



## CHAPTER I INTRODUCTION

### 1.1 Introduction

Today's environment contains more toxic gases produced from many industries; hydrogen sulfide ( $H_2S$ ), sulfur dioxide ( $SO_2$ ), and hydrocarbon gases from petrochemical industry, ammonia ( $NH_3$ ) from fertilizer industry and carbon monoxide ( $CO$ ), nitrogen monoxide ( $NO$ ) and carbon dioxide ( $CO_2$ ) from the vehicle exhausts. Development of the gas sensor devices for detecting these gas pollutants is in urgent need. Typically, gas sensor devices are based on metallic oxide,  $SnO$  or  $ZnO$ , as sensing material. However, the problems with metallic oxide as a sensing material are: the need to operate at high temperature ( $>200^{\circ}C$ ), lack of sensitivity and selectivity to toxic gases at low concentrations, poor cross-sensitivities to other gases, and the very small signals to monitor.

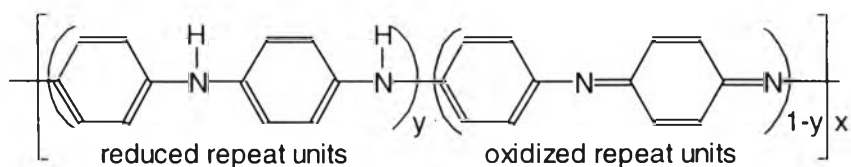
In the recent years, many researchers have developed conductive polymers, polyacetylene, polypyrrole, polyaniline, polythiophene, phthalocyanine and poly(p-phenylene), for using as sensing materials in the gas sensor applications. The advantages of these sensing materials based on conductive polymer are the ability to operate at low temperature and sensitivity to toxic gases at low concentrations down to a few part per million (ppm). The sensitivity and selectivity of many conductive polymers can be modified by redox doping process.

In this work, prepared and characterized polyaniline is used as a sensing material. The electrical conductivity of polyaniline can be varied by

protonation doping process. There are two mechanisms to explain how polyaniline can detect the toxic gases. When the doped polyaniline is exposed to an electron supplying gas such as ammonia ( $\text{NH}_3$ ) gas, the number of hole charge carriers of the doped polyaniline are reduced due to the deprotonation process and a decrease in the electrical conductivity. The change in electrical conductivity of the doped polyaniline is proportional to the gas concentration in the system. When the doped polyaniline is exposed to an electron withdrawing gas such as nitrogen dioxide ( $\text{NO}_2$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ) and sulfur dioxide ( $\text{SO}_2$ ) gases. The number of hole charge carriers of the doped polyaniline increase and so the electrical conductivity increases.

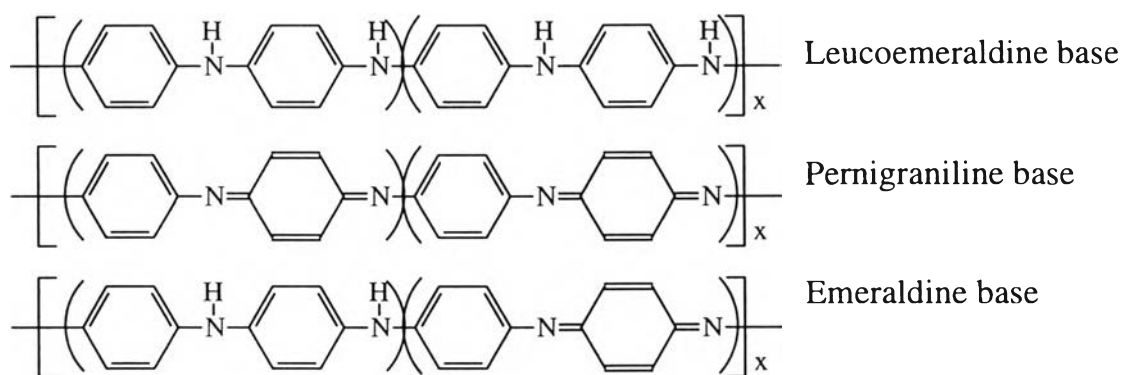
## 1.2 Polyaniline Background

Polyaniline is one of the conductive polymers synthesized by chemical oxidation or by electrochemically polymerization in the presence of acid media. Polyaniline has a general formula containing reduced repeat units, and oxidized repeat units. The general formula of polyaniline is shown in Figure 1.1.



