การพัฒนาแก๊สเซ็นเซอร์จากพอลิเมอร์คอมพอสิตนำไฟฟ้าที่มีพอลิ(3,4-เอทิลีนไดออกซีไทโอฟีน)

นางสาวละอองดาว เม่นบางผึ้ง

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DEVELOPMENT OF GAS SENSOR FROM CONDUCTING POLYMER COMPOSITE CONTAINING POLY(3,4-ETHYLENEDIOXYTHIOPHENE)

Miss Laongdao Menbangpung

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2009

Thesis Title	DEVELOPMENT OF GAS SENSOR FROM CONDUCTING POLYMER COMPOSITE CONTAINING POLY(3,4-ETHYLENEDIOXYTHIOPHENE)
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Field of Study	Petrochemistry and Polymer Science
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งานวิจัยนี้ศึกษาการขึ้นรูปฟิล์มพอลิเมอร์คอมพอสิตนำไฟฟ้าที่มี พอลิ(3,4-เอทิลีนไดออกซีไทโอฟีน) เป็นองค์ประกอบ โดยอาศัยปฏิกิริยาพอลิเมอไรเซชันในวัฏภาคของแข็งของ 2,5-ไดโบรโม-3,4-เอทีลีนไดออกซีไทโอฟีนในพอลิเมอร์เมทริกซ์บนขั้วไฟฟ้าเพื่อประยุกต์ใช้งานเป็นแก๊สเซ็นเซอร์ จากการศึกษาพบว่าสภาวะที่เหมาะสมที่สุดในการเตรียมฟิล์มคอมพอสิตที่มี 2,5-ไดโบรโม-3,4-เอทีลีนไดออกซีไทโอฟีน เป็นองค์ประกอบคือ การเคลือบแบบหมุนเหวี่ยงของสารละลายผสมในโทลูอีนที่มีอัตราส่วนโดยน้ำหนักระหว่างพอลิบิวทาไดอีนและ 2,5-ไดโบรโม-3,4-เอทีลีนไดออกซีไทโอฟีนเป็น 1 ต่อ 10 บนขั้วไฟฟ้าโดยใช้ความเร็วรอบในการหมุนเหวี่ยงเท่ากับ 1,500 รอบต่อนาที เป็นเวลา 60 วินาที จากนั้นจึงเหนี่ยวนำให้เกิดพอลิเมอไรเซชันในวัฏภาคของแข็งเพื่อเปลี่ยน 2,5-ไดโบรโม-3,4-เอทีลีนไดออกซีไทโอฟีนเป็นพอลิ(3,4-เอทิลีนไดออกซีไทโอฟีน) ที่นำไฟฟ้าได้โดยการให้ความร้อนฟิล์มคอมพอสิตของพอลิบิวทาไดอีน/2,5-ไดโบรโม-3,4-เอทีลีนไดออกซีไทโอฟีนที่ 60 องศาเซลเซียส เป็นเวลา 8 ชั่วโมง ฟิล์มคอมพอสิตของพอลิบิวทาไดอีน/พอลิ(3,4-เอทิลีนไดออกซีไทโอฟีน) ที่มีความต้านทานประมาณ 10^3 โอห์ม ถูกนำไปทดสอบการตอบสนองกับสารเคมีระเหยชนิดต่างๆ ผลการทดลองพบว่าค่าความต้านทานของฟิล์มคอมพอสิตพอลิบิวทาไดอีน/พอลิ(3,4-เอทิลีนไดออกซีไทโอฟีน) มีการเปลี่ยนแปลงอย่างเป็นระบบขึ้นกับสภาพขั้วของสารเคมี เซ็นเซอร์ที่มีพอลิ(3,4-เอทิลีนไดออกซีไทโอฟีน) เป็นองค์ประกอบนี้ให้การตอบสนองที่ดีกับตัวทำละลายมีขั้ว เช่น เมทานอล เอทานอล และน้ำ นอกจากนี้ยังได้มีการศึกษาการใช้ซ้ำและความไวในการตอบสนองของเซ็นเซอร์ที่พัฒนาขึ้นอีกด้วย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต
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4973412923 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS : PEDOT / CONDUCTING POLYMER/SOLID STATE POLYMERIZATION / GAS SENSOR / PEDOT/POLYMER COMPOSITE

LAONGDAO MENBANGPUNG: DEVELOPMENT OF GAS SENSOR FROM CONDUCTING POLYMER COMPOSITE CONTAINING POLY(3,4-ETHYLENEDIOXYTHIOPHENE). THESIS ADVISOR: ASST. PROF. VORAVEE P. HOVEN, Ph. D., THESIS CO-ADVISOR:ASST. PROF. YONGSAK SRITANA-ANANT, Ph. D., 91 pp.

This research aims to study film processing of the conducting polymer composites containing poly(3,4-ethylenedioxythiophene) (PEDOT) using solid state polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in the polymer matrix on the interdigitated electrode (IDE) for gas sensing applications. The most appropriate condition for preparing DBEDOT-containing composite film was to spin casting the mixed solution of polybutadiene (PB) and DBEDOT dissolved in toluene at 1:10 (w/w) of PB:DBEDOT on IDE with a spin speed of 1500 rpm for 60 sec, and induced SSP of DBEDOT to conductive PEDOT by heating the PB/DBEDOT composite film at 60 ^{o}C for 8 h. The PB/PEDOT composite film having a resistance of 10^3 ohm was chosen for testing against a number of volatile chemicals. The resistivity of the PB/PEDOT composite film was systematically changed with the polarity of the chemical. The PEDOT-based sensor gave good responses to polar solvents such as methanol, ethanol, and water. The repeatability and sensitivity of the developed sensor were also determined.

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Student's Signature:
Advisor's Signature:
Co-Advisor's Signature:

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LIST OF SCHEMES

LIST OF ABBREVIATION

VOCs : volatile organic compounds
CO : carbon monoxide
CO_2 : carbon dioxide
O_2 : oxygen
E-nose : electronic nose
PA : polyacetylene
PANI : polyaniline
PPy : polypyrrole
PTh : polythiophene
PPV : poly(phenylene vinylene)
PS : polystyrene
PB : polybutadiene
PMMA : poly(methyl methacrylate)
MOSFET : metal oxide semiconductor field-effect transistor
QCM : quartz crystal microbalance
SAW : surface acoustic wave
SPR : surface plasmon resonance
CPs : conducting polymers
LB : Langmuir Blodgett
HOMO : highest occupied molecular orbital
LOMO : lowest occupied molecular orbital
T_c : critical temperature
$CHCl_3$: chloroform
CH_2Cl_2 : dichloromethane
DBEDOT : 2,5-dibromo-3,4-ethylenedioxythiophene
PEDOT : Poly(3,4-ethylenedioxythiophene)
EDOT : 3,4-ethylenedioxythiophene
CH_3COOH : acetic acid
NBS : *N*-bromosuccinimide
min : minute

mL	: milliliter
°C	: degree celsius
$CDCl_3$	: deuterated chloroform
g	: gram
h	: hour
NMR	: Nuclear magnetic resonance spectroscopy
MS	: mass spectrometry
SSP	: solid state polymerization
Mw	: average molecular weight
S	: seimens
eq	: equivalence
w/w	: weight by weight
$NaHCO_3$	: sodium hydrogen carbonate
ppm	: part per million
Br_2	: bromine
nm	: nanometer
N/A	: not available
I_2	: iodine

CHAPTER I

INTRODUCTION

1.1 Statement of Problem

Recently, gas sensor becomes increasingly important in many fields such as health, industry, security, household, and medicine. For example, the sensor can be used to monitor toxic gas in chemical process, environment, exhaust from food production or chemical industry, to detect quantity of alcohol in wine processing. Gas sensor that is based on the detection of chemical or “chemosensor” is a device that is capable of converting a chemical entity into a quantitatively detectable change of signal such as electronic, thermal, optical or mass. The gas sensor that relies on the change of electronic signal generally requires a conductive component. Conjugated polymers (CPs) are among the most frequently used conductive materials for sensing applications. Polymers hold several advantages over inorganic-based materials. They can provide high sensitivity and short response time. They possess good mechanical properties, are easy to be fabricated, and the measurement can be operated at ambient temperature. CPs are polymeric macromolecules that can either conduct electricity or acts as electrical semiconductors. Since the structure of the CP consists of alternating single and double carbon-carbon bond along the backbone, electrons can delocalize under doping condition. CPs that are well known for their applications as chemosensor especially for monitoring humidity, ammonia, and alcohol are polyaniline (PAN), polypyrrole (PPy), polythiophene (PTh).

Poly(3,4-ethylenedioxythiophene) (PEDOT), first discovered in 1980s, is one of polythiophene derivatives that has received much attention in recent years due to its remarkably high conductivity (> 200 S/cm in the electrochemical doped state) and excellent environmental stability. The most success of PEDOT lies on the industrial applications of PEDOT-doped polystyrene sulfonic acid (PEDOT/PSS), known commercially as BaytronP, for antistatic coatings of photographic films and hole transporting material in many electronic devices. The PEDOT synthesis is conventionally based on chemical or electrochemical oxidation of ethylenedioxythiophene solution. Until recently, it has been discovered by Meng and coworkers that blue-black crystals of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) can undergo solid state polymerization (SSP) through debromination and coupling. Without the use of initiators or catalysts, SSP could give rise to a nearly defect-free and highly ordered bromine-doped PEDOT with high conductivity (20-80 S/cm). And the SSP can also be accelerated by heat treatment.

Taking advantage of DBEDOT being able to dissolve in a number of common organic solvents and can be converted to conductive PEDOT via a simple heat treatment, this research aims to prepare a thin film of PEDOT/polymer composite that can act as a sensing material for gas sensor applications by first spin casting the mixed solution between DBEDOT and a designated polymer on interdigitated electrode (IDE). SSP of the DBEDOT/polymer composite is then induced by heating. The physical appearance and resistivity of the resulting PEDOT-containing composite film were evaluated by optical microscope and Keithley digital multimeter, respectively. The developed PEDOT-based sensor is then subjected to testing against volatile chemicals having varied polarity such as water, methanol, ethanol, chloroform, acetone, toluene and hexane.

1.2 Objectives

1. To prepare gas sensor containing conductive PEDOT/polymer composite via solid state polymerization.
2. To determine the sensor response against volatile chemicals by conductivity measurement.

1.3 Scope of Investigation

The stepwise investigation was carried out as follows:

1. Literature survey for related research work
2. To synthesize DBEDOT
3. To prepare IDE as an electrode for gas sensor via vacuum thermal evaporator

4. To fabricate DBEDOT /polymer composite film on IDE by spin casting and followed by SSP by heat treatment to prepare PEDOT/polymer composite film. Several parameters involving the fabrication are tested:
   - Solvent
   - Polymer matrix
   - Spin speed
   - DBEDOT/polymer weight ratio
5. To determine the resistivity and morphology of the PEDOT/polymer composite film
6. To study response and sensitivity of the PEDOT-based sensor against volatile chemicals

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Introduction of gas sensor technology [1-4]

Gas sensor technology is very useful in many fields such as medical and diagnostics and health monitoring, process monitoring, food and beverage quality assurance, environmental monitoring, automotive and aerospace applications, detection of explosives, recognition of natural products, cosmetics and fragrance, etc. The development of sensor was developed to response with the toxic gas, combustible gas, volatile organic compounds (VOCs), hydrocarbon compounds, and single gas detection such as O_3, NO_x, CO, CO_2 and O_2.

The development of sensing materials design in gas sensor is a continuing research. Some of the basic requirements are that the sensor should be small, low cost, consume low power, easily operate and maintain and expected to give high sensitivity, selectivity and reliability. In the market, there are gas sensor devices performed in either stationary or portable instruments for detecting different chemicals. The technology of sensor covered on variety of solid support such as electrochemical or infrared probes, thin film or catalytic beads. Some of these examples are shown in Figure 2.1.

Among a number of chemical sensors available for field measurements, the gas sensor device known as an Electronic nose (E-nose) was particularly caught attention recently. It is an electronic instrument that is capable of detecting and recognizing many gas and odors. It usually comprises an array of several chemical sensors in the system. For example, Guadarrama and coworkers reported an array of conducting polymers synthesized by electrochemical polymerization, which had been used in an E-nose system. This system could be applied to distinguish the quality of the olive oil aroma [4].

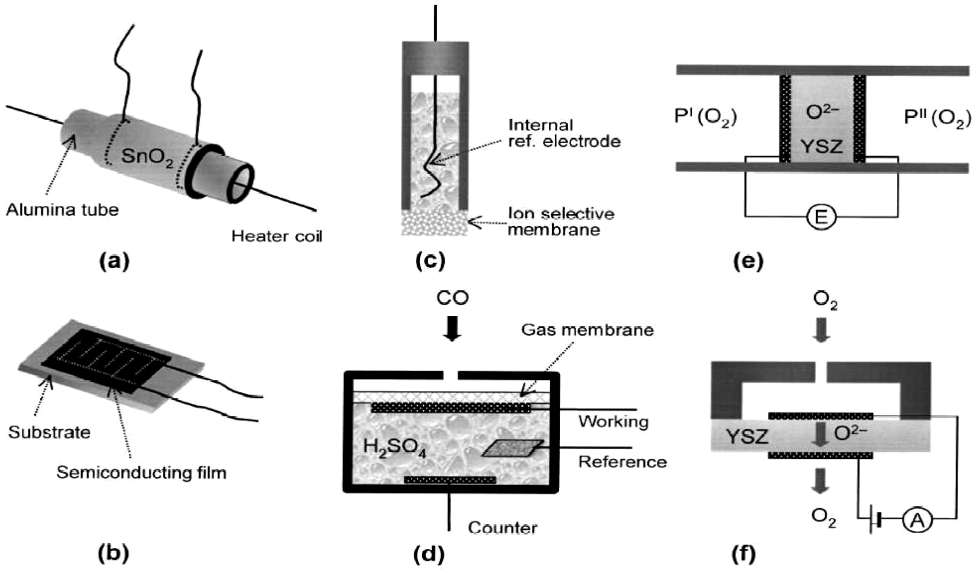


Figure 2.1 Typical chemical sensors: (a) tubular type SnO_2 gas sensor; (b) planar semiconductor sensor; (c) ion selective electrode (potentiometric); (d) amperometric gas sensor with liquid electrolyte; (e) potentiometric solid electrolyte O_2 sensor; (f) amperometric solid electrolyte O_2 sensor.

2.2 Chemoresistor sensor: Conducting polymer [5-6]

A chemosensor is a device that is capable of converting a chemical related quality into an electrical signal. The principles of the sensing interactions with gas molecules may be electrical, thermal, optical or mass changed. The different applications of chemosensors ranged from chemocapacitor, metal oxide semiconductor field-effect transistors (MOSFET), quartz crystal microbalance (QCM), surface acoustic wave (SAW), surface plasmon resonance (SPR), fluorescence and many others. Inorganic semiconductor, metal oxides, composite and organic conducting polymer were commonly used as the sensing materials.

Chemoresistors based on the conductivity change of organic conducting polymers (CPs) due to chemical reactions with gas molecules are among the simplest types of gas sensors. Thin films, fibers and bulk materials could be utilized as the sensing elements of chemoresistors. Using conducting polymers as the sensing film bring several advantages in device fabrication and operation. Conducting polymers are easy to be processed into films by many techniques such as electrochemical deposition, spin coating, Langmuir Blodgett (LB) technique, etc. Most of these methods could be operated in room temperature.

Chemoresistors consist of one or several pairs of electrodes and a layer of conducting polymer in contacting between the electrodes, as shown in Figure 2.2. The electrical resistance change of the sensing material is measured as the output using a simple ohmmeter. Figure 2.3 shows the configuration of the interdigitated electrode that is widely used for chemoresistor sensor.

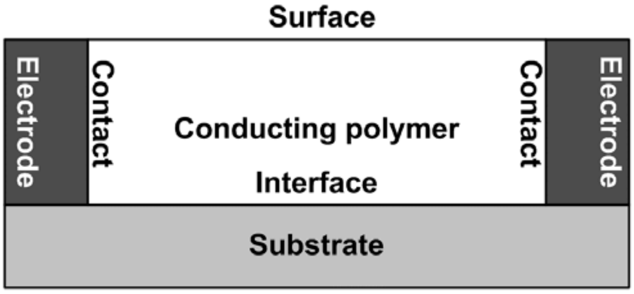


Figure 2.2 Configuration of a chemoresistor

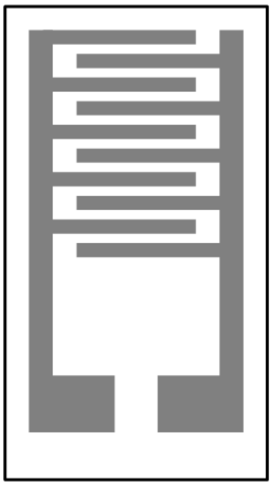


Figure 2.3 Interdigitated electrodes: the dark pattern is the conducting part while the white area is the insulating supporting substrate

Gas sensors have appeared in commercial devices such as ethanol sensor, flame sensor, toxic gas sensor, humidity sensor, etc. The sensing applications may relied on the response with analyte vapor with only one or an array many sensors (e-nose).

2.3 Conjugated polymer: organic semiconductor [7-9]

Conjugated polymers (CPs) are polymers that conduct electricity or act as electrical semiconductors due the alternating single and double carbon-carbon bonds along the backbone based on sp^2 hybridized linear carbon chains. Conducting polymer was first discovered by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa who earned the Noble prizes in 2000.

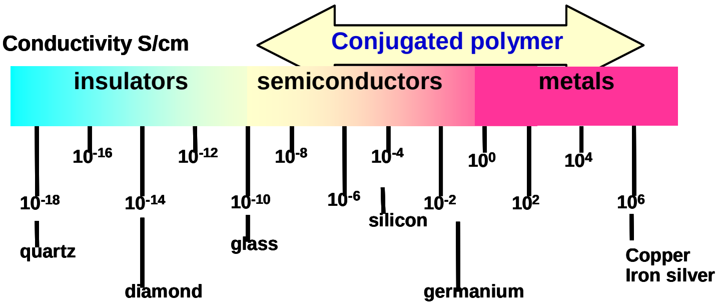


Figure 2.4 Conductivity of different materials

Polypyrrole, PPy

Poly(3,4-ethylenedioxythiophene), PEDOT

Polythiophene,PTh

Polyaniline, PANI

Polyacetylene, PA

Poly(phenylene vinylene, PPV)

Figure 2.5 The structure of conducting polymer

The alternating single and double bonds created an extended π-network. Electron movements within this π-framework are the source of conductivity, with respect to electronic energy levels, hardly differ from inorganic semiconductors. Both types of semiconductor have their electrons organized in bands rather than in discrete levels and their ground state energy bands are either completely filled or completely empty. The band structure of a conjugated polymer originates from the interaction of the π-orbitals of the repeating units throughout the chain. Figure 2.5 shows commonly known conjugated polymers that are conductive.

The highest occupied band (originating from the HOMO of a single monomer unit) is called the valence band, while the lowest unoccupied band (originating from the LUMO of a single thiophene unit) is called the conduction band. The difference in energy between these energy band levels is called the band gap energy or simply, band gap (Eg). Generally speaking, because conducting polymers posses delocalized electrons in π-conjugated system along the whole polymeric chain, their conductivity is much higher than that of other polymers with no conjugated system. These latter non-conjugated polymers are usually known to be insulators.

