CHAPTER I
INTRODUCTION

Conducting polymers or CPS are the complex dynamic structures which consist of the oxidative or reductive groups used in the research work as the smart materials. Conducting polymers not only exhibit conducting properties, but they also possess some extraordinary properties such as electronic, magnetic, optical properties, mechanical, and microwave-absorbing properties. Therefore, many of research work have been done to find new applications of conducting polymers such as electronic nano devices, polymer light emitting diodes (LEDs), catalysis, electromagnetic materials, sensor technologies, energy storage, super-capacitors, electrochromic devices, and etc., as shown in Figure 1.1. By rationally choosing the materials, it is possible to prepare multifunctional molecular structures that open possibilities for almost any desired applications (Ates *et al.*, 2012; Das *et al.*, 2014).

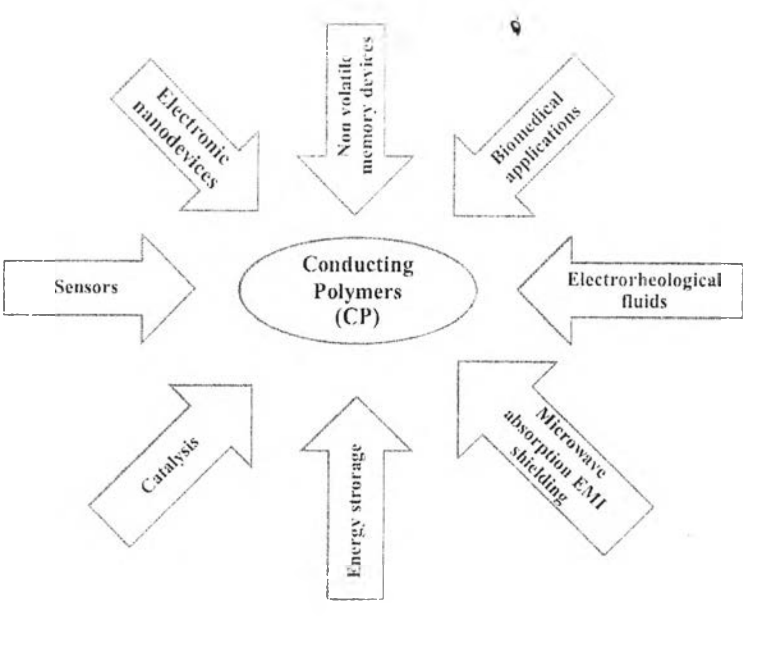

Figure 1.1 Applications of conducting polymers (Das *et al.*, 2014).

Due to their unique properties, various types of conducting polymers for example poly(acetylene) (PA), poly(aniline) (PANI), poly(pyrrole) (PPY), poly(p-phenylene vinylene) (PPV), poly(3,4-ethylene dioxythiophene) (PEDOT), poly(furan) (PF) and other poly(thiophene) (PTs) derivatives, and etc., have drawn special attentions in the many research fields. Particularly, conducting polymers are the common materials to develop as a sensor. Although they have some similarities to conventional polymers, they can be considered to be a smart sensor which a several advantages: room temperature operation, less toxicity and corrosion, low cost, and light weight.

Poly(*para*-phenylene vinylene) (PPV) is an alternating copolymer between PA and PPP which combines between the high electrical conductivity of alternated double bond and the phenylene group as shown the PPV structure in Figure 1.2. PPV is an important polymer in many electronic applications such as LEDs and photovoltaic devices which is due to the small optical band gap and its fluorescent properties. Furthermore, it can be easily doped to form electrically conductive materials. PPV is mostly synthesized by using chemical process. However, PPV based devices still have drawbacks because of the photo-degradation. However, PPV and its derivatives are used to develop various applications especially in sensor field due to the high electrical conductivity, good chemical and environmental stability, and light weight (Collins *et al.*, 1996; Das *et al.*, 2014).

