



CHAPTER I INTRODUCTION

Presently, safety requirements of human being become more and more stringent. There are many circumstances in which a gas sensor* is desired for detecting a specific gas or gases in an environment; for instance, various pollutants in the atmosphere, the leakage of anesthetic gases in hospital, the leakage of toxic gases in laboratory, and the emission of odors from food indicating its condition. Many combustible and toxic gas detectors using metals and polymers have been developed. Some of them are briefly described here (Loughlin, 1993).

The most widely used gas monitor is an *electrochemical sensor* with an anode and a cathode separated by an electrolyte. The current generated by this system depends on the concentration of gas absorbed and oxidized or reduced on the electrode surface. If the oxygen level is less than 1%, it will need a fresh air purging for 30 minutes every hour. A *metal oxide semiconductor* (e.g. tin oxide and zinc oxide) is a popular gas detector. Its electrical conductivity changes when gas molecules are adsorbed onto its surface. Even though its low selectivity has been improved (Pijolat *et al.*, 1999), its operating temperature needs to be as high as 300 – 400 °C which remains a problem. Moreover, it usually takes a few days to obtain a really stable readout signal. A *catalytic detector* works on the basic of oxidation reaction of flammable gas which releases energy and raises its temperature. However, the early catalytic sensors could be poisoned temporarily by compounds containing halogen or sulfur. The example of this class is a catalytic pellistor sensor (<http://www.crowcon.com>) which has to be operated at 500 °C.

Spanning more than two decades, *conductive polymers* have been developed with the aim to be an intelligent gas sensor because of many advantages: they can be operated at room temperature; they are light, non-corrosive and can be prepared and cast on various substrates easily. Polypyrrole, PPy, has been one of the most interested amongst several conductive polymers due to its high electrical conductivity (Truong *et al.*, 1992), relatively high environmental stability (Truong *et al.*, 1995), and the ease of being doped under various dopants.

* In this specification, the term “gas” refers to material which is in the gas state at room temperature, including vapor and odor.

1.1 Theoretical Background

1.1.1 Electrically Conductive Polymers

Electrically conductive polymers are polymers that possess electrical conductivity due to the fact that there are π -electrons delocalizing along the backbone. They are the conjugated polymers which can be chemically or electrochemically synthesized. The neutral forms of conductive polymers can be insulator or semi-conductor. The examples of this class of polymer are polyacetylene, polythiophene, PPy, and polyaniline. The chemical structures of their neutral forms are shown in Figure 1.

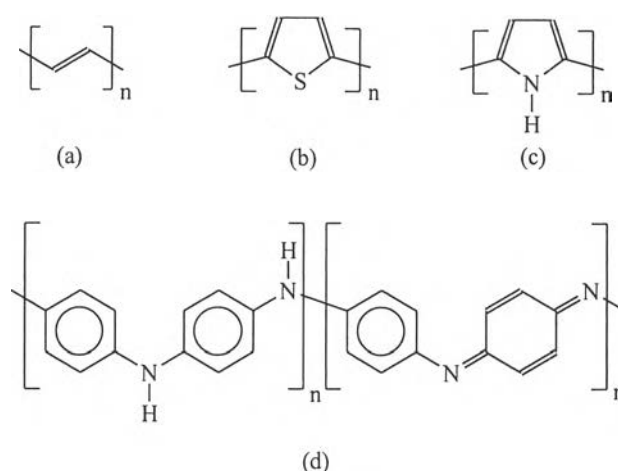


Figure 1 The chemical structures of the neutral form of: a) polyacetylene; b) polythiophene; c) PPy; and d) polyaniline.

