

CHAPTER I

INTRODUCTION

1.1 Electrically Conductive Polymers

1.1.1 Basic Concepts

Electrically conductive polymers are composed of conjugated polymer chains with π -electrons delocalized along the backbone. Figure 1.1 shows the chemical repeat units of undoped forms of several families of conducting polymers. They display unusual electronic properties such as low energy optical transitions, low ionization potentials, and high electron affinities therefore they can be oxidized or reduced more easily and more reversibly than conventional polymers and can behave like semiconductors.

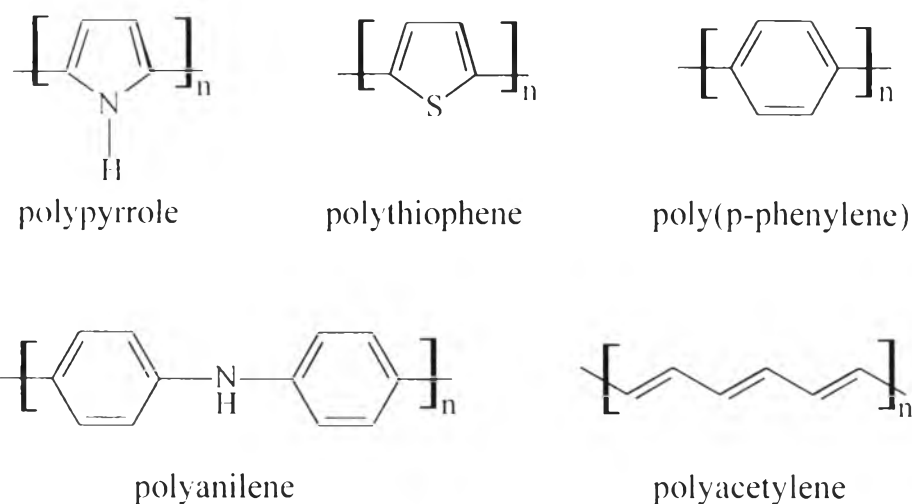


Figure 1.1 Repeat unit of several electrically conductive polymers.

The electrical conduction properties of conductive polymers are controlled by the addition of small quantities of foreign atoms into the host polymer matrix. Both *n-type* (electron donating) and *p-type* (electron accepting) dopants have been utilized to induce an insulator-metal transition in conductive polymers. New dopant energy levels are introduced into the band gap and conduction is facilitated. The conductivity level attained depends strongly on the concentration of donor or acceptor species incorporated.

The partial oxidation of the polymer chain is termed p-doping. The basic process involves the removal of electrons from the π -electrons delocalized network to form a positively charged repeat unit :



where P represents the basic monomeric repeat unit in the polymer, A^- indicates a p-type dopant. x and y are balanced coefficients. If the polymer chain is partially reduced, one has n-type doping as follows :



where M^+ indicates a n-type dopant. These processes are called *doping reaction*. From these reactions the insulating polymers are converted to conducting polymers because the delocalized charges on the polymer chains are mobile and are thus the current-carrying species for conduction. Charge balance is accomplished by the incorporation of an oppositely charged counter ion into the polymer matrix.

1.1.2 Charge Carriers and Conductivity in Electrically Conductive Polymers

A brief summary of band theory is useful at this point. Electrical conductivity depends on a number of fundamental parameters such as the density of mobile charge carriers (n), the carrier charge (q), and the carrier mobility (μ). The relationship between the conductivity (σ) and the latter quantities is expressed *via* the general relationship :

$$\sigma = nq\mu \quad (1.3)$$

Conduction in solids is usually expressed in terms of the well-established band theory. In this model it is assumed that a solid consists of an N -atom system where the atoms are tightly packed together. Each individual electronic energy state splits into N levels. Typically there are about 10^{22} atoms/cm³ in a crystalline solid, and so the energy levels are spaced very close together. Hence one may ignore the discreteness of the levels and consider a continuous energy band. Due to the periodic nature of a crystalline solid, one will have energy gaps between the various energy bands. The highest occupied energy band is termed the valence band, whereas the lowest unoccupied energy band is termed the conduction band. Only charge carriers with energies near the top of the valence band can contribute to the electronic conduction by being thermally promoted to the empty conduction band where they are free to move under the influence of an applied electric field.

