CHAPTER I
INTRODUCTION

1.1 Introduction

Nowadays, petrochemical industry is one of the most important industry in Thailand as well as in other countries due to the increasing demands for gases, oil and petroleum products. In 1980, the world consumption of 23 of major petroleum products is higher than 250 million metric tons per year. These products are involved in combustion process, cracking process and so on, which release a significant amount of gases to the atmosphere. These gases can be rendered into hydrocarbons (HC), carbonmonoxide (CO), sulfur dioxide (SO_2), nitrogen oxide (NO_x), and other particulate as shown in Figure 1.1

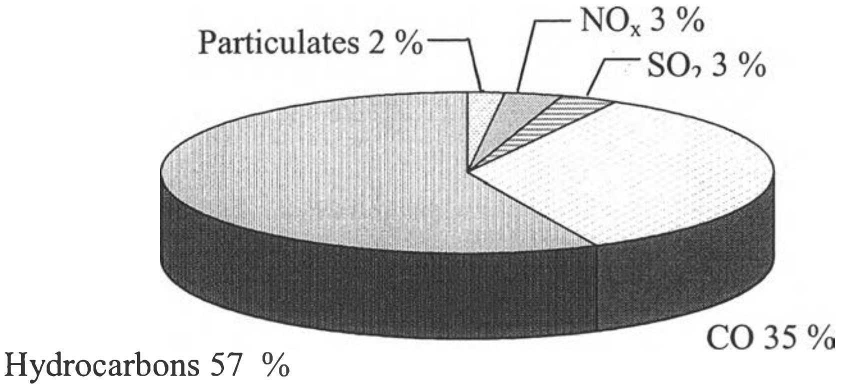

Figure 1.1 Contribution of different sector of petrochemical industrial emission (Brett B.M., 1987).

The rapid expansion of these industries has induced greater concerns on public health and environment. Better process design, proper combustion unit or even effective waste recovery can lead to a better control for the emission of gases. Therefore, an effective tool to monitor the release of these gases or a gas sensor is desirable. There are several types of gas sensors: electrochemical, infrared, catalytic bead, photoionization and solid-state. The most widely used gas sensor is made of a metal oxide such as SnO_2 or ZnO based. However, they have many disadvantages, the lack of sensitivity and selectivity at low concentrations, and the requirement in many applications to be operated at 300 °C or above (Garder *et al.*, 1994).

Gas-sensing devices based on semiconducting polymeric materials are becoming more popular due to its electrical conductivity, environmental stability, inexpensiveness and low power consumption. However, the major drawback of conductive polymer to be used as gas sensor in petroleum gas monitoring is its instability at high temperatures.

The challenge of producing blends and composites with conducting polymers has been pursued by many researchers in the last few years. Some researchers have improved thermal stability of conductive polymers by fabricating several polymer blends. These thermally stable conductive polymer blends were used as selective membranes, conductive films and coating; whereas the use as gas sensor is still very limited.

1.2 Background

Conductive Polymer

For the last two decades, conducting polymers has been widely studied by physicists, chemists and material scientists. Conducting polymers have shown not only an unusual conductive behavior presenting a strong theoretical challenge for fundamental study, but also a great potential for technological and commercial exploitation which have been reported to be applicable to batteries, electronic devices, functional coatings, chemical and biological sensors, etc. (MacDiarmid *et al.*, 1985a,b).

The first electrically organic conductive polymer, polyacetylene, was synthesized in 1977. It is known as the 'Shirikawa' type, which was synthesized via the Ziegler-Natta polymerization. Recently, several kinds of conductive polymers have been discovered such as poly(p-phenylene) or PPP, polypyrrole or PPY, polythiophene or PTH, polyaniline or PANI and so on. The important distinguishable feature of these chemicals is the conjugation of π-electrons, which is formed by the overlap of the carbon p-orbital along the backbone. The high electrical conductivity can be accomplished after the 'doping process', which can be divided into two different processes: the protonic acid doping and the oxidative doping (Genis *et al.*, 1985).

The mechanisms of how semiconducting polymer responds to toxic gas can be briefly explained. For electron donor gases, such as ammonia (NH_3) or hydrogen sulfide (H_2S), its electrical conductivity increases. On the other hand, for electron acceptor gases, such as sulfur dioxide (SO_2) or nitrogen oxide (NO_x) or carbonmonoxide (CO), its electrical conductivity decreases. This is because a p-type semiconducting polymer consists of a number of holes as charge carriers (Allode *et al.*, 1990).

For homogenous semi-conducting materials, the conductivity σ (S/cm) is proportional to the product of the free-carrier concentration, n (number/cm^3), and the carrier mobility, μ (m^2/V-sec), as in the following equation:

$$\sigma = ne\mu \tag{1}$$

where e is the unit electronic charge, 1.6×10^{-9} (s.A). For semi-conducting material, the morphology also effectively influences the conductivity of polymer. The more crystalline or the more metallic-like states displayed, the larger conductivity of polymer can be expected. Crystallinity can be induced by mechanical stretching, interchain interaction or increasing the localization length.

Polyaniline.

Polyaniline (PANI) has emerged as one of the most promising conducting polymers because it is an inexpensive monomer, its relative ease of synthesis, good environmental stability and moderately high value of dc conductivity, and the excellent chemical stability in conductive form both in aqueous and ambient media (Stejskal *et al.*, 1996). Polyaniline can be synthesized via both chemical and electrochemical oxidative polymerizations of aniline in aqueous acid media by variety of oxidizing agents. It has a general structure in emeraldine base, which consists of alternating reduced and oxidized repeating unit as shown in Figure 1.2 (MacDiarmid *et al.*, 1985a).