Delocalized charge carriers could be introduced by donating electrons to or withdrawing electrons from polymer chain via reduction or oxidation reaction, respectively. This process is known as ‘doping process’. When electrons are removed from the valence band by an oxidizing agent, p-type conducting polymer is formed with positive charges which can delocalize as charge carriers. *Vise versa* when electrons are added by a reducing agent, n-type conducting polymer is formed. For most of conductive polymers, the former structure is more thermodynamically stable and it is much more widely studied. Oxidation breaks one double bond in polymer chain, leaving a free radical and a positive charge on the chain. This form is called

'polaron'. At a higher extent of oxidation, when a concentration of polaron is so high that they can meet with each other, two of radicals in particular two polarons combine with each other to form one covalent bond. This form of charge carriers consists of two positive charges remaining from the combination of those two polarons: it is called 'bipolaron'. These induced charge carriers must be stabilized by ions from the reaction medium. These counter ions are called 'dopant'. The large range of conductivity is obtained by a doping process, which mainly depends on type of dopant (Yamaura *et al.*, 1988; Wang, *et al.*, 1990; Cao *et al.*, 1992; Shirakawa *et al.*, 1994) and dopant concentration used (Heeger and MacDiarmid, 1980). Polyacetylene can have the specific conductivity as high as 10^4 S/cm when it is doped with I_3^- (Shirakawa *et al.*, 1994). The highest specific conductivity of PPy that has been reported is 10^3 S/cm when it is doped with PF_6^- (Yamaura *et al.*, 1988).

1.1.2 Polypyrrole

Polypyrrole, PPy is one of poly(heterocycles) that possess high environmental stability over polyacetylene which composes of only hydrocarbon. PPy can be easily synthesized easily via electrochemical (Dall'Olio *et al.*, 1969; Diaz *et al.*, 1979) or chemical oxidative coupling polymerization (Angeli, 1916). These advantages make it, nowadays, the most frequently used in commercial applications (Rodríguez *et al.*, 1997).

The principal advantage of a chemical synthesis over an electrochemical one is the possibility of mass production at low cost. The neutral form of PPy obtained from chemical oxidative coupling polymerization has the specific conductivity on the order of $10^{-10} - 10^{-11}$ S/cm. The general scheme of polymerization mechanism is shown in Figure 2. Upon an oxidative doping, a more stable p-type doped form of PPy is formed with polaron or bipolaron as charge carriers. The structure of PPy along with the charge carriers and all possible chemical defects, e.g. branching, carbonyl group, are shown in Figure 3.

