



CHAPTER I INTRODUCTION

Recently, the most common problems forming in many countries of the world are rigorous environmental standards and regulation on volatile organic compounds (VOCs). In particular, the VOCs are the primary alcohol such as methanol, n-propanol, ethanol, butanol, pentanol, heptanol. The primary alcohols are widely used in the chemical industrial engineering and production technology processes (Penza *et al.*, 2002). But the natural toxicity of these primary alcohols is dangerous for human beings with very serious irreversible effect through breathing and in contact with skin (Nagle *et al.*, 1998).

Therefore, the high performance sensors are required to identify and measure various kinds and quantities of VOCs. Conductive polymers, CPs have been highlighted as effective gas sensors owing to many advantages over metal oxide materials. Because CPs have light weight, less expensive, high sensitive and short response time at room temperature, ease to synthesize, and their molecular chain structure can be modified conveniently by copolymerization and structure derivations (Bai *et al.*, 2007). Polyaniline and their derivatives have been reported to exhibit good response for alcohol vapors, especially methanol, ethanol, and propanol (Athaware *et al.*, 2000) due to its outstanding properties; inexpensive monomer, ease of synthesis, and good environmental stability (Agbor *et al.*, 1995). However it has the problem of solubility and processibility. This problem can be overcome by using N-aryl substituted derivatives of polyaniline; polydiphenylamine (PDPA). PDPA was prepared by chemical or electrochemical oxidative polymerization of diphenylamine which occurred through a 4, 4' C-C phenyl-phenyl coupling mechanism instead of the head-to-tail polymerization of polyaniline (Hua *et al.*, 2003). Thus, PDPA combines the chemical structures of polyaniline and poly(p-phenylene) which are expected to improve solubility and processibility (Li *et al.*, 2007). Furthermore, PDPA can be doped with sulfonic acid or methane sulfonic acid, grafted with hydrophilic side chain, hyperbranched, and blended with other polymers to improve their solubility (Li *et al.*, 2008; Wen *et al.*, 2002; Hua and Ruckenstein, 2005; and Hua and Ruckenstein, 2003).

The sensitivity of chemical gas sensors is strongly affected by the specific surface of sensing materials (Gopel, 1995 and Lee *et al.*, 1999). Hence a higher specific surface of a sensing material can lead to higher sensor sensitivity. Electrospun nanofibers generally have a larger surface area and can be modified as a sensor material having augmented sensor characteristics (Manesh *et al.*, 2007).

1.1 Conductive Polymer

Polymers have long been considered as insulating materials which are used to coat electric wire to protect them from short circuits. Since in 1958, polyacetylene was first synthesized by Natta *et al.* as a black powder. This was found to be a semiconductor with conductivity between 7×10^{-11} to $7 \times 10^{-3} \text{ Scm}^{-1}$. In 1970, Shirakawa and co-worker prepared a silver film from polyacetylene and used it in Ziegler-Natta as a catalyst (K. Ziegler and G. Natta, 1974). But despite its metallic appearance, it was not a conductor. However, Shirakawa *et al.* (1977) discovered that the oxidation with chlorine, bromine, or iodine vapors made polyacetylene films 109 times more conductive than they were in the original state. The treatment with a halogen is called doping. The doped form of polyacetylene had a conductivity of 10^5 Scm^{-1} (Shirakawa *et al.*, 1977).

Conductive polymers have conjugated double bonds along the backbone. Every bond contains a strong sigma (σ) bond and a weaker pi (π) bond, so the conjugation can occur along the polymer backbone. However, the electrical conductivity of pure conductive polymers is rather low, thus doping process is necessary to achieve highly electrical conductivity.

Other polymers extensively studied since early 1980s are polypyrrole (PPy), polythiophene (PTh), polyphenylene vinylene (PPV) and polyaniline (PAni). Polyacetylene is very sensitive to O_2 in air and humidity. Polypyrrole and polythiophene differ from polyacetylene; it can be synthesized directly in the doped form and is very stable in air (Kumar and Sharma, 1998). Conductive polymers are widely used in many applications because of their advantages: light weight, less expensive, highly sensitive and short response time at room temperature, easy to

synthesis, and their molecular chain structure can be modified conveniently by copolymerization and structure derivations (Bai *et al.*, 2007).

