

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Conductive Polymer

Since the discovery of conductivity in polymer in 1961 by Hatano and coworkers (Hatano *et al.*, 1961), the so-called Intrinsically Conducting Polymer (ICPs) has been investigated extensively. Hatano *et al.* discovered that a polyacetylene sample had conductivity of the order of  $10^{-5}$  S/cm. A very important result was obtained in 1977, when Shirakawa, MacDiarmid, Heeger and coworkers reported that the conductivity of freestanding polyacetylene films increased up to 12 orders of magnitude upon exposure to halogen vapors (Shirakawa *et al.*, 1977; Chiang *et al.*, 1977; Chaing *et al.*, 1978). This can be attributed to the formation of free charge carriers in the polymer chain upon reduction or oxidation of the ICP and this process is called doping. But polyacetylene has drawbacks because of its processing difficulty and the rapid decrease in conductivity upon exposure to air. Therefore other ICPs that are more environmentally stable and that can be polymerized in an electrochemical synthesis have been developed. Thus new ICPs has been synthesized and investigated: polyacetylene, polypyrrole (PPy), polyaniline (PANI), polythiophene (PTH), and polyphenylene vinylene (PPV) (Figure 1).

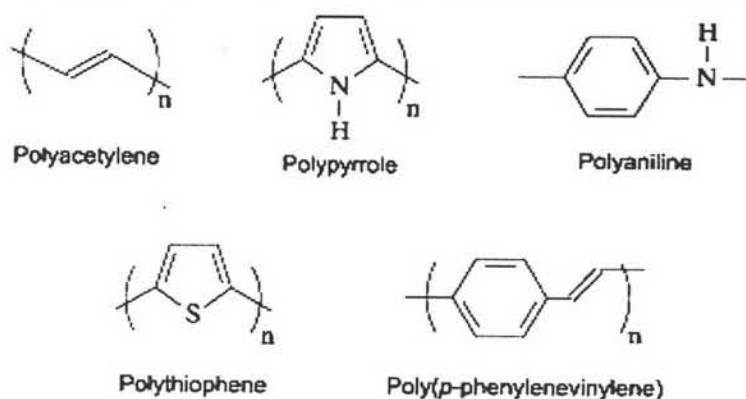
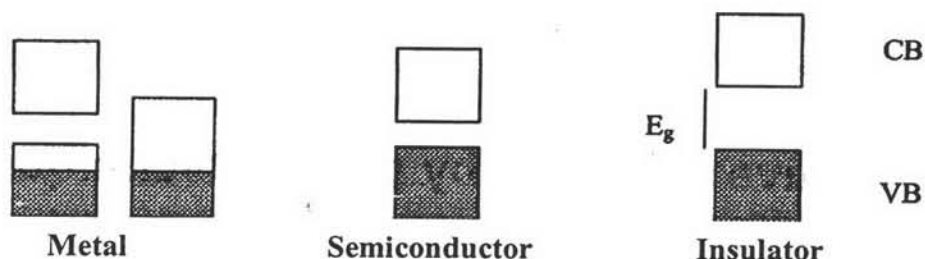


Figure 2.1 Intrinsically Conducting Polymers.

Generally, conductive polymers are organic material which comprised of C, H and simple heteroatom such as N and S and consisting of unique  $\pi$ -conjugation electrons. Conjugation is important characteristic because it provides a pathway for electrons to migrate along a polymer chain and to jump from one chain to another chain. So, conjugated polymers have the ability to conduct electricity by the delocalization of  $\pi$ -bonded electrons over the polymeric backbone, exhibiting unusual electronic properties, such as low energy optical transitions, low ionization potentials and high electron affinities (De Paoli and Gazotti, 2002). These phenomena present electric, electronic, magnetic and optical properties inherent to metals or semiconductors, while retain the mechanical properties of conventional polymers. Those properties are intrinsic to the doped materials: they are completely different from those originated from a physical mixture of a non-conductive polymer with a conducting material, such as metal or carbon powder (Patil *et al.*, 1988). Furthermore it has several advantages: low density and cost, ease of processing, relative robustness, and lightweight, so it is widely used in many applications such as gas sensing, light-emitting cells and diodes, rechargeable batteries, electronic cells, controlled-release applications, actuators, and polymeric electronics such as transistors (Van Vught *et al.*, 2000).