Metallic conductors are characterized either by a partially filled valence band or by the presence of a marked degree of overlap between the valence and conduction bands. On the other hand, semiconductors/conductive polymers are characterized by the presence of an appreciable band gap between the top of the valence band and the bottom of the conduction band. Hence the ease of promotion of electrons across the band gap to generate mobile

conducting carriers in the conduction band will depend on the magnitude of the band gap. In simple terms semiconductors/conductive polymers have reasonably low band gaps whereas the gap for insulators is rather large. The situation is outlined schematically in Figure 1.2

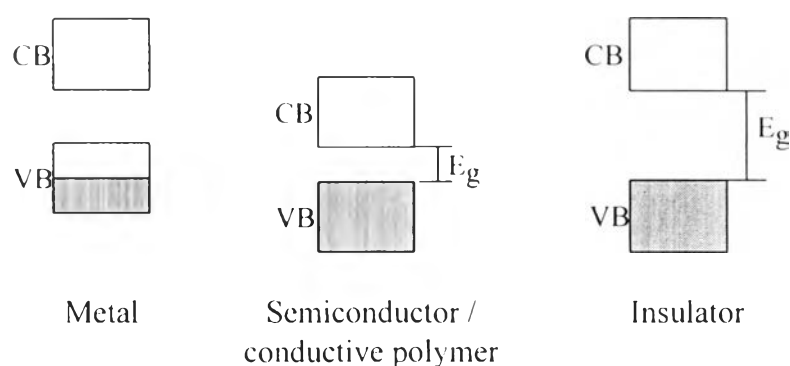


Figure 1.2 Schematic representation of band structure of metal, semiconductor / conductive polymer, and insulator. VB and CB represent valence and conduction bands, respectively. Shaded regions denote filled electronic states, whereas unshaded regions represent unoccupied electronic states.

Charge carriers in conducting polymers differ from metals [Chance *et al.* (1984)]. Metals have unpaired electrons. Electronic conductivity results from the fact that the electrons can move readily under an electric field since there is no forbidden gap. Conductivity is limited, therefore, by defects in lattice and vibrational distortions (also called *phonons*). Since this phonon activity increases with elevated temperatures, the conductivity of metals is reduced as temperature increases. In the case of conducting polymers, as in inorganic semiconductors, the electrons are paired, creating a band gap. The energy difference between these bands gives rise to the intrinsic insulating or semiconducting properties of conjugated organic polymers. The moderate

conductivity of these materials is a result of thermal excitation of valence electrons into the conduction band. Therefore, the conductivity of semiconductors and conjugated organic polymers increases with increasing temperature in the neutral or undoped state.

The charge carriers or charge defects could be formed when the conductive polymer is doped. When one electron is removed (or added) to the polymer chain a radical cation (or anion) is formed. This results in a lattice distortion which leads to an upward shift for the valence band and a downward shift for the conduction band. This radical ion associated with a lattice distortion is called a *polaron*. A similar argument can be used when a second electron is removed from (or added to) this site. The resulting species is a dication (or dianion), with a lattice distortion separating the two charges. This species is termed a *bipolaron*. At high doping levels the bipolarons interact to form bipolaron bands within the energy gap. This process is illustrated in Figure 1.3.

