

# CHAPTER I

## INTRODUCTION



### 1.1 Introduction

Nowadays, the environment contains more toxic gases that are quite dangerous to human being. They are produced from many sources; for example, hydrogen sulfide ( $H_2S$ ), sulfur dioxide ( $SO_2$ ) and hydrocarbon gases from petrochemical industry; carbon monoxide ( $CO$ ), nitrogen monoxide ( $NO$ ) and carbon dioxide ( $CO_2$ ) from the vehicle exhausts; and ammonia ( $NH_3$ ) from fertilizer industry. Increasing concern for the environment together with requirements for more accurate process control has created a need for new or improved sensors for measuring these toxic gases. Generally, gas sensor devices are based on metallic oxide,  $SnO_2$  or  $ZnO$ , as sensing material. However, they have many disadvantages: lack of sensitivity and selectivity to toxic gases at low concentrations, lack of sensitivity to ambient moisture and the requirement in most applications for operation at  $300^\circ C$  or above (Miasik *et al.*, 1986).

In recent years, many researches have developed new types of gas-sensing materials, which could be sensitive to a wider range of gases and particularly to toxic gases, which could show significant sensitivity at low concentrations down to a few part per million (ppm) and could also be operated at ambient temperature. These gas-sensing materials are based on semiconducting polymeric organic materials (Miasik *et al.*, 1986).

There are two mechanisms responsible for a conductive polymer to respond to toxic gases. When a conductive polymer is exposed to an electron supplying gas such as ammonia ( $NH_3$ ) gas, the number of hole

charge carriers of the doped polymer are reduced due to the deprotonation process and hence the electrical conductivity is decreased. When the doped polymer is exposed to an electron withdrawing gas such as sulfur dioxide gas (SO<sub>2</sub>) and nitrogen dioxide gas (NO<sub>2</sub>), the number of hole charge carriers of the polymer increases and so the electrical conductivity increases (Kukla *et al.*, 1996).

## 1.2 Background

### Conductive Polymer

The conductive polymer is one type of polymer which has a special property that differ from other polymers, viz. electrical conductivity. It is a macromolecule in the solid state which possesses the electronic conduction. For conductive polymers, electrons (or their counterparts, positive holes) can migrate along a polymer chain and to jump from one chain to another. This process resembles the electronic conduction in metals or metalloid semi-conductors. In polymers, the process generally depends on the presence of arrays of conjugated, delocalized double bonds (Allcock *et al.*, 1990). Most of the conductive polymers have skeletal systems with long sequences of formally alternating single and double bonds. The electrical conductivity of conductive polymers can be improved by an injection or removal of electrons by an external source (James, 1996). Electron might be injected by the addition of small-molecule electron donor chemicals or by a reduction of a polymer in an electrochemical cell. Alternatively, electrons can be removed by treatment of the polymer with electron acceptors or by electrochemical oxidation. This is known as *doping* (James, 1996). Examples of conductive polymers are Polyacetylene [(CH)<sub>x</sub>], Polypyrrole (PPy), Polythiophene (PT), Polyaniline (PANI), Poly(p-phenylene) (PPP) etc. The discovery year of

some important conductive polymers are listed in Table 1 (Stenger-Smith, 1998).

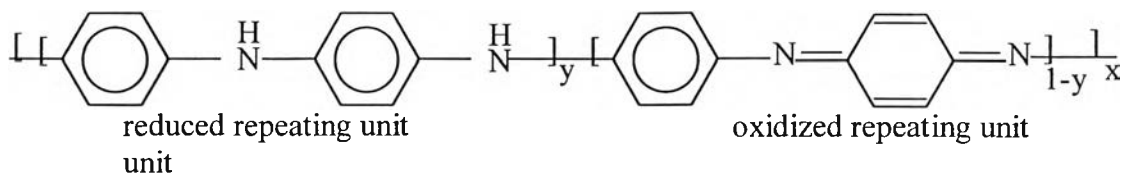
**Table 1.** The discovery year of the important conductive polymer types

Polymer	Year of discovery	Reference
Poly(sulfurnitride)	1960	Stenger-Smith, 1998
Polyacetylene	1977	MacDiarmid, 1986
Polyaniline	1988	Reynolds <i>et al.</i> , 1988

In 1977, the first electronically conductive organic polymer, doped polyacetylene was discovered (MacDiarmid, 1986). Polyacetylene, which is a very poor conductor in the pure state, could be turned into a highly conductive polymer by conversion to the salt on reacting it with  $I_2$  (Cowie, 1991).

