การเตรียมพอลิเมอร์คอมพอสิตนำไฟฟ้าโดยปฏิกิริยาพอลิเมอไรเซชันในวัฏภาคของแข็งของ

2,5-ไดโบรโม-3,4-เอทิลีนไดออกซีไทโอฟีน

นางสาวสไบ กุศลส่ง

PREPARATION OF CONDUCTING POLYMER COMPOSITES BY SOLID STATE POLYMERIZATION OF 2,5-DIBROMO-3,4-ETHYLENEDIOXYTHIOPHENE

Miss Sabai Kusonsong

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 2007

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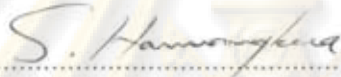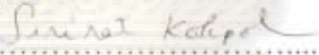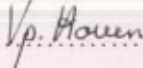|	
Thesis Title	PREPARATION OF CONDUCTING POLYMER COMPOSITES BY SOLID STATE POLYMERIZATION OF 2,5-DIBROMO-3,4-ETHYLENEDIOXYTHIOPHENE
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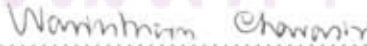
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เตรียมพอลิเมอร์คอมพอสิตนำไฟฟ้าที่มี พอลิ 3,4-เอทิลีนไดออกซีไทโอฟีน (พีอีดีโอที) เป็นองค์ประกอบได้โดยปฏิกิริยาพอลิเมอไรเซชันในวัฏภาคของแข็งของ 2,5-ไดโบรโม-3,4-เอ ทิลีนไดออกซีไทโอฟีน (ดีบีอีดีโอที) ในเมทริกซ์พอลิสไตรีน (พีเอส) หรือพอลิบิวทะไดอีน (พีบี) ได้เปอร์เซนต์ผลผลิตของพีอีดีโอทีสูงถึง 85 เปอร์เซนต์ สามารถวิเคราะห์พีอีดีโอทีที่มีอยู่ในพอลิ เมอร์คอมพอสิตได้ด้วยเทคนิคเอฟที-ไออาร์สเปกโตรสโกปี, ยูวี-วิสิเบิล สเปกโตรสโกปี, ทีจีเอ และ เอ็กซ์อาร์ดี จากการวัดด้วยโฟร์พอยท์โพรบคอนดักโทมิเตอร์พบว่าพีอีดีโอที/พีเอสคอมพอสิตฟิล์ม ให้ค่าการนำไฟฟ้าสูงถึง 58 ซีเมน/เซนติเมตร โดยภาวะในการเตรียมที่เหมาะสมคือ ใช้อัตราส่วน โดยน้ำหนักระหว่างดีบีอีดีโอทีและพีเอส เป็น 3 ต่อ 1 ความเข้มข้นของดีบีอีดีโอที 0.225 กรัมต่อ มิลลิลิตร และทำปฏิกิริยาพอลิเมอไรเซชันในวัฏภาคของแข็งที่ 50 องศาเซลเซียส เป็นเวลา 7 ชั่วโมง ค่าการนำไฟฟ้าของพีอีดีโอที/พีบีคอมพอสิตฟิล์มมีค่าต่ำกว่าพีอีดีโอที/พีเอสคอมพอสิตฟิล์ม อย่างมีนัยสำคัญ ทั้งนี้เชื่อว่าการที่พีบีมีค่าอุณหภูมิกลาสทรานซิชันต่ำส่งผลให้ทั้งดีบีอีดีโอทีและพีอี ดีโอทีเคลื่อนที่ได้ระหว่างการทำปฏิกิริยาพอลิเมอไรเซชันในวัฏภาคของแข็ง ดังนั้นพีอีดีโอทีที่ สังเคราะห์ได้จึงมีคอนฟอร์เมชันที่เป็นระเบียบต่ำ ส่งผลให้ค่าการนำไฟฟ้าที่ต่ำด้วย นอกจากนี้ยัง พบว่าการเก็บพอลิเมอร์คอมพอสิตไว้ทำให้ค่าการนำไฟฟ้าลดลงเนื่องจากการสูญเสียโบรมีน อย่างไรก็ตามสามารถทำให้พอลิเมอร์คอมพอสิตมีค่าการนำไฟฟ้ากลับขึ้นมาสูงอีกครั้งได้โดยการ โด๊ปด้วยไอโอดีนในกรณีของพีอีดีโอที/พีเอสคอมพอสิตฟิล์ม แต่ทำไม่ได้ในกรณีของพีอีดีโอที/พีบี คอมพอสิตฟิล์ม