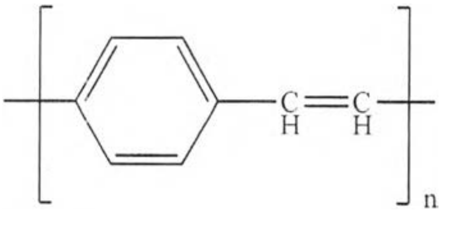

Figure 1.2 PPV structure (Das *et al.*, 2014).

The development of gas sensor is an essential topic due to increasing environmental problems. The problems can be from the nature or man made as results of the expansion of the worldwide population resulting in the increase for the demand of energy and petrochemical products. Many processes in industry, transportation, and residence generally release various volatile organic compounds or VOCs which are typically contaminated with toxic gases and chemical vapors causing a wide range of diseases in the long-term as shown in Figure 1.3. For example, sulfur dioxide (SO_2) can induce a lung disease and respiratory problem. Therefore, the development of devices to detect and reduce the pollutants will be a significant challenge. A gas detector is one instrument which is used to detect the leakage and concentration of toxic gases and chemical vapors in atmosphere originating from industrial plants, hospitals, and school laboratories (Fanget *et al.*, 2011). Consequently, there is a great deal of interest in developing alternative sensor technologies, noting that chemical sensors are an attractive tool which can rapidly monitor environmental contaminants.

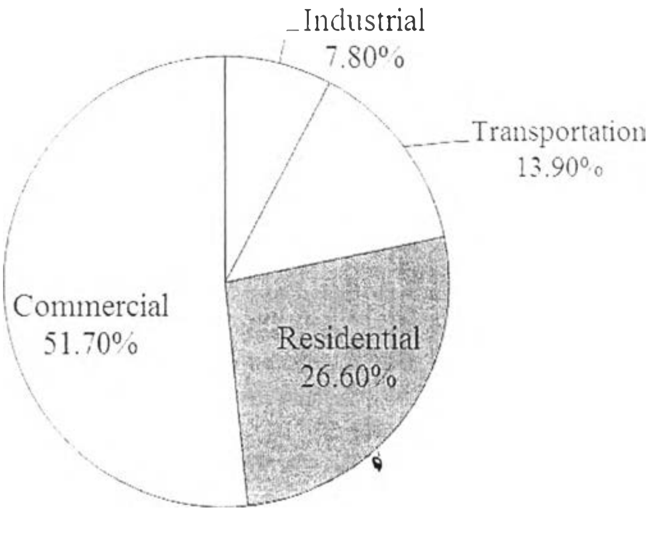

Figure 1.3 The percentages of energy usage in various fields as of 2012 (Fanget *et al.*, 2011).

Various methods are available to screen the level or concentration of toxic components. Generally, a catalytic sensor is one of many gas detectors which is widely used to monitor toxic gases and chemical vapors. They work on the principle of a gas or air combustion is in contact with a hot surface of catalyst. The heat increases the temperature of the sensing element and changes the thermal resistance of the catalyst surface during toxic gas and chemical vapor exposures. The thermal resistance change can be related to the toxic gas and chemical vapor concentration. Although the catalytic gas sensor is easy to use, they could be contaminated by cathode when immersed in a common electrolyte solution. The last popular gas detector is the semiconducting gas sensors. They are made from semiconducting materials (metal oxide, conductive materials, and carbon nanotube) along with several advantages such as the possibility as a universal gas detector, low fabricating cost, and ease of usage as shown the schematic in Figure 1.4.