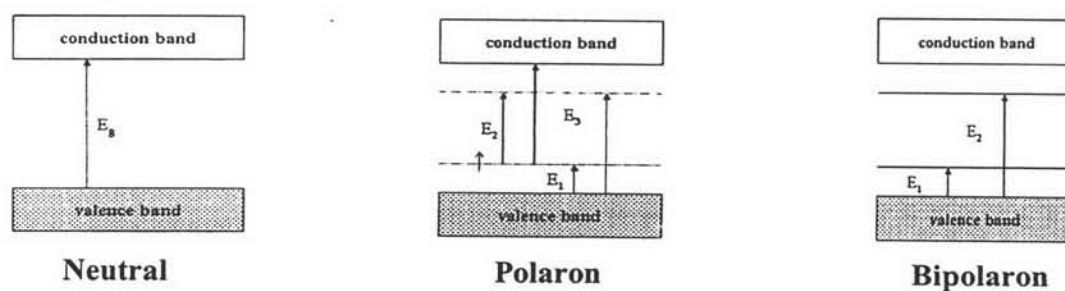
## 2.2 Semiconductor Model

Materials in the world can be classified into three categories according to their room temperature conductivity properties: Insulators, Semiconductors and Conductor. These materials contain two electronic band, valence and conduction band that occur by overlapping of molecular electronic states. Each material has different electric model that illustrate in figure 2.2



**Figure 2.2** Schematic diagram of the band structure of metals, semiconductors, and insulators ( $E_g$  is the energy gap between the valence band (VB) and the conduction band (CB)).

If the gap between conduction (CB) and valence band (VB) is large, electrons are difficult excited from valence to the conduction band which is characteristic of insulator. In case semiconductor has small gap, electrons are easily excited into the conduction band by thermal excitation, vibrational excitation, or excitation by photons. Conductive polymers have different electronic state after doping, solitons, polarons or bipolarons. These defects or the charge carriers generate localized electronic states in the middle of the energy gap between the valence band and the conduction band. This effectively reduces the energy gap and the charge carriers can jump into conduction band and electrical conductivity is enhanced (Kumar and Sharma, 1998; Chandrasekhar, 1999; Van Vught *et al.*, 2000).



**Figure 2.3** Schematic diagram neutral, polaron, bipolaron state.

The polaron has form of radical cation (one unpaired electron), which is locally associated with a structural distortion in conductive polymer and conduction band remains empty and the valence band remain full. Therefore, electrical conduction can only take place when electron is removed from valence band into the conduction band. If the second electron is removed from the polaron itself, bipolaron will be achieved (Chandrasekhar, 1999).

### 2.3 Concept of Doping

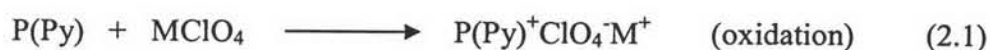
In intrinsic conducting polymers, also known as conjugated polymers, they are distinguished by alternating single and double bonds between carbon atoms on the polymer backbone or the main chain contains  $\pi$ -conjugation. The naturally  $\pi$ -conjugated electrons systems on conductive polymer backbone are not sufficient to render them highly conductivity; trans-polyacetylene possesses only  $10^{-6}$  S.cm<sup>-1</sup>. The high electrical conductivity is achieved by the process called the “doping process”. This process was firstly discovered by Shirakawa and Ikeda by doping of polyacetylene (PA) with iodine, and conductivity increases by 9-13 orders of magnitude (Kumar and Sharma, 1998).

The concept of doping distinguishes conducting polymers from all other kinds of polymers. The controlled addition of known, small (< 10 %) non-stoichiometric amounts of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical and structural properties of the polymer (De Paoli and Gazotti, 2002). Doping of pristine conductive polymer can be accomplished by using chemical and electrochemical method via oxidation or reduction reaction. In chemical method, conjugate polymer is directly exposed with a solution or vapor of the dopant. If the oxidation in the polymer occurs, it extracts electrons from the valence band (electrons from the polymer to the dopant), creating “holes” in the valence band, which is then known as “p-doping”. It generates a positively charged conductive polymer and an associated anion. When the reduction on the polymer occurs, it adds electrons to the

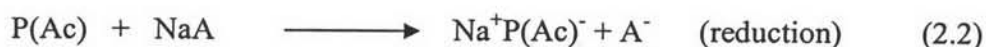
conduction band (electrons from the dopants to the polymer), increasing conducting electrons in this band, which is known as the “n-doping”. This generates a negatively charged conductive polymer with an associated cation (Chandrasekhar, 1999).