สาขาวิชา	ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์	ลายมือชื่อนิสิต.................
ปีการศึกษา	2550	ลายมือชื่ออาจารย์ที่ปรึกษา.................
		ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.................

4672450223: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORD: PEDOT CONDUCTIVE COMPOSITE SOLID STATE POLYMERIZATION POLYSTYRENE

SABAI KUSONSONG: PREPARATION OF CONDUCTING POLYMER COMPOSITES BY SOLID STATE POLYMERIZATION OF 2,5-DIBROMO-3,4-ETHYLENEDIOXYTHIOPHENE. THESIS ADVISOR: ASST. PROF. VORAVEE P. HOVEN, Ph.D., THESIS CO-ADVISOR: ASST. PROF. YONGSAK SRITANA-ANANT, Ph.D., 59 pp.

Conducting polymer composites containing poly(3,4-ethylenedioxythiophene) (PEDOT) was prepared by solid state polymerization (SSP) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in the presence of either polystyrene (PS) or polybutadiene (PB) matrix. The percentage yield of up to 85 % of the PEDOT could be obtained. The presence of PEDOT in the polymer composite was verified by FT-IR spectroscopy, UV-VIS spectroscopy, TGA, and XRD. As measured by four-point probe conductometer, the conductivity of the PEDOT/PS composite film can reach as high as 58 S/cm. The optimal condition to obtain the highest conductivity of the PEDOT/PS composite was to use 3:1 DBEDOT:PS weight ratio, 0.225 g/mL of DBEDOT and conducting the SSP at 50°C for 7 h. The PEDOT/PB composite films possess significantly lower conductivities than the PEDOT/PS composite film. It is believed that the low T_g of PB allows the DBEDOT as well as PEDOT to move during SSP and resulting in the PEDOT with less ordered conformation and lower conductivity. The conductivity of the PEDOT composite films was found to decrease upon storage due to the loss of Br_2. The conductivity can be completely recovered after re-doping with I_2 in the case of PEDOT/PS composite films but cannot be recovered in the case of PEDOT/PB composite films.

Field of study Petrochemistry and Polymer Science   Student's signature S. Kusonsong

Academic year 2007   Advisor's signature Vp. Hoven

Co-advisor's signature

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATION

CH_3COOH	: acetic acid
NBS	: *N*-bromosuccinimide
cm	: centimeter
min	: minute
mL	: milliliter
°C	: degree celsius
$CDCl_3$	: deuterated chloroform
DBEDOT	: 2,5-dibromo-3,4-ethylenedioxythiophene
PEDOT	: Poly(3,4-ethylenedioxythiophene)
EDOT	: 3,4-ethylenedioxythiophene
g	: gram
h	: hour
HOMO	: highest occupied molecular orbital
LOMO	: lowest occupied molecular orbital
FT-IR	: fourier-transform infrared spectrophotometer
NMR	: Nuclear magnetic resonance spectroscopy
TGA	: thermogravimetric analysis
UV	: ultra-violet
VIS	: visible
XRD	: x-ray diffractometer
MS	: mass spectrometry
SSP	: solid state polymerization
Mw	: average molecular weight
S	: seimens
eq	: equivalence
T_g	: glass transition temperature
w/w	: weight by wiegh
$NaHCO_3$	: sodium hydrogen carbonate
I_2	: Iodine

ppm	: part per million
Br_2	: bromine
nm	: nanometer
PS	: polystyrene
PB	: polybutadiene
2θ	: 2theta
I&V	: current and voltage
conc.	: concentration
N/A	: not available