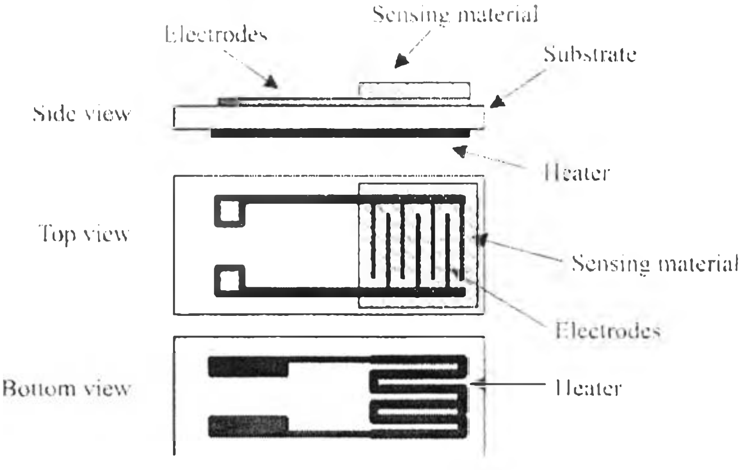

Figure 1.4 The schematic semiconducting gas sensor (Liu *et al.*, 2012).

Sensor materials for toxic gas and chemical vapor detection are mostly polymers as shown Figure 1.5. Conducting polymer gas sensors is one type of polymeric gas sensors which provide many advantages such as high sensitivity, short response, the low fabricating cost, simple and portable structures. On the other hand, they also exhibit some disadvantages such as long-time instability, irreversibility, and poor selectivity. Furthermore, the development of conducting polymer for sensing materials still needs a clearer and more convincing explanation (Liu *et al.*, 2012).

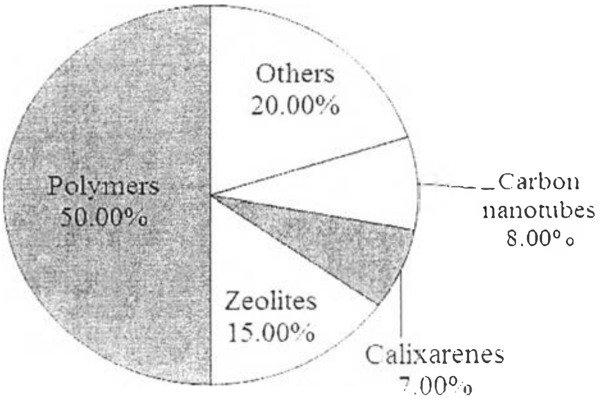

Figure 1.5 Materials used in sensor application. Note other groups comprises of inorganic metal oxide, semiconductors, and organic film (Pejcic *et al.*, 2007).

Moreover, porous materials are the other types to use and study in the sensor field. Zeolite is a porous material which consists of the hydrated alumino-silicates of group I and group II, sodium, ammonium, calcium, strontium, and etc. The structures of zeolite are frameworks of aluminosilcates. They are used in various applications such as petrochemical cracking, gas separation, removal of gases and solvent, and as gas detector materials. From theirs porous properties, the gas and liquid can be adsorbed into the zeolite framework resulting in the change of ionic conductivity of the zeolite as shown Figure 1.6 (Sahner *et al.*, 2008).

The two most important sensor properties are sensitivity and selectivity and a great deal of effort has been directly towards charactering the sensor in term of these parameters. Typically, the electrical conductivity sensitivity values of zeolite materials are low. One method to enhance their sensitivity properties of a zeolite is by using a conductive polymer as a filler.

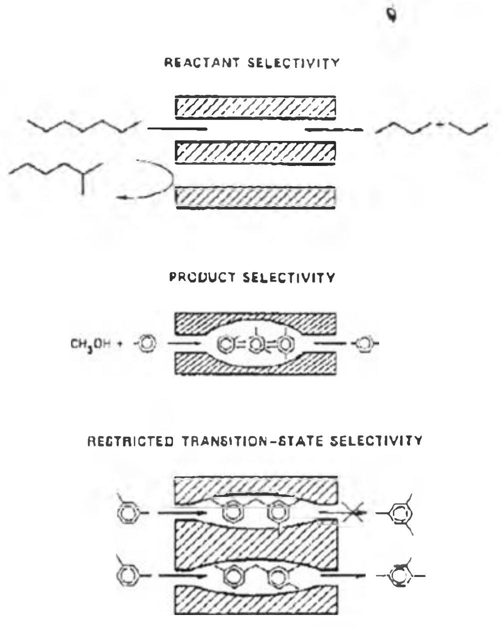

Figure 1.6 Different types of reaction selectivity imposed by rigid pore structure of zeolite (Auerbach *et al.*, 2003).