Doping processes are summarized in the schematic below, where M and A are the cation and the anion, respectively:

*Anionic doping (p-doping):*



*Cationic doping (n-doping):*



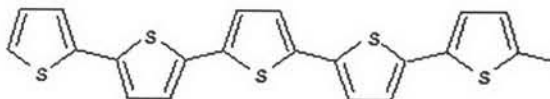
Dopants are generally incorporated into the conductive polymer at the time or later of synthesis. Usually, dopants are small anions or cations, eg.  $\text{ClO}_4^-$  or  $\text{Na}^+$ , or large polymeric species, such as the “polyelectrolytes” poly(styrene sulfonic acid) and poly(vinyl sulfonic acid). These counter-ions neutralizing charge on conductive polymer can influence the mobility of the charge carriers (Van Vught *et al.*, 2000). If counter-ions are large so the degree of charge delocalization is stronger. That means the stability of the conductivity can be affected by the size of the counter-ions. Moreover, conductivity can be increased via creation of more mobile charges by increasing doping level or using different dopants.

The doping with n-type dopants, anion conductive polymer is formed which is highly unstable in air and water. So, the conductivity which is generated by n-type dopants e.g. Na, Li is less stable than by p-type dopants e.g.  $\text{I}_2$ ,  $\text{AsF}_5$ ,  $\text{FeCl}_3$ ,  $\text{HClO}_4$ . Therefore p-type dopants are more frequently used (Kumar and Sharma, 1998; Chandrasekhar, 1999; Van Vught *et al.*, 2000).

## 2.4 Polythiophene

Polythiophene (PT) is an important conducting polymer belonging to the rigid-rod polymer host family. It can be polymerized by specific chemical methods or via electrochemical synthesis by oxidation reaction (Liaw *et al.*, 1999). After doping process the color of this polymer changes from red to blue.

This polymer has many advantages: high conductivity (some cases approaching that of metals); large amounts of charge can be stored; high stabilities in aqueous media and air; the polymerization and doping methods are simple and giving high yield; exhibits electrically triggered molecular conformational transition; ease of chemical modification; flexible; lightweight, and ease of fabricating thin films (Kumar and Sharma, 1998; Mu and Park, 1995; Anquetil *et al.*, 2002).

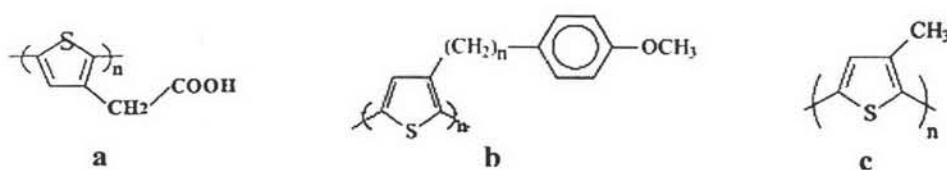


**Figure 2.4** polythiophene.

Poly(thiophene)s and derivatives (Fig.3) are potentially useful components in field-effect transistors, optical and electronic sensors, light-emitting devices, nonlinear optical materials, and etc (Ribeiro *et al.*, 2004). Because polythiophene derivative are modified in particular ways, some properties are improved such as solvent solubility, fusibility, environmental stability, electrical conductivity and optical properties through introducing various substituent groups as the side chains with electron donating and accepting nature. Polythiophene derivatives may possess different substituted groups and lengths on the thiophene ring, so polythiophene has many derivatives. Poly(3-alkylthiophene) are polythiophene derivatives that have soluble and flexible side chain substituted onto  $\pi$ -conjugated polymers. They are easily processible materials and still

may have the extended  $\pi$ -electron delocalization typical of the corresponding unsubstituted parent polymer (Andreani *et al.*, 2000).