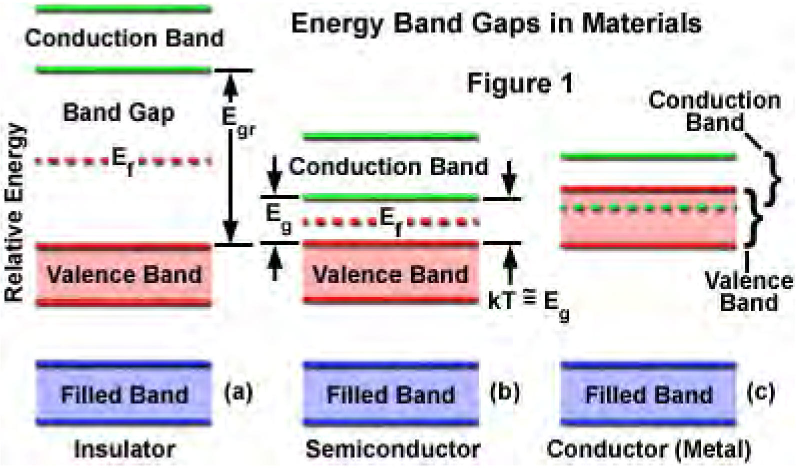


Figure 2.6 Energy bands and band gaps in materials

The different between π-conjugated polymers and metals is that in metals, the orbitals of the atoms overlap with the equivalent orbitals of their neighboring atoms in all directions to form molecular orbitals similar to those of isolated molecules. With N numbers of interacting atomic orbitals, there would be N molecular orbitals. In the metals or any continuous solid-state structures, N will be a very large number (typically 10^{22} for 1 cm^3 metal piece). With so many molecular orbitals spaced together in a given range of energies, they form an apparently continuous band of energies

In insulators, the electrons in the valence band are separated by a large gap from the conduction band. However, in conductors like metals, the valence band overlaps with the conduction band. And in semiconductors, there is a small enough gap between the valence and conduction bands that thermal excitations can bridge the gap. With such a small gap, the presence of small percentage of a doping material can increase conductivity dramatically.

An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperature. The position of the Fermi level which related to the conduction band is a crucial factor in determining electrical properties. The conductivity of the metal is due either to partly-filled valence or conduction band, or to the band gap being near zero, so that with any weak electric field the electrons easily redistribute. Electrons are excited to the higher energy bands and leave unfilled bands or “hole” at lower energy. Metals and conducting polymers exhibit opposite directions of conducting behavior as a function of temperature. For metallic materials, the conductivity increases as the temperature falls (some of which become superconducting below certain critical temperature, T_c) while it generally decreases with lowered temperature for polymeric semiconductors and insulators.

Since π-conjugated polymers allow virtually endless manipulation of their chemical structures; the control of the band gap of these semiconductors is a research issue of ongoing interest. This “band gap engineering” may give the polymer its desired electrical and optical properties. Reduction of the band gap to approximately zero is expected to afford an intrinsic conductor like metal.

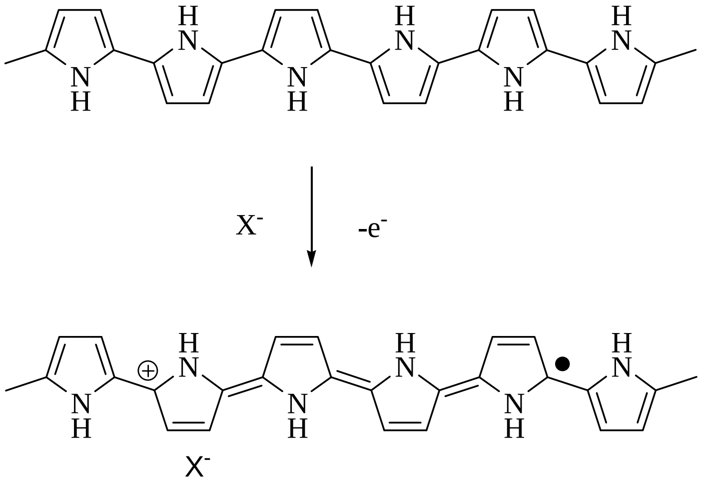
2.4 Conducting polymer in gas sensor applications [10-14]

Conducting polymers such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and their derivatives are most widely used for volatile sensing materials that show the advantage over other materials with high sensitivity, short response time, good mechanical properties, easy fabrication, and ability to operate at room temperature. (Table 2.1) Moreover, these conducting polymers can be easily synthesized via chemical oxidation or electrochemical polymerization. Their structures can be modified or incorporate into copolymers or other different structures.

Table 2.1 The comparison of conducting polymers and metal oxides

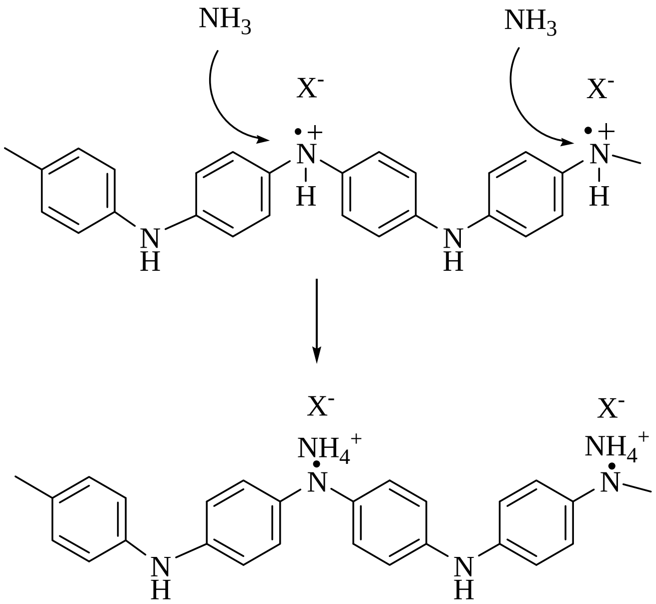
Properties	Conducting polymer	SnO_2 (thin film)
Synthesis/Fabrication	Oxidation/ Many casting method	Sol-gel, Sputtering
Choice of material	Large varieties	Limited
Operating temperature	10-110 °C	250-600 °C
Response time	60 s	20 s
Power consumption	< 10 mW	80 mW
Stability	Moderate	Poor
Interference	Acidic gas, water	SO_2, Cl_2, water

Most of the conducting polymers are doped/undoped by redox reactions; therefore, their doping level can be altered by transferring electrons from or to the analytes. Electron transferring can cause the changes in resistance and work function of the sensing material.



Scheme 2.1 Oxidative doping of polypyrrole

PANI is a special conducting polymer that is widely used to detect acidic and basic gases because its doped state can be controlled by acid/base reactions. In ammonia detector, PANI was exposed to ammonia gas and underwent dedoping by deprotonation. (Scheme 2.2)



Scheme 2.2 Polyaniline interacts with ammonia by deprotonation.

The protons on –NH– groups were transferred to NH_3 molecules to form ammonium ions while PANI itself turned into its base form. This process is reversible, and in fact, when ammonia atmosphere is removed, the ammonium ion can be decomposed to ammonia gas and a proton. This process causes the resistance of PANI to increase. In contrast, when PANI reacts with acidic gas such as HCl, H_2S and CO_2, it will be doped and cause the decrease of the resistance.

Similar processes occurred when PPy, PTh and in some case PANI films exposed in NH_3, NO_2, I_2, H_2S and other redox-active gases. Electron acceptors, such as NO_2 and I_2, can remove electrons from the aromatic rings of conducting polymers. When this occurs in a p-type conducting polymer, the doping level as well as the electric conductance of the conducting polymer are enhanced. An opposite process will occur when detecting electron-donating gas.

2.5 Preparation of conducting polymer film

Active layer of gas sensitive materials is the heart of a sensor. Various techniques have been developed to prepare conducting polymer films, in order to adapt to different sensing materials and different types of sensor configurations. These techniques include:

Electrochemical deposition Electrochemical deposition is the most convenient method to deposit conducting polymer films. The thickness of the film can be controlled by the total charge passed through the electrochemical cell during film growing process. Moreover, the film can be deposited on patterned microelectrodes [15]. The deposition must be carried out on a conducting substrate.

Dip-coating When dipping a substrate into a chemical polymerization solution, part of the polymer will be deposited onto its surface [17, 18]. This process occurs on different substrates, and the thickness of the film is usually controlled by dipping time. Another similar process involves alternatively immersing a substrate into the monomer and oxidant solutions. The adsorbed monomers will be polymerized on the surface of the substrate [19, 20].

Spin-coating Spin-coating is a simple method for preparing films from soluble conducting polymers. In this process, the conducting polymer solution is spread on a rotating substrate [21, 22]. After evaporation of solvent, a thin film was formed (Figure 2.7). Repeating above process is feasible, which can control the thickness of the film. Concentration of the solution and rotating rate of the substrate are also play important roles in adjusting the thickness of the formed film. This method can coat conducting polymers on both conducting and insulating substrates.

Langmuir-Blodgett (LB) technique LB technique is a famous method to produce a thin film of polymer and surfactant. The operation of LB technique has been described in many books and literatures. Two different ways are reported to deposit a conducting polymer film by LB technique: directly depositing polymer and depositing monomer followed by polymerization on the substrate. LB film is usually ultrathin (monomolecular layer). A thicker film can be obtained by repeating the procedure of LB deposition.

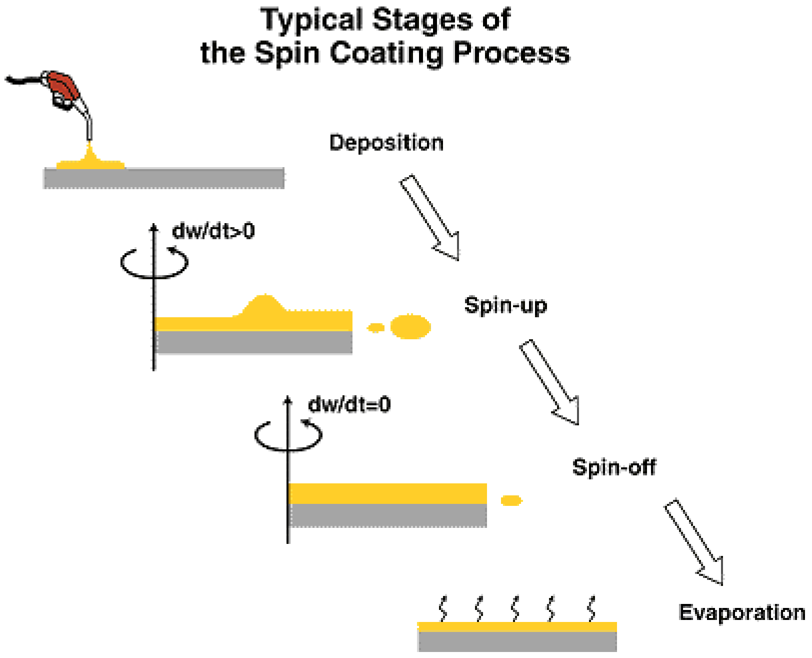


Figure 2.7 The typical stages of the spin coating process

Layer-by-layer (LBL) self-assembly technique By alternatately immersing the substrate into a polymeric anion solution and a polymeric cation solution, an alternate composite film (layer by layer) consists of the two polymeric electrolytes is fabricated [23, 24]. Doped conducting polymers, such as PANI, bring positive charge on their backbone, which allow it to be deposited with a polymeric anion. The thickness of the LBL film depends on the number of repeating times.

Thermal evaporation This technology can be realized by heating conducting polymer under vacuum. The evaporated conducting polymer deposits on the target substrate. The thickness of the film is determined by the evaporation duration [25].

Drop-coating A polymer solution is dropped onto a substrate and dried [27, 28], or some drops of the monomer and the oxidant solutions are dropped and reacted together on a substrate. This technology is rather simple. However, the resulting film is usually not uniform.

Other methods An electric field induced electrochemical polymerization can fabricate patterned conducting polymer film. The polymerization of pyrrole occurs between an electrode gap (5 μm) when a voltage is applied in the saturated vapor of pyrrole [29]. Colloidal suspension of PANI is controlled to directionally deposited on microelectrodes at controlled voltages [30]. For soluble conducting polymers, inkjet-printing also is a convenient method for producing thin films [31]. Some researchers also packed conducting polymer powders into pellets to fabricate the active layers [32, 33].

2.6 Sensing mechanism of conducting polymer [34-39]

Chemical vapor interacting with CP can be divided in two main classes: chemical interaction and physical interaction. Different gas and vapor interact with conducting polymers is shown in Table 2.2.

Physical interactions do not change the doping level of conducting polymer, but occur as absorbing or swelling of the polymer. Absorption of the analyte molecules on the surface of sensing film is widely used in gas sensing. In fact, absorption is the first step in all the sensing techniques, especially in some quartz crystal microbalance sensors. The absorption of organic gases on conducting polymers has been experimentally studied.

Chemical reactions lead to changes in the doping level of CP and hence their physical properties like resistance or optical absorption. Electron acceptors like NO_2, I_2, O_3, O_2 are able to oxidize partially reduced CP and therefore increase their doping level. To oxidize, the gas analyte should have a higher electron affinity than the CP. NO_2 was found to increase the number of charge carriers in PANI and P3HT through oxidative doping with NO_2^-.

The protonation of PANI or PPy by HCl vapor leads to an increase of the polymer conductivity. On the other hand, deprotonation of PPy or PANI by ammonia leads to increase of the polymer resistance. The mechanism of NH_3 deprotonation of PANI was shown in Scheme 2.2

Table 2.2 Interaction of gas with conducting polymer

Interaction mechanism with CPs		Chemical vapor
Physical	Swelling or absorption	$CHCl_3$, CH_2Cl_2, alcohols, acetone, acetonitrile, alkanes, cyclohexane, benzene THF and toluene
Chemical	Oxidation	NO_2, SO_2,O_3
	Reduction	H_2, N_2H_4, NH_3, H_2S
	Protonation/ deprotonation	HCl, NH_3

2.7 Poly (3,4-ethylenedioxythiophene) [40-45]

Chemical modifications of polythiophene have been widely carried out in recent years to satisfy different application requirements. The most familiar and important one is regioregular poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT is also one of the few examples within the conjugated polymer family which is both p- and n-dopable. It is well known that upon electrochemical p-doping (n-doping) conducting polymers undergo oxidation (reduction) of the polymer backbone resulting not only in an increase of their electronic conductivity but also in structural transitions which give rise to spectral changes.

Poly(3,4-ethylenedioxythiophene) (PEDOT) are widely studied because of their high conductivity for their use as hole injecting layers in light emitting diodes, solar cells and semiconductor device fabrication. PEDOT has been developed into one of the most successful materials from both fundamental and practical perspectives. It possesses several advantageous properties as compared with other polythiophene derivatives: it combines a low oxidation potential and moderate band gap with good stability in the oxidized state. Also, by blocking the β-positions of the heterocyclic ring, the formation of α-β linkages during polymerization is prevented, resulting in a more regiochemically defined material. In addition to a high conductivity (550 S/cm in the electrochemical doped state), PEDOT is found to be highly transparent in thin, oxidized films. As a result, PEDOT derivatives are now utilized in several industrial applications including antistatic coatings for photographic films, electrode material in solid-state capacitors, substrates for electroless metal deposition in printed circuit boards, indium tin oxide (ITO) electrode-replacement material in inorganic electroluminescent lamps, and hole conducting material in organic/polymer-based light-emitting diodes (OLEDs/PLEDs).

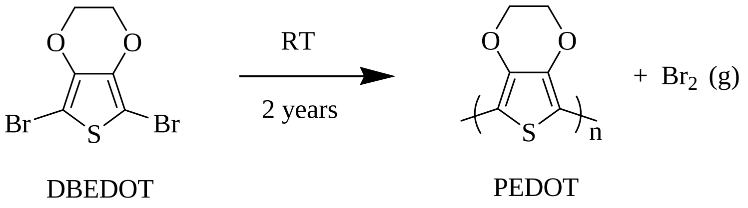
3,4-Ethylenedioxythiophene (EDOT) is a commercially available, oxidatively polymerizable monomer which polymerizes at relatively low applied potentials (+1.0 V vs Ag/Ag+). Jonas and Heywang [42] first polymerized EDOT to poly(3,4-ethylenedioxythiophene) (PEDOT) and found the polymer to be useful for antistatic coatings. Inganas and co-workers [44] showed the usefulness of PEDOT as a potential material for electrochromic devices due to its ability to cycle between an opaque blue-black in the reduced (undoped) state and a transmissive sky blue in the oxidized (doped) state. Conductivities reported for PEDOT prepared electrochemically range from 10 to 100 S/cm, and these conductivites have been found to be stable for up to 1000 h at 120 °C in a laboratory atmosphere.

2.8 Solid state synthesis of PEDOT [46-47]

Polymerization of PEDOT by traditional oxidative polymerization with $FeCl_3$ in organic solvents gives an insoluble blue-black polymer powder. The limitations of traditional polymerization methods can be a serious problem for PEDOT applications as well as for in-depth investigation of molecular order in this conducting polymer. It is generally not possible to obtain a well-defined polymer structure, unless the synthesis of conducting polymers is carried out via pure chemical polymerization routes, without adding any catalysts. A possible solution for this lies in a solid-state polymerization of a structurally pre-organized crystalline monomer.

The advantages of solid-state polymerization (SSP) include low operating temperatures, which restrain side reactions and thermal degradation of the product, while requiring inexpensive equipment, and uncomplicated and environmentally sound procedures. Also by-products can be easily removed by application of vacuum or through convection caused by passing an inert gas.

In 2003, Meng et al. [46-47] reported that the solid-state polymerization (SSP) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) was discovered by chance as a result of prolonged storage (2 years) of the monomer at room temperature.The colorless crystalline DBEDOT, with time, transformed into a black blue material without apparent change of morphology. Surprisingly, the conductivity of this decomposition product appeared to be very high (up to 80 S/cm) for an organic solid. Even though this type of non catalytic coupling was not known in organic chemistry, indeed, the most likely explanation for the observed transformation was polymerization with formation of bromine-doped PEDOT. The following characterizations unequivocally confirmed the proposed structure (see below).



Scheme 2.3 Solid state polymerization of DBEDOT

The room-temperature conductivity of different SSP-PEDOT samples was measured by the four point probe method (Table 2.3). The highest conductivity belongs to the polymer prepared at lowest temperature and longest reaction time, which may reflect achievement of a higher degree of order. Indeed, heating above the monomer’s melting point results in dramatically reduced conductivity (0.1 S/cm), which rises up to only 5.8 S/cm after doping with iodine, approaching the value of an $FeCl_3$-synthesized PEDOT (7.6 S/cm). Not very significant, but certain increase in conductivity of SSP-PEDOT (about 2 times) was found on exposing a sample to iodine vapor.

Traditional PEDOT synthesis has limitations especially in molecular order. In comparison, solid state polymerization via single crystal or power has great advantages because no further purification is necessary, and the resulted polymer has a high degree of molecular order and often shows less defect.

Table 2.3 Conductivity data of PEDOT polymers

	σ_{rt} (SSP-PEDOT)/ Scm^{-1}				σ_{rt} ($FeCl_3$-PEDOT)/ Scm^{-1}
Reaction Temperature (°C)	20	60	80	120	0-5
Reaction time	2 years	24 h	4 h	24 h	24 h
"crystals"/ "fibers"	80	33	20	NA	N/A
pellets as synthesized	30	18	16	0.1	N/A
pellets after I_2 doping	53	30	27	5.8	7.6
thin films	N/A	23	N/A	N/A	N/A
Thin films after I_2 doping	N/A	48	N/A	N/A	N/A

N/A = Not available

2.9 Polythiophene and PEDOT in gas sensor applications [48-50]

Conductive polymer PEDOT/PSS fabricated on the polyester film by inkjet printing was used as the sensing element to organic vapor [48]. The inkjet method offers particular advantages over other methods for forming thin films: patterning thin film capability; reduction of waste products, high speed and low cost fabrication, room temperature deposition, and printing onto large area and flexible substrates. The resistance of fresh sensor achieved about 1-40 MΩ depended on the number of inkjet print layer. When exposed to alcohol vapor, the film exhibited a sharp and nonreversible increase of the resistance. The higher sensitivity to methanol may because of the small size of methanol molecules, allowing them to interact and diffuse efficiently in the polymer layer. Furthermore, the high dielectric constant of methanol (33), compared to ethanol (23), probably resulted in better interaction between its molecules and the polymer film.

Multilayer ultrathin films of PEDOT/stearic acid (PEDOT/SA) were fabricated using a modified Langmuir-Blodgett (LB) technique [49]. The electrical conductivity of 40 layers of the composite LB film was about 0.52 S cm $^{-1}$. The response of film coated QCM to NH_3 has fast response and recovery time to 10 ppm NH_3 with good reversibility and recovery performance. At identical concentration QCM sensitivity was enhanced with increasing layer of LB film less than 80 layers and the decrease of QCM sensitivity was observed in the case of layer number over 80 layers.