Therefore, the objective of this work is to develop the composites between dPPV and zeolite Y for using as a flammable vapors sensor. PPV was synthesized and systematically characterized. Zeolite Y (Si/Al=5.1 and Na^+) was ion exchanged with alkaline cations (K^+, Mg^{2+}, and Ca^{2+}) and alkaline (Cu^{2+}, Ni^{2+}, and Fe^{2+}) to improve the electrical sensitivity towards flammable vapors. Moreover, the cation exchange level, chemical vapor concentration, cyclic interval and the percentages of dPPV on the composites materials on the electrical conductivity sensitivity towards flammable solvent were systematically investigated. Zeolite Y (Si/Al=5.1 and Na^+), zeolite mordenite (Si/Al=18 and Na^+), and zeolite 5A (Si/Al=1 and Na^+) were ion exchnged with Cu^{2+} to study the selective properties towards two different flammable vapors (polar vapor and non polar vapor). The selectivity of each chemical vapor depended on the zeolite type. The physical and chemical interactions between a flammable vapor and its composite were investigated by FTIR and AFM techniques. It was expected that dPPV/zeolite can be used as a selective sensor.

Scope of Research Work

Research Work 1: Sensitive and Selective Response of Poly(p-Phenylene Vinylene)/Zeolite Y-Based Sensors towards Ketone Vapors

The poly(p-phenylene vinylene) (PPV) was synthesized by the reaction between α, α' dicloro-p-xylene with tetrahydrothiophene. The composites of PPV and zeolite Y were fabricated by dry mixing a hydraulic press. The effects of dPPV concentrtion, cation types of zeolite Y, and the ketone vapors on the electrical conductivity response of the composite were investigated. The work also focused on the temporal response and induction time when the composites were exposed to three different ketone vapors.

Research Work 2: Poly(p-phenylene vinylene)/zeolite Y Composite as a Ketone Vapors Sensor: Effect of Alkaline Cations

This work investigated the effects of alkaline cation type and cation concentration of zeolite Y at a fixed Si/Al ratio at 5.1 on the electrical conductivity sensitivity of zeolite Y/PPV composite towards three different ketone vapors. In addition, the effect the cyclic interval was also investigated. The FTIR techniques was used to study the interaction between the composites and the ketone vapors.

Research Work 3: Effect of Transition Metals on the Electrical Conductivity Response of dPPV/Zeolite Y Composites towards Ketone Vapors

DPPV was mixed with zeolite Y (Si/Al=5.1 and Na^{+}) which was ion exchanged with 3 different transition metals (Cu^{2+}, Ni^{2+}, and Fe^{2+}) to improve the electrical conductivity responses towards three different ketone vapors (acetone, MEK, and MIBK). The effects of transition metal type, dPPV, and chemical vapor concentration were investigated in this work. Moreover, the interaction of the composite between dPPV and zeolite Y was studied by using the FTIR and AFM techniques.

Research Work 4: Improving Selective Properties of dPPV/(Zeolite Y, Mordenite, 5A) and Response towards Chemical Vapors

Zeolite Y (Si/Al=5.1 and Na^+), zeolite mordenite (Si/Al=18 and Na^+), and zeolite 5A (Si/Al=1 and Na^+) were ion exchanged with Cu^{2+} to improve the electrical conductivity sensitivity and to study the selectivity towards two different flammable vapors (polar vapor: acetone and methanol and nonpolar vapor: n-heptane). DPPV was used to blend with the zeolite to improve their electrical conductivities. In this work, the effects of zeolite types, polarity of flammable vapor, and vapor concentration were investigated. The AFM technique was used to study the interaction between the composites and the chemical vapors.