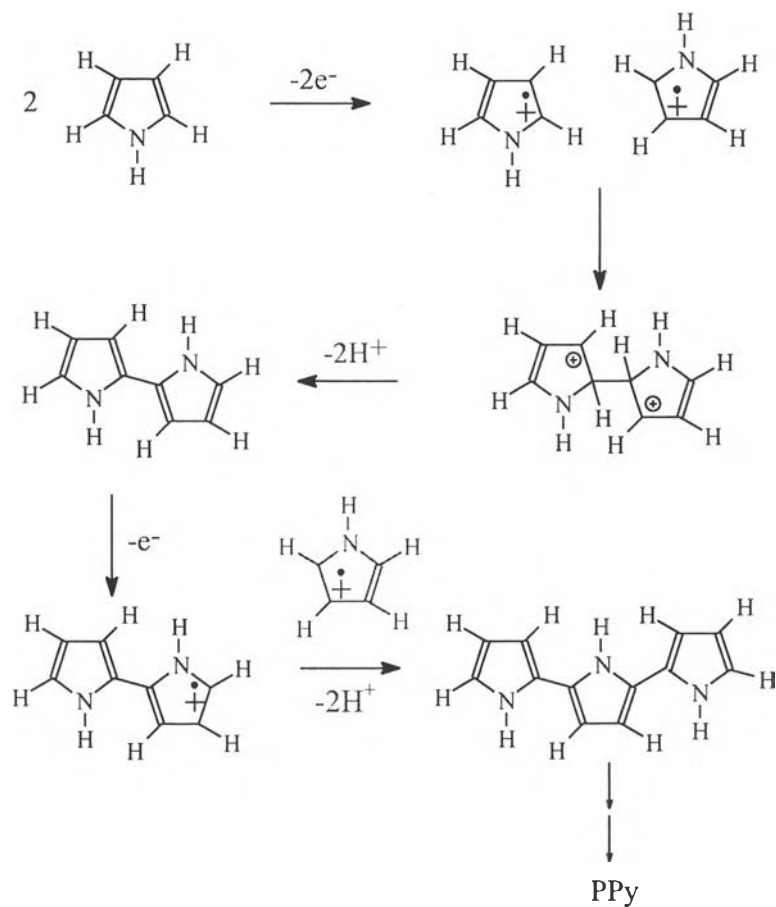


Figure 2 The proposed mechanism of chemical oxidative coupling polymerization of PPy (Zotti, 1997).

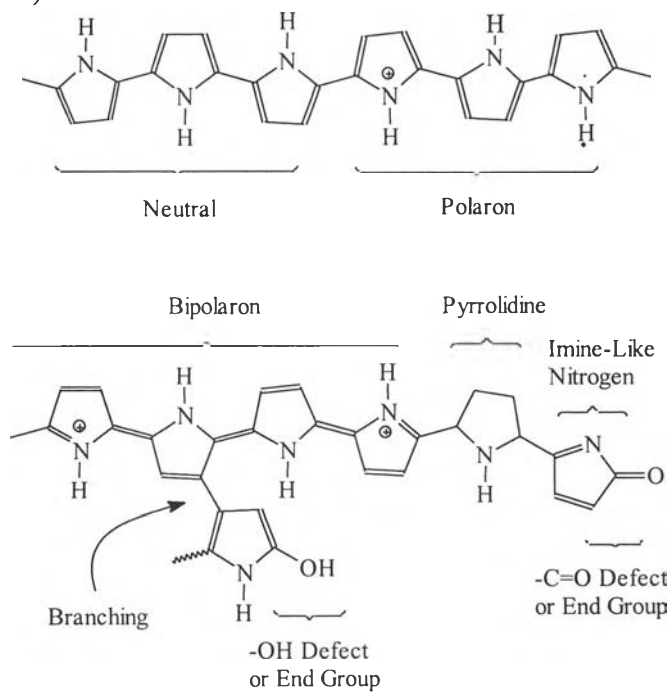


Figure 3 The structure of PPy with its possible chemical defects.

1.1.3 Application of Conductive Polymers as Gas Sensor

The electrical conductivity sensitivity of conductive polymers when they are exposed to various chemicals has been a subject of many studies which focus on sensing applications (Kanazawa *et al.* 1979/1980; Miasik *et al.*, 1986; Gustafsson and Lundström, 1987; Hanawa *et al.*, 1988; Philip and Sim, 1989; Hanawa and Yoneyama, 1989). There are three mechanisms for the specific electrical conductivity to change when a conductive polymer is exposed to a gas. The first mechanism occurs with gas molecules with specific charge transfer properties. Electron-accepting gases like NO₂ (Hanawa *et al.*, 1988) withdraw electrons from polymer chains. If the conductive polymer is a p-type-doped polymer which have positive charges as the charge carriers, its electrical conductivity will increase with NO₂. The FT-IR spectral investigation evidently shows that NO₂ oxidatively dopes the conductive polymer and becomes the dopant anion NO₂⁻ (Miasik *et al.*, 1986; Hanawa *et al.*, 1988). On the other hand, electron-donating gases like ammonia (NH₃) (Hanawa and Yoneyama, 1989) reduce the amount of positive charges in p-type-doped polymer chains and hence decrease the electrical conductivity.

The second mechanism possibly involves conformation changes and/or degree of crystallinity in the polymer matrix itself due to the incorporation of guest molecules which do not have the distinct charge transfer properties by themselves. This mechanism induces a greater or lower charge mobility which in turn enhances or reduces electrical conductivity.

The third mechanism involves the migration of dopant anion molecules which are attached electrostatically to a polymer chain; this process can be referred as an ionic conductivity (Cassignol *et al.*, 1998).