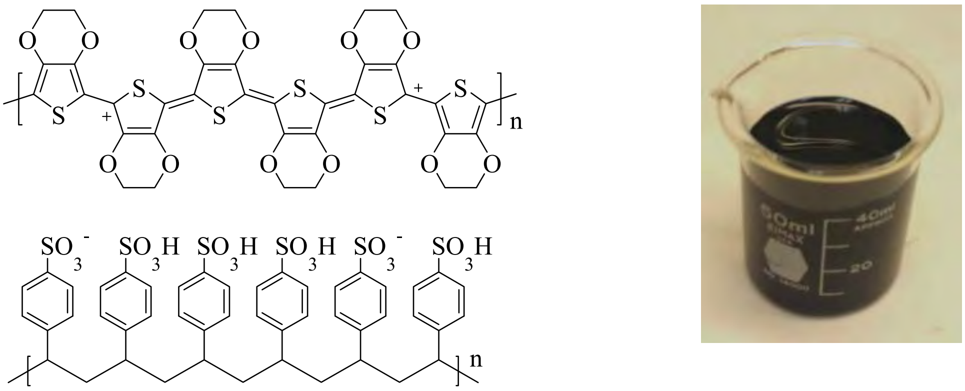


Figure 2.8 Chemical structure of PEDOT:PSS (left) and commercial PEDOT:PSS (Baytron ®P)

Bendikov and Harmon have developed and fabricated of the potentiometric solid state sensor from perchlorate ion doped poly(3,4-ethylenedioxythiophene) (PEDOT (ClO_4^-)) as sensing materials in ion selective electrode [50]. The electrode was successful for sensing perchlorate and exhibited very high environmental stability in the oxidized state over 8 months.

CHAPTER III

EXPERIMENTAL

3.1 Materials

3,4-Ethylenedioxythiophene was obtained from Sigma-Aldrich (USA). *N*-bromosuccinimide was purchased from Acros Organic. Methanol, ethanol, 2-propanol, 1-butanol, tetrahydrofuran, toluene, hexane, acetic acid, acetone and chloroform were purchased from Lab-scan (Thailand). 1-Heptanol, 1-hexanol, 1-pentanol and ammonia were purchased from Merck (Germany). All reagents were analytical grade and used without further purification. Polybutadiene (Mw = $4x10^4$), polystyrene (Mw = $3x10^5$) and poly(methyl methacrylate) (Mw = $1x10^5$) were obtained from DOW Chemical (USA). All chemicals used were of analytical grade and used as received without further purification.

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

All spectra were recorded in solution of $CDCl_3$ by a Varian, model Mercury plus 400 nuclear magnetic resonance spectrometer (USA) operating at 400 MHz for ^1H and 100 MHz for ^{13}C nuclei.

3.2.2 Mass Spectrometry (MS)

Molecular weight of DBEDOT was analyzed by mass spectrometer (Micromass Quattro Micro API, USA), using chloroform as the solvent. The instrument were operated by using CP-sil 8 column (30 m x 0.25 mm), injection volume = 1 µL, split ratio = 200, column flow = 2 mL/min and column oven = 250 ^oC at 10^oC/min.

3.2.3 Optical Microscope (OM)

The surface morphology of DBEDOT, PEDOT and PEDOT/polymer composite films was visualized at a magnification of 40x by transmission mode of

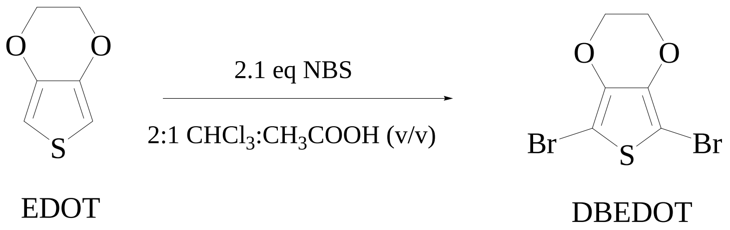
Compound biological microscope with digital camera model DC4-156-5 (National Optical & Scientific Instrument Inc., USA).

3.2.4 Spin Coater

Thin film of DBEDOT and DBEDOT/polymer composite were fabricated on interdigitated electrode by a P-6000 spin coater, model P6206 SCS-special coating system, Inc., USA.

3.3 Method

3.3.1 Synthesis of 2,5-Dibromo-3,4-Ethylenedioxythiophene (DBEDOT)



To a stirred solution of 3,4-ehylenedioxythiophene (EDOT) (1.14 g, 8 mmol) dissolved in a 2:1 (v/v) mixture of chloroform (18 mL) and glacial acetic acid (9 mL) was added slowly 2.1 eq. *N*-bromosuccinimide (NBS) (2.99 g, 16.2 mmol). The reaction was carried out at 0-5 ^{o}C under nitrogen atmosphere for 8 h. The mixture was then quenched and washed with 1.5% sodium hydrogen carbonate solution (100 mL x 3 times). The organic layer was separated and the aqueous layer was extracted. The combined chloroform extract was dried with anhydrous magnesium sulfate. During the solvent removal by rotary evaporator, 3 mL of ethanol was added to the evaporating flask when 2 mL of the chloroform solution was left. DBEDOT product obtained as white needle-like crystals in 1.9 g (80%) was characterized by ^{1}H-NMR, ^{13}C-NMR and MS.

3.3.2 Preparation of Interdigitated Electrode

Glass slides were cleaned by refluxing in Piranha reagent (a mixture of 30% hydrogen peroxide and sulfuric acid (3:7 v/v) for 1 h, rinsed extensively with deionized water, and then blow dried with nitrogen gas. After that, a desired mask made of nickel was put on top of the cleaned glass slide which was later placed in a chamber of a vacuum thermal evaporator (EDWARDS model Auto 306, England).

The chamber was evacuated until the pressure inside the chamber reached 5x10^{-6} mBar. Chromium (20 nm) and gold (200 nm) layer was consecutively coated on the masked glass slide by applying a current of 60 mA and 40 mA to a boat containing chromium and gold, respectively. Total film thickness was measured by QCM detector. The configuration of interdigitated electrode (IDE) is shown in Figure 3.2

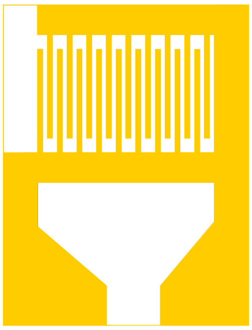


Figure 3.1 The configuration of interdigitated electrode

3.3.3 Preparation of Polymer/PEDOT Composite

A toluene solution of 0.02 g of selected polymer and 0.20 g DBEDOT was sonicated in an ultrasonic bath (Elmasonic S30 H, Germany) for 15 min. The solution (35 µl) was spun cast on the IDE electrode prepared from 3.3.2 with a spin speed 1500 rpm for 60 sec. After solvent evaporation, solid state polymerization of the DBEDOT crystals embedded in the polymer matrix was then induced by heating (60-80 °C for 8 h. The morphology and thickness of conducting PEDOT/polymer composite film was characterized by optical microscope (transmission mode) and surface profiler. After that the resistance of film was measured by Keithley digital multimeter. Then the sensor was placed in sensor chamber and then tested with various organic chemical solvent such as methanol, ethanol, toluene, hexane and ammonia etc.

3.3.4 Gas Sensor Testing

The sensor testing system (shown in Figure 3.2) consists of a gas flow controller, a sensor chamber, a digital multimeter (Keithley 2700, USA), and a computer for data collection and calculation. Nitrogen gas (N_2), purity 99.99%, used as the carrier gas was flowed into a sensor chamber for 1 h before testing in order to calibrate the sensor resistance. The flow rate of carrier gas was fixed at 300 mL/min. For the process of testing, the carrier gas was flowed into the sensor chamber for 60 sec in order to obtain baseline resistance (Rb). After that, the saturated chemical vapor generated by passing nitrogen gas into the chemical was carried to the sensor chamber for 20 sec. Upon interacting with the chemical vapor, the resistance of the composite film was changed. Finally, nitrogen gas was flowed into the chamber again for 360 sec in order to purge off the chemical vapor from the surface and bulk of the sensing material and ready for the next testing.

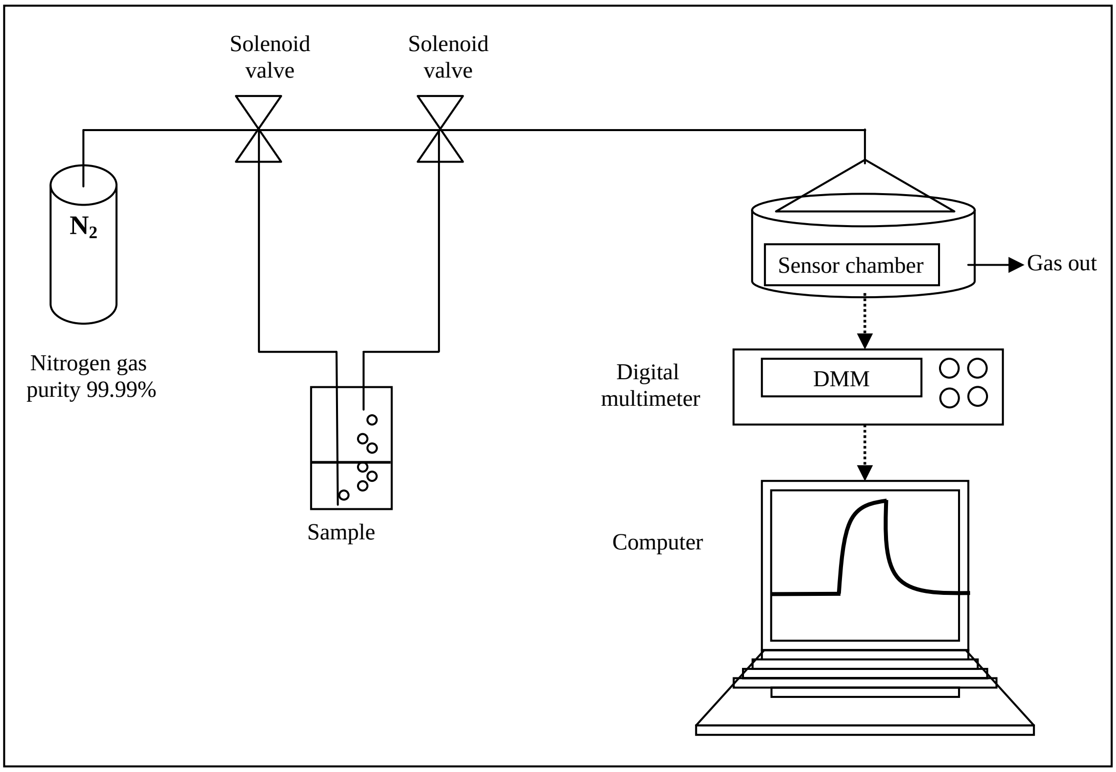


Figure 3.2 Schematic of gas sensor testing system.

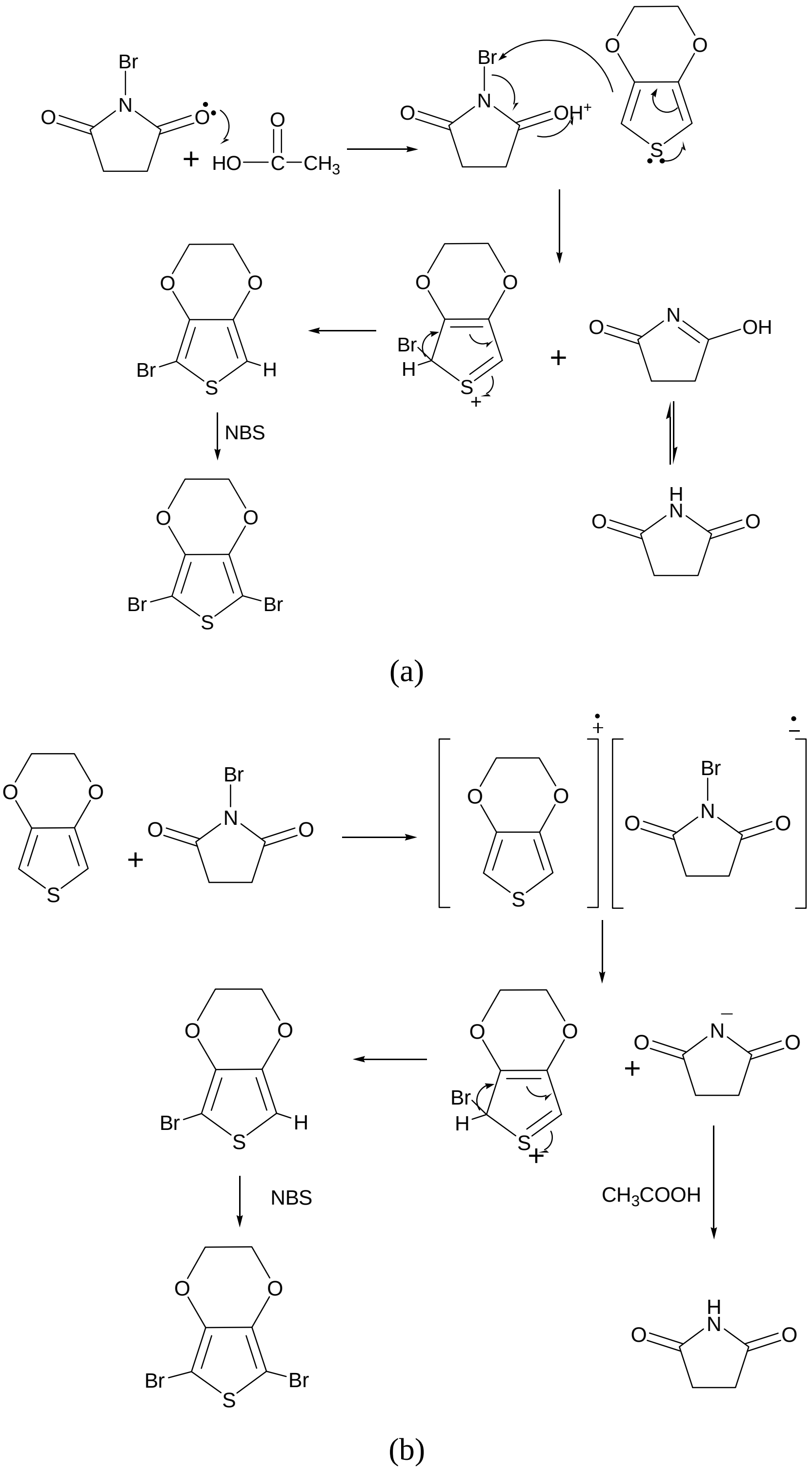
CHAPTER IV

RESULTS AND DISCUSSION

The aim of this work is to develop gas sensor from conducting polymer composite of poly (3,4-ethylenedioxythiophene) and commercial polymer by spin coating DBEDOT/polymer solution on IDE electrode and then polymerized DBEDOT by solid state polymerization. This chapter is divided into 3 parts. The first part involves a synthesis of DBEDOT by bromination of ethylenedioxythiophene (EDOT). The second part is dedicated to preparation of PEDOT/polymer composite film as a sensing material for gas sensor application. Several parameters that can affect physical morphology and conductivity of the composite films were investigated including solvent, polymer matrix, DBEDOT/polymer weight ratio, time and temperature used in the step of solid state polymerization (SSP). The last part concentrates on testing the efficiency of the developed gas sensor in terms of response, sensitivity, repeatability and stability.

4.1 Synthesis of 2, 5-Dibromo-3, 4-ethylenedioxythiophene (DBEDOT)

DBEDOT is the monomer to be used for solid state polymerization to form PEDOT. As proposed by Meng and coworkers, there are two possible pathways for bromination of EDOT as shown in Scheme 4.1 [46-47]. Unlike the method conducted by Meng and coworkers, the bromination of EDOT using *N*-bromosuccinimide (NBS) in this work is a one step process. The quenching and neutralization were done simultaneously by washing the chloroform layer by 1.5% $NaHCO_3$ solution (100 mL x 3 times). The crystallization of DBEDOT product was then induced by addition of a small amount of ethanol (3 mL) to a concentrated chloroform solution (containing ~ 2 mL of chloroform) after most of chloroform was removed under reduced pressure using rotary evaporator. White needle-like crystal with 80% yield was recovered after all the solvent (both chloroform and ethanol) was removed without further purification by column chromatography. The product was characterized by ^{1}H-NMR, ^{13}C-NMR and MS.



(a)

(b)

Scheme 4.1 Bromination of EDOT through (a) electrophilic aromatic substitution and (b) radical-based single electron transfer followed by aromatic substitution.

^{1}H-NMR spectra of the synthesized DBEDOT and EDOT are shown in Figure 4.1. The absence of a signal at 6.4 ppm suggested that the protons of EDOT at α-position to sulfur were substituted by bromine atoms after bromination by NBS. There are three signals appearing in the ^{13}C-NMR spectrum of the synthesized DBEDOT shown in Figure 4.2. The signal at 65 ppm belongs to two carbons at the ethylene bridge. The signals at 86 and 140 ppm can be assigned to two carbons at –C-O position in thiophene ring (2) and two carbons at –C-S position (3), respectively. MS spectrum of the synthesized DBEDOT is displayed in Figure 4.3. The spectrum gives the corresponding molecular weight of DBEDOT and exhibits the characteristic 1:2:1 triplet molecular signal of two bromine atoms.

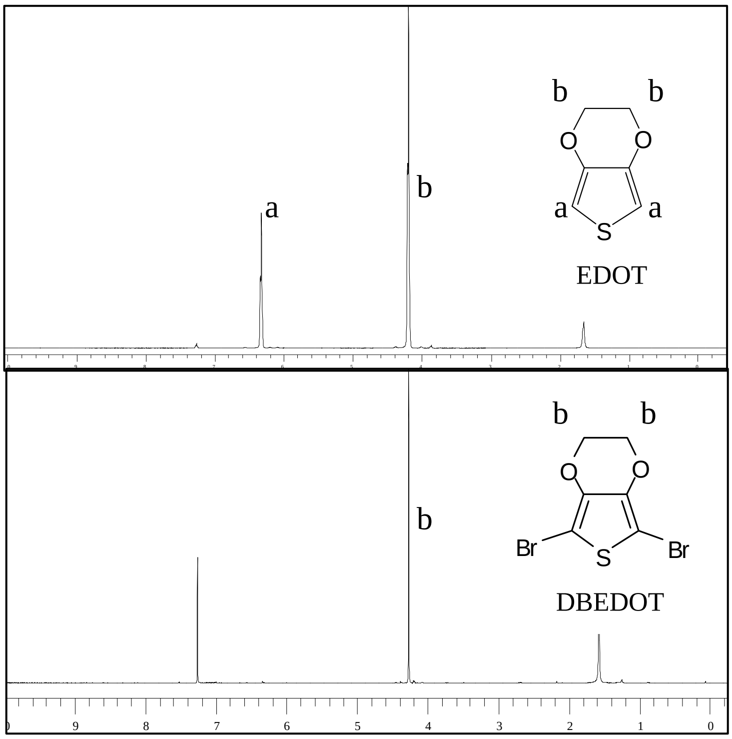


Figure 4.1 ^{1}H-NMR spectra of DBEDOT and EDOT.

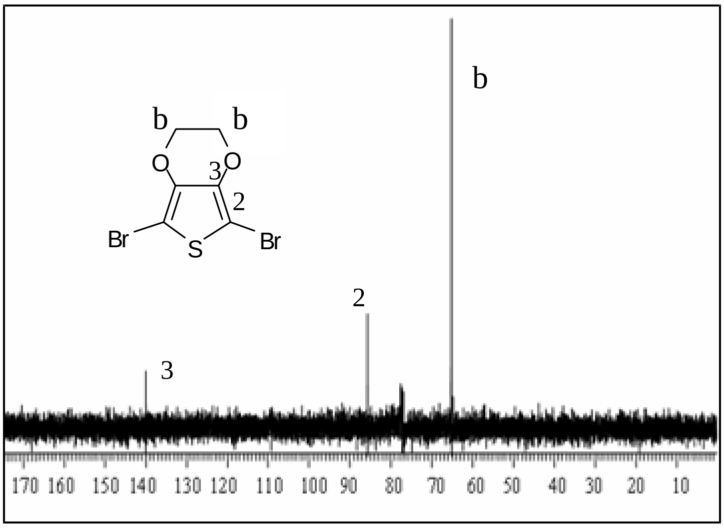


Figure 4.2 ^{13}C-NMR spectrum of DBEDOT.