### Polyaniline

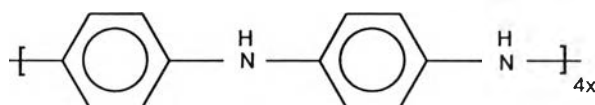
Polyaniline has attracted a considerable attention since MacDiarmid *et al.* (1977) reinvestigated this material as a conductive polymer. Polyaniline is attractive because the monomer (aniline monomer) is relatively inexpensive; the polymerization of monomer to polyaniline is straightforward; and polymerization reaction proceeds with a high yield. The important point is that the conductive form of polyaniline has an excellent chemical stability combined with relatively a high level of electrical conductivity. Polyaniline can be synthesized by both electrical and chemical oxidation polymerizations in the presence of acid media (Cowie, 1991). Reaction of aniline monomer with an oxidant in aqueous HCl produces polyaniline as a dark blue powder (Cowie, 1991). Polyaniline has the generalized composition containing reduced repeating units and oxidize repeat units. The general composition of polyaniline is shown in Figure 1.1.



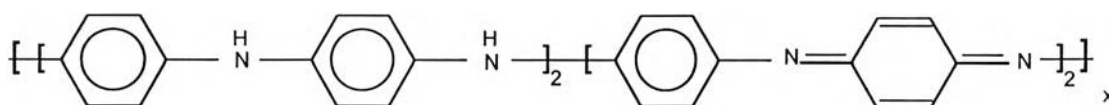
**Figure 1.1** The general composition of polyaniline.

Polyaniline has three different oxidation states depending on the oxidation level. Each of the states which are listed below has a particular name and color (MacDiarmid, 1986).

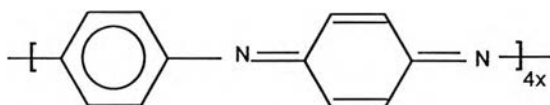
- Leucoemeraldine base: fully reduced material, it is colorless.



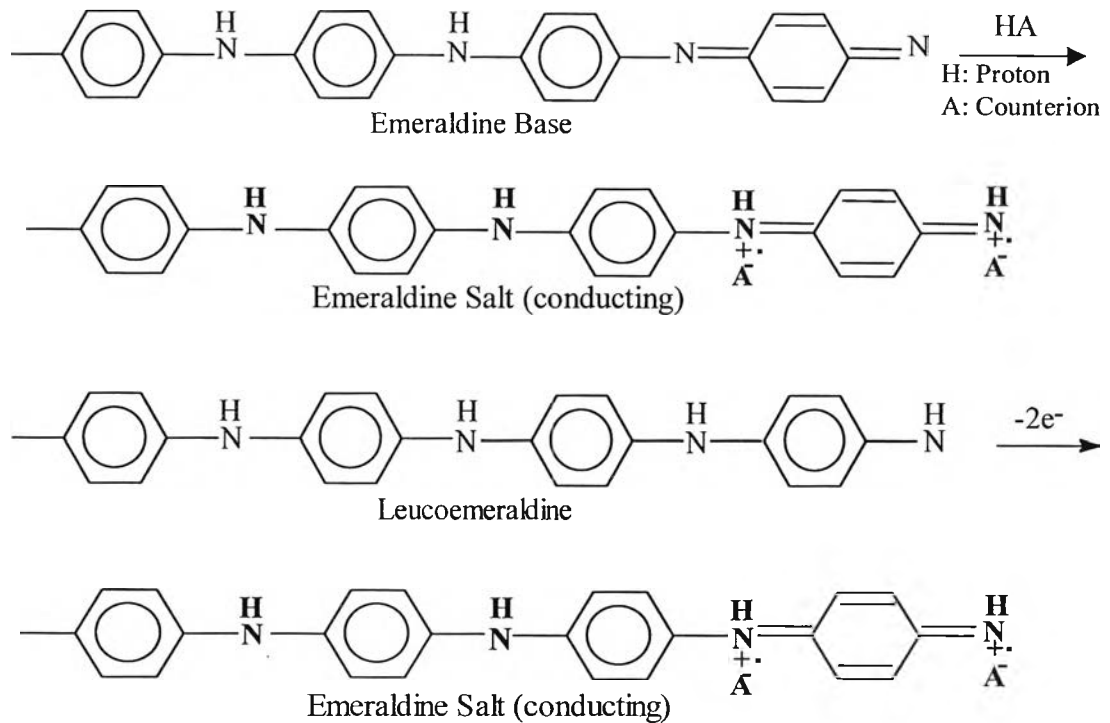
- Emeraldine base: It has dark blue color.