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

Polyaniline can exist in three different oxidation states with differences in colors. The fully reduced form of polyaniline, “Leucoemeraldine”, corresponds to a value of  $y = 1$ ; the fully oxidized form of polyaniline, “Pernigraniline”, corresponds to a value of  $y = 0$ ; and the half-oxidized form of polyaniline, “Emeraldine”, corresponds to a value of  $y = 0.5$ . The different oxidation states of polyaniline are shown in Figure 1.2.

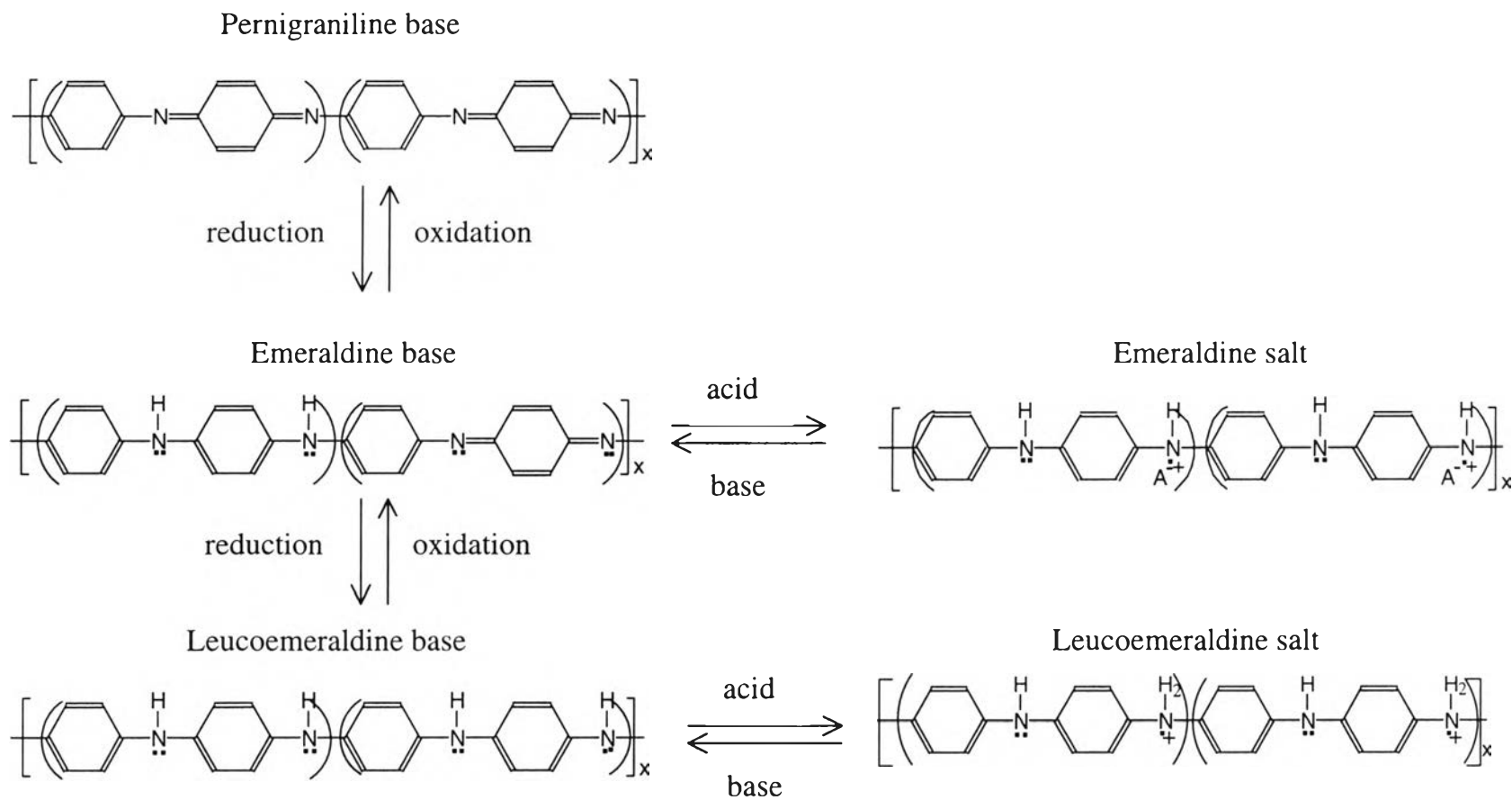


**Figure 1.2** The different oxidation states of polyaniline.

Each oxidation state can exist in the form of its base or its protonated form (salt) by treatment with an acid. The different oxidation states of polyaniline can interconvert between each other under appropriate conditions. The schematic of the interconversion process of polyaniline is shown in Figure 1.3.

The insulating emeraldine base form of polyaniline can be converted to the conducting emeraldine salt form by two independent doping methods:

- 1) Oxidation doping method by chemical reaction with an appropriate oxidizing agent such as  $\text{FeCl}_3$  and electrochemical charge transfer reaction. The charge transfer reaction causes a change in the total number of  $\pi$ -electrons on the conjugated chain.



**Figure 1.3** A reaction diagram consistent with the interconversion of different oxidation and protonation states of polyaniline.

2) Protonation doping with acid-base reaction in the aqueous media with pH less than 2-3. There is no change in the number of  $\pi$ -electrons.

The main disadvantages of polyaniline are an intractable material and insoluble in common organic solvents. The intractable material is referred to the material that decomposes before melting. Heeger *et al.* (1995) reported that polyaniline can be dissolved in some organic solvent such as 1-methyl-2-pyrrolidone (NMP), specific amines, and concentrated sulfuric acids. Cao *et al.* (1992) reported that the solubility of polyaniline emeraldine salt can be increased by using dodecylbenzene sulfonic acid, camphor sulfonic acid, or the others functionalized sulfonic acids as a protonic acid or dopant.