CHAPTER I

INTRODUCTION

1.1 Statement of the Problem

Poly(3,4-ethylenedioxythiophene) (PEDOT) has received much attention in recent years for its unique electrical properties. Due to its high stereo-regularity, PEDOT possesses very high conductivity up to 550 S/cm in the electrochemical doped state and remarkable stability as compared with other conducting polymers. In early phases of development, the materials were insoluble and not processible. This shortcoming was later overcome by the incorporation of a water soluble counter-anion poly(styrene sulfonate) (PSS). Chemical polymerization of 3,4-ethylenedioxythiophene (EDOT) in the presence of PSS yields the well-known commercial product "Baytron P" which is PEDOT/PSS composite in the form of dispersion in water. However, PEDOT:PSS composite still possesses quite low conductivity of less than 1 S/cm.

Here, we propose to use solid-state polymerization (SSP) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in a polymer matrix as a way to enhance the processibility of PEDOT. Because DBEDOT is soluble in a wide range of organic solvents, it can be homogeneously mixed with a number of commonly used polymers such as polystyrene, polybutadiene. After the removal of the solvent, the crystalline DBEDOT in the polymer matrix should be capable of undergoing SSP yielding conductive PEDOT-containing composite. Also, doping can simultaneously take place as a result of entrapped bromine (Br_2), a by-product generated during SSP.

1.2 Objectives

1. To prepare conductive polymer composites containing 3,4-polyethylenedioxy thiophene (PEDOT) using solid state polymerization (SSP) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)

1.3 Scope of Investigation

The stepwise investigation was carried out as follows.

1. Literature survey for related research work

2. To synthesize 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)

3. To prepare PEDOT/ polymer composite films by solid state polymerization of DBEDOT by varying a number of processing parameters:

    - polymer matrix i.e. polystyrene (PS) and polybutadiene (PB)
    - DBEDOT: polymer weight ratio
    - DBEDOT concentration
    - polymerization time
    - polymerization temperature

4. To characterize PEDOT/ polymer composite films by Thermal gravimetric analysis (TGA), UV-Vis Spectroscopy

5. To determine the conductivity of the PEDOT/ polymer composite films

6. To characterize the PEDOT extracted from PEDOT/ polymer composite films by x-ray diffraction, UV-Vis spectroscopy, FT-IR spectroscopy

7. To investigate the effect of storage on the conductivity of the PEDOT/ polymer composite films

8. To study the effect of doping with I_2 on the conductivity of the PEDOT/ polymer composite films

ศูนย์วิทยทรัพยากร

จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Introduction of electronic organic [1-4]

During the last few decades, much attention has been paid to the filed of organic electronics. Electrical devices made out of plastic materials provide great advantages due to their special chemical and electrical behavior as compared with standard semiconductors. Organic light emitting diodes (OLEDs), plastic solar cells or organic field effect transistors (OFETs) are some of the new devices in this area. Great progress has been made to investigate, understand, improve and utilize their unique physical features. Commercial products are entering the consumer markets and show the potential of this new technology. The foundation of the field of organic electronics was established back in the seventies with the discovery that the conductivity of polyacetylene films can be changed over several orders of magnitude by chemical doping. For their groundbreaking work in this area, MacDiarmid, Heeger and Shirakawa were awarded the Nobel Prize in Chemistry 2000. Excellent introductions into the field of organic electronics are their Nobel lectures. Intrinsic conducting plastic materials and semiconductors, both electron (n-type) and hole transport (p-type) materials with band-like structures, could now be made. Since the early work, many innovative materials in pure form have been developed and characterized for the usage in electronic applications. An overview of the conductivity of different materials from insulators to metals and the span organic materials cover is shown in figure 2.1.
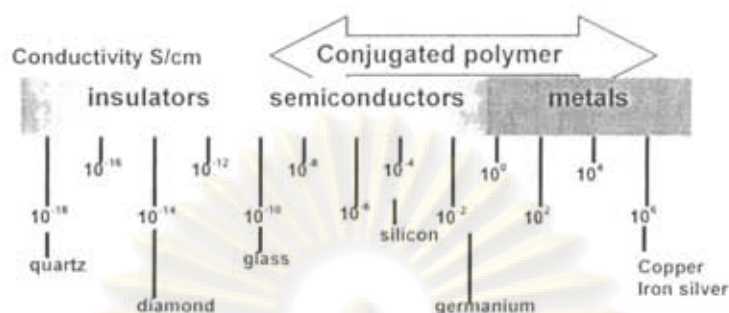
Figure 2.1 Conductivity of different materials.