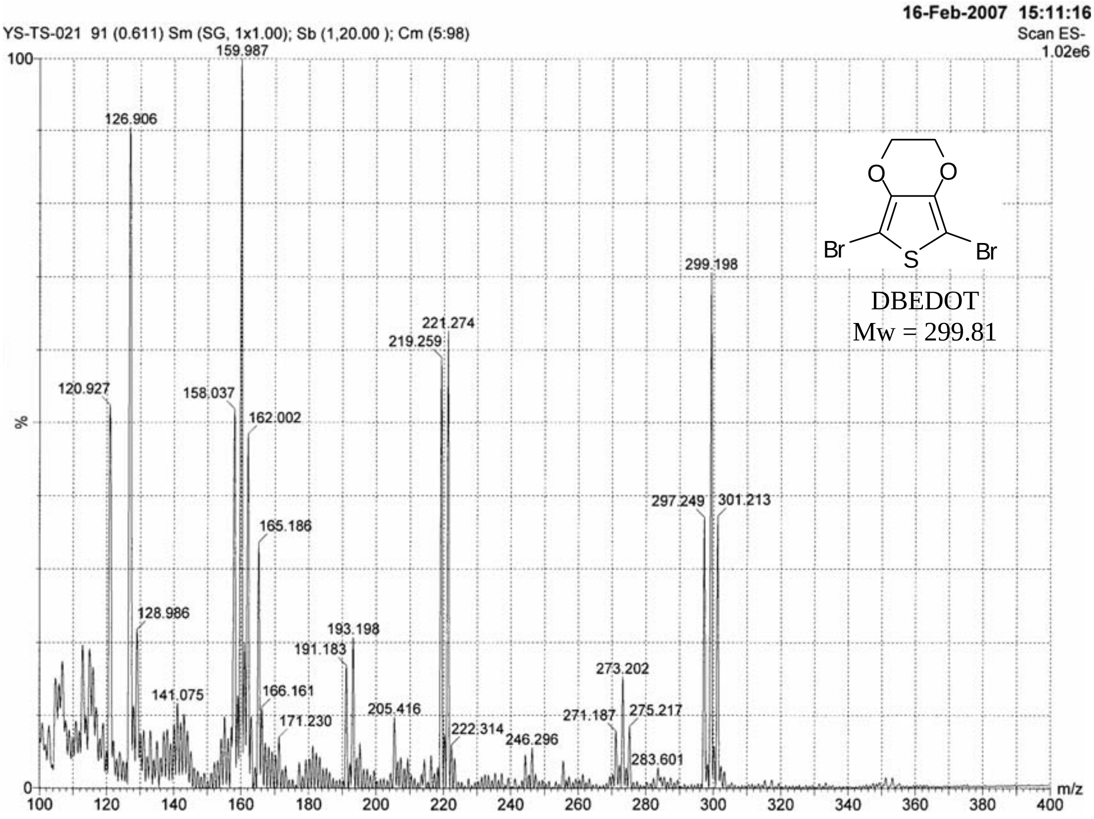
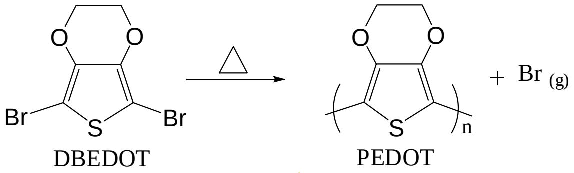


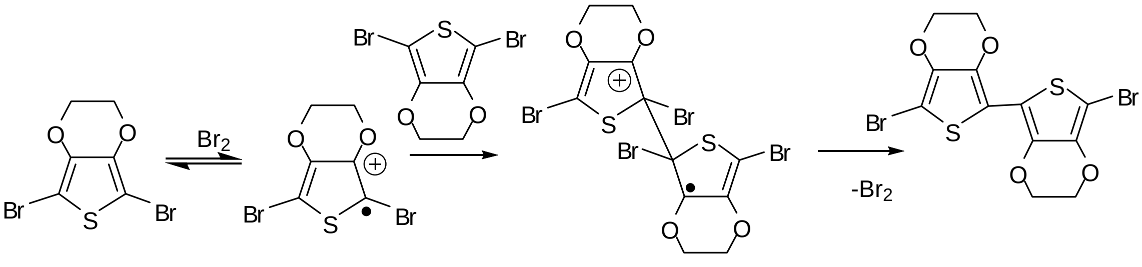
Figure 4.3 MS spectrum of DBEDOT.

4.2 Preparation of PEDOT/Polymer Composite

In this study, conductive PEDOT was synthesized by solid-state polymerization (SSP) of colorless DBEDOT monomer through debromination and coupling, yielding nearly defect-free and highly ordered bromine-doped conductive PEDOT, without the need of initiators or catalysts (Scheme 4.2). The mechanism of SSP of DBEDOT (Scheme 4.3) has been proposed by Meng and et.al. [47]. DBEDOT molecules in the form of crystal pack closely in parallel fashion which facilitates polymerization process in solid state. Most likely, the polymerization occurs along the stacks of the monomer and must be accompanied by significant rotation and some movement of the molecules. DBEDOT can transform to PEDOT by condensation during heat treatment. The initiation involves oxidation of DBEDOT by bromine (Br_2) and generates DBEDOT radical carbocation. In the propagation step, this radical carbocation first reacts with another DBEDOT to form DBEDOT dimer, also in the form of radical carbocation. The elimination of bromine then yields DBEDOT dimer which undergoes propagation and eventually forms PEDOT. The presence of bromine in the reaction, in fact, facilitates polymerization in the initiation step.



Scheme 4.2 Solid state polymerization of DBEDOT.

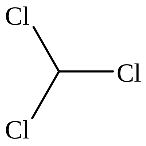
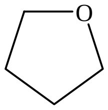
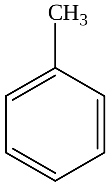


Scheme 4.3 Mechanism of solid state polymerization of DBEDOT.

Prior to the investigation on the preparation of composite film, solubility and spinnability of the monomer, DBEDOT, was first tested in selected organic solvents.

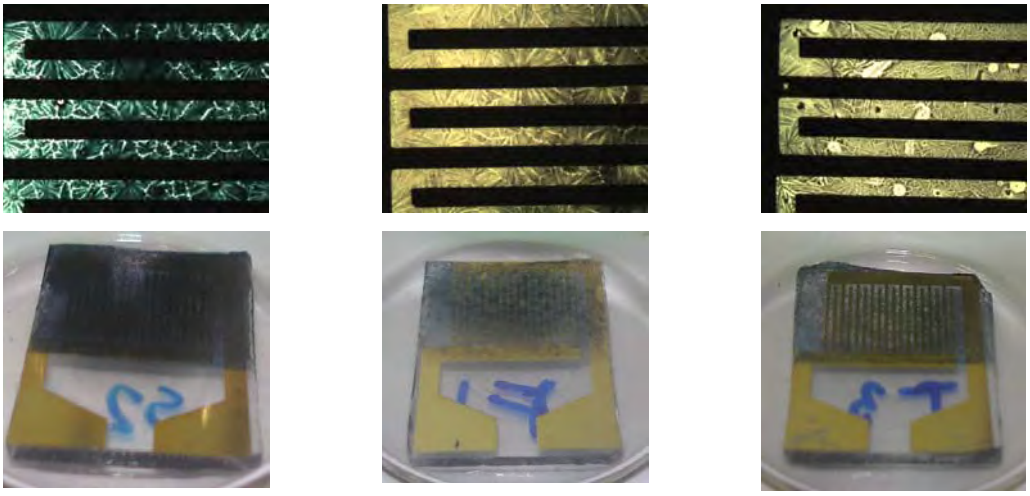
According to Kusonsong [51], DBEDOT is highly soluble in many organic solvents. In this study, chloroform, tetrahydrofuran (THF) and toluene were chosen as solvents for solubilizing both DBEDOT and polymer matrix in order to prepare solution for composite film fabrication on IDE electrode by spin coating. The physical and chemical properties of these three organic solvents are demonstrated in Table 4.1.

Table 4.1 Physical and chemical properties of organic solvents used for making DBEDOT solution

Organic solvent	**Chloroform**  	**THF**  	**Toluene** 
Molar mass (g/mol)	119.38	72.11	92.14
Boiling point (°C)	61	65-66	111
Density (g/cm^3)	1.48	0.89	0.87
Vapor pressure (kPa)	26.2	21.6	3.79
Dipole moment	1.04	1.63	0.37

Although they were different in polarity, all of them possess not too high boiling point so they should not be difficult to be removed after the spin coating. By fixing the weight of DBEDOT at 0.050 g it can be easily dissolved in 0.2 mL of all solvents after putting in an ultrasonic for 5 min (DBEDOT concentration = 0.25 g/mL). Then, the DBEDOT solution was spun coated on IDE electrode with a spin speed of 2,000 rpm for 60 sec. After solvent evaporation, DBEDOT crystals were spread across the pairs of IDE. Dark blue PEDOT film was produced upon heating the coated DBEDOT in an oven at 60 °C for 8 h. The morphology and the resistance of PEDOT film were determined.

Figure 4.4 illustrates morphology which was inspected under optical microscope and physical appearance of the PEDOT film fabricated directly from the DBEDOT solution which were prepared from different solvents. Having the same concentration, the DBEDOT dissolved in chloroform seems to give better PEDOT coverage than THF and toluene. With the lowest boiling point, chloroform can evaporate during and/or after the spin coating so rapidly that the DBEDOT and the resulting PEDOT were evenly covered the IDE. The PEDOT film fabricated from chloroform, toluene, and THF exhibited a resistance of 154, 2,437 and 119,691 ohm, respectively. In spite of their workable range of resistivity for gas sensor application, the morphology of the pure PEDOT film fabricated directly from the DBEDOT solution was not homogeneous. It is thus believed that fabricating the PEDOT in the form of composite should be a better alternative for PEDOT processing. In fact, there are many studies reporting the success based on a similar strategy by using polymer matrix which is usually insulating as a processing aid for conducting polymer and filler [52].



(a) (b) (c)

Figure 4.4 Morphology (top) and physical appearance (bottom) of PEDOT film on IDE fabricated directly from the DBEDOT solution prepared from (a) chloroform, (b) THF, and (c) toluene.

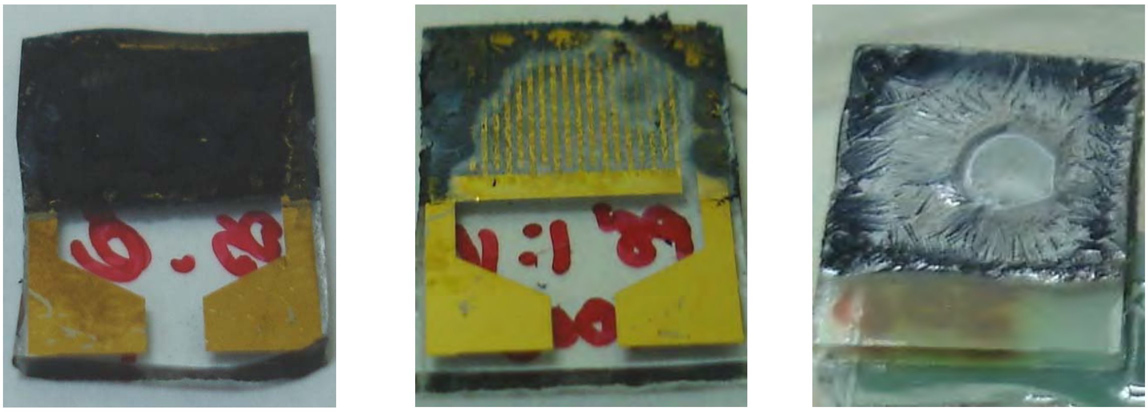
The rest of this section focuses on the preparation of the composite film containing PEDOT as a sensing layer for gas sensor applications. Several parameters such as polymer matrix, DBEDOT/polymer weight ratio, spin speed of spin coater were investigated. The preparation efficiency was determined based on morphology and resistance of the resulting composite film coated on IDE electrode.

4.2.1 Effect of polymer matrix

To improve the morphology of PEDOT film, easily processable commercial polymers such as polybutadiene (PB), polystyrene (PS) and poly(methyl methacrylate) (PMMA) were used tested as an insulating polymer to facilitate processing of conductive PEDOT/polymer composite sensor. Previous work by Kusonsong has demonstrated that conductive PEDOT composite films can be fabricated by drop casting the mixed solution between DBEDOT and polymer matrix of PS and PB in toluene followed by heat treatment to induce SSP [51]. Such method, however, is not appropriate for fabricating sensing layer to be used for gas sensor preparation. The resulting composite film was rather thick and quite rough (Figure 4.5 (a)). To be able to produce thinner and smoother film, spin casting method was therefore chosen.

In this experiment, 0.20 g of white crystal of DBEDOT and 0.02 g of commercial polymer (PS, PMMA and PB) were first dissolved in 1 mL of solvent (toluene, THF and toluene) yielding the weight ratio of polymer/DBEDOT of 1:10. Then, the mixed solution was spun casted on IDE with a spin speed of 1,500 rpm for 60 sec followed by heat treatment at 60 ^{o}C for 8 h to induce SSP of DBEDOT.

PS was the first matrix to be tested. Using the spin speed of 1500 rpm, it was found that the DBEDOT crystals as well as the resulting PEDOT composite were accumulated at the edge of electrode (Figure 4.5(b)). It was suspected that the centrifugal force introduced during the spin coating had a strong tendency to push the small molecule of DBEDOT to the edge of electrode. The same kind of force should have less impact on PS. With its higher molecular weight (Mw = $3x10^5$), their inter- and intra-chain interactions and chain entanglement should help holding them in the center of electrode. Uneven coverage of the PEDOT composite film led to the inconsistent, and sometimes unmeasurable resistivity. An attempt to reduce the effect of centrifugal force by decreasing the spin speed down to 500 rpm was also failed. The same problem still persisted. Using toluene as the solvent for making the mixed solution of PS and DBEDOT, it is also possible that the high boiling point and the slow evaporation rate of toluene would give enough time for DBEDOT of which polarity is higher than PS to phase separate from the non-polar PS matrix. This may be another reason why the fabrication of PS/PEDOT was not successful.



(a) (b) (b)

Figure 4.5 Physical appearance of PEDOT/PS composite film on IDE prepared by (a) drop casting, (b) spin casting at 1500 rpm, and (c) spin casting at 500 rpm.

Having greater polarity, PMMA (Mw = 1x10^5) was originally expected to be more compatible with DBEDOT than PS. And the problem from the phase separation may be suppressed. As can be seen from Figure 4.6(a), the coating of the mixed solution between PMMA and DBEDOT using the spin speed of 1,500 rpm seems to be homogeneous. However, the content of DBEDOT remained on the IDE was so low that there was almost no PEDOT on the IDE after SSP (Figure 4.6(b)). This outcome suggested that most of DBEDOT was spun away from the IDE. The problem due to phase separation was even more obvious at the lower spin speed of 500 rpm.

(a) (b) (c)

Figure 4.6 Physical appearance of (a) a film just cast on IDE from the mixed solution of PMMA using the spin speed of 1500 rpm and PEDOT/PMMA composite film prepared using the spin speed of (b) 1500 rpm and (c) 500 rpm.

Unlike PS and PMMA, the composite film prepared by SSP at 60 ^{o}C, 8 h of the spun cast film of the mixed solution of DBEDOT and PB (Mw = 4x10^{4}) was quite homogeneous and evenly covered the IDE. The resistance of about 1 kΩ made the PEDOT/PB composite film applicable for sensing applications.

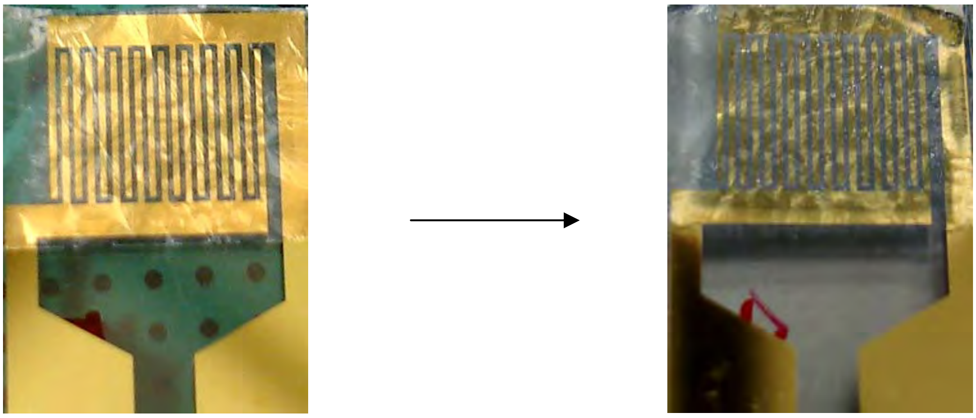


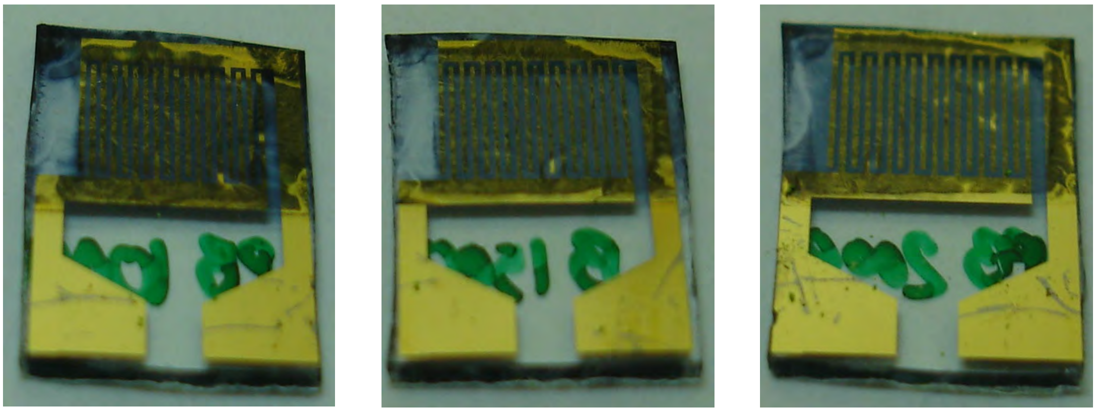
Figure 4.7 Physical appearance of a film just cast on IDE from the mixed solution of PB and DBEDOT (left) and PEDOT/PB composite film on IDE (right)

4.2.2 The effect of spin speed

Having the weight ratio of PB to DBEDOT of 1:10, the mixed solution (1 mL) was spun cast on IDE with a spin speed of 1,000, 1,500 and 2000 rpm for 60 sec followed by heat treatment at 60 ^{o}C for 8 h to induce SSP of the DBEDOT. The physical appearance shown in Figure 4.8 suggested that the coverage seems to be independent of the spin speed. Upon using different spin speed, the spherulite of the DBEDOT crystals growing across each pair of electrode (Figure 4.9, top) observed under optical microscope before SSP was quite similar in size. The spherulites of the dark-blue PEDOT obtained after SSP was apparently smaller than those of the DBEDOT at all spin speed. The feature seems to be smaller and finer when the spin speed was raised higher to 2000 rpm.