Basically, attaching substitute groups to the 3- and/or 4- positions of the thiophene ring minimizes the occurrence of  $\alpha$ - $\beta$  coupling during polymer synthesis, producing more regular structures with enhanced properties. Various types of soluble poly(3-alkylthiophene)s with a long alkyl chain at the 3-position have been extensively studied (Ribeiro *et al.*, 2004). The long substituted alkyl chain has also been used to produce more regioregular structures. These neutral polythiophenes, bearing properly designed side chains, can undergo striking conformational changes when exposed to heat, light, electric fields or various chemical moieties giving rise to reversible thermochromism, photochromism, electrochromism, or ionochromism. These optical changes are believed to be related to a reversible planar-to-nonplanar conformational transition of the conjugated main chain (Kim *et al.*, 1999). The length of the alkyl chain was related to the solubility and the electrical conductivity of the product. An alkyl side chain of appropriate length also contributes to make the polymer more soluble, enhancing the possibility of using it in technological applications (Ribeiro *et al.*, 2004)



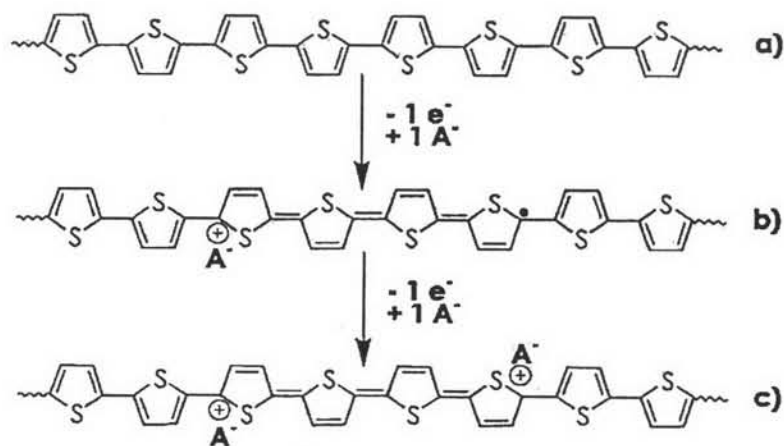
**Figure 2.5** polythiophene derivatives: (a) poly(3-thiopheneacetic acid), (b) poly-3-[ $\omega$ -(p-methoxyphenoxy) alkyl]thiophene, (c) poly(3-methylthiophene).

Another derivative, poly (3-thiopheneacetic acid) (PTAA) has attracted much attention due to its bioelectrochemical and photochemical properties in homogeneous competitive immunoassays. Although the PTAA salt form shows high water-solubility, the PTAA acid form is not soluble in water due to the strong hydrogen bonds between

the carboxyl groups. Moreover, the carboxyl group of PTAA can react with a desirable compound or can interact with an antigen, a desirable feature for biological devices (De Souza *et al.*, 2001).

The aqueous electrochemistry of the conducting poly(3-thiopheneacetic acid) film has been investigated (Albery *et al.*, 1991; Albery and Li, 1991). Its self-doping process was found to be pH-dependent in an aqueous solution because of the weakly acidic nature of the carboxylic acid group. The limited applications are primarily attributed to its brittle property (Liaw *et al.*, 1999).

Polythiophene can conduct electricity via p-doping or n-doping process that new state of polymer occurs. New forms are polaron and bipolaron that appear at lower and higher doping level, respectively (figure 2.6).



**Figure 2.6** p-Type doping of polythiophene: (a) Neutral form, (b) Polaron form, (c) Bipolaron form.

## 2.5 Zeolite

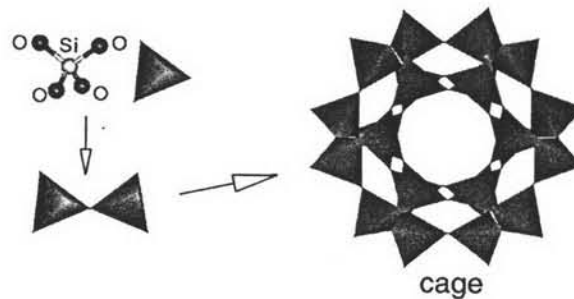
Zeolites were discovered in 1756 by the Swedish mineralogist Axel Fredrick Cronstedt. He named the class of materials zeolites from the classical Greek words



meaning 'boiling stones' which describe the escape of water molecules from the cavities of zeolites (Tomlinson, 1998).

R. Barrer and J. Sameshima worked extensively on zeolite synthesis that zeolites were first synthesized during the 1930's. In 1948, Richard Barrer first produced a synthetic zeolite that did not have a natural counterpart. At approximately the same time, Milton made the first materials that had no natural counterpart such as zeolite A.