2.2 Advantages and drawbacks [5-14]

Organic materials, in general, possess some unique features. Their chemical structure can be altered and adapted to the need of the application. Especially polymers have advanced far since their first appearance in the early nineteen hundreds. The success of thermoplastics as a cheap and endurable material used widely in our daily life is only but one example. There, the material was designed to be moldable to simplify fabrication but also to exhibit good mechanical characteristics and chemical stability. By changing part of the molecular structure, the behavior of the matter can be modified. For example, adding polar OH side groups to a molecule will result in a better solubility in water. The same approach can be used to adjust the properties of organic electronic material. The common technologies and techniques to modify the chemical structure can now be applied to adjust the electrical behavior of molecules out of this new class of organic electronic materials. Because there are an almost infinite number of combinations available, the possibilities seem to be virtually unlimited. This is an advantage of organic electronics over the established microelectronic technology. When inorganic single-crystals are used, the electrical properties are changed only by doping. The substrate material itself remains unchanged. Some examples where the versatility of organic electronic materials is used can be given out of the field of optoelectronics. For a full color display, the pixels have to emit light at different wavelengths for red, green and blue. Materials for OLEDs have been developed for all three colors and can even be stacked on each other to achieve a higher pixel density.

Because plastics can be used as substrate material, the combination provides an opportunity to build flexible devices, something that was not possible with silicon

based technology. The bases for the novel materials are known components in organic chemistry. This makes them potentially low cost, at least if the fabrication process is not too affording and the material can be mass-produced. Since the materials are assembled out of organic building blocks, they can be made bio-compatible. Thus, they can be implanted and used *in vivo* without causing immune reactions. Organic layers are already used as coating material for *in situ* electrodes to record neural activity. More all-plastic, bio-compatible sensors are likely to be developed in the near future monitoring critical data like local blood pressure or blood sugar concentration.

With the organic origin of the novel materials, there is also a major drawback inherited. They easily degrade under environmental conditions due to humidity, oxygen and light. In fact, this is the major obstacle that has to be overcome before such products can be introduced into the consumer market. The principal limitation of organic materials is their confined lifetime. Requirements for many applications are in the range of several tens of thousands of hours. This is orders of magnitude beyond most numbers published to date. The performance of the electronic devices built with organic materials nowadays is far from competing with the established silicon technology. But the idea is not replacement but expansion of the application of electronic devices into new low cost/low performance markets. One example could be the so often mentioned RF-ID tag for supermarket products to simplify logistics and payment. But the field of possible applications is much wider once functional and endurable devices can be mass produced. As important as the material itself are the technologies to fabricate functional devices as will be explained in the next section.

2.3 Fabrication technologies [15-18]

Many of the new organic materials are soluble and can therefore be applied in liquid form. When the side groups of the building blocks of a polymeric material are modified, their solubility can be altered. This approach was successfully used for many materials such as poly(phenylenevinylene) (PPV)-derivatives. Using this material, the first organic LED based on a polymer was made by spin-casting a solution processable precursor [15]. The polymerization process was carried out after the thin film had been applied. If the electro-active molecules cannot be mixed with a

solvent to form a solution, dispersions may be available which still allow the application of liquid-based processing technologies.