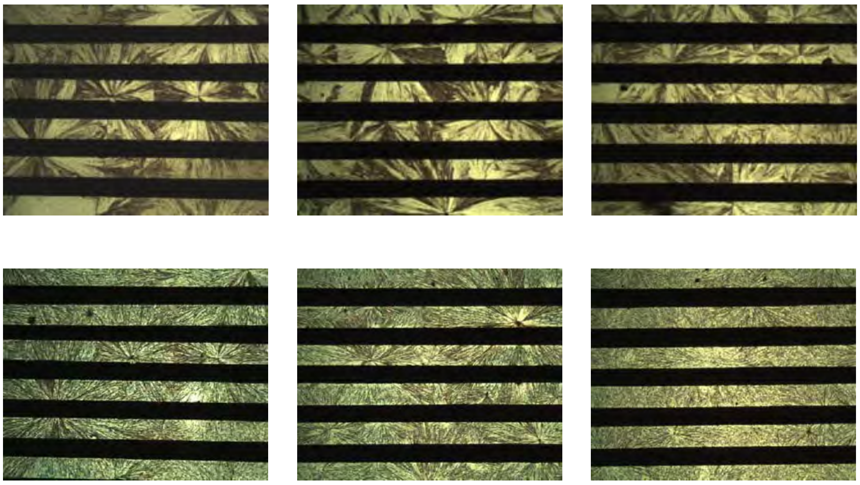
Nonetheless, increasing the spin speed tended to give a negative impact on the resistivity of the PEDOT film. The spin speed of 1500 and 2000 rpm yielded the PEDOT film having relatively high resistance which was 1.73 and 4.15 MΩ, respectively.

The resistance was several magnitude lower when the spin speed used for spin coating was 1,000 rpm. This trend strongly suggested that there should be higher content of conductive PEDOT on the IDE that was processed at lower spin speed. This is reasonable considering that there was more tendency for the material to be spun away from the IDE at high spin speed than the lower one.



(a) (b) (c)

Figure 4.8 Physical appearance of PEDOT/PB composite film on IDE prepared using a spin speed of (a) 1000 rpm, (b) 1500 rpm, and (c) 2000 rpm.



(a) (b) (b)

Figure 4.9 Morphology of PEDOT-PB composite film on IDE prepared using a spin speed of (a) 1,000 rpm, (b) 1,500 rpm, and (c) 2,000 rpm.

Interestingly, it was later found that the resistivity of the PEDOT/PB composite film continuously decreased as a function of time. After storing for 4 month in a dessicator, the resistance eventually went down to ~10^2 ohm for the film processed at the spin speed of 1,000 rpm and 10^3 ohm for the films processed at the spin speed of 1,500 and 2,000 rpm. The resistance was not significantly changed upon further storage for another 4 months. We explained the deterioration of the PEDOT resistance as a result of incomplete polymerization of the DBEDOT at the as-prepared stage. This discovery suggested that the heat treatment (60°C, 8 h) did help promoting the polymerization of DBEDOT in solid state to a certain extent. But such treatment is not powerful enough to induce SSP of the entire DBEDOT present in the composite film. The majority of polymerization slowly occurred thereafter at ambient temperature. This is in good agreement with the results reported by Meng and coworkers [47] that the SSP of the DBEDOT was extremely slow at ambient temperature, yet more effective in producing highly conductive PEDOT than the thermal-accelerated process.

Although the PB/PEDOT composite films prepared at the spin speed of 1,000 rpm possessed the highest conductivity, their response towards the organic vapor (results shown in section 4.3) was less sensitive than those prepared at the spin speed of 1,500 rpm, of which the resistivity is 10 times lower. This corresponds with the value called percolation threshold of which detail will be explained in the next section. For this reason, the speed 1,500 rpm was identified as the most appropriate spin speed to be used for further studies.

Table 4.2 Resistance of the PB/DBEDOT composite film prepared using different spin speed upon storage for up to 8 months

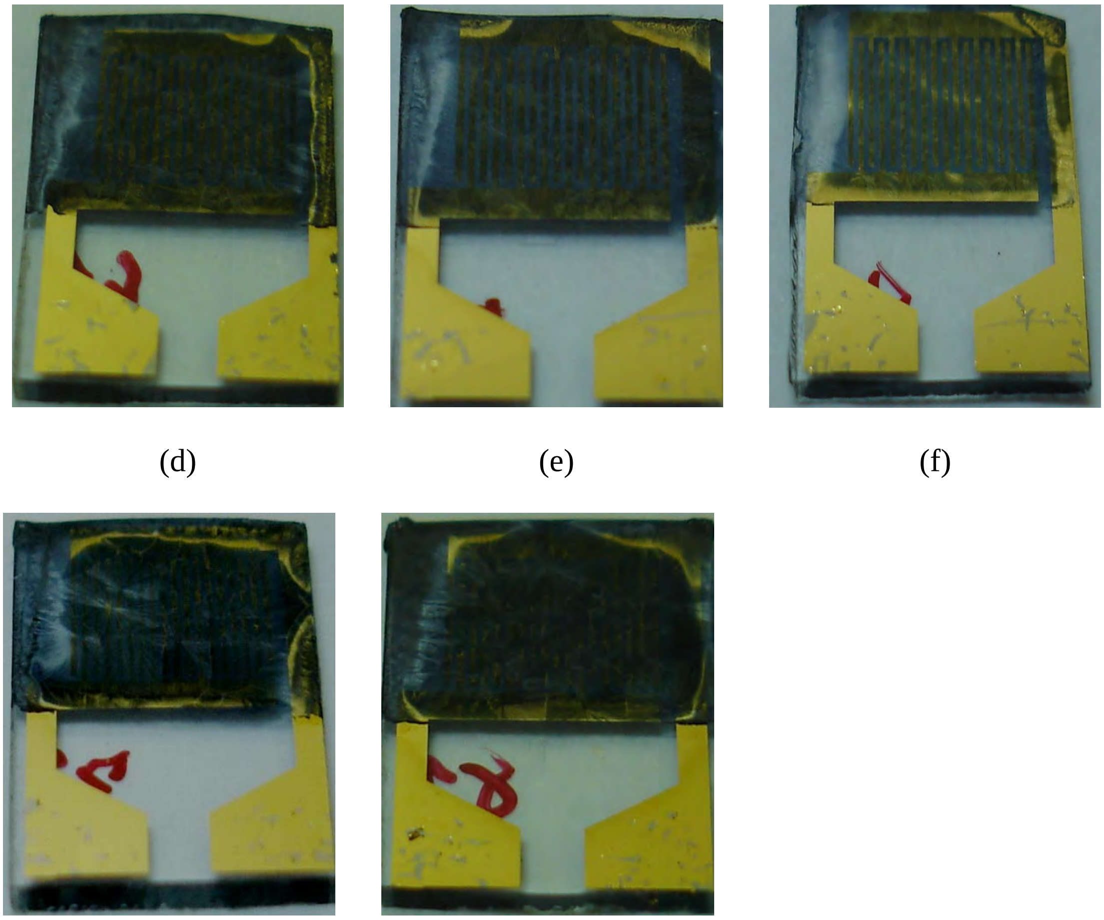
Time after SSP (day)	Resistance (ohm)		
	Spin speed (rpm)		
	1,000	1,500	2,000
1	2.24×10^4	1.73×10^6	4.15×10^6
2	5.45×10^3	1.81×10^6	6.40×10^5
3	3.44×10^3	1.19×10^6	6.60×10^5
6	2.46×10^3	2.50×10^5	8.00×10^5
8	1.05×10^3	5.00×10^4	1.4×10^5
120	1.23×10^2	7.80×10^2	7.88×10^2
180	1.32×10^2	6.97×10^2	9.39×10^2
240	1.60×10^2	1.13×10^3	1.12×10^3

4.2.3 Polymer:DBEDOT weight ratio

Using the spin speed of 1,500 rpm, polymerization temperature and time of 60°C and 8 h. It was found that the PEDOT/PB composite films prepared from the mixed solutions having the PB/DBEDOT weight ratio of 1:2.5, 1:5, and 1:7.5 did not appear as dark-blue films (Figure 4.10). In comparison with the previously used ratio of 1:10, the DBEDOT quantity on the IDE spun cast from the mixed solutions having those ratios may be so low and the DBEDOT were so far apart that they cannot lead to effective SSP. This speculation was verified by the fact that their resistances were not measurable, suggesting that the PEDOT/PB composite films possessed higher resistivity than the detection limit of the Keithley digital multimeter used in this research which is 100 MΩ. Upon increasing the PB/DBEDOT weight ratio much further to 1:10, 1:12.5, 1: 15.0, 1:17.5, and 1:20, there is no significant variation in the physical appearance of the resulting PEDOT/PB composite films.

The PB/PEDOT composite films were prepared by using various weight ratios of PB to DBEDOT, e.g., 1:2.5, 1:5, 1:7.5, 1:10, 1:12.5, 1:15, 1:17.5, and 1:20, it was found that the PEDOT/PB composite films prepared from the mixed solutions having the PB/DBEDOT weight ratio of 1:2.5, 1:5, and 1:7.5 were not detectable their resistances. On the other hand, the resistances of the PB/DBEDOT with the weight ratio of 1:10, 1:12.5, 1:15, 1:17.5, and 1:20 were measured by the Keithley digital multimeter, and reported in term of the resistances (log R) upon storage for 1, 30, 60, and 120 day, as shown in Figure 4.11. The resistance of the PB/DBEDOT weight ratio of 1:10, 1:12.5, and 1:15.0 after SSP for 1 day were 4.92, 3.72, and 3.62 log(ohm), respectively, whereas the resistance of the PB/DBEDOT weight ratio of 1:17.5, and 1:20 after SSP for 1 day were 7.83 and 7.32 log(ohm), respectively. The higher resistance values of the PB/DBEDOT weight ratio of 1:17.5 and 1:20 were a result of incomplete polymerization of the DBEDOT contacted with surface of the pairs of interdigitated electrode because of the increased thickness of film. The film thickness was increased with an increasing amount of DBEDOT. It indicated that the polymerization of DBEDOT in the bulk of film was more complete than the monomer DBEDOT at the surface of electrode at the as-prepared stage.

(a) (b) (c)



(d) (e) (f)

(g) (h)

Figure 4.10 Physical appearance of PEDOT/PB composite film on IDE prepared from the mixed solution having weight ratio of PB/DBEDOT of (a) 1:2.5, (b) 1:5, (c) 1:7.5, (d) 1:10, (e) 1:12.5, (f) 1: 15.0, (g) 1:17.5, and (h) 1:20.

After SSP, the PB/PEDOT composite films were stored at room temperature for 1, 30, 60 and 120 day. The results showed that as the storage time increased, resistance decreased as shown in Figure 4.11. It clearly indicated that polymerization of the DBEDOT was incomplete at the beginning. The polymerization of DBEDOT slowly occurred thereafter at ambient temperature. It was noted that the polymerization of DBEDOT was dependent on the function of time as corresponding with results in 4.2.2 (the effect of spin speed).

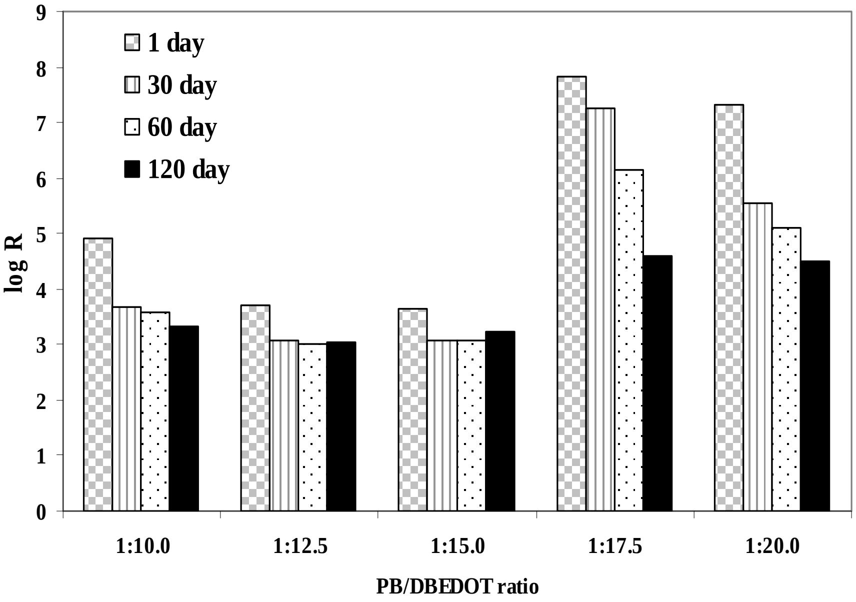


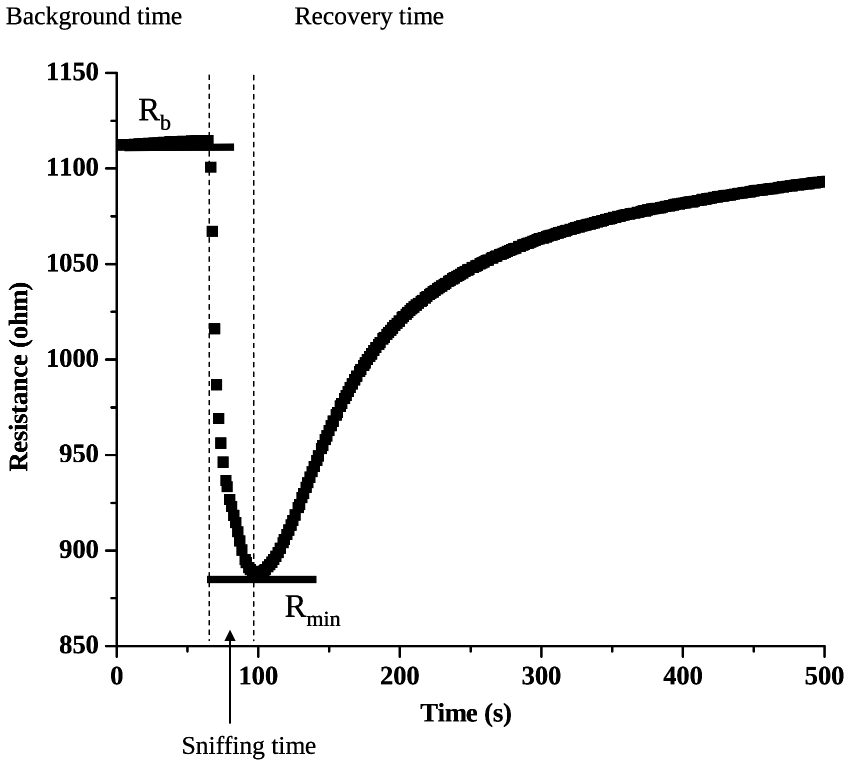
Figure 4.11 Resistance of the PB/DBEDOT composite film prepared using various weight ratios of PB to DBEDOT (1:10, 1:12.5, 1:15, 1:17.5, and 1:20) upon storage for 1, 30, 60, and 120 days.

4.3 Gas sensor testing

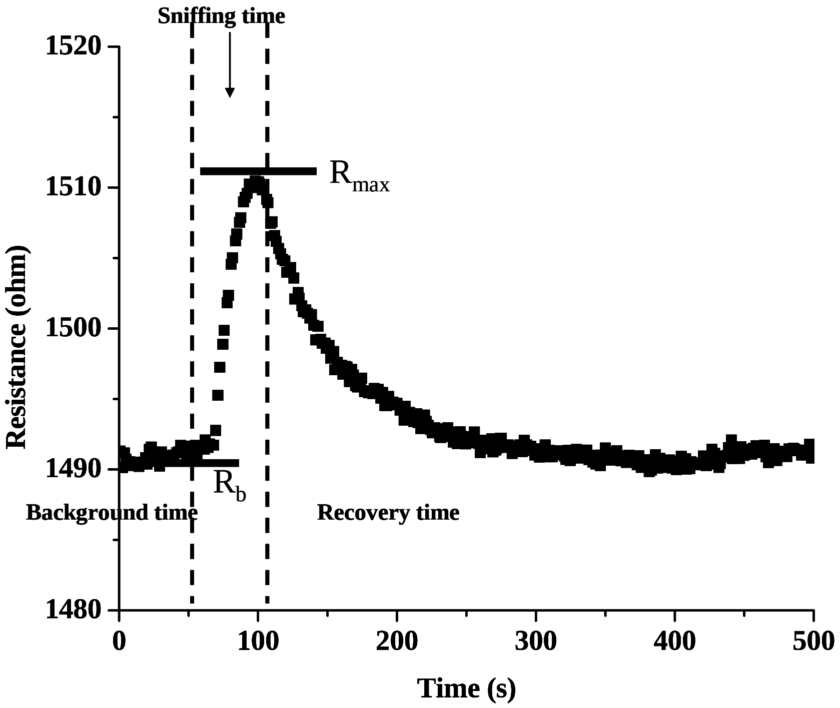
To study the response to volatile chemical, the selected PEDOT/PB composite sensor was placed in sensor chamber and the carrier gas was flowed into sensor chamber at flow rate of 300 mL/min for 1 h before testing in order to calibrate the sensor resistance. For the process of testing, the carrier gas flowed into the sensor chamber for 60 sec in order to obtain baseline resistance (R_b). After that, the saturated chemical vapor generated by passing nitrogen gas into chemical was carried out to the sensor chamber for 20 sec. Upon interacting with the chemical vapor, the resistance of the composite film was changed. Finally, nitrogen gas was flowed into the chamber again for 360 sec in order to purge off the chemical vapor from the surface and bulk of the sensing material and the sensor is ready for the next testing. There are two possible patterns of sensor response when being contacted with the vapor of chemical (Figure 4.12). Initially, the resistance can either decrease ((Figure 4.12(a)) or increase ((Figure 4.12(b)) depending on the type of chemical and then recovers back to the initial resistance value. The change of resistance value can be converted to response of the sensor using the following equation:

$$\text{Response} = dR/R_b \tag{4.1}$$

Where dR is the difference of resistance value between the maximum or minimum peak and the starting point of sensing curve and R_b is the resistance value at the starting point of sensing curve.



(a)



(b)

Figure 4.12 Pattern of sensor response: (a) initial decrease in resistance and (b) initial increase in resistance before recovery back to the baseline resistance.

4.3.1 Effect of spin speed on sensor response

The PEDOT/PB composite films were prepared from 1:10 (w/w) PB/DBEDOT solution using a different spin speed of 1,000, 1,500 or 2000 rpm for 60 sec. The condition for SSP was to heat the PB/DBEDOT composite films at 60 °C for 8 h. The composite sensors were then stored at ambient temperature for 4 months in order to allow the SSP reach its maximum extent and achieve the lowest resistance values which are 123, 780, and 788 ohm for the composite films prepared using the spin speed of 1,000, 1,500 and 2000 rpm, respectively. The response values of the prepared PEDOT/PB composite sensors against 3 selected chemicals which are methanol, ethanol and water are shown in Figure 4.13. Since all chemicals tested in this particular study are polar, the sensors showed negative responses implying that the resistance of the sensor decreased upon contacting with the vapor of polar solvent. The reason for such response will be explained in the next section. Although the resistance of the sensor prepared using the spin speed of 1,500 rpm was not much different from that prepared using the spin speed of 2,000 rpm, the former one seems to give a better performance in all chemical evaluated. For this reason, the PEDOT/PB composite sensor prepared by the spin speed of 1,500 rpm was selected for further investigation.