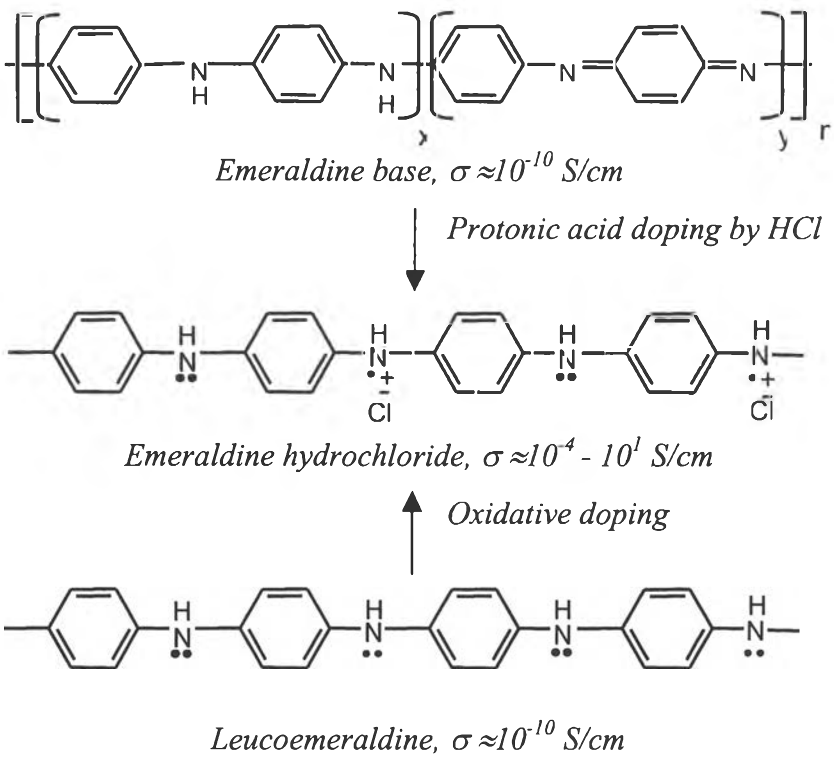

Figure 1.2 Protonic acid doping and oxidative doping of polyaniline.

Polyaniline can be converted into 4 different oxidation states by variation of oxidation level (Stejskal *et al.*, 1996). The first one is pernigraniline form (x = 1), which is fully oxidized, providing a violet color. The second one is the emeraldine base from (x = 0.5) which is a general state of polyaniline with a dark blue color. The third one is the leucoemeraldine base form (x = 0), which is a fully reduced material with a yellow color. The last one is the polyaniline salt, which possesses a green color.

To prepare a conductive form of polyaniline, an emeraldine base is converted to an emeraldine salt via a doping process. The doping process can be rendered through two independent doping routes which are an oxidation process electrochemically or chemically or a protonation through acid-base (Kang *et al.*, 1995).

In spite of various benefits of polyaniline, it also has some technical problems such as a difficult processability because of its insolubility in most common solvents and the conducting form of polyaniline are inherently brittle. However, one of the methods to improve the mechanical properties and to broaden the range of industrial applications has been through the blending with other polymers such as polyethylene; PE (Valenciano *et al.*, 2000), poly(methyl methacrylate); PMMA (Kahol, 2001), acrylonitrile-butadiene-styrene; ABS (Cao *et al.*, 1992), polyimide; PI (Han *et al.*, 1998-2000) etc.

Polyimide

Polyimide is well known as a high temperature engineering polymer, which plays an important role as coating materials in the microelectronics industry due to their outstanding thermal stability (>500 °C), electrical resistance, inertness to solvent and mechanical toughness. Polyimide can be synthesized by a two-stage classical method. The first stage starts with poly(amic acid) obtained from polycondensation of diamine and dianhydride in polar aprotic solvent followed by cyclodehydration of poly(amic acid) to polyimide either by thermally heating or chemically imidisation (Ghosh *et al.*, 1996).

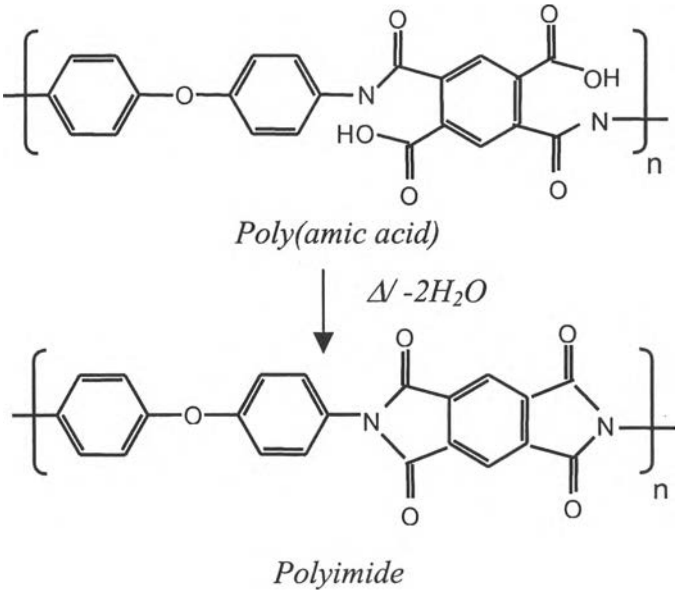

Figure 1.3 Two-step synthesis of polyimide.

The preparation of the blends can be achieved by electrochemical deposition, in situ chemical polymerization, powder dispersion, melt blending and solution blending. In this work, powder dispersion of conducting polyaniline and insulating matrix polyimide was performed by a dry mixing of the polyaniline complex with polyimide, a grinding of the two polymers together followed by compression into a pellet. Through this method, a well-dispersed blend of a conducting polymer in an insulating matrix could be achieved.