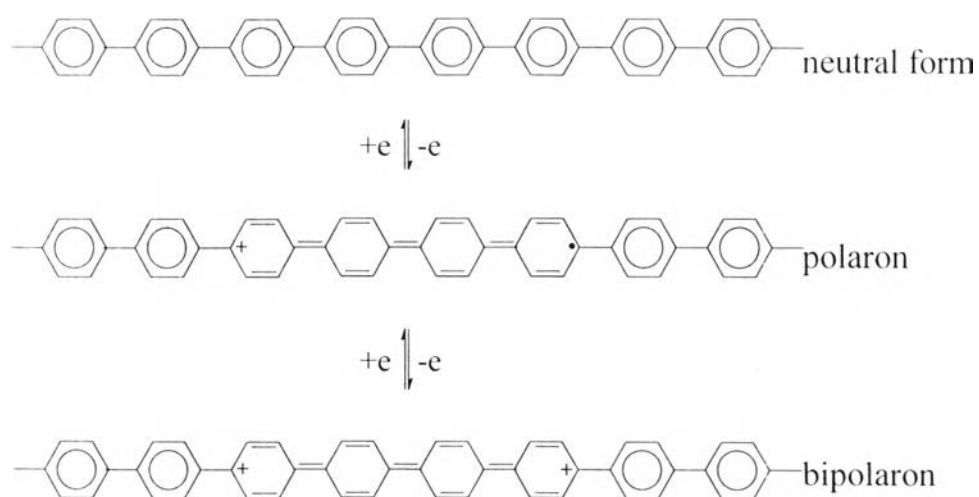


Figure 1.3 Generation of polaron and bipolaron defects in conjugated organic polymer such as poly(p-phenylene).

In the doped form, transition between the band edges and newly formed intragap electronic states are observed in the optical spectra of conducting polymers. When polarons are present as charge carriers, an additional transition is apparent which corresponds to the electronic transitions between the two gap states. Since the intragap electronic states are taken from the band edges, the band gap increases with increasing doping levels. Also, since a bipolaron creates a larger lattice distortion than a polaron, the gap states are farther away from the band edges in the bipolaron model. The band structure of doped conductive polymer is shown in Figure 1.4.

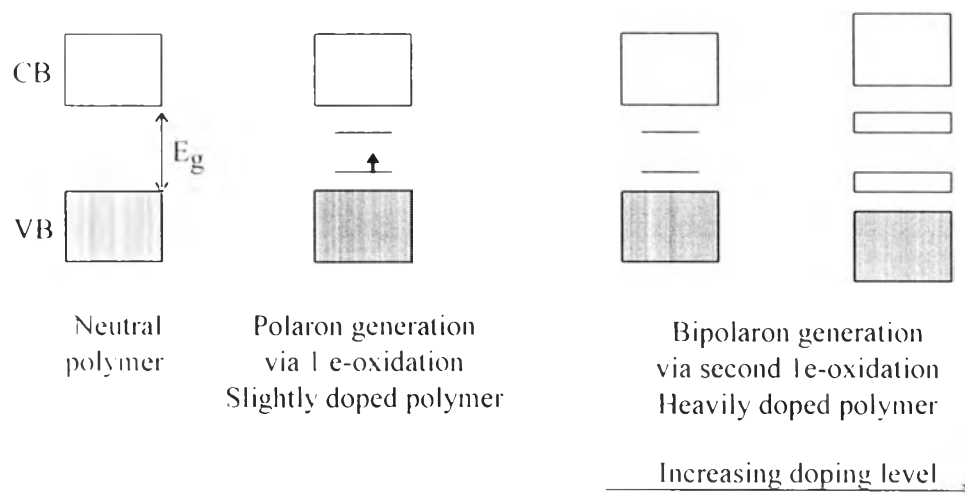


Figure 1.4 Band structure of conjugated polymer as function of doping level illustrating polaronic and bipolaronic states in band gap. Electronic conduction involves both polarons and bipolarons.

1.2 Conductive Polymer Films in Gas Sensor Applications

Recently, after the discovery of conducting polymers, it became clear that their properties made them attractive candidates for gas sensing applications, replacing metal sensing devices. Conducting polymers offer a lot of advantages for sensor technologies [*Gabor (1995)*];

- they are relatively low cost materials because a wide variety of polymers are available
- their fabrication techniques are quite simple (there is no need for special clean room and/or high temperature process)
- they can be deposited on various types of substrates
- in many cases these materials exhibit fast reversible changes in conductivity when exposed to gases and vapors at room temperature
- the wide choice of their molecular structure and the possibility to build in side chains, charged or neutral particles and even grains of specific behavior into the bulk material or on its surface region enables producing films with various physical and chemical properties.