1.1.4 Flammable Chemicals

One of the main causes of fire accident on construction sites and also in chemical stores is the presence of the flammable chemicals, e.g. acetone. Acetone and toluene are the main ingredients in lacquer, the material used for interior decoration. When their concentrations in the air are between their lower and upper explosive limits: 2.5 - 12.8 vol.% for acetone and 1.1 - 7.6 vol.% for toluene (Chou 2000), they can be instantly ignited. Within this decade, there have been at least two

serious fire accidents during hotel constructions in Bangkok, Thailand. There have been a number of fire accidents in chemical stores all over the country.

1.2 Literature Survey

1.2.1 Preparation of PPy

The first report on the chemical oxidation of pyrrole appeared in 1888, then the subsequently reports on the polymerization in the presence of hydrogen peroxide to yield what was commonly referred to as 'pyrrole black' had to wait until 1916. More than 50 years later, the first report of electrochemical production of PPy appeared (Dall'Olio *et al.*, 1969). Until now, many other ways to synthesize PPy have been developed. Sun and Ruckenstein (1996) polymerized PPy films on a surface of a hot 2 wt.% poly(vinyl alcohol). However the highest electrical conductivity from this method was only 1 S/cm. More recently, the *in-situ* doped polymerization has been suggested by Shen and Wan (1997). Dopant was introduced into PPy matrix during polymerization. This method provides the β -naphthalene sulfonate doped PPy with the specific conductivity as high as 27 S/cm.

1.2.2 Application of PPy as Gas Sensor

During the 1970s, reports began to appear on the gas detecting properties of PPy. In 1986, Miasik *et al.* investigated interactions between ammonia, nitroendioxide (NO₂) and hydrogensulphide (H₂S) and PPy coated onto electrodes, and the responses were found to be reversible. However the response to NH₃ concentrations was not linear. After that, many studies have focused on mechanisms of these interactions, especially that caused by NH₃ (Gustafsson and Lundström, 1987; Hanawa and Yoneyama, 1989). In 1987, Josowicz *et al.* demonstrated that under suitable electropolymerization conditions, where aromatic solvents such as nitrotoluenes were incorporated into the PPy metric, PPy exhibited the selective sensitivity to vapor of aromatic compounds. The responses of PPy films to 4 kinds of organic vapors were studied by Philip and Sim in 1989. Methanol and ethanol vapors gave a stable and reproducible decrease in film conductivity but the response of ethanol was much slower. For toluene, acetone and ether vapors, the

responses were much smaller. Moreover for acetone, the baseline resistance of the film drifted towards lower conductivity. In the recent years, Slater and Watt (1992) studied the response of bromine doped PPy, which was coated on piezoelectric quartz crystal microbalance on methanol, hexane, 2,2-dimethylbutane, ammonia and hydrogensulfide. There were changes in both conductivity and mass. The reduction in specific conductivity of PPy caused by NH_3 was nearly reversible (Gustafsson and Lundström, 1987). However, irreversible changes may result with a prolonged exposure time, concentration of NH_3 , and the presence of water vapor (Gustafsson and Lundström, 1987). Other gases studied were AsF_5 , Br_2 (Kanazawa, *et al.*, 1979/1980), O_2 in N_2 (Blanc *et al.*, 1990), CH_2Cl_2 , and HCN (Langmaier and Janata, 1991).

The studies of the guest vapor molecules having no distinct charge transfer properties are: cyclohexane and ethyl acetate (Blanc *et al.*, 1990); hexane, triethylamine, butanal, butan-1-ol, hexan-1-ol, and nonan-1-ol (Deng *et al.*, 1997); ethyl acetate, acetone, and ethanol (Musio and Ferrara, 1997); and water (Okuzaki *et al.*, 1997; Okuzaki *et al.*, 1999). Nigorikawa *et al.* (1995) found an increase in resistivity of PPy upon an acetone vapor exposure. A lower electronegativity of acetone as compared to the work function of PPy suggests the reduction of PPy caused by acetone. An exposure of Langmuir-Blodgett film of PPy to acetone (Milella *et al.*, 1996) caused a stable and reproducible resistance changes. The response increases with chemical's polarity; for acetone, the response is smaller than for those of methanol and ethanol, but bigger than those of ethyl acetate and toluene. The good correlation between resistance changes and the number of monolayers in the film indicated a bulk effect.