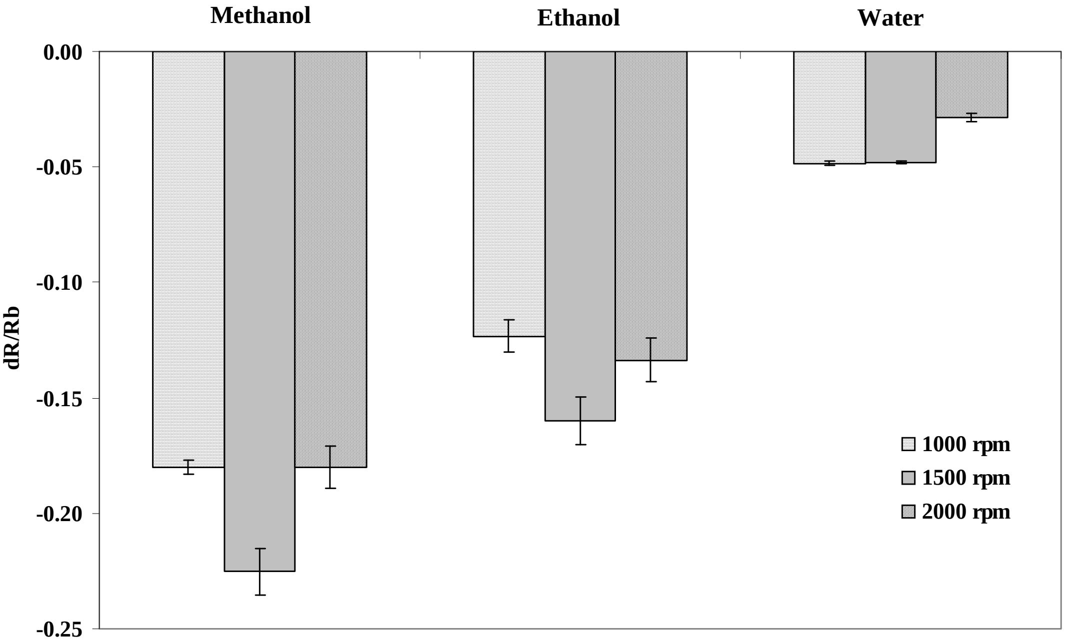


Figure 4.13 Response value of the PEDOT/PB composite sensor prepared by spin coating 1:10 (w/w) PB/DBEDOT solution on IDE with a different spin speed against methanol, ethanol and water. The SSP was conducted at 60 ^{o}C for 8 h. The sensor was kept at ambient temperature for 4 months prior to the test.

4.3.2 Response of PEDOT/PB composite sensor against chemical volatile

Figure 4.14 shows response values of the PEDOT/PB composite sensors upon contacting with the vapor of chemicals having different polarity which can be judged from their dielectric constants shown in Table 4.3. The sensors gave high responses with the chemicals having relatively high polarity, especially methanol and ethanol. The negative response of the polar solvents may be explained as a consequence of screening effect of this polar compound. The screening effect should reduce the

Coulomb interactions between the PEDOT and the bromine dopant, thereby enhancing the charge mobility, hopping rate, and conductivity.

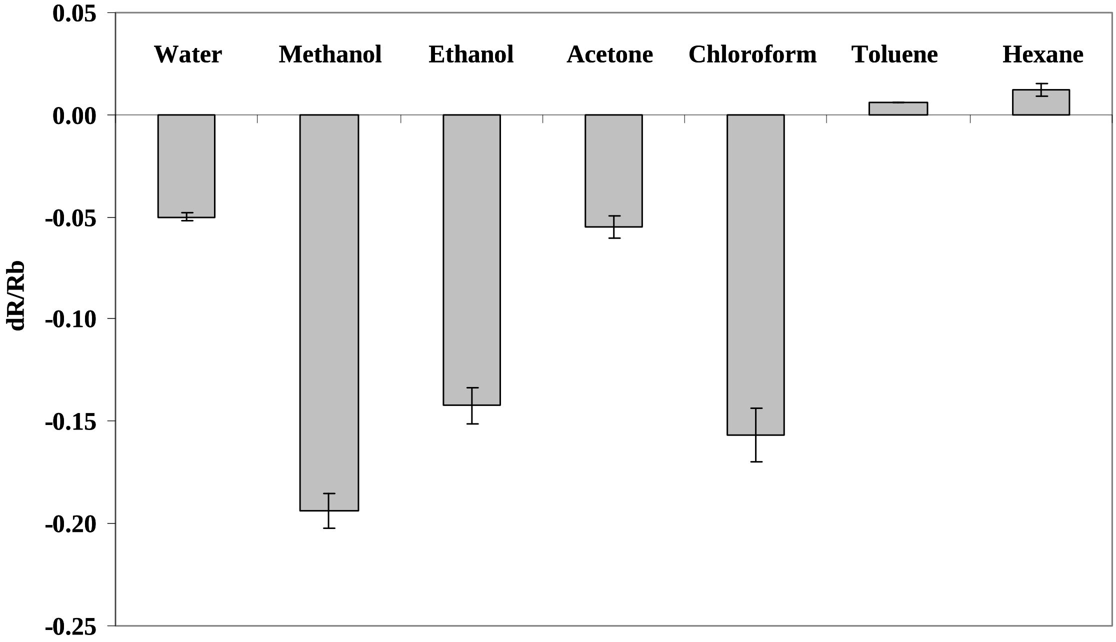


Figure 4.14 Response value of the PEDOT/PB composite sensor against different volatile chemicals.

Table 4.3 Dielectric constant, boiling point, response and sensitivity values of the PEDOT/PB composite sensors when tested against different volatile chemicals

. Solvent	Dielectric constant	Boiling point (°C)	Response (ΔR/Rb)	Vapor concentration (ppm)	Sensitivity (10^{-6})/ppm)
Water	80.0	100	-0.050 ± 0.002	2.67×10^4	-1.85
Methanol	33.0	68	-0.194 ± 0.008	1.26×10^5	-1.54
Ethanol	24.3	78	-0.142 ± 0.009	5.83×10^4	-2.45
Acetone	20.7	56	-0.055 ± 0.005	2.28×10^5	-0.24
Chloroform	2.0	62	-0.157 ± 0.013	1.91×10^5	-0.81
Toluene	4.8	111	0.006 ± 0.000	3.30×10^4	0.18
Hexane	2.4	69	0.012 ± 0.003	1.47×10^5	0.08

The positive response of toluene and hexane can be ascribed to their ability to swell the nonpolar component in the composite which is PB, in this particular case. The more the swelling of the PB, the further apart the PEDOT chains. As a result, the resistance of the composite increased. In other words, the composite became less conductive upon contacting with the non-polar solvent. Since the content of the PB (only 1 to 10 by weight in comparison with the DBEDOT) in the composite was rather low, the variation in resistance as a result of swelling was also small. As a result, the sensor was not able to response well with the non-polar solvents. Because each chemical has different boiling point and vapor pressure, it is not reasonable to compare the effectiveness of the sensor by considering the response alone. Taking into account how well the chemical can evaporate and how much the vapor in the chamber during the measurement that was conducted for the same period of time, the ability of the sensor to response to each chemical can then be calculated and expressed in term of sensitivity (See Table 4.3, last column). It should be emphasized that the amount of the vapor in the chamber can be calculated by measuring the quantity of the chemical left in the vessel after each experiment. According to the sensitivity values, the PEDOT/PB composite film gave the best sensing performance to ethanol.

The composite sensor was also subjected to the tests with a series of alcohol having different alkyl chain length from C1 to C7. As can be seen in Figure 4.15, the response was proportional to the hydrocarbon chain length. The longer the hydrocarbon chain length, the lower the polarity (See dielectric constant in Table 4.4), and the lesser the response. The response has shifted from the negative value to the positive value when the number of carbon in the chain increased from 4 (butanol) to 5 (pentanol). The explanations based on screening effect and swelling can also be applied in this case. Despite the variation in their responses, all alcohols except 1-heptanol, exhibited comparable sensitivity ranging from ~1.5 to ~3.0.

In contrast, the composite sensor exhibits a sharp and irreversible increase in the resistance after it exposed to ammonia vapor. It is believed that ammonia which is a reducing agent caused permanent change in the chemical structure of PEDOT. Not only can ammonia reduce bromine which acts as the dopant, but it can also interact with the positively charged PEDOT chains and subsequently suppressed the charge transportation in the composite film. The PEDOT/PB composite film is thus not a suitable material for sensing chemicals that have reducing power.

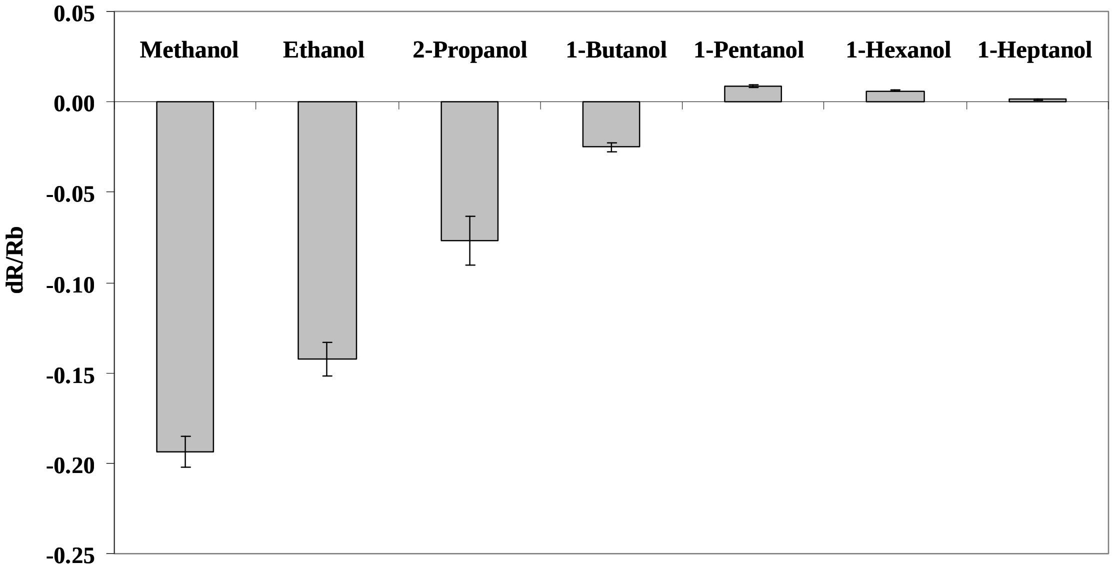


Figure 4.15 Response value of the PEDOT/PB composite sensor against a series of alcohol.

Table 4.4 Dielectric constant, response and sensitivity values of the PEDOT/PB composite sensors when tested against a series of alcohol

. Solvent	Dielectric constant	Boiling point (°C)	Response (ΔR/Rb)	Vapor concentration (ppm)	Sensitivity (10^{-6})/ppm)
Methanol	33.0	68	-0.050 ± 0.002	1.26 x 10^5	-1.85
Ethanol	20.3	78	-0.194 ± 0.008	5.83 x 10^4	-1.54
2-Propanol	20.0	82	-0.142 ± 0.009	5.34 x 10^4	-2.45
1-Butanol	17.8	118	-0.055 ± 0.005	1.03 x 10^4	-0.24
1-Pentanol	13.9	138	-0.157 ± 0.013	4.43 x 10^3	-0.81
1-Hexanol	13.3	157	0.006 ± 0.000	1.33 x 10^3	0.18
1-Heptanol	6.7	175	0.012 ± 0.003	1.53 x 10^3	0.08

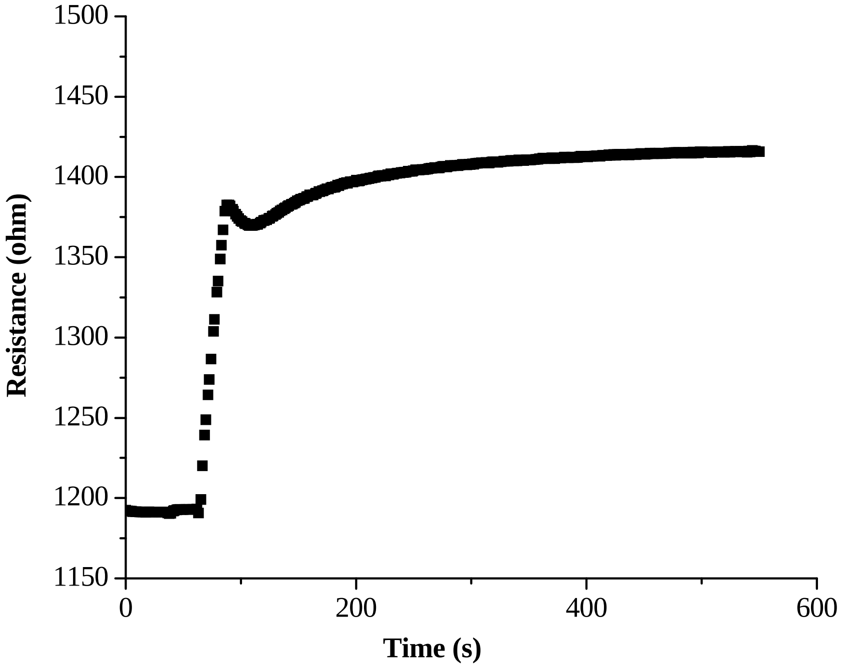


Figure 4.16 Response value of the PB/PEDOT composite sensor against ammonia.

4.3.3 The repeatability and stability of sensor

The fact that the resistance of the composite sensor can be recovered back to the initial value (Figure 4.17) after the on/off cycle exposure to ethanol vapor implying that the PEDOT-based sensor is quite stable and the PEDOT/PB composite did not have specific interactions with the vapor of ethanol. Besides ethanol, the recoverable responses were also observed in other chemicals; methanol and water. These results provide good evidences demonstrating the versatility of the sensor. As outlined in Table 4.5, the responses towards selected polar chemicals, water, methanol, and ethanol decreased as a function of storage time. This is presumably caused by a decreasing resistivity of the composite film. The resistance of the sensor decreased respectively.

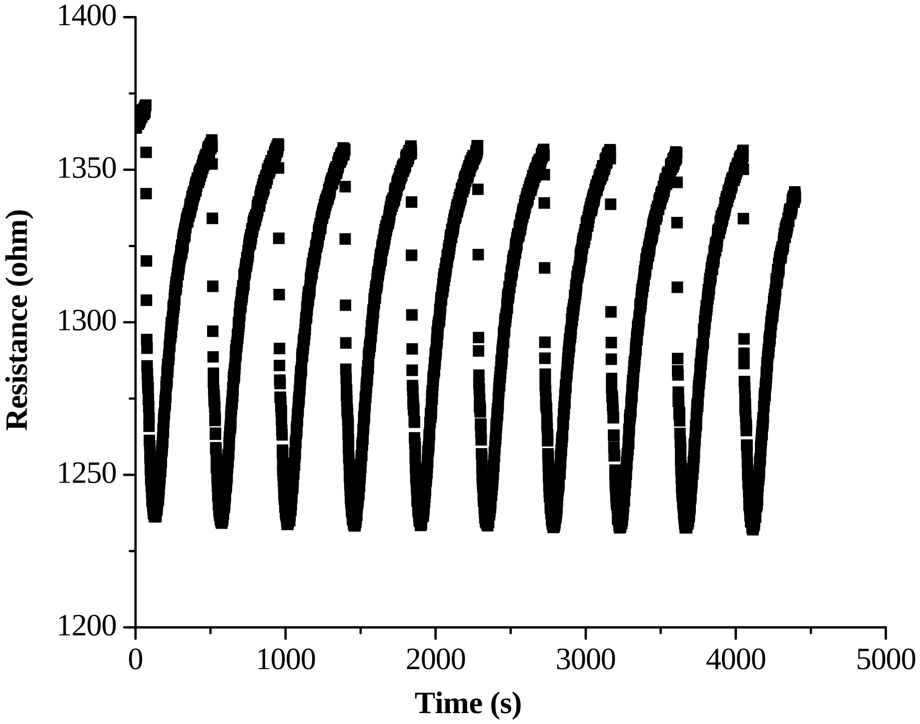


Figure 4.17 Response value of the PEDOT/PB composite sensor after the repeated contact with ethanol vapor.

Table 4.5 Response value of the PB/PEDOT composite sensor that was repeatedly used for sensing the vapor of selected polar chemicals for up to 8 months

Solvent	Dielectric constant	Response (ΔR/Rb)		
		1 month	4 month	8 month
Water	80.0	-0.048 ± 0.001	-0.050 ± 0.002	-0.032 ± 0.002
Methanol	33.0	-0.225 ± 0.010	-0.194 ± 0.008	-0.153 ± 0.007
Ethanol	24.3	-0.160 ± 0.010	-0.142 ± 0.009	-0.105 ± 0.009

CHAPTER V

CONCLUSION AND SUGGESTION

Development of chemiresistor gas sensor utilizing conducting polymer composite film containing poly(3,4-ethylenedioxythiophene) (PEDOT) was successfully prepared by spin casting the mixed solution of polybutadiene (PB) (Mw = $4x10^4$) and 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) at weight ratio of 1:10 on interdigitated gold-coated electrode (IDE) followed by heat-induced solid state polymerization (SSP) of at 60 °C for 8 h to convert DBEDOT into PEDOT. The presence of well distributed spherulites across the IDE on both the PB/DBEDOT and PB/PEDOT composite films indicated the well coverage of the material on the IDE both before and after SSP. In particular, the resistance of the PB/PEDOT composite film continuously decreased from $1.73 \times 10^6\ \Omega$ to $1.13 \times 10^3\ \Omega$ after 4-month storage and remained relatively constant at $\sim 10^3\ \Omega$ for up to five months. The PB/PEDOT based sensor showed high response and sensitivity against vapor of the chemicals having high polarity, especially water, methanol, and ethanol implying its great potential for gas sensing applications.

In this research, attempts to use polystyrene (PS) and poly(methyl methacrylate) (PMMA) as the polymer matrix for preparing the PEDOT-containing composite film as sensing material was not successful. The DBEDOT crystals cannot disperse evenly in the polymer matrix and failed to homogeneously and entirely cover the IDE by using spin casting of the DBEDOT/polymer solution. It is interesting to investigate the preparation of PEDOT/PS and PEDOT/PMMA composite films using an alternative fabrication process such as electrospinning. This method should improve the composite film uniformity, smoothness, and conductivity of PEDOT/PS and PEDOT/PMMA films. The ability to use a variety of polymer matrices for fabrication should expand the applicability of the PEDOT-containing composite for sensing applications.

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APPENDICES

APPENDIX A

Pattern response of PEDOT/PB sensor tested with the volatile chemical

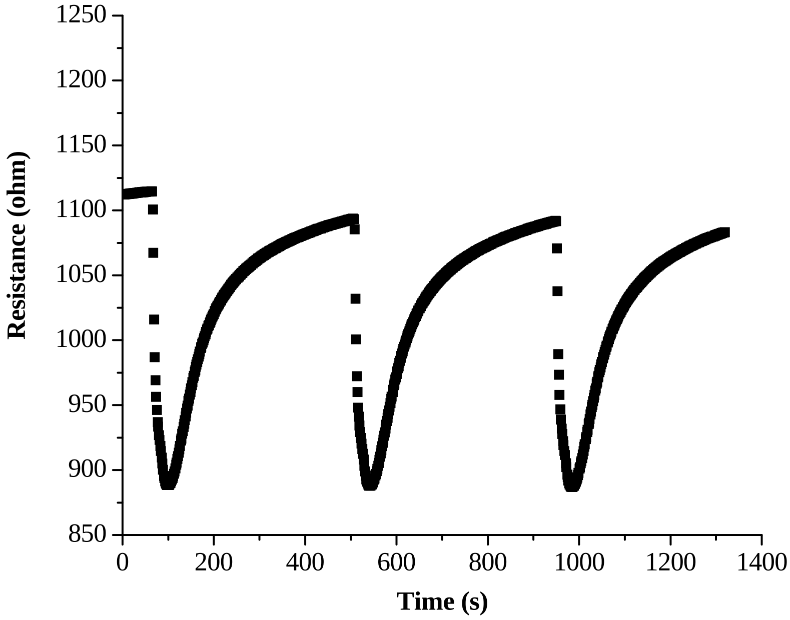


Figure A-1 Pattern response and repeatability of PEDOT/PB sensor against saturated methanol vapor.