The electrical conductivity is related to the redox interaction with certain gases. A variation of doping level of conducting polymer can be modulated by interaction with various substrates. The conductive polymer gives many responses to certain gases.

The general adsorption of gas molecules to conductive polymers is strongly due to the electronic effects. Electrophilic gases such as NO_2 withdraw electrons from the polymer, thereby increasing the number of charge carriers and hence the conductivity, while nucleophilic gases such as NH_3 have the opposite effect resulting in a conductivity decrease. However, *Esther et al.*

(1991) attempted to study the other mechanism for describing the response of conductive polymers to organic vapors where the electronic theory is not a satisfactory explanation. It has been shown that certain vapors such as methanol, have a solvent type action on the polymer, causing it to swell and this dimension change was accompanied by a conductivity change. In this work, we focused on SO_2 because it is an environmentally hazardous gas that exhibits electron accepting behavior and is present in forms of SO_3^- , SO_4^{2-} .

1.3 Polypyrrole

Polypyrrole is one of the most attractive polymers to come from a new class of materials which have special electrical properties. Polypyrrole can fulfill almost all of the requirements listed above for an ideal conductive polymer and exhibit excellent thermal and electrical properties. It has found wide applications in the gas sensing technology.

In general, polypyrrole polymerized either electrochemically or chemically is known to be insoluble and infusible due to the strong inter- and intra-molecular interactions and crosslinkings [Qian *et al.* (1993)]. The poor processibility of polypyrrole has limited its applications.

In this project, I used a new synthetic route to chemical polymerization of polypyrrole soluble in an inorganic solvent and electrically conductive in the dried state [Lee *et al.* (1995)].

1.4 General Objectives

The objective of this research project is to evaluate a suitable polymer for gas sensing application. The desired specifications include ;

1. the polymer must be a conducting polymer
2. the polymer has high sensitivity for gases which are environmentally harmful or pose health hazards
3. the polymer can be deposited on a substrate in form of thin film
4. the polymer has to be stable over a wide range of temperatures
5. the polymer exhibits reversible behavior in the conductivity change after exposure to certain gases.

1.5 Literature Survey

Polypyrrole is very popular in gas sensing technology over other conducting polymers because of ease in synthesis and its relatively high stability. *Street et al. (1982)* studied the environmental stability of polypyrrole and found that air stability was demonstrated as long as the polymer was held in its doped, conductive state. Polypyrrole can be synthesized by both chemical and electrochemical polymerizations. An important problem for many applications of the both synthesized polypyrrole and other conductive polymers is their solubility because of strong inter- and intra-molecular interactions and crosslinkings. There were some researchers who have been trying to improve the solubility. *Lee et al. (1995)* reported that a polypyrrole, synthesized at low temperature and doped with dodecylbenzene sulfonic acid (DBSA) dissolved in

m-cresol and partially dissolved in chloroform. The resulting polypyrrole film exhibited a conductivity of about 0.5 - 2 S/cm.

The sensitivity of electrical properties of conductive polymers to chemical stimuli suggests they may prove useful in a number of sensing applications. Conductivity is heavily dependent on the level of primary doping. Addition of another type of electroactive molecule to the polymer can be viewed as a secondary doping and, as expected, it also affects the conductivity of conducting polymer, albeit usually less than the primary doping. Nevertheless, this incremental change of conductivity is the basis for operation of conductimetric chemical sensors.