In the recent years, polyaniline has attracted much attention in many applications due to a number of important reasons: its conductive form has an excellent chemical stability with relative high electrical conductivity, aniline monomer is inexpensive, and its polymerization is straightforward with high yield reaction. Polyaniline has potential in many applications such as electromagnetic shielding, rechargeable batteries, light emitting diodes, non-linear optical device, static film for transparent packaging of electronic components, sensors for medicine and pharmaceuticals, and membranes for separation of gas mixtures.

### 1.3 Literature Survey

MacDiarmid *et al.* (1985) reported that polyaniline could be synthesized by both chemical and electrochemical polymerization. The quinoid-benzenoid-diimine form, an insulator, was doped in dilute aqueous protonic acid to give the corresponding iminium salt in the metallic state. The conductivity of the compressed pellet of polyaniline was equal to  $5 \text{ ohm}^{-1} \text{ cm}^{-1}$ . A new type of p-doping phenomenon in a conducting polymer was reported. Both the insulator and conductive forms of polyaniline were stable

in the presence of air or water. The reversibility between reduced and oxidized form of polyaniline was studied by cyclic voltammetry technique.

MacDiarmid et al. (1986) reported that the emeraldine salt form of polyaniline obtained by electrochemical synthesis had a fibrillar morphology, the same as the morphology of polyacetylene. Cyclic voltammograms of the chemically and electrochemically synthesized polyaniline were identical. The emeraldine salt form of polyaniline had a symmetrical structure with extensive charge delocalization.

Show-An Chen (1987) reported that polyaniline film was prepared by electrical synthesis with sulfuric acid as the protonic acid. This film was brittle and could not be peeled off to form a free-standing film. They also reported that the fibrillar network morphology of polyaniline was obtained by electrical synthesis with tetrafluoroboric acid ( $\text{HBF}_4$ ) solution as an electrolyte. When acetonitrile was used to replace the water, polyaniline layer formed on the electrode surface with a stack of irregular lumps. If the protonic acids were replaced by hydrochloric acid ( $\text{HCl}$ ) or sulfuric acid ( $\text{H}_2\text{SO}_4$ ) in the aqueous solution, polyaniline was of granular structure.