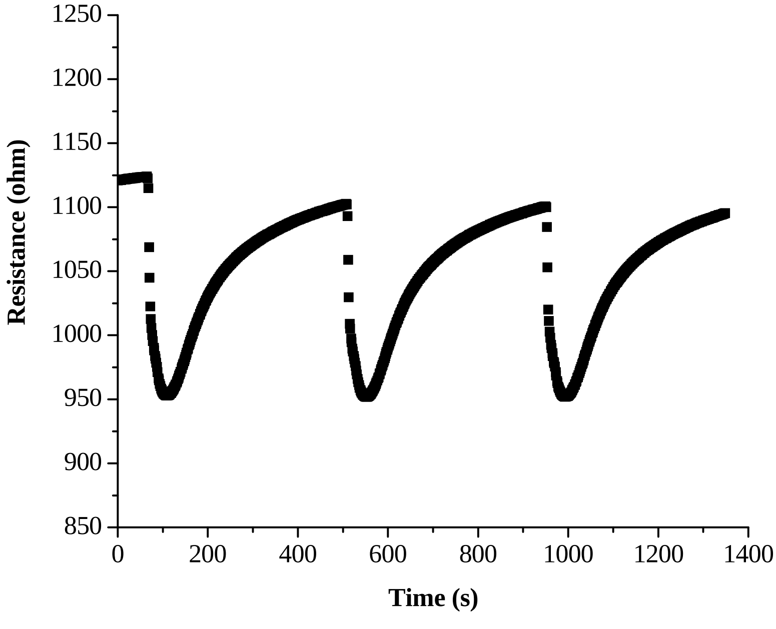


Figure A-2 Pattern response and repeatability of PEDOT/PB sensor against saturated ethanol vapor.

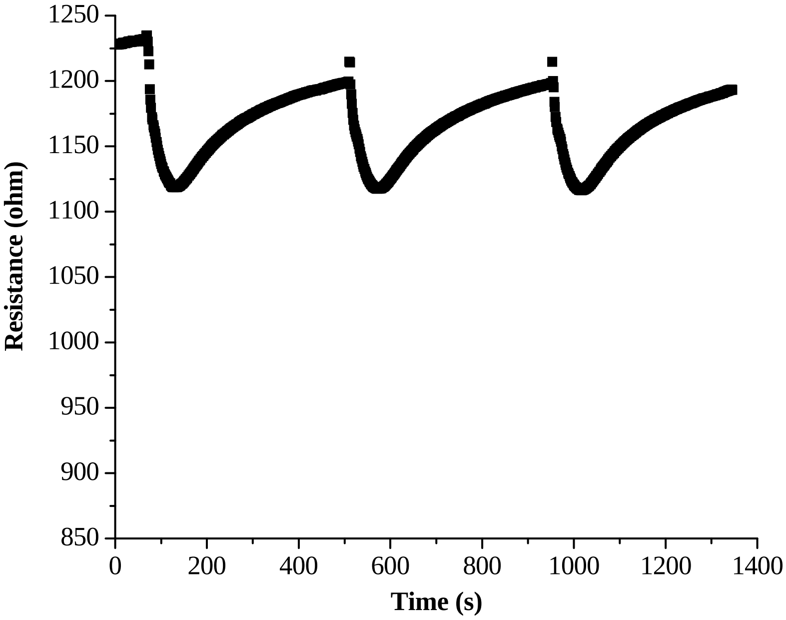


Figure A-3 Pattern response and repeatability of PEDOT/PB sensor against saturated 2-propanol vapor.

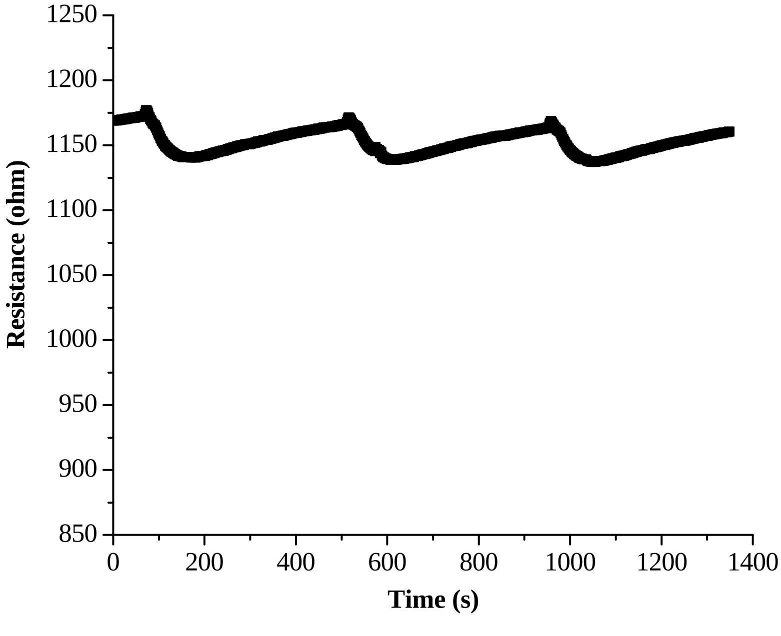


Figure A-4 Pattern response and repeatability of PEDOT/PB sensor against saturated 1-butanol vapor.

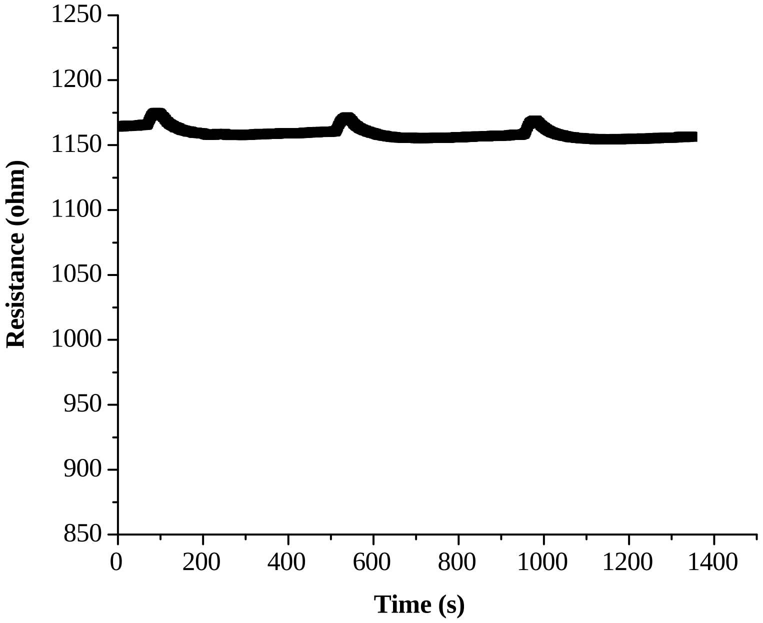


Figure A-5 Pattern response and repeatability of PEDOT/PB sensor against saturated 1-pentanol vapor.

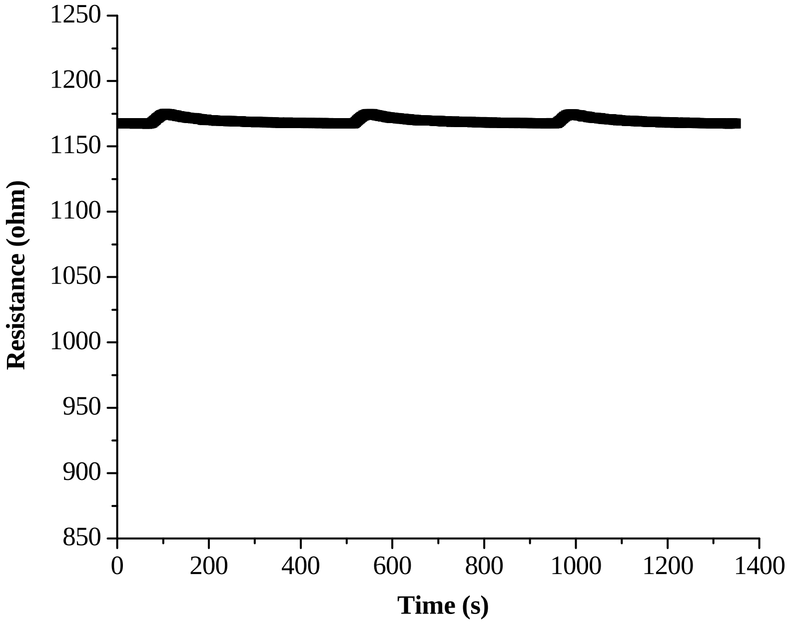


Figure A-6 Pattern response and repeatability of PEDOT/PB sensor against saturated 1-hexanol vapor.

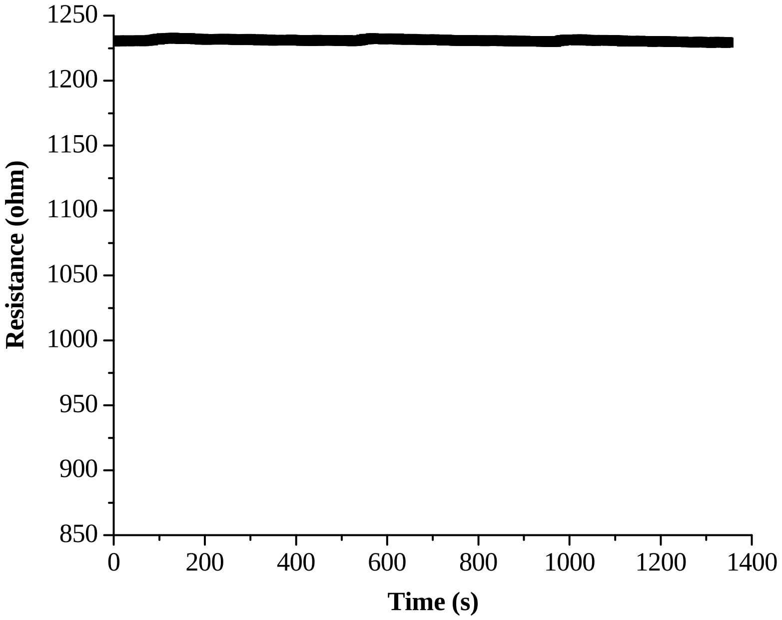


Figure A-7 Pattern response and repeatability of PEDOT/PB sensor against saturated 1-heptanol vapor.

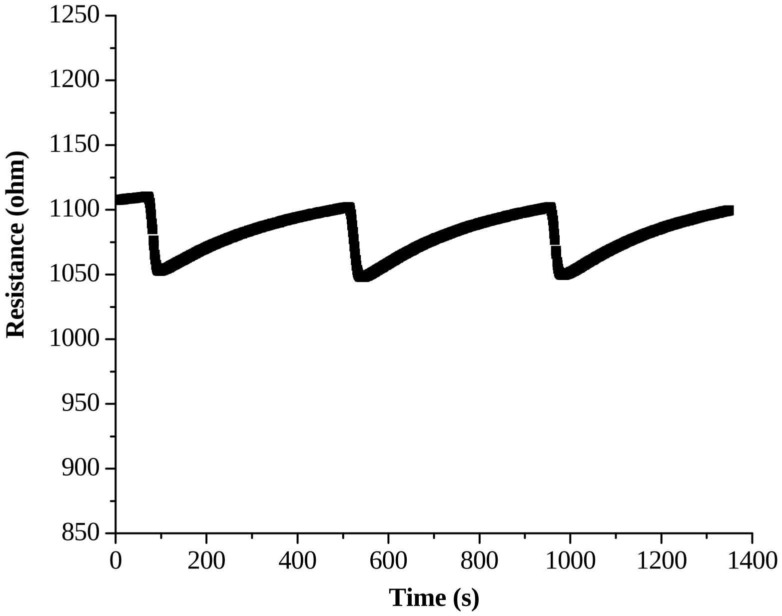


Figure A-8 Pattern response and repeatability of PEDOT/PB sensor against saturated water vapor.

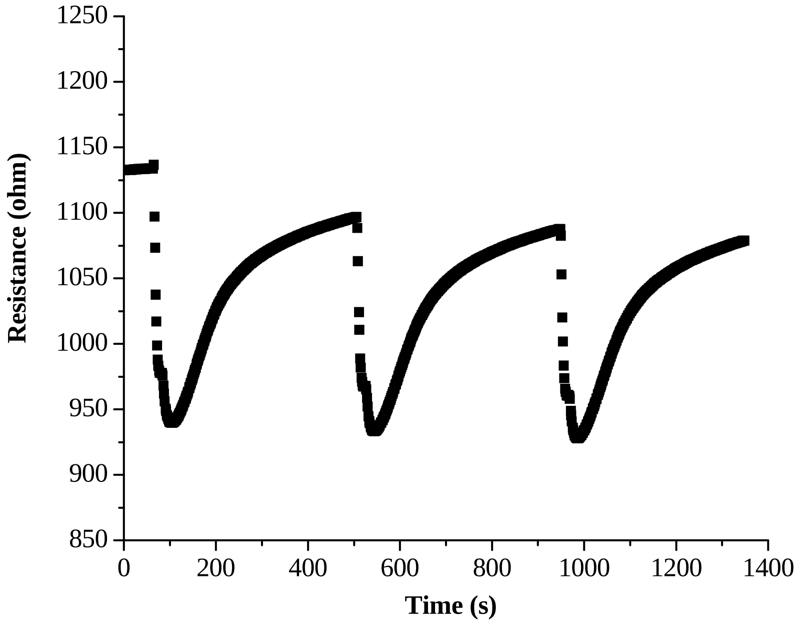


Figure A-9 Pattern response and repeatability of PEDOT/PB sensor against saturated chloroform vapor.

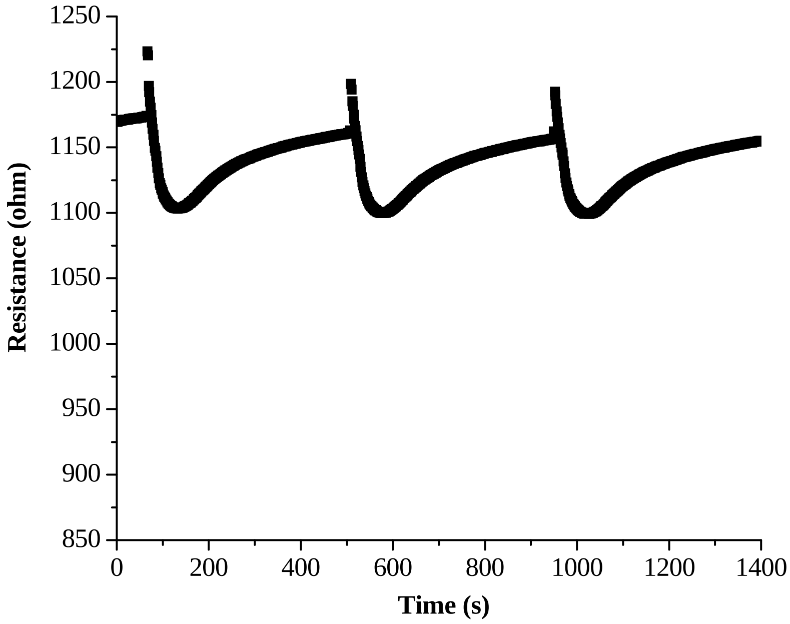


Figure A-10 Pattern response and repeatability of PEDOT/PB sensor against saturated acetone vapor.

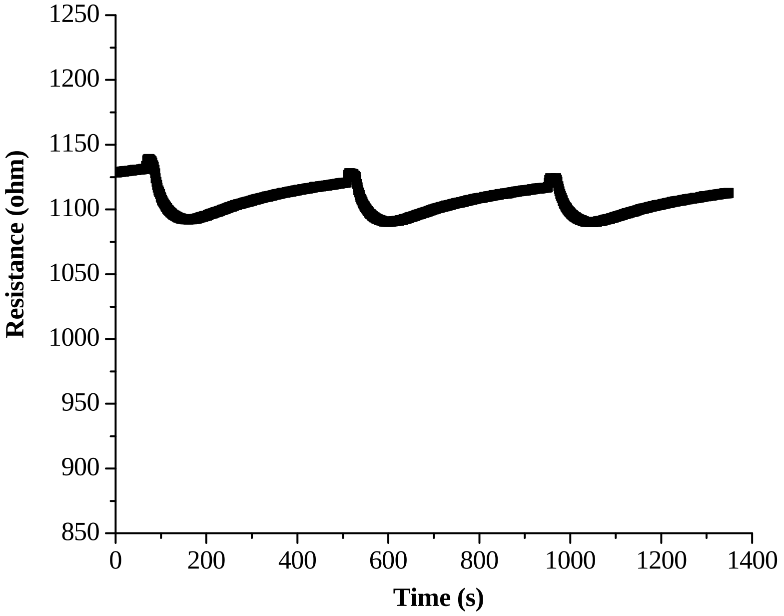


Figure A-11 Pattern response and repeatability of PEDOT/PB sensor against saturated toluene vapor.

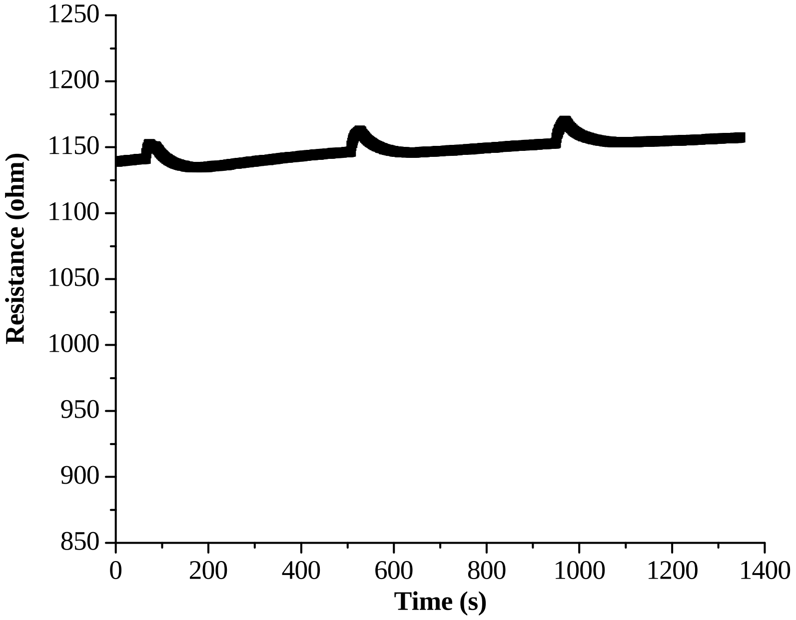


Figure A-12 Pattern response and repeatability of PEDOT/PB sensor against saturated hexane vapor.

Response calculation

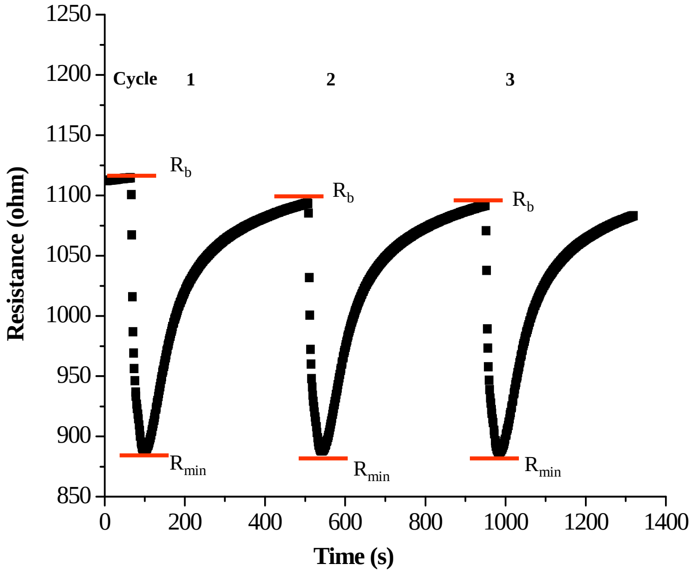


Figure A-13 Pattern response of PEDOT/PB sensor against the methanol vapor.

$$\text{Response} = dR/R_b$$

dR = the difference of resistance value between the maximum or minimum peak and the starting point of sensing curve

$$dR = R_{min} - R_b$$

R_b = the resistance value at the starting point of sensing curve

Table A-1 Response of the PEDOT/PB composite sensors when tested with methanol vapor.

Cycle	Resistance (Ω)		dR (Ω)	dR/Rb
	R_b	Rmin	(R_{min}-R_b)	
1	1114.7	888.4	-226.3	-0.204
2	1093.6	887.9	-205.7	-0.189
3	1091.9	886.9	-205.0	-0.189

Table A-2 Response and average response values of the PEDOT/PB composite sensors when tested with different chemical vapor.