Interdigitated electrodes covered by a polypyrrole layer have been tested by *Miasik et al. (1986)* for the detection of NH_3 , NO_2 and H_2S gases. These sensors proved to be quite sensitive with large conductance changes occurring with exposure to an atmosphere containing 0.01 - 0.1% of the reactive gas since Polypyrrole is p-doped, electron-donating gases like NH_3 reduce the carrier density hence there is a conductivity decrease on exposure to NH_3 . In contrast, NO_2 withdraws electrons and increases conductivity. In all three cases the reactions were shown to be reversible as removal of the gas from the atmosphere led to recovering of the original conductivity.

Yoshino et al. (1986) reported that undoped poly(p-phenylene)(PPP) and poly(p-phenylenevinylene) also showed reversible changes upon ammonia exposure, but in this case the conductivity increased in contrast to Polypyrrole, where the conductivity decreases reversibly upon ammonia exposure. The conductivity of conducting polymers like doped PPP and doped polyacetylene were, as reported by *Chiang et al. (1977)* decreased irreversibly by several orders of magnitude when they were exposed to ammonia.

The influence of ammonia on electrochemically prepared polypyrrole was reported by *Gustafsson et al. (1987)* It was demonstrated that both a

reversible and irreversible change of the electronic properties of the polymer occurred. Some possible origins of these changes were discussed, such as the formation of ammonia-anion complexes and a breaking of the polymer chains. Later *Gustafsson et al.* (1989) showed that in addition to the previously reported change, there was also a large irreversible change if the material was exposed to high concentrations of ammonia and ammonia plus water vapor for a long period of time. The FT-IR, X-ray photoelectron spectroscopy and elemental analysis also indicated that amide-type carbonyl groups, amine groups and ammonium ions could also be present in the irreversibly changed polymer.

Tetsuro et al. (1989) observed the response of the electrochemically synthesized polypyrrole when exposed to the electron acceptor gases. Electropolymerized polypyrrole films exhibited noticeable gas sensitivities to PCl_3 , SO_2 and NO_2 at room temperature only when they were reduced electrochemically, and the resistance decrease was larger with the gas of larger electron affinity.

The optical property change of polypyrrole and poly(p-phenylene) films exposed to various vapors, such as MeOH, CHCl_3 , CH_2Cl_2 , was studied by *Blackwood et al.* (1991). They clearly demonstrated that the chemical doping caused by these gas exposures presented a change in optical densities. And they found that this chemical doping was not as high as that achieved by the primary electrochemical doping. The resulting chemical doping was clearly dominated by the carrier change density present in the film affecting conductivity.

When conductive polymer is exposed to the reactive gases, a redox interaction occurs and then the charge carriers are created on the polymer chain. These charges introduced are compensated by ions from the reaction medium, so a mass change of polymer may occur. Therefore *Esther et al.* (1991) studied this mass change. They reported polypyrrole, electrochemically prepared and

doped with anion, has been found to be a responsive coating for a piezoelectric gas detection system. It was found that samples of ammonia gas cause a measurable frequency decrease, interpreted as adsorption by the polymer coating of the quartz crystal. The linear range of responses was 0.05 - 1 % for mixtures of gas in nitrogen. These signals were found to correspond to simultaneous conductivity changes of a similarly prepared polypyrrole sample.

Jonathan et al. (1992) showed that the resistance change and mass change of polypyrrole layer occurred using a piezoelectric quartz crystal microbalance of bromide-doped films exposed to methanol, hexane, 2-2-dimethylbutane, ammonia and hydrogen sulfide. The response mechanism of polypyrrole sensing of different gases and vapors was due to a mixed response involving electronic effects and physical effects.

Polypyrrole has low gas-transport selectivity which has been attributed to the microporous morphology obtained when thin films of them are prepared by conventional synthetic methods. *Parthasarathy et al. (1997)* showed that polypyrrole with a dense morphology could be prepared by slowing down the rate of the polymerization reaction. They demonstrated that a partially oxidized form of this material showed extraordinary gas-transport properties. The O_2 versus N_2 selectivity coefficient was found to increase with decreasing partial pressure of O_2 in the feed-gas stream.