous doping.
2) Solution doping.
3) Electrochemical doping.
4) Self doping.
5) Radiation-induced doping.

In gaseous doping, polymers are exposed to the vapours of the dopent under low pressure. In the solution method the dopant is dissolved in the appropriate solvent
in which all the products of doping are soluble. Only low level doping is achieved by this method. In electrochemical doping both polymerization and doping occur simultaneously. In self doping process, ionizable groups covalently linked to the polymer chain serve as dopants. Doping can also be achieved by irradiating the polymer. High energy radiation is used to augment doping of polymers by neutral dopants. Neutron radiation, for example, was used for radiation induced doping of thiophene by iodine.

1.7 Effect of doping on polymers

The principal objective of doping of polymers is to enhance their electrical conductivity. In most cases phenomenal increase in conductivity of the order of $10^8$-$10^{12}$ results. The electrical conductivity of the doped polymers depends on the nature of dopents used, the process of doping and doping level of the dopant in the polymer, and temperature.

Since doping involves a redox type reaction, the reduction or oxidation potential of the dopent determines its suitability for being used as the dopant for a particular polymer. For example iodine is too week to oxidize PPS or PPP, but AsF$_5$ is strong enough for this oxidation.
Doping conditions and doping techniques also influence the conductivity of doped polymers. In the process of doping of PPS with AsF$_5$ the saturation level of conductivity is achieved within 2 hours at 50°C, but at room temperature, it requires 24 hours. Electrochemical doping is sensitive to the presence of oxygen and moisture in the electrolyte. For example, the conductivity value increases 25 to 75 times when the electrochemical doping of poly(3-methyl) thiophene with perchlorate is carried out in the absence of oxygen and moisture. On doping, conducting polymers become more unstable in environmental conditions. Thus the rate of decrease of conductivity in doped polymers is greater than that in undoped polymers. In general, polymers on doping become more unstable in outdoor conditions and sensitive to higher temperatures.

Polymers are insulators because of the intrinsic property of the C-C covalent bond. They lack conducting paths as well as charge carriers while conjugation in the polymer chain provides path for carrier movement. Doping or complex formation with electron donor or acceptor species generates charge carriers and converts insulating polymers into conductors.
1.8 Stable and processable conducting polymers

It is well known that extended carbon chain conjugated polymers such as polyacetylene have two drawbacks: poor stability and poor processibility. Any attempt to overcome these drawbacks results in the reduction of electrical conductivity of the polymer. A good design of a conducting polymer may consist of a polymer backbone which will be embedded, so to say, in electron clouds not only from the delocalized \( \pi \) electrons of carbon-carbon multiple bonds but also from non-bonding electrons of heteroatoms such as nitrogen, sulphur, phosphorus etc. Maiti et al. have utilized this concept and synthesized two polymers, one containing sulphur atoms and the other phosphorus atoms in the backbone. Both the polymers synthesized, are soluble in organic aprotic solvents and possess remarkable thermal and environmental stability.

1.9 Electrochemical property - Cyclic voltammetry

The electropolymerized films of conducting polymers show cyclic voltammetry responses. That is, the electrochemically prepared polymer films are electroactive and can be switched between the neutral and non-conducting state to the oxidized and conducting state. This behaviour was first demonstrated with thin polypyrrole
films of thickness 200-400 Å. The anodic and cathodic waves in the cyclic voltammetry of a conductive polymer are not symmetrical and in some cases (thiophenes) the cathodic region is complex and shows two peaks, the first one corresponding to an intermediate state of the polymer. The shape of the two waves and the value of the potential separation between the peaks suggest that the electrochemical reaction is quasireversible and that the reduction and oxidation kinetics which are limited by a slow ion diffusion in the film and/or a slow electron transfer may be different.

The peak currents increase linearly with the thickness of the film and within the scan rate up to 200 mv/sec. The peak-to-peak separation increases when the scan rate increases and the redox waves become broader when the thickness increases. The peak positions depend on the nature of the supporting electrolyte, and shape of the voltammograms may be different. In the case of polypyrrole films, the oxidation reaction is chemically reversible and can be driven repeatedly without loss of electroactivity.

1.10 Progress towards technology

Present interest in conducting polymers is primarily due to various novel applications envisaged for such
polymers. Some of the possible areas of application are polymer battery electrodes, rechargeable batteries, EMI Shielding and solar cells. In all these applications low density, low cost, ease of fabrication, flexibility of design, colourability, low energy and labour requirements for fabrication and processing, etc. are the advantages polymers generally enjoy over other materials. Many limitations of the present-day polymers have to be overcome. Future Research and development activities should address to the following aspects.

1) Stability of virgin and doped polymers.

2) Better processability.

3) Achieving higher molecular weights for better mechanical and durability properties.

4) Metallic conductivity at low levels of doping.

Most conducting polymers such as doped polyacetylene, polyphenylene, and poly(P-phenylene sulfide) are not stable in air. Reaction with atmospheric water vapour appears to be an important factor contributing to the degradation of conductivity on exposure of the doped materials to air. Donor doped polymers have poor stability in air, presumably due to reaction with oxygen and water. Only recently have several air-stable
conducting polymers been discovered. These include polythiophene, polypyrrole and polyaniline. In polypyrrole, air stability has been demonstrated as long as the polymer is held in its doped, conductive state. Since environmental stability is crucial for many applications, detailed research work needs to be undertaken in order to clarify the mechanistic origins of the observed instabilities and stabilities in conducting polymers.

1.11 Work undertaken in the present study

As mentioned in section 1.2 of this chapter a variety of conducting polymers have been developed since the synthesis of polyacetelyne film by Sherakawa et al. Some of them are fairly stable at ambient conditions and at elevated temperatures but some others are much less stable and are not suitable for practical applications. For the present studies, the author has chosen polypyrrole in view of its fairly good stability at ambient conditions and at elevated temperatures, ease of its preparation and its wide range of practical applications.

Polypyrrole films containing various counter ions have been synthesized by many researchers using chemical and electrochemical polymerization reactions and their conductivity properties has been studied in detail. But
polypyrrole films containing both \((\text{MoO}_4)^{2-}\) and \((\text{SO}_4)^{2-}\), \((\text{MoO}_4)^{2-}\), \((\text{PO}_4)^{3-}\) have been not studied so far. In this thesis the author reports the detailed electrochemical and chemical methods of synthesis and the characterization of polypyrroles using these anions.
References