Different methods are used to form thin films. Spin-coating is one of them and probably the most widely used due to its simplicity. Especially in laboratory applications, this method has become a standard. The film thickness can be adjusted by setting the spin-speed and time. A drawback is the large amount of waste considering the quantity of material applied compared to the one effectively making up the thin film. Therefore, spin-coating is not often used for high volume fabrication.

Another technique is dip-coating, where the sample is submerged into the solution and pulled out again. When the solution is applied to the substrate using a mold, the term film casting is used. For large area processing, spraying is the most adequate method, since only the required material is applied. The ink-jet process is highly analogous to graphical ink-jet printing, tiny droplets of polymer solution are propelled onto the substrate in carefully controlled pattern.

All the technologies mentioned above are low temperature processes. This allows using substrates that would not withstand high temperatures such as most plastic materials. Flexible, all plastic electronic devices can be built with the novel organic conductive and semi-conductive materials and using the fabrication technologies explained above.

2.4 Conjugated polymers: organic semiconductors [19-21]

Conjugated polymers (CPs) are organic semiconductors. These polymers consist of alternating single and double bonds, creating an extended p-network. Electron movement within this p-framework is the source of conductivity, with respect to electronic energy levels, hardly differs from inorganic semiconductors. Both 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-orbital of the repeating units throughout the chain. Figure 2.2 shows commonly known conjugated polymers that are conductive.
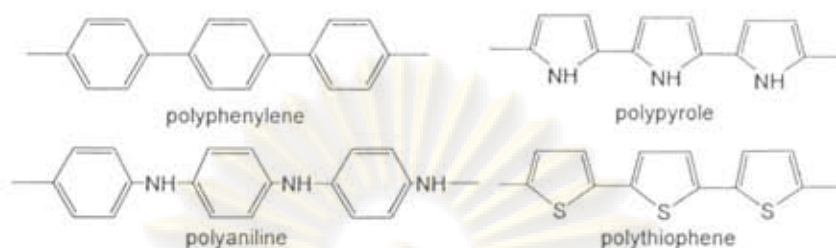
Figure 2.2 Conjugated polymers

Analogous to semiconductors, the highest occupied band (originating from the HOMO of a single thiophene 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 (E_g). 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.
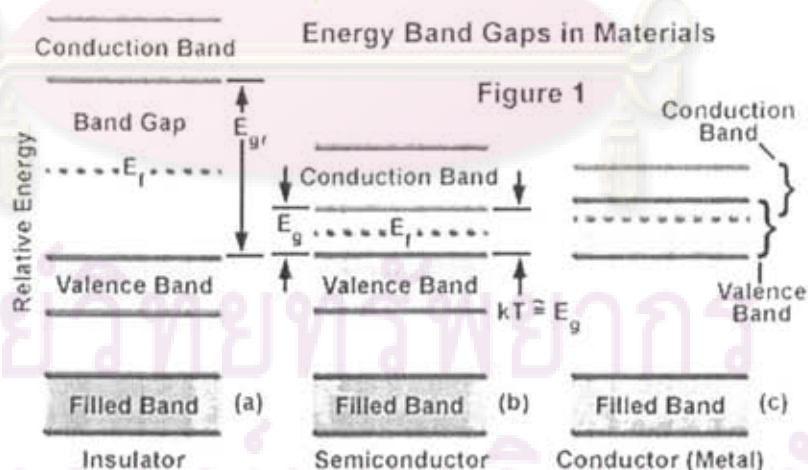
Figure 2.3 Energy band gaps in materials

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 1022 for 1 cm³ 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 of other excitations can bridge the gap. With such a small gap, the presence of a 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 with relate 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, (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.

2.5 Poly (3,4-ethylenedioxythiophen) (PEDOT) [22-27]

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.