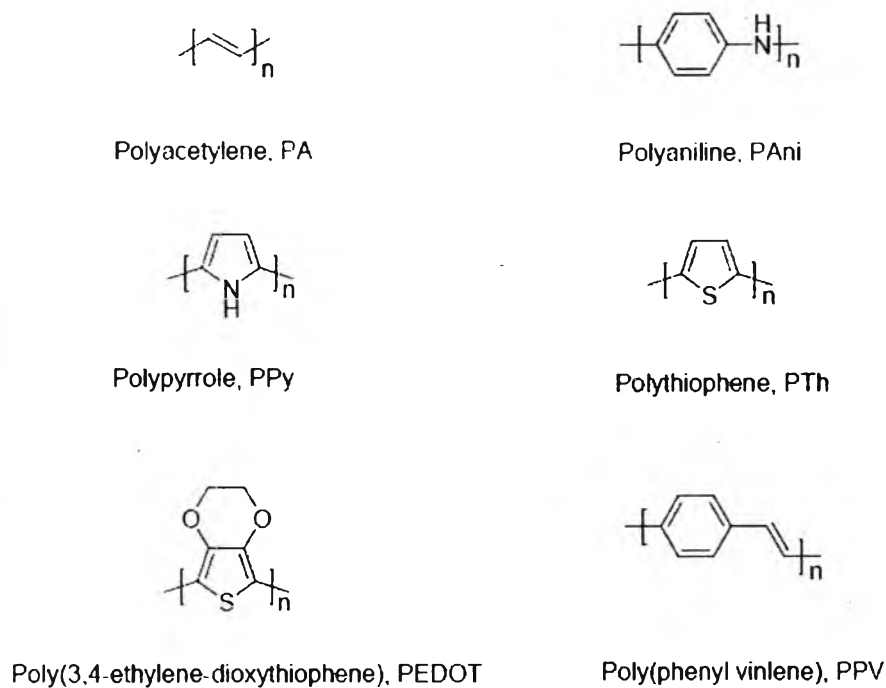


Figure 1.1 The chemical structure of conductive polymers (Bai *et al.*, 2007).

1.2 Doping Process

Conductive polymers have conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized sigma (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a weak localized pi (π) bond. However, conjugation is not enough to make the polymer conductive. In order to increase the conductivity of the conductive polymer, a doping process is necessary (Shirakawa *et al.*, 1977).

Doping of conductive polymers can be done either chemically or electrochemically. In the chemical doping, the oxidation is accomplished by exposing the conductive polymers to oxidizing vapors. The primary methods of

doping conductive polymers are the n-doping and the p-doping. For the n-doping process, a dopant, an electron donor, is injected into a polymer, the extra electron jumps to the neighboring bond. Hence a charge carrier occurs on the polymer backbone. An increase in the electrical conductivity of the conductive polymer occurs. For the p-doping process, a dopant, an electron acceptor, is injected to create a hole on the polymer backbone, so the electron from neighboring bond jumps to fill the hole. Thus, the electrical conductivity of conductive polymer increases (Shirakawa *et al.*, 1977).

1.3 Polydiphenylamine

Diphenylamine (DPA), an N-substituted aniline derivative, can be synthesized to polydiphenylamine by the electrochemical or the oxidative polymerizations (Orlov *et al.*, 2006). This reaction occurs via a 4, 4' C-C phenyl-phenyl coupling mechanism. The PDPA's structure is intermediate between polyaniline and poly(p-phenylene) (Hua *et al.*, 2003). PDPA can be synthesized directly in the doped form or easily doped with HCl solution to obtain the polaron or bipolaron forms. PDPA has many properties that are not comparable with another polymer of N-substituted aniline derivative; these include electrochemistry, conductivity, and electrochromism (Dao *et al.*, 1989 and Guay *et al.*, 1990).

