CHAPTER I

INTRODUCTION

1.1.Conducting Polymer

An organic polymer that possesses the electrical, electronic, magnetic, optical properties, and meanwhile retaining the mechanical properties, processability of a conventional polymer is termed an 'intrinsically conducting polymer' (ICP), more commonly known as a 'synthetic metal' (Salaneck *et al.*, 1993). For the past 50 years, conventional insulating polymer systems have been increasingly used as substitutes for structural materials such as wood, ceramics, and metals because of their light weight, high strength, ease of chemical modification/customization, and processability at low temperatures. In 1977, the first electrically conducting organic polymer, doped polyacetylene, was reported, spurring interest in 'conducting polymers'. The common electronic feature of pristine (undoped) conducting polymers is the π- conjugated system which is formed by the overlap of carbon p_z orbitals and alternating carbon-carbon bond lengths (Mark *et al.*, 1996) shown in schematically in Fig.1. Other conducting polymers found are, for examples, poly(p-phenylene)(PPP), polypyrrole (PPy) , poly(p-phenylene)sulfide (PPS), polythiophene (PT), polycarbazole (PCB), polyquinoline , and polyaniline(PANI) (Salaneck *et al., 1993)*.
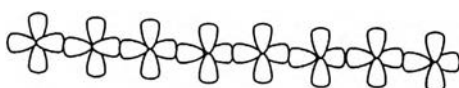
**Figure 1.1** Schematic of the π- conjugated system in polyacetylene.

1.2.Conduction Mechanisms

Electrical conductivity is a function of the number of charge carriers of species 'i'(n_i), the charge on each carrier (ε_i), and carrier mobilities (μ_i) . Conduction in solids is usually explained in terms of the band theory which is described by the relation $\sigma = \Sigma\mu_i\ n_i\ \varepsilon_i$ where the unit of conductivity is S cm^{-1}. It is postulated that when atoms or molecules are formed in the solid state, the outer atomic orbitals containing the valence electrons are split into bonding and antibonding orbitals, and are mixed to form two series of closely-spaced energy levels. These are usually called the valence band and the conduction band, respectively. If the valence band is only partly filled by available electrons, or if the two bands overlap so that no energy gap exists between them, then application of an electrical potential will raise some of the electrons into empty levels where they will be free to move throughout the solid thereby producing a current. This is the description of a *conductor*. If, on the other hand, the valence band is full and is separated from the empty conduction band by an energy gap, then there can be no net flow of electrons under the influence of an external field unless electrons are elevated into the empty band and this process will require a considerable expenditure of energy. Such materials are either semiconductors or insulators, depending on how large the energy gap may be. The band model then assumes that the electrons are delocalized and can extend over the lattice. The majority of polymers are insulators

For the electrical conduction in a polymer, the band theory is not totally suitable because the atoms are covalently bonded to one another, forming polymeric chains that experience weak intermolecular interactions. Thus macroscopic conduction will require electron movements, not only along chains but also from one chain to another (Mark *et al.*, 1996).

1.3.Polyaniline

Polyaniline (PANI), the oldest organic polymer ever synthesized, has received renewed scientific and technological interest due to its richness in its chemistry/physics and its potential/practical applications in electrical devices (Xia *et al.*, 1994). Furthermore, the electrical properties can be substantially improved through secondary doping. Traditionally, the aniline polymers have the general formula $[(-B-NH-B-NH-)_y(-B-N=Q=N-)_{1-y}]_x$, in which B and Q denote the C_6H_4 rings in the benzenoid and quinonoid forms, respsctively. Thus, aniline polymers are basically poly(p-phenyleneimineamine), in which the neutral intrinsic redox states can vary from that of the fully oxidized pernigraniline (PNA, y=0), to that of the fully reduced leucoemeraldine(LM, y=1). The 50% intrinsically oxidized polymer has been termed emeraldine (EM, y=0.5), and the 75% intrinsically oxidized polymer, is termed nigraniline (NA, y=0.75). Fig.2 shows the octameric representation of the various intrinsic redox states of polyaniline (PANI) (Kang *et al.*, 1998).