Zeolites are porous crystalline aluminosilicate solids with well-defined structures. Most occur naturally as minerals, and are extensively used in many parts of the world. Others are synthetic, and are made commercially for specific uses. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. Their frameworks based on an extensive three-dimensional network of oxygen ions that are made up of 4-connected networks of atoms with a silicon atom in the middle and oxygen atoms at the corners. This framework linked tetrahedral that can link together by their corners to form a variety of structures (Fig. 2.7). The  $AlO_2$  tetrahedra in the structure determine the framework charge. It attracts the positive cations inside within and may contain linked cages, cavities or channels, which are of the right size to allow small molecules to enter. The framework charge is balanced by cations that occupy nonframework positions (Szostak, 1989).



**Figure 2.7** Zeolite framework structure as the tetrahedral.

The vacant spaces or cages in their structures can accommodate large cations such as sodium, potassium, barium and calcium and even relatively large molecules and cation groups such as water, ammonia, carbonate ions and nitrate ions. These channels permit the easy movement of the resident ions and molecules into and out of the structure (Amerthyst Galleries, Inc, 1999, 2000).

Zeolites are used in a variety of applications such as petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are often also referred to as molecular sieves.

## 2.6 Applications of Zeolites

### 2.6.1 Adsorption and Separation

The shape-selective properties of zeolites are the basis for their use in molecular adsorption. The ability to adsorb certain molecules causes several of molecular sieving applications. The size and shape of pores controlling different types of molecule enter the zeolite. Some molecules diffuse through the channels more quickly.

Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find application in gas separation of gases as ammonia, hydrogen sulfide, carbon monoxide, carbon dioxide, sulfur dioxide, water vapor, oxygen, nitrogen, formaldehyde, and others. Molecules are separated on the basis of their electrostatic interactions with the metal ions. So Zeolites can separate molecules based on differences of size, shape and polarity.

### 2.6.2 Catalysis

Zeolites act as catalysts for chemical reactions which take place inside the cavities. An important class of reactions is that catalyzed by hydrogen-exchanged zeolites. The framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerisation and fuel synthesis.

Zeolites can serve as oxidation or reduction catalysts by introducing metals into the framework.

The unique structure has a steric influence on the reaction, controlling the access of reactants and products. Increasingly, attention has focused on the properties of zeolite catalysts in order to carry out very specific syntheses of high-value chemicals e.g. pharmaceuticals and cosmetics.

### 2.6.3 Ion Exchange

The loosely-bound nature of extra-framework metal ions (such as in zeolite NaA, right) means that they are often exchanged for other types of metal when in aqueous solution. This is exploited in a major in water softening, where alkali metals such as sodium or potassium prefer to exchange out of the zeolite, being replaced by the "hard" calcium and magnesium ions from the water. Many commercial washing powders contain substantial amounts of zeolite. Commercial waste water containing heavy metals and nuclear effluents containing radioactive isotopes can also be cleaned up using such zeolites.

Recently, zeolite is interested to use for gas sensor applications by mixing with conductive polymer such as polyaniline, polyphenylene vinylene and polythiophene. Because the well-define structure of zeolite can separate the desire gas molecules and the efficiency of gas sensor can measure by electrical conductivity changing of conductive polymer.

## 2.7 Polythiophene Synthesis and Derivatives

In 1999, Liaw *et al.* improved the brittle property of poly(3-thiopheneacetic acid) film via a net-work formation by using 3,3'-bithiophene or hexamethylene diisocyanate-bithiophene as a crosslink agent. The network film crosslinked by 3, 3'-bithiophene exhibited a large volume change when temperature exceeded 100°C. After

doping with iodine, the decrease in conductivity was observed along with the changes of IR spectra of poly(3-thiopheneacetic acid) film and networks.