(a)   (b)
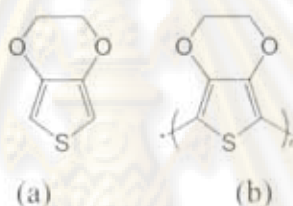
Figure 2.4 EDOT (a) and PEDOT (b)

PEDOT has been developed into one of the most successful materials from both fundamental and practical perspective. 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 [24] first polymerized EDOT to poly(3,4-

ethylenedioxythiophene), (PEDOT), and found the polymer to be useful for antistatic coatings. Inganas and co-workers [26] 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.

2.6 Solid state synthesis of PEDOT [28-30]

Polymerization of PEDOT by traditional oxidative polymerization with FeCl3 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. [29-30] reported that the solid-state polymerization (SSP) of 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).
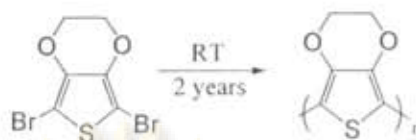
Scheme 2.1 Solid state polymerization of DBEDOT

The room-temperature conductivity of different SSP-PEDOT samples was measured by the four point probe method (Table 2.1). 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 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.

From the experiment, they concluded that heating DBEDOT in the solid state resulted in an unprecedented self-coupling reaction and gave highly conduction and relatively well-ordered bromine-doped PEDOT. Furthermore, heating DBEDOT above its melting point led to polymer with a lower conductivity.

Table 2.1 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

2.7 Processibility

Poly(3,4-ethylenedioxythiophene) (PEDOT) and other conductive polymer are convenient for oxidative polymerization by using oxidizing agents such as iodine and $FeCl_3$ and other way by electrochemical polymerization. These methods yielded non processible polymers product with hard, brittle, insoluble in most solvent and nonfusible even by heating up to their decomposition temperature.

Out of this thinking came the first exploratory polymerizations by Bayer and AGFA of PEDOT with the intent of applying it to the fields of antistatic coatings and photographic films. Chemical polymerization, aqueous dispersions of PEDOT: PSS, Baytron[@] synthesized by Inganäs et al.[26], is successfully used and the fabrication volume of coated photographic film per year exceeds 108 m^2. Poly(styrenesulfonate) (PSS) is used as a dopant for PEDOT. The doping process of the conjugated polymer is done by acid- rather than redox-doping. Thus, the PEDOT does not act as an electron donor but accepts a proton from the sulfonate group of the PSS dopant. A C=C π-bond of the EDOT opens up and the C bonds to an H^+ donated by the acid. As a result, there is a net positive charge on the PEDOT chain that will strongly attract the negative charge left on the acid. Since this happens at many points along the polymer, PEDOT and PSS become closely intertwined. An unpaired π- electron remains on the PEDOT chain that is highly mobile along the conjugated backbone and leads to a high conductivity. Other dopants reported in literature include Tosylate and inorganic materials such as Phosphomolybdate.
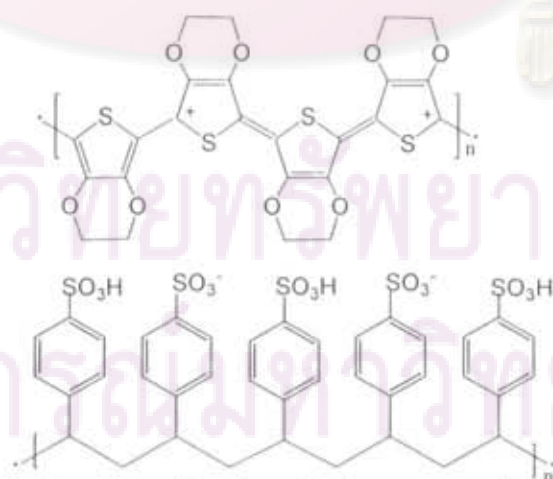
Figure 2.5 Poly(3,4-ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT/PSS)

However, PEDOT:PSS also suffers from low conductivity of less than 1 S/cm, which is lower than that of some good conducting polymers by one to two orders of magnitude. Also, it is typically laid down in an acidic water-based solution whose corrosive properties cause other problems [31].