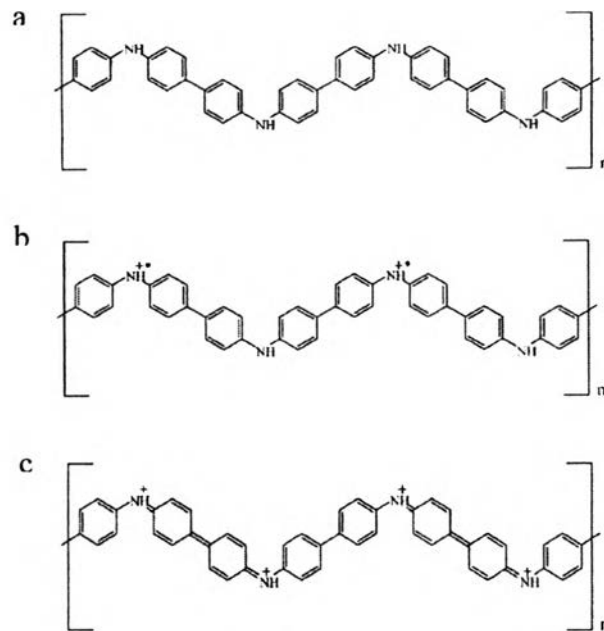


Figure 1.2 a) Neutral structure of PDPA, b) Polaron structure of PDPA, c) Bipolaron structure of PDPA (Wen *et al.*, 2002).

Athawale *et al.* (1999) studied the polymerization of polydiphenylamine by the electrochemical polymerization under the galvanostatic condition in nonaqueous acetonitrile media at different monomer concentrations. The result showed that the rate of polymerization of polydiphenylamine increased with the monomer concentration, because the higher monomer concentration, the larger the number of unreacted monomer molecules were available in the solution. However, as monomer concentration increased, the dispersity in polymer phase formation occurred.

1.4 Gas Sensors Based on Conductive Polymers

Many different types of gas sensors have been employed for the analysis of volatile organic compounds (VOCs). Perhaps the most competitive type is based on the change in electrical DC resistance (or ac impedance) when a semi-conductive material is exposed to a vapor (Li *et al.*, 2008). These sensors are often made from metal oxide semiconductors or conductive polymers (James *et al.*, 2005). Conductive polymers-based sensors demonstrate a number of attractive features including reversible operation at ambient temperature, high sensitivity to a wide range of VOCs, large possibilities of structural variations and relative low cost (Li *et al.*,

2008). The most commonly used conductive polymers for gas-sensing purposes have been polypyrrole, polyaniline, and polythiophene (Melo *et al.*, 2005; Anitha *et al.*, 2003; Carvalho *et al.*, 2007; and Chang *et al.*, 2006).

1.5 Gas Sensors Based on Electrospun Nanofibers

Electrospinning is an efficient, relatively simple, and low cost way to produce polymer and composite fibers with diameters ranging from several nanometers to a few micrometers by applying a high voltage to a polymer solution or melt ejected from a micro-syringe pump (Reneker *et al.*, 1996; Doshi *et al.*, 1999; and Fong *et al.*, 1999). The ultrafine fibers produced via electrospinning are assembled as a three dimensional structured fibrous membrane with controllable pore structure and high specific surface area. The utilization of electrospun nanofibers with large specific surface as gas sensing materials has received great attention (Dong *et al.*, 1997; Jin *et al.*, 1998; and Matsumiya *et al.*, 2003). Various gas sensors comprising of electrospun nanofibers of polyelectrolytes, conducting polymer composites, and semiconducting metal oxides were successfully fabricated with ultrahigh sensitivity, very short response and recovery time, good reversibility, reproducibility, and stability based on various sensing techniques and principles (Ding *et al.*, 2009). The fine structure of electrospun fibers was proven to be an excellent candidate instead of the current widely used solid flat films to further increase the sensor sensitivity. It opens a new way to fabricate the ultrasensitive sensors (Ding *et al.*, 2009).

In this work, we synthesized PDPA via the oxidative polymerization and doped it with 5M HCl at various doping levels. PDPA and its blends with PEO at various ratios were also fabricated into fibers by an electrospinning process. Then we investigated the effects of doping level and the amount of polyethylene oxide on the electrical conductivity and sensitivity of de-doped PDPA pellets, doped-PDPA pellets and PDPA fibers towards methanol vapor.