1.3 Research Philosophy

1.3.1 The Driving Force of Research Work

Because of the grave dangers from fire accidents described above, a sensor for those flammable chemicals is needed. An appropriate sensor should be simple, cheap, light and portable, so that every construction sites and chemical stores in poor countries can afford to use it practically. The sensor array of conductive

polymers seems to work excellently, but its high cost and complexity make it unsuitable for these requirements. The appropriate sensor should be developed from the single PPy sensing materials that have high sensitivity and high selectivity toward acetone and toluene over other interference from lacquer and from environment. Moreover, it should have a high stability under the alternating weather all over its working life.

With the advantages of PPy-based gas sensor as mentioned, it has some practical disadvantages. Firstly, the variety of gases and chemical vapors that may change the electrical conductivity of PPy as referred above indicates its low selectivity. To overcome this problem, many researchers fabricate sensor arrays from different sensing materials: the conductive polymers that are environmental stable, e.g. PPy, polyaniline, and polythiophene; and their derivatives (Hodgins, 1995; Harris *et al.*, 1997). Those arrays work well on the basis of pattern recognition but they have to be initially calibrated with all target gases. They are complicated and need expensive software to operate: furthermore, they are not portable. Secondly, PPy generally has poor mechanical properties. Many researchers introduced blending PPy with common polymer, e.g. PE, PP, PMMA (Omastová *et al.*, 1996), PVA, polyamide, polyester, and PTFE (Lin *et al.*, 1999; Hwang *et al.*, 1999).

1.3.2 Objectives

Our objective for this dissertation is to develop PPy-based sensors for detecting acetone and toluene vapors, which are flammable chemicals in lacquer. The sensors must have a high sensitivity, a high selectivity, and a high stability in signal under various humidity values.

We have accomplished the sensor requirements by means of: a) *chemical modifications* of PPy chains by varying type of dopant and dopant concentration and; b) *physical modifications* of the PPy, which is doped with the best dopant and at the optimum dopant concentration, by means of blending with common polymers. The results of chemical modifications are reported in Chapter II and Chapter III in this dissertation, whereas those of physical modifications are reported in Chapter IV and V.

An additional objective was initiated upon an X-ray photoelectron measurement of PPy. X-ray beam has been reported to be harmful for many polymeric materials (Chang and Thomas, 1982; Bocchi and Gardini, 1986; and Briggs, 1998). To answer the question how reliable the results of our sample from this technique were, the surface degradation induced by X-ray beam was studied.

1.3.3 Research Strategies

1.3.3.1 *The Sensitivity Improvement*

It has been shown that different chemical structures and properties of dopants can modify the properties of PPy, e.g. the surface morphology (Topart and Josowicz, 1992), the solubility (Shen and Wan, 1998), the moisture content (Cassagnol *et al.*, 1998), and the degree of water sorption (Okuzaki *et al.*, 1999). However, the properties of PPy doped with various dopants from various research groups cannot be compared directly due to some differences in polymerization conditions, handling, processing and storage conditions. This work aims to report the effect of dopant anions and dopant concentrations on the physical, chemical, and electrical properties of PPy. Then, the PPy with acceptable properties will be selected to further study its electrical response of PPy toward acetone vapor. The sensitivity and the temporal response of a conductive polymer are expected to be improved if the film is sufficiently thin (Partridge *et al.*, 1996). However, because of the low solubility of PPy (Salaneck *et al.*, 1993) and the aim of this work is to detect the flammable acetone at a very high concentration, PPy is better prepared as a thick pellet in order to have a high susceptibility to chemical vapor.