- Pernigraniline base: fully oxidized material, it has violet color.

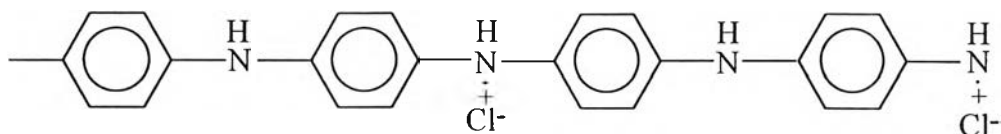


The insulating emeraldine base form of polyaniline can be converted to the conducting emeraldine salt form by a protonic acid doping and an oxidative doping as shown in Figure 1.2 (Stenger-Smith, 1998).



**Figure 1.2** The conversion of polyaniline from the insulating form into the conducting form.

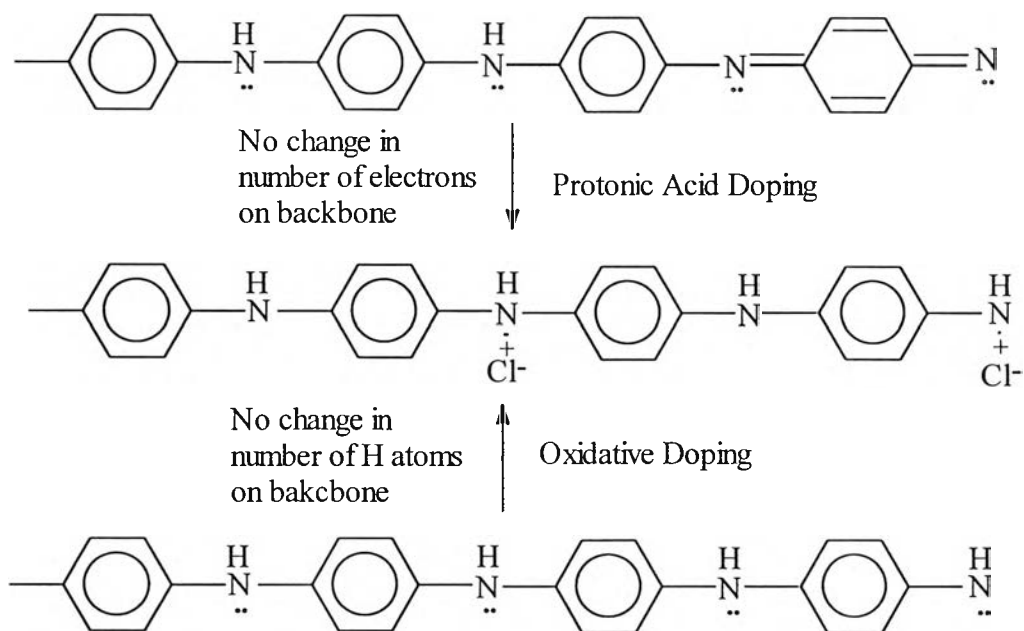
Protonic Acid Doping: This protonation reaction does not change the number of electrons in the polymer backbone. In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts. The degree of the protonation of the polymeric base depending on its oxidation state and on the pH of the aqueous acid. After doping, the protonated polyaniline is actually present in the form of poly-semiquinone radical cation, one resonance form consisting of two separated polarons. The structure of poly-semiquinone radical cation is shown in Figure 1.3 (Salaneck, 1980).