In 1999, Kim *et al.* synthesized poly (3-thiophene acetic acid) (P3TAA) and its copolymer with 3-n-methylthiophene or with 3-n-octadecylthiophene by chemical oxidative polymerization using  $\text{FeCl}_3$  as an oxidant. Some properties were investigated by potentiometric titration, viscosity measurements, and UV-visible spectroscopy in different conditions such as varies pH, alkali concentrations, solvent and temperature. When the ionic strength of P3TAA water solution was changed from 1.0 to 2.0 M NaCl, the dissociation of P3TAA was suppressed because of strong electro static repulsion between dissociated groups and found two slope of graph between pH and  $\log [\alpha/(1-\alpha)]$ . The transition of slope at around pH=6 indicated that increase difficulty of the dissociation of polymer. In viscosity, it decreased suddenly at pH=5.05 and almost constant above pH=6. This suggests that conformational changed from the aggregate state to the extended state. Similar explanation in the changing  $\lambda_{\text{max}}$  at rang of pH 5 to 6 increased dramatically and became almost constant above pH=6. The temperature dependence of  $\lambda_{\text{max}}$  of the P3TAA solution at pH=11.1 and 6.3,  $\lambda_{\text{max}}$  increased with increasing temperature that inversed at pH=5.2 because extended state become aggregate state and aggregate state become extended state.

In 1999, Masuda *et al.* synthesized poly(3-methoxymethylthiophene) (PMOMT) and poly(3-ethoxymethylthiophene) (PEOMT) by electrochemical polymerization with various kinds of tetrabutylammonium salt. EOMT and MOMT were prepared by the reaction of 3-lithiophene with chloromethyl ethyl ether. The conductivity of PEOMT was higher than that of POMT. The characteristic IR bands of the C-O-C stretching vibration of the ether groups of PEOMT and PMOMT were observed at  $1097 \text{ cm}^{-1}$  and  $1094 \text{ cm}^{-1}$ . NMR peaks values and shape of cyclic voltammograms (CV) were very similar to those of poly(3-nonylthiophene) (PNOT) and poly (3-undecylthiophene) (PUOT). PMOMT and PEOMT showed similar properties to those of poly(3-alkylthiophene) and poly(3-alkoxythiophene).

In 2001, Masuda *et al.* studied the conductivity of poly(3-alkyl-2,2'-bithiophene)s (poly-ArBT); they are poly(3-hexyl-2,2'-bithiophene), poly(3-dodecyl-2,2'-bithiophene) and poly(3-eicosyl-2,2'-bithiophene) by using different oxidations and solvents. The copper (II) and iron (III) ions are effective oxidants for the chemical polymerization. Chemically prepared poly-ARBT was found to be more soluble and conductivity than electrochemically prepared.

## 2.8 Polythiophene as Gas and Chemical Sensors

In 1999, Tanaka *et al.* studied electrical and optical properties of poly(3-octyloxythiophene); PAOT-8 exhibited stable doped state and a stronger interaction with electron accepting molecules such as fullerene because it has strong electron donating nature of the alkoxy group. So it can be used as gas sensor material. In this case Ethylisovalerate ( $(\text{CH}_3)_2\text{CHCH}_2\text{COOC}_2\text{H}_5$ ), a gas which is contained in various kinds of fruit such as strawberry was used to investigate the effect of gas concentration on conductivity; they found that electrical conductivity increased with gas concentration. When the test gas was replaced by  $\text{N}_2\text{-O}_2$  gas, the original resistance recovered, indicating reversibility of the gas sensor.

In 1999, Schottland *et al.* synthesized and characterized different soluble polythiophenes including poly(3-octylthiophene), poly(3-octylthiophene-co-thienylethanol) copolymers and  $\text{C}_{14}$ -alkylated polymer(3,4-ethylenedioxythiophene methanol) for  $\text{NO}_2$  sensing applications. These polymers were synthesized by a chemical polymerization and deposited by spray coating on an adapted substrate. When gas  $\text{NO}_2$  was exposed to polymer, copolymer containing alcohol functions did not provide better detection but P3OT and PEDTM-C14 showed drastic changes in conductivity and the latter was the most sensitive. However, P3OT has better reversibility; it seems to be the most interesting material for building gas sensors.

In 2002, Sakurai *et al.* developed gas sensor devices by using polythiophene(pTh) film and poly(3-n-dodecylthiophene) (pDpTh) film coated over pTh

film with the electrochemical polymerization using different solvents (propylene carbonate and acetonitrile), and  $\text{BF}_4^-$  or  $\text{ClO}_4^-$  as doping agent. The response characteristics of the conducting polymer films against various sample gases over a range of temperature of the sensitive layer were investigated. The pTh film responded to ammonia gas and pDpTh films responded to hydrophobic gases such as chloroform, methane and ethanol because pDpTh has a long alkyl chain that can interact with hydrophobic gases.