Leucoemeraldine

Emeraldine

Nigraniline

Pernigraniline
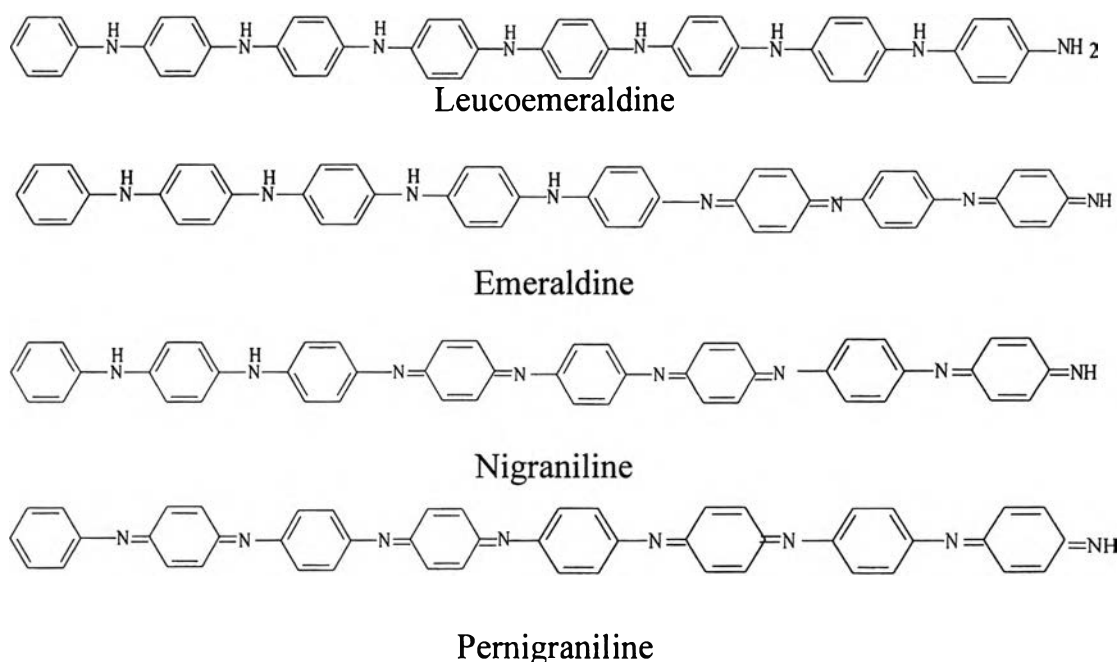
Figure 1.2 Octamer structures of polyaniline in various intrinsic redox states.

In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depending on its oxidation state and on pH of the aqueous acid. Moreover, it can also form a rich set of structures dependent upon the processing sequence and dopant (Show-An Chen *et al.*, 1995).

The high electrical conductivity is achieved by the method known as 'doping process'.

1.4. The Concept of Doping

The doping of all conducting polymers is accomplished by the so called redox doping. This involves the partial addition (reduction) or removal (oxidation) of electrons to or from the π system of the polymer backbone.

The concept of doping is of a unique underlying theme which distinguishes conducting polymers from all other types of polymers. During the doping process, an organic polymer, either an insulator or semiconductor, having a small conductivity, typically in the range 10^{-10} to 10^{-5} Scm^{-1}, is converted to the polymer which resides in the 'metallic' conducting regime (≈ 1 to 10^4 Scm^{-1}). The controlled addition of known, usually small ($< 10\%$) and non-stoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer. Doping can be reversible to produce the original polymer with a little or no degradation of the polymer backbone. Doping and undoping processes, involving dopant counterions which stabilize the doped state, maybe carried out chemically or electrochemically.

In the 'doped' state, the polymer backbone of a conducting polymer consists of a delocalized π system. In the 'undoped' state, the polymer may have a conjugated backbone such as in trans-(CH)$_x$ or it may have a non-conjugated backbone, as in polyaniline (leucoemeraldine base form), which becomes conjugated only after doping or a non-conjugated structure as in the
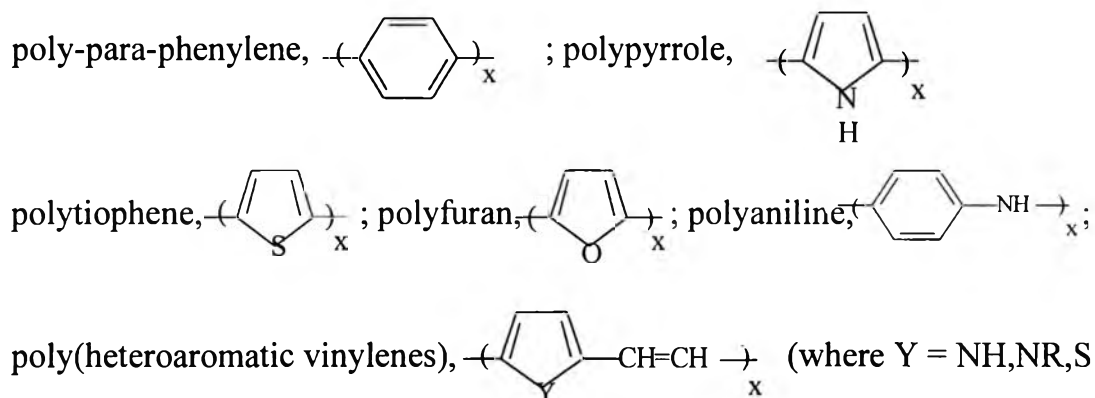
emeraldine base form of polyaniline which becomes conjugated only after protonic acid doping.