Eptein (1990) reported that the first protonic acid self-doped polyaniline was prepared by chemical polymerization with sulfuric acid as a protonic acid. Without external doping, polyaniline had a conductivity equal to 0.1 S/cm. Eptein (1991) reported that the heat treatment of emeraldine base of polyaniline produced oriented partially crystalline film. Polyaniline emeraldine base films were prepared by casting emeraldine base form which was dissolved in NMP onto glass substrate. This film contained 20 % by weight of NMP. The film was heated at an elevated temperature ( $T \geq 110^\circ\text{C}$ ) and the stress was applied at the same time. This polymer film was elongated with  $I/I_0$  up to 4.5. The mechanical properties with tensile strengths of polyaniline film were improved from an average of 54 Mpa for the unstretched film to an average of 124 Mpa for the 4-fold uniaxially stretched film. Both

the optical and electrical properties of polyaniline emeraldine base and salt forms were improved.

Kamer (1991) reported that permeability for a series of gases through polyaniline film. Specific selectivity for gas pairs including  $H_2/N_2$ ,  $O_2/N_2$ , and  $CO_2/CH_4$  were investigated. The doped polyaniline had a higher selectivity for these gases than non-conjugated polymer such as poly (trifluorochloroethylene) and cellulose nitrate. The process for improvement the gas selectivity of polyaniline membrane involved the permeability of gas with small diameter by doping and undoping the film with a counter-anion size. The higher selectivity was achieved by decreasing the permeability of larger gases by controlled redoping of the polymer.

Jieshan (1992) reported that the conductivity of polyaniline at room temperature depended on the protonation state and temperature. The activation energies, conductivity at various pH, XPS, ESR and UV-Visible absorption spectra for free-standing films of polymer were measured. All results were in agreement with the metallic island model in which polaron was formed by protonation process and separated by insulating medium.

Eptein (1992) reported the mechanical and thermal properties of polyaniline films as studied by DMA, DSC and TGA. Thin film of polyaniline had a storage modulus of  $\sim 200$  MPa – 2 GPa at temperature below  $T_g$ . The glass transition of polyaniline film was strongly dependent on the condition of residual NMP solvent in the film. In the case of the residual solvent remaining in the film at  $\sim 16\%$ ,  $T_g$  was determined to be  $\sim 105$ - $220^\circ\text{C}$  by DMA, and DSC.

Palaniappan (1994) reported that five different polyaniline salts were prepared by chemical polymerization of aniline in different acid solutions. Polyaniline was heat treated at various temperatures of 150, 200, 275 and  $375^\circ\text{C}$ . Thermal stability of these films was studied by thermal analysis. Their results showed that polyaniline salt had a three-step weight

loss process in the heating cycle. The first step at temperature up to 110°C was related to the loss of water molecule from the polymer chain. In the second step at temperature range 110-275°C the loss was due to a small amount of acid evaporated out as a volatile gas. The last step at temperature higher than 275°C corresponded to the oxidative thermal degradation of polymer chain. This result showed that thermal stability of polyaniline salt depended on the counteranion. The thermal stability of polyaniline was stable up to 250°C.

Chan (1994) reported that they synthesized polyaniline by post-treatment of polyaniline base with three different phosphonic acids. They found that the phosphonic acid doped polyaniline had a higher conductivity and thermal stability than hydrochloric acid doped polyaniline. The best of the doped polymers studied were PAN-BnPA and PAN-Bu/EtPA that had a doping level and conductivity very similar to PAN-HCl.

Lin (1995) reported that polyaniline could be doped by ionic salt such as LiClO<sub>4</sub>, LiBF<sub>4</sub>, and Zn(ClO<sub>4</sub>)<sub>2</sub>. The ionic salt was used to dope polyaniline by mixing an ionic salt with polyaniline in NMP solvent and then casting the solution into a film. UV-Visible, FTIR, XPS spectrophotometer, DMA, SEM, and conductivity measurement investigated the structure and property of doped polyaniline. The LiBF<sub>4</sub>-doped PAN film retains conductivity at 10<sup>-1</sup> S/cm in the temperature range 25-140°C. The conductivity decayed to 10<sup>-3</sup> S/cm at 175°C.