In 2003, Torsi *et al.* used poly-(3,3''-didodecyl-2,2':5',2''-terthiophene) (Poly DDT) and poly-(3,3''-dipentoxy-2,2':5',2''-terthiophene)(Poly DPOT) as active layers in sensing organic thin films transistors (OTFTS). The TFT device: showed the I-V characteristics of using Poly DDT as thin film that had an on/off ration better than  $10^3$  and mobility of  $5 \times 10^{-4} \text{ m}^2/\text{Vs}$  and lower performance level was achieved using Poly DPOT as active layer but it had good degree of regioregularity of sensing layer. In the AFM micrographs, both polymer surfaces showed a polycrystalline material property but Poly DDT had smaller grains than poly DPOT. Both films were considered in the films with ethanol and 1-hexanol and both responses show a good degree of reversibility. Poly DDT was insensitive to ethanol but sensitive to 1-hexanol. On the other hand, Poly DPOT was sensitive to both gases. The different response of both films arised from the different dipole moment and long linear alkyl chain. The considering in interaction between films and alcohols molecules showed no swelling of the film, so indicative that surface interaction occuring.

Alkoxy-substituted polyterthiophene thin films were synthesized to use as active layer in a-thin-film-transistor (TFT) and in a quartz crystal microbalance (QCM) by Torsi *et al.* in 2004. Dipentoxy substituted polyterthiophene (Poly-DPOT) solution in chloroform was casted on transistor substrate or on the quartz crytal. The surface morphology of the Poly-DPOT films exhibited continuous nanoscopic grains that corresponded with high packing stability. When 1-hexanol or ethanol was exposed to the QCM device, it exhibited fast and reversible responses that corresponded to the hypothesis of a surface-interaction and the best extrapolated sensitivity was as good as

0.7 ng/ppm. Further more it gave higher response to 1-hexanol than to ethanol. Those results were exhibited as same in the TFT device.

## 2.9 Other Applications of Polythiophene

In 2003, Chotpattananont *et al.* studied electrorheological properties in oscillatory shear of perchloric acid doped poly(3-thiopheneacetic acid) (PTAA), particles suspended in a silicone oil, examining the effects of field strength, particle concentration, doping degree, operating, operating temperature, and nonionic surfactant on the yield stress. The PTAA/silicon oil suspensions showed the typical ER response of Bingham flow behavior upon the application of electric field. The yield stress at specified electric field strength increased with particle concentration, and at specified concentration, increased as the electric field strength increased. The particles volume fraction decreased and when the doping level of the particles decreased. The yield stress increased with temperature up to 25°C and the electric fields had above 1.5 kv/mm by adding small amounts of a nonionic surfactant.

In 2001, De Souza and Pereira prepared aqueous solution of poly(3-thiopheneacetic acid) (PTAA) by using various kind of solvent such as PVA, water ethanol and ethylene glycol for investigating the optical properties. Stable aqueous of PTAA was obtained by using PVA. In PTAA salt-PVA solution, the absorption spectrum shifts from 480 to 415 nm when acid condition are established that indicated the molecular conformation open coil (expanded structure) become compact coil structure. The chain stretched due to the electrostatic repulsive force between the carboxylate groups and coil-compacted due to the hydrogen bonds between the carboxyl groups. In others solution, the maximum of absorption showed ethanol as poor solvent whereas ethylene glycol and water as good solvent for PTAA salt. The emission spectra of PTAA salt in PVA solution showed two emission bands that one from absorbing species and another from protonating during excitation or to a few chain segments of

PTAA acid present in ground state. In water and ethylene glycol, luminescence was quenched that mean the luminescence intensity increased in poor solvents.

### 2.10 Conductive Polymer as Gas Sensor

In 2000, Prissanaroon *et al.* investigated the electrical conductivity of polypyrrole films as a gas sensor by using dodecylbenzene sulfonic acid as a dopant. The specific conductivity increased with SO<sub>2</sub> concentration and the gas sensitivity of the film depended on the doping level. The specific electrical conductivity change can be correlated with changes in morphology observed by SEM. As the dopant level increased, the morphology changed from three dimensional random coils (granular structures) to rigid rod-like (fibrils structures).