1.5.Doping process

Doping process can be divided into three main types:

<u>1.5.1 Redox doping involving dopant ions</u>

All conducting polymers (and most of their derivatives), e.g.

poly-para-phenylene, ; polypyrrole,

polytiophene, ; polyfuran, ; polyaniline,

poly(heteroaromatic vinylenes), (where Y = NH,NR,S

and O) ; etc, undergo either *p*- and/or *n*-redox doping by chemical and/or electrochemical processes during which the number of electrons associated with the polymer backbone changes.

1.5.1.1 Chemical and electrochemical p-doping

P-doping, partial oxidation of the π backbone of an organic polymer, was first discovered by treating *trans*-polyacetylene with an oxidizing agent such as iodine (Salaneck *et al.,* 1993), viz.

$$trans\text{-}[CH]_x + 1.5\,xy\,I_2 \longrightarrow [CH^{+y}(I^3)^-_y]_x \qquad (y < 0.07)$$

This process was accompanied by an increase in conductivity from $\approx 10^{-5}$ to $\approx 10^3$ Scm^{-1}.

1.5.1.2 Chemical and electrochemical n-doping

N-doping, partial reduction of the backbone π system of an organic polymer, was also discovered by using *trans*-(CH)$_x$ and treating it with a

reducing agent such as liquid sodium amalgum or preferably sodium napthalide (Salaneck *et al.,* 1993), viz.

$Trans\text{-}[CH]_x + (xy)Na^+(Naphth)^- \longrightarrow [Na_y^+(CH)^{-y}]_x + Naphth \ (y < 0.1)$

The antibonding π^* system is partially populated by this process which is accompanied by an increase in conductivity of $\approx 10^3 \ Scm^{-1}$.

1.5.2 Redox doping involving no dopant ions

1.5.2.1 Photo-doping

When *trans*-$(CH)_x$, for example, is exposed to a radiation of energy greater than its band gap electrons are protonated across the gap and the polymer undergoes 'photo-doping'.
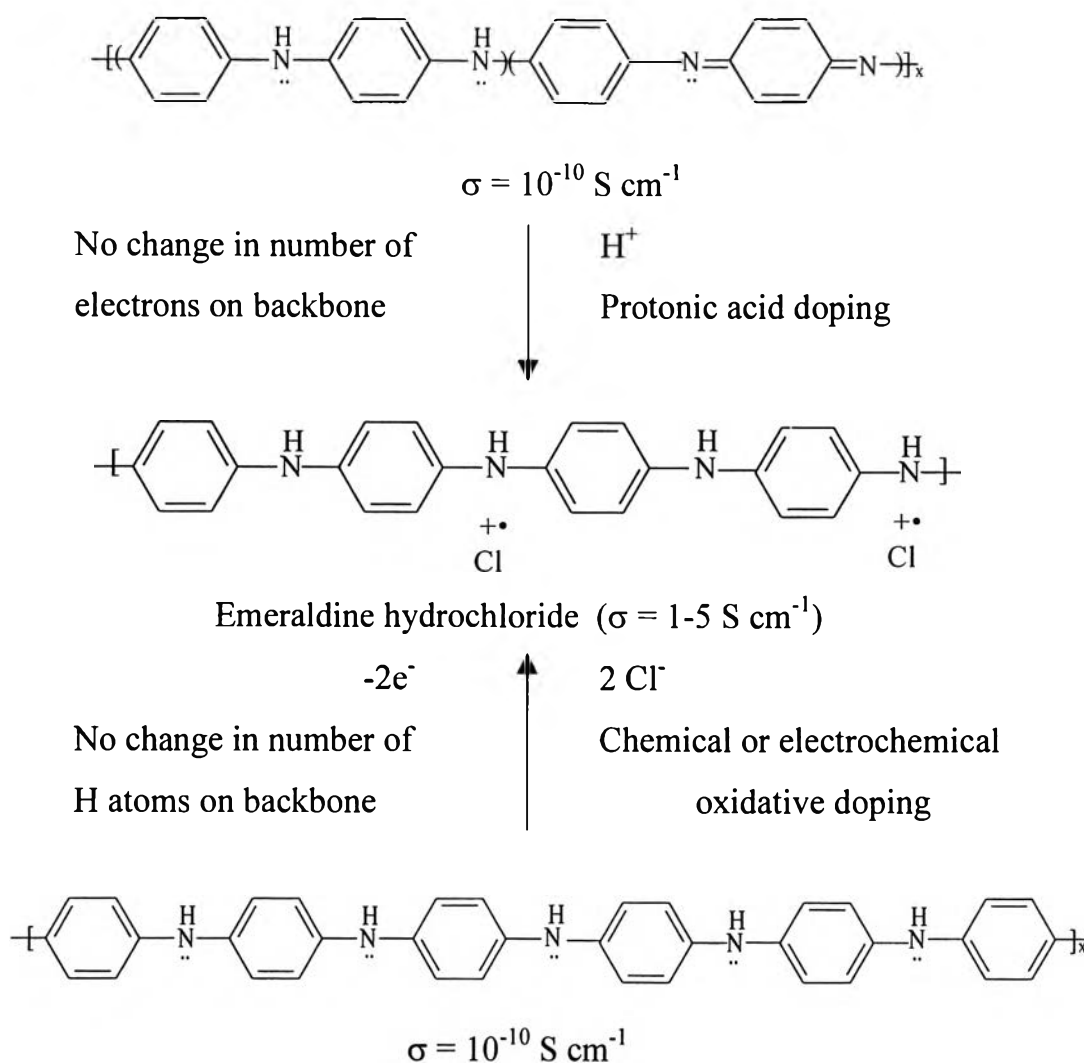
1.5.2.2 Charge-injection doping