1.3.3.2 *The Selectivity Improvement*

Despite the large number of publications on the sensing properties of PPy, no work has been done to improve the selectivity of a PPy sensing material towards a particular chemical. This work attempts to improve the selectivity of PPy towards flammable chemicals in lacquer; i.e. acetone and toluene. It is ideal to reduce the sensitivity toward acetic acid and water. Acetic acid is the other major ingredient in lacquer which is non-flammable: it normally exists in lacquer up to 20

vol.%. Water is present in air as the moisture. The most promising PPy from the previous step, the sensitivity improvement, will be modified physically.

Polymeric materials composed of conducting polypyrrole, PPy, and insulating polymers have been prepared for some special applications. PPy has been electrochemically polymerized onto the matrix of poly(vinyl alcohol) (Lindsey and Street, 1984) or poly(urethane) (Chiu *et al.*, 1992). It has also been chemically synthesized in the presence of PE, PP, or PMMA microbeads (Omastová *et al.*, 1996). At 8.9 wt% of PPy, PP particles were totally covered with a 60 nm thick PPy layer. The specific conductivity values of composites were as high as 10^{-2} S/cm. The potential applications for these materials are anti-static packaging and electromagnetic radiation shielding. PPy-polyamide composite was reported as a gas sensor by Selampinar *et al.* (1995). Upon exposure to CO₂, the resistance decreased and reached a steady value within 50 min, 5 times faster than that of pristine PPy. For NH₃ exposure (Selampinar *et al.*, 1995), both temporal response and sensitivity were evidently improved. However, there has been no report about selectivity improvement.

The swelling effect is one of the proposed mechanisms of the electrical conductivity change in PPy upon exposure to chemical vapors. Meanwhile, the variation in the solubility parameter of some common polymers indicates not only the differences in dissolving but also in swelling when exposed to different solvents. Utilizing polymers that swell under the presence of acetone and toluene but do not swell in acetic acid and water is expected to improve the selectivity of PPy. From Table 1, by considering the solubility parameters of acetone, toluene, acetic acid, water, and polymers in solvents with different hydrogen bonding ability, the polymers that can be used to improve the selectivity of PPy by this strategy are PMMA, PS and ABS. However, PEO, polymethacrylic acid, and PE will be also studied. These polymers will be introduced into PPy matrix by means of dry blending, solution blending, and coating. The coating of PMMA onto PPy pellet surface is proposed to protect PPy totally from water and acetic acid.

Table 1 Solubility parameter, δ in $[\text{MPa}]^{1/2}$ of chemicals (shown in parentheses) and some insulating polymers (Grulke, 1989)

Polymer	Solvent Hydrogen Bonding		
	Poor	Moderate	Strong
	Toluene (18.2)	Acetone (20.3)	Water (47.9) Acetic Acid (21.3)
PEO	18.2 – 26.0	17.4 – 30.1	19.4 – 29.7
Polymethacrylic acid	0	20.3	20.6 – 29.7
PMMA	18.2 – 26.0	17.4 – 27.2	0
PS (Koppers KTPL-A)	16.4 – 21.7	16.6 – 20.3	0
ABS		16.5 – 21.0	
85%styrene/15%acrylonitrile	18.2 – 22.7	19.0 – 24.8	0

1.3.3.3 *The Stability Improvement*

Finally, the successfully modified PPy is tested for the other sensing performances, e.g. signal stability under the changing environmental humidity. The PPy blend that insensitive to liquid of water is expected to be insensitive to moisture as well. Moreover, its mechanical properties is expected to be improved at the same time.

1.3.3.4 *A Study of Surface Degradation of PPy during X-Ray Photoelectron Measurement*

According to the additional objective as stated above, a surface degradation of PPy samples was investigated. The expected cause of degradation is heat, which has been suggested by Buncick *et al.* (2000) and Briggs (1998) without any supporting experimental data. This hypothesis was tested in this dissertation by carrying the XPS experiments for PPy repetitively under a lower temperature using liquid nitrogen, and results are compared with the results taking at uncontrolled temperature.