Levon (1995) reported that doped polyaniline could be obtained by introducing the dopant molecule, dodecylbenzene sulfonic acid, into the undoped polyaniline without the use of an auxiliary solvent. Complex formation between the dopant molecule and undoped polyaniline occurred at an elevated temperature. This method improved the solubility and processability of the doped polyaniline.



Lianyan et al. (1996) reported that Langmuir-Blodgett films of metal porpyhrin derivative were studied for gas sensor application. The metal porpyhrin film was deposited on a specially designed FET. The results showed that the selectivity of the gas sensor was dependent on the central metal ion of metal porphyrin. When the central metal of metal porphyrin derivatives was Cobalt (Co), it could easily detect to  $\text{NO}_2$  at a few ppm of 0.5 ppm. However, the cobalt porphyrin was not sensitive to CO,  $\text{H}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and alcohol at 500 ppm. Other films of metal porphyrin were not sensitive to ambient gas. The sensitivity and stability of metal porphyrin derivatives was dependent on the length of aliphatic chain of porphyrin derivatives producing high sensitivity, fast responsibility and good stability.

Piletsky et al. (1996) reported that polyaniline was used as the sensitive element for ammonia sensor. Ammonia microsensor was constructed based on a multi-purposed silicon chip with a system of heaters and thermometers. The sensor characteristic of polyaniline was studied by monitoring the sensitivity of polymer film with a wide range of ammonia gas concentration in the range of 1-2000 ppm. A physicochemical model described the changed in the conductivity of polyaniline with the absorbed ammonia molecules. It was shown that the changed in conductivity occurred due to the reversible protonation of polyaniline molecules in ammonia removal. Polyaniline was used for ammonia sensor because of high chemical stability in oxidizing ambient.

Monkman et al. (1997) showed that polyaniline film could be prepared by Langmuir-Blodgett technique. The surface phasmon resonance technique was used to characterize this polymer film. Exposing polyaniline film to  $\text{NO}_2$  and  $\text{H}_2\text{S}$  produced the increased in the reflectivity and resonance angle. In case of  $\text{NO}_2$ , the changed in the reflectivity and resonance angle was similar to the changed in the electrical conductivity of polyaniline sensor. The

surface plasmon resonance result showed poorer response to H<sub>2</sub>S than the electrical sensor.

Dhawan et al. (1997) reported that a prototype chemical sensor was studied by exposing polyaniline to aqueous ammonia and observed the changed in the resistance of polymer film. The changed in the resistance of polyaniline film on exposure to aqueous ammonia was due to the deprotonation in the doped polyaniline film. The surface resistance of the doped polyaniline changed from 10<sup>2</sup> to 10<sup>10</sup> ohms on the exposure to the aqueous ammonia. In this research, polyaniline was synthesized by electrochemical polymerization. 5-Sulphosalicylic acid and p-toluene sulphonic acid were used as protonic acids.

Barker (1997) studied the humidity sensor by using polyaniline film. The fabrication of gas sensing device was based on polyaniline /silicon hybride field effect transistor to improve the signal-to-noise ratio. They studied the effect of different humidity levels in the range of 15-50 % on the initial gradient. For humidity in the range of 15-30 %, the sensitivity increased gradually.

Larson (1997) reported that the fully dense films of polyaniline and polyimide blend were successfully prepared from the solution. The blend film at 50:50 ratio of polyaniline and polyimide provided a higher permeability than homopolymer. The separation property of the blend film was higher than polyimide homopolymer, but lower or equivalent to polyaniline base. In the blend film at 25:75 ratio of polyaniline and polyimide, it showed higher measuring than polyaniline homopolymer film. The selectivity of the blend film was higher than the undoped polyaniline.

## 1.4 Objectives

The objectives of this study are:

- 1) To synthesis and characterize polyaniline.
- 2) To study the preparation method and characterizations of undoped and doped polyaniline films.
- 3) To study effect of aging, acid concentrations, exposure time and exposure temperature on the electrical properties of doped polyaniline films under nitrogen atmosphere.
- 4) To determine suitable conditions for the electrical conductivity of polyaniline film under SO<sub>2</sub> atmosphere.