**Figure 1.3** The structure of poly-semiquinone radical cation.

Oxidative Doping: This process actually involves the oxidation of the  $\sigma/\pi$  system rather than just the  $\pi$  system of the polymer. The leucoemeraldine base form of polyaniline can also be oxidized to the poly-semiquinone radical cation in aqueous HCl. Its reaction with a solution of chlorine in carbon tetrachloride proceeds to give the emeraldine salt. This process changes the total number of  $\pi$ -electrons on the conjugated chain, thus differing from the protonation doping (Stenger-Smith, 1998).

The relationship between the protonic acid doping and the oxidative doping from different forms of nonconductive polyaniline to give the same conducting material is listed below in Figure 1.4.



**Figure 1.4** The relationship between protonic acid doping and oxidative doping of polyaniline (Salaneck, 1980).

In all of the conductive polymers being investigated, polyaniline is a material having the highest potential for commercial applications (Stenger-Smith, 1998). However, processing of polyaniline has remained a difficult problem. Polyaniline has been generally classified as an intracable material. They are quite insoluble in most common solvents. Cao et al. (1992) reported that polyaniline can be dissolved without changing the molecular structure of the polymer in N-methylpyrrolidone (NMP), in specific amines, or in concentrated sulfuric and other strong acids. In addition, the solubility of the emeraldine salt form of polyaniline can be increased by using functionalized protonic acid to dope polyaniline. This conductive form can be dissolved in common nonpolar or weakly polar organic solvents. A functionalized protonic acid is generally denoted as  $H^+(MR)$ , in which the counterion anionic species,  $(MR)$ , contains the R functional group which is chosen to be compatible with nonpolar or weakly polar organic solvent (Cao *et al.*, 1992).

### Conductive Polymer Sensor

One of the advanced applications of electrically conductive polymers is as a sensing device. The use of conductive polymers as gas sensors and solution sensors for detection of chemical and biochemical species are of more interest recently. Gas sensor is desired to detect a specific gas or gases in the environment; for instance, the presence of pollutants, the leakage of toxic gas, the emission of gases from food and released gases from fermentation. Since conductive polymers change their properties by incorporation of ions and solvents, it is possible to develop ion-specific sensors based on conductive polymers. Conductive polymers also change volume depending on their oxidation state. Therefore, it is possible for conductive polymers to convert electrical energy into mechanical work (Stenger-smith, 1998).

Polyaniline is attractive to be used as a sensing device material. Many researchers reported that polyaniline can be used as a gas sensor; for example, conducting polyaniline as sensor material for different vapors like methanol, ethanol, acetone and benzene (Grummt, 1997), ammonium sensors based on sensitive polyaniline films (Younan, 1995). In addition, the use of Polyaniline film which does not involve its electrical properties is in gas separation process. Polyaniline membranes are far superior in the selectivity to all known gas separation membranes for many simple gas mixtures such as O<sub>2</sub> and N<sub>2</sub> (Kukla, 1996).

### 1.3 Objectives

The objectives of this study are:

1. To synthesis and characterize polyaniline.
2. To study the preparation method and characteristics of undoped and doped polyaniline films.
3. To study the effect of various acid dopants and dopant concentration on the electrical conductivity of polyaniline films.
4. To study the electrical conductivity of doped polyaniline films at various dopant concentrations when exposed to SO<sub>2</sub> gas at various concentrations.