In 2002, Kiattibutr *et al.* showed electrical conductivity of PANI/HCl films higher than PANI/CSA film in all doping level, moisture and humidity content due to the more closely packed water molecules which induced ionic conduction. But PANI/HCl films did not respond to SO<sub>2</sub>. The PANI/CSA responded to SO<sub>2</sub> because of large free volumes. The response was reversible and depended on doping level. The electrical conductivity of PANI/CSA films increased with SO<sub>2</sub> concentration with a lowest detectable limit of 200 ppm.

### 2.11 Zeolite for Gas Sensor Application

In 1995, Triebe and Tezel studied on various molecular sieves including H-Mordenite, 4A and 5A zeolite, a natural clinoptilolite and an activated carbon in order to investigate the adsorption of N<sub>2</sub>, CO, CO<sub>2</sub> and NO. Adsorption of CO<sub>2</sub> on the clinoptilolite was too strong and irreversible. The clinoptilolite showed the strongest adsorption of CO, NO and N<sub>2</sub> between 323 and 473 K. Further more, the clinoptilolite gives the best separation factors of CO/N<sub>2</sub> and NO/N<sub>2</sub> at the temperature range 273-398



K. Micropore diffusion proved to be the dominant mass transfer mechanism for both CO and N<sub>2</sub> in clinoptilolite under the conditions examined between 348 and 423K.

In 2000, Kaneyasu *et al.* produced carbondioxide gas sensor by using a combination of a Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> (NASICON) as solid electrolyte and Li<sub>2</sub>CO<sub>3</sub> as a carbonate phase. The sensor's emf showed a linear relationship with the logarithm of the CO<sub>2</sub> concentration and was slightly affected by interfering gases (CO and EtOH) through the use zeolite filter (Na/Y type). When the sensor was exposed to a high humidity atmosphere, the emf decreased but  $\Delta$ emf stayed fairly stable, so CO<sub>2</sub> concentration can be measured by calculating  $\Delta$ emf. The output of CO<sub>2</sub> monitor corresponded to a NDIR analyzer, so this sensor could be useful for air quality control.

In 2002, Sasaki *et al.* used three different zeolites, which are zeolite A, silicate-1 and sodalite, were deposited on quartz crystal microbalance (QCM) oscillators with resonance frequency of 4.7 MHz. The QCMs were exposed to single gases such as NO, SO<sub>2</sub> and H<sub>2</sub>O in He at 443 K. The differential values were effective to improve the drifts and response time of QCM. Using the principal component analysis (PCA), single gases and mix gases (NO and SO<sub>2</sub>) were qualified and quantified using the differential values which represent sorption-kinetics, instead of the frequency shifts representing sorption-equilibrium. The performance of the sensor system was successfully improved by employing the differential values.

## 2.12 Conductive Polymer/Zeolite Composites

In 2005, Densakulprasert *et al.* studied electrical conductivity of polyaniline/zeolite composites that responded to carbon monoxide (CO) by using zeolite Y, 13X and AlMCM41 that have the pore sizes of 7, 10, 36 Å and have the common cation Cu<sup>2+</sup> inside. The Cu<sup>2+</sup> exchanged capacities of 0.161, 0.087 and 0.044 mol/g. The doping agent is maleic acid (MA). For PANI-10MA/zeolite-13X, the sensitivity and temporal response time increased with zeolite content because of larger total pore volume per unit area, so more CO molecules interacted with PANI chains. PANI-

10MA/Zeolite-13X had pore size and sensitivity higher than PANI-10MA/10-Y because of a greater pore free volume and distribution of  $\text{Cu}^{2+}$  ions. PANI-10MA/10-AIMCM41 had the lowest sensitivity because of large pore size and the longest response time because of the lowest  $\text{Cu}^{2+}$  exchange capacity.

In 2005, Chuapradit *et al.* investigated electrical conductivity response of polyaniline/zeolite composites towards CO by using different dopant type, dopant concentration, zeolite LTA content and zeolite pore size. At same doping level, maleic acid (MA) doped PANI showed a slightly higher conductivity than hydrochloric doped one. Addition of zeolite 4A up to 40% w/w, the conductivity and the response to CO decreased with zeolite content. At 20% w/w zeolite content, zeolite 5A is the most effective in terms of response and sensitivity because it has the largest pore size (5 Å) that promotes interaction between CO and polyaniline.