Volatile chemical	Response			Average Response	SD
	1	2	3		
Water	-0.052	-0.050	-0.048	-0.050	0.002
Methanol	-0.204	-0.189	-0.189	-0.194	0.008
Ethanol	-0.153	-0.138	-0.136	-0.142	0.009
Acetone	-0.060	-0.054	-0.050	-0.055	0.005
Chloroform	-0.172	-0.150	-0.148	-0.157	0.013
Toluene	0.006	0.006	0.006	0.006	0.000
Hexane	0.009	0.014	0.015	0.012	0.003

Table A-3 Response and average response values of the PEDOT/PB composite sensors when tested with a series of alcohol.

Chemical	Response			Average Response	SD
	1	2	3		
Methanol	-0.204	-0.189	-0.189	-0.194	0.008
Ethanol	-0.153	-0.138	-0.136	-0.142	0.009
2-Propanol	-0.093	-0.069	-0.069	-0.077	0.014
1-Butanol	-0.028	-0.024	-0.023	-0.025	0.003
1-Pentanol	0.008	0.009	0.009	0.009	0.001
1-Hexanol	0.006	0.006	0.006	0.006	0.000
1-Heptanol	0.002	0.001	0.001	0.001	0.000

Vapor concentration calculation

- **Determination of weight loss of volatile chemical**

Table A-4 Weight loss of volatile chemical determined by flowing nitrogen gas into chemical chamber at a flow rate 300 mL/min for 30 minutes at 25 °C

Chemical	Weight of solvent (g)		Weight loss (g)	Average weight loss (g)	SD
	Before	After			
Water	197.3028	197.1136	0.1892	0.1818	0.0068
	197.1136	196.9333	0.1803		
	196.9333	196.7575	0.1758		
Methanol	188.0038	186.2499	1.7539	1.6927	0.0532
	186.2499	184.5926	1.6573		
	184.5926	182.9257	1.6669		
Ethanol	188.1505	187.0493	1.1012	1.0496	0.0449
	188.9951	187.9673	1.0278		
	187.9668	186.9471	1.0197		
Acetone	194.1840	187.8323	6.3517	6.3675	0.0935
	191.3409	185.0579	6.2830		
	192.4261	185.9582	6.4679		
Chloroform	214.2811	203.7852	10.4959	10.6008	0.4907
	219.2732	208.1377	11.1355		
	216.0293	205.8582	10.1711		
Toluene	191.6722	190.5077	1.1645	1.1560	0.0435
	190.5077	189.3130	1.1947		
	189.3130	188.2041	1.1089		
Hexane	184.2887	178.4930	5.7957	5.4537	0.3156
	178.4930	173.1015	5.3915		
	173.1015	167.9277	5.1738		

Table A-5 Weight loss of alcohols determined by flowing nitrogen gas into chemical chamber at a flow rate 300 mL/min for 30 minutes at 25 °C

Alcohol	Average weight loss (g)	SD
Methanol	0.1818	0.0532
Ethanol	1.0496	0.0449
2-Propanol	1.2494	N/A
1-Butanol	0.2837	N/A
1-Heptanol	0.1444	N/A
1-Hexanol	0.0505	N/A
1-Heptanol	0.0670	N/A

N/A not available

- **Calculation of chemical vapor**

Mol. loss = weight loss/ formular weight of chemical

Volume loss (L) = Mol. loss x 24.25

$PV = nRT$
$P = 1\text{atm}$
$R = 0.0821\ \text{L.atm.mol}^{-1}.\text{K}^{-1}$
$n = 1$
Temp. 25 °C = 298 K

<u>V = 24.45 L</u>

Volume loss/min = Volume loss (L) / 30 minute

Volume loss at 20 second (L) = Volume loss/min/3

Volume loss at 20 second (mL) = Volume loss at 20 second (L)*1,000

Total volume = Volume loss of chemical (mL) + Volume loss of nitrogen gas (mL)

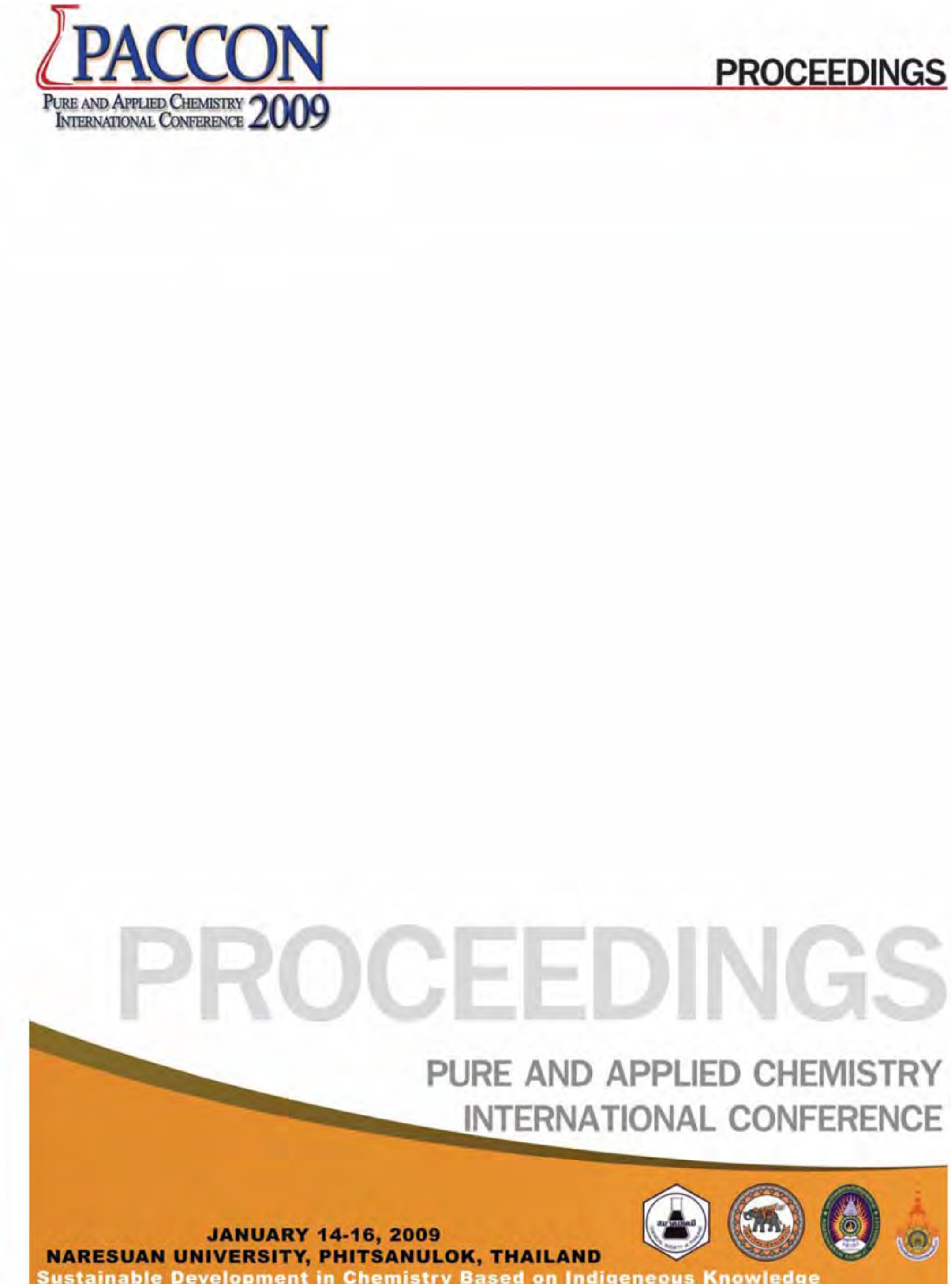
$$\text{Concentration of chemical vapor (ppm)} = \frac{\text{Volume loss of chemical (mL)} \times 1{,}000{,}000}{\text{Total volume (mL)}}$$

Table A-6 Concentration of chemical vapor (ppm) calculated from weight loss of volatile chemical by flowing nitrogen gas into chemical chamber at a flow rate 300 mL/min for 30 minutes at 25 °C

Solvent	Fw.	Avg Weight loss (g)	Mol. loss	Volume loss (L)	Volume loss (L/min)	Volume loss at 20 second (L)	Volume loss at 20 second (mL)	Volume of N_2 at 20 second	Total volume (ml)	ppm
Hexane	86.18	5.4537	0.0633	1.5473	0.0516	0.0172	17.2	100	117	1.47×10^5
Toluene	92.13	1.1560	0.0125	0.3068	0.0102	0.0034	3.4	100	103	3.30×10^4
Ethanol	46.07	1.0496	0.0228	0.5570	0.0186	0.0062	6.2	100	106	5.83×10^4
Methanol	32	1.6927	0.0529	1.2933	0.0431	0.0144	14.4	100	114	1.26×10^5
Water	18	0.1818	0.0101	0.2469	0.0082	0.0027	2.7	100	103	2.67×10^4
Acetone	58.08	6.3675	0.1096	2.6805	0.0894	0.0298	29.8	101	131	2.28×10^5
Chloroform	119.38	10.6008	0.0888	2.1711	0.0724	0.0241	24.1	102	126	1.91×10^5

Solvent	Fw.	Avg. Weight loss (g)	Mol. loss	Volume loss (L)	Volume loss (L/min)	Volume loss at 20 second (L)	Volume loss at 20 second (mL)	Volume of N_2 at 20 second	Total volume (ml)	ppm
Methanol	32.04	1.6927	0.0528	1.2917	0.0431	0.0144	14.4	100	114	1.26×10^5
Ethanol	46.07	1.0496	0.0228	0.5570	0.0186	0.0062	6.2	100	106	5.83×10^4
2-Propanol	60.1	1.2494	0.0208	0.5083	0.0169	0.0056	5.6	100	106	5.34×10^4
1-Butanol	74.12	0.2837	0.0038	0.0936	0.0031	0.0010	1.0	100	101	1.03×10^4
1-Pentanol	88.15	0.1444	0.0016	0.0401	0.0013	0.0004	0.4	100	100	4.43×10^3
1-Hexanol	102.17	0.0505	0.0005	0.0121	0.0004	0.0001	0.1	100	101	1.33×10^3
1-Heptanol	116.2	0.0670	0.0006	0.0141	0.0005	0.0002	0.2	100	102	1.53×10^3

APPENDIX B



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Sustainable Development in Chemistry Based on Indigeneous Knowledge

DEVELOPMENT OF GAS SENSOR FROM CONDUCTING POLYMER COMPOSITES CONTAINING POLY(3,4-ETHYLENEDIOXYTHIOPHENE)

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Abstract: It has been recently discovered that crystals of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) can undergo solid state polymerization (SSP) through debromination and coupling, yielding nearly defect-free and highly ordered bromine-doped conductive poly(3,4-ethylenedioxythiophene) or PEDOT, without the need of initiators or catalysts. Taking advantages of DBEDOT solubility in many common organic solvents together with its capability of undergoing SSP, this research aims to prepare conducting polymer composites containing PEDOT and to determine the possibility of using them for gas sensing applications. A mixed solution between DBEDOT and an insulating host polymer, polybutadiene (PB), was first fabricated into thin films on chromium/gold interdigitated electrode (IDE) by spin coating. After solvent evaporation, SSP of the DBEDOT crystals embedded in the PB matrix was then induced by heating (60°C, 8h). The physical appearance and resistivity of the dark blue composite film containing PEDOT were evaluated by optical microscope and Keithley digital multimeter, respectively. The composite film deposited on the IDE was tested for gas sensing against vapor of a number of organic solvents having varied polarity such as water, methanol, ethanol, chloroform, acetone, toluene and hexane. Upon the exposure to chemical vapor of most tested solvents, the resistance of the composite film decreased. The results indicated that the PEDOT composite film can be applicable for gas sensing, especially the vapor of polar organic solvents. The repeatability, sensitivity and stability of the PEDOT-based sensor were also determined.

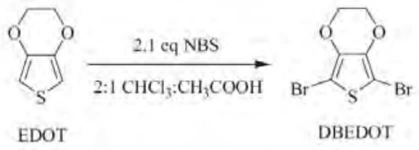
Introduction

Nowadays, gas sensor technology is most widely used in many fields such as environmental monitoring, chemical processing, and food production for detecting quantity or quality of the chemical volatile compound. Conducting polymers are attractive materials for sensing applications due to many advantages [1,2]. They can be easily synthesized via chemical or electrochemical methods. The sensors produced from them can be operated at room temperature and have high sensitivity as well as short response time. Furthermore, they have good mechanical properties, which allow fabricating to thin film or fiber. A number of conducting polymers that have been used as sensing materials in gas sensing applications include polypyrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives [3-5]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a well-known PTh derivative that has high conductivity (> 200 S/cm), transparency and possesses great environmental stability. However, this material is insoluble in water or organic solvents. It is thus difficult to fabricate PEDOT using casting or spin-coating techniques. The recently discovered solid state polymerization (SSP) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) (Scheme 1) provides an alternative route to synthesize PEDOT and simultaneously to overcome the fabrication limitation [6]. In this work, we aim to prepare gas sensor from PEDOT-PB composite films spun-coated on chromium/gold interdigitated electrode and test the sensing performance against different chemical vapors.

Scheme 1: Synthesis of PEDOT by solid state polymerization of DBEDOT.

Materials and Method

Materials: Polybutadiene(PB), average molecular weight of 40,000 g/mol, was obtained from DOW chemical. Methanol, ethanol, chloroform, acetone, toluene and hexane were purchased from Labscan. Chromium/gold interdigitated electrode (IDE) and gas sensor testing system were provided by National Metal and Materials Technology Center (MTEC). 2,5-Dibromo-3,4-ethylenedioxythiophene (DBEDOT) was synthesized by bromination of ethylenedioxythiophene (EDOT) as shown in Scheme 2. DBEDOT was later used as a monomer for PEDOT synthesis.



Scheme 2: Bromination of EDOT

Preparation of PEDOT-PB Composite Sensor: 0.20 g of white crystal of DBEDOT and 0.02 g of PB were dissolved in 1 mL toluene. The composite film was fabricated on chromium/gold IDE by spin casting of the composite solution with a spin speed of 1500 rpm for 60 sec. After solvent evaporation, SSP of the DBEDOT crystals embedded in the PB matrix was then induced by heating at 60^0C for 8 h. The physical appearance and resistivity of the dark blue composite film containing PEDOT were evaluated by transmission optical microscope and Keithley digital multimeter, respectively. Finally the composite sensor was placed in sensor chamber for testing with the vapor of organic solvents.

Sensor testing and response calculation: The sensor testing system (shown in Figure 1) consists of a gas flow controller, a sensor chamber, a digital multimeter (Keithley 2700), and a computer for data collection and calculation. Nitrogen gas (N_2), purity 99.99%, used as the carrier gas was flowed into sensor chamber for 1 h before testing in order to calibrate the sensor resistance. The flow rate of carrier gas was fixed at 300 mL/min. For the process of testing, the carrier gas flowed into the sensor chamber for 60 sec in order to obtain baseline resistance (Rb). After that, the saturated chemical vapor generated by passing nitrogen gas into chemical was carried to the sensor chamber for 20 sec. Upon interacting with the chemical vapor, the resistance of the composite film was changed. Finally, nitrogen gas was flowed into the chamber again for 360 sec in order to purse off the chemical vapor from the surface and bulk of the sensing material and ready for the next testing. The change of resistance value can be converted to response of the sensor using the following equation:

$$\text{Response} = dR/Rb \qquad (1)$$

Where, dR = the difference of resistance value between the maximum or minimum peak and the starting point of sensing curve and Rb = the resistance value at the starting point of sensing curve.

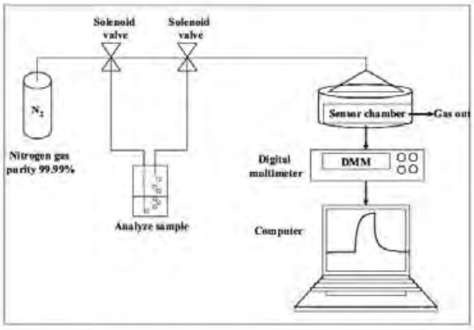


Figure 1: Schematic of gas sensor testing system

Results and Discussion

The optical image shown in Figure 2(a) indicates thorough coverage of as-spun DBEDOT-PB composite film on the IDE. The appearance of the spherulite growth across each pair of electrode verified the presence of DBEDOT white crystal in the film. Upon heating at 60 ^{0}C for 8 h, the resulting dark-blue crystal spherulites of PEDOT seemed to be smaller and finer as can be seen from Figure 2(b).

Figure 2: The morphology of the composite films at the magnitude of 40X: (a) before SSP and (b) after SSP

As measured by the digital multimeter, the resistance of the PEDOT-PB composite film was about 1,000 ohms. The fact that the resistance of the composite film remains essentially constant for up to 5 months suggests that the resistance of the film is quite stable. This is a desirable characteristic for material to be used in gas sensing applications.

Sensor response against chemical vapor: After the PEDOT-PB composite sensor was exposed to the chemical vapor, the resistance of the film was changed. The responses of the sensor against selected organic solvent are shown in Table 1. The results show that when the sensor was exposed to polar solvents, the resistance of the film decreased, giving negative responses. On the other hand, the resistance of the film increased when it was exposed to non-polar solvent, giving positive responses as can be observed in the cases of toluene and hexane. The dipole interactions between polar solvents and the polar PEDOT in the composite film was believed to facilitate the charge or electron transfer and led to the elevation of film conductivity. In contrast, the absorption of the non-polar solvents by PB matrix may cause swelling of the polymer composite. Being further apart from one another of the conducting PEDOT chains may be the reason why the conductivity of the composite film was deteriorated.

Table 1: The dielectric constant, response and sensitivity of sensor with various organic solvents

Solvent	Dielectric constant	Response	Sensitivity (10^{-3})
Water	80	-0.050 ± 0.002	1.85
Methanol	33	-0.194 ± 0.008	1.54
Ethanol	24.3	-0.142 ± 0.009	2.45
Acetone	20.7	-0.055 ± 0.005	0.24
Chloroform	4.8	-0.157 ± 0.013	0.81
Toluene	2.4	0.006 ± 0.000	0.18
Hexane	2.02	0.012 ± 0.003	0.08

Figure 3 shows the repeatability of the PEDOT-PB composite sensor when it was exposed to ethanol vapor. The resistance of the film decreased after the exposure to ethanol vapor (on). The resistance of the sensor was slowly recovered (within 200 sec) to baseline value after the flow of ethanol vapor was stopped (off). The complete recovery of the signal after each on-off cycle of the exposure to ethanol vapor indicated that the PEDOT-PB composite is a good sensing material for gas sensing applications.

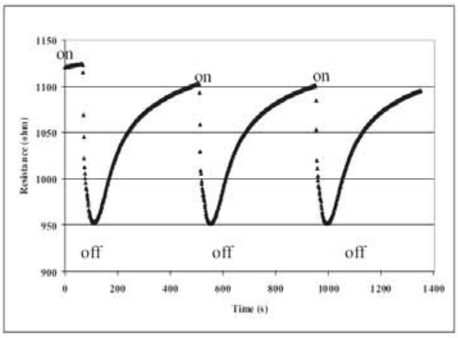


Figure 3: The repeatability of sensor response with ethanol vapor

Conclusion

Conducting PEDOT-PB composite films fabricated on IDE produced by solid state polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene possessed desirable performance suggesting that they can be used as sensing material for gas sensing applications. This sensor shows high response and sensitivity towards highly polar organic solvents especially ethanol, water, and methanol. In particular, sensor resistance is quite stable after storage for up to five months. This research has also indicated that PEDOT-based composite films hold a great potential in the development of sensor array. It may be applied in electronic nose system for detecting the complicated chemical vapor.

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FOR THE OUTSTANDING POSTER PRESENTATION AWARD
THE PURE AND APPLIED CHEMISTRY INTERNATIONAL CONFERENCE 2009
NARESUAN UNIVERSITY, PHITSANULOK, THAILAND
JANUARY 14 –16, 2009

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Award:

- The Outstanding Poster Presentation Award (PACCON2009) Pure and Applied Chemistry International Conference 2009, Naresuan University, Phitsanulok, Thailand 14-16 January 2009, “Development of Gas Sensor from Conducting Polymer Composites Containing Poly(3,4-ethylenedioxythiophene)”.