It is the most conveniently carried out using a metal/insulator/semiconductor (MIS) configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator. Application of an appropriate potential across the structure can give rise, for example, to a surface charge layer, the 'accumulation' layer which has been extensively investigated for conducting polymers. The resulting charges in the polymer, e.g. $(CH)_x$ or poly(3-hexylthinylene), are present without any associated dopant ions so that the spectroscopic properties of the charged species so formed can be examined in the absence of dopant ion. However, the coulombic interaction between charges on the chain and the dopant ions is a very strong interaction and one that can totally alter the energetics of the system. Studies of this type of polymers strongly suggest that the formation and role of bipolarons in chemically and/or electrochemically doped polymers should be carefully re-examined since they may be stable only in the presence of the dopant counterion.

1.5.3 Non-redox doping

This type of doping differs from the redox doping described above in that the number of electrons associated with the polymer backbone does not

change during the doping process. It is accomplished by treating an emeraldine base with aqueous protonic acids and is accomplished by a nine to ten order of magnitude increase in conductivity (up to$\approx 10^2$ Scm^{-1}) to produce the protonated emeraldine base (Salaneck *et al.*, 1993), viz.

Scheme 1.1 Doping process of emeraldine base by protonic acids.

1.6. Doping of Polyaniline

Polyaniline holds a special position amongst conducting polymers in that its most highly conducting doped form can be obtained by two completely different processes - protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base units with, for example 1M aqueous HCl results in complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine hydrochloride salt.

The relationship between protonic acid doping and oxidative doping of different forms of polyaniline to give the same conducting material is illustrated diagrammatically below (Salaneck *et al.*, 1993):

$\sigma = 10^{-10} \text{ S cm}^{-1}$

No change in number of electrons on backbone

H^+

Protonic acid doping

Emeraldine hydrochloride ($\sigma = 1\text{-}5 \text{ S cm}^{-1}$)

$-2e^-$

No change in number of H atoms on backbone

2 Cl^-

Chemical or electrochemical oxidative doping

$\sigma = 10^{-10} \text{ S cm}^{-1}$

Scheme 1.2 Doping diagram of polyaniline.

1.7. Applications Associated with the Various Redox States

A large number of applications and potential applications arising from the presence of the various redox states, their inter-conversions and their charge transfer interactions have been reported in the patent and scientific literature (Salamone , 1996).

The ability of PANI to assume a number of stable intrinsic oxidation states and the ability of these intrinsic oxidation states to undergo reversible protonation/deprotonation and charge transfer interactions have resulted in a

large number of recent claims of PANI and its derivatives as elements for gas, chemical and pH sensors, as components of electroactive composites and as selectively permeable membranes. For example, a thin film of PANI in the reduced or oxidized states can be used to determine the presence of an oxidant or a reductant, respectively, in a particular environment through the simple measurement of color changes (Cui *et al.*, 1995). The ability of PANI to exhibit a number of intrinsic oxidation states has also been utilized in the inhibition of corrosion of metals (Wessling, 1995). The chemical process leading to the passive state of metal surface by PANI is not yet fully understood. For EM base coated on steel, depending on the open-circuit voltage of the electroactive polymer in the corrosive medium with respect to that of stainless steel, the polymer can undergo reduction to passive the steel. The reduced polymer will then be re-oxidized by air. The polymer in this case will function indefinitely (Ahmad *et al.*, 1996). Alternatively, in the case where the polymer has a high open-circuit voltage in the corrosive medium, the electroactive polymer will function as a sacrificial metal in the cathodic protection of the steel until it is completely consumed (Wessling , 1995).