In this study, we have purposed the newly way to overcome the mechanical properties of PEDOT is to blend it with another insulating polymer. Composites have been formed by directly dispersing a soluble precursor polymer, DBEDOT, into an insulating polymer matrix which can form solid film by casting then transformed into PEDOT/polymer by thermal treatment or solid state polymerization. Polymer matrix, polystyrene and polybutadiene are chosen as matrices because they are readily available, and are easy to cast into desired forms maintaining the mechanical integrity of the matrix. Most of all, they can be easily mixed with DBEDOT in organic solvent. The following is work related to the preparation of conducting polymer composite based on polystyrene.

In 2002, Costa et al. [32] produced new conductive composite material, polystyrene/polypyrrole particles, and investigated percolating system in this composite by the electrical and dielectrical properties. The electrical conductivity of PS/PPy particles was observed when used percolation threshold at a volume concentration about 12% of PPy. At the same concentration, true dielectric response of polymer could be found at low frequency. Analysis of the data indicates that the onset of the percolating path can be seen in the conductivity data as well as in the true dielectric response data.

In 1998, Roichman and coworkers [33] developed PS/PANI-DBSA composite by synthesized PANI-H_2SO_4 powder then de-dope and re-dope with functionalized protonic acid and dodecyl benzene sulfonic acid (DBSA), respectively, in order to induce solubility in xylene and compatibility with PS. The best blend integration was observed at high quality of the PANI-DBSA dispersion and the highest amount of excess DBSA. Least dense of PANI resulted in a higher conductivity. Therefore, to synthesize PANI-DBSA, it would be advantageous to prevent the formation of a dense complex structure by using condition, namely, high oxidant addition rate, an excess of oxidant, relatively high polymerization temperature and short synthesis duration.

2.8 Effect of doping [34]

The doping is an addition of an agent into the polymer and is expected to improve the conductivity of the polymer. Reversible "doping" of conducting polymers, with associated control of the electrical conductivity over the full range from insulator to metal, can be accomplished either by chemical doping or by electrical doping. Concurrent with the doping, the electrochemical potential is moved either by a redox reaction or an acid base reaction into a region of energy where there is a high density of electronic states; charge neutrality is maintained by the introduction of counter-ions. Metallic polymers are, therefore, salts. Consequently, doped conjugated polymers are good conductors for two reasons:

1. Doping introduces carriers into the electronic structure. Since every repeating unit is a potential redox site, conjugated polymers can be doped n-type (reduce) or p-type (oxidized) to a relatively high density of charge carriers.

   p-type

   $(\pi\text{-polymer})_n + 3/2 \, ny \, (I_2) \longrightarrow [(\pi\text{-polymer})^{+y} \, (I_3^-)y]_n$

   n-type

   $(\pi\text{-polymer})_n + [Na^+(naphthalide)^\bullet]_y \longrightarrow [(Na^+)_y((\pi\text{-polymer})^{-y}]_n$
   $+ (naphthalene)^\bullet$
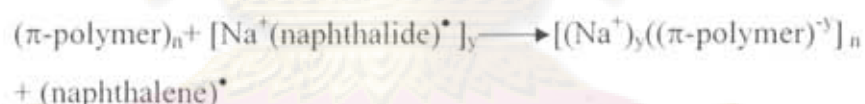
   When the doping level is sufficiently high, the electronic structure evolves toward that of a metal.

2. The attraction of an electron in one unit to the nuclei in the neighboring units leads to carrier delocalization along the polymer chain and to charge carrier mobility, which is extended into three dimensions through interchain electron transfer.

Disorder, however, limits the carrier mobility and in the metallic state, limits the electrical conductivity. Indeed, research directed towards conjugated polymers with improved structural order and hence higher mobility is a focus of current activity in the field. Charge injection onto conjugated, semi-conducting macromolecular chains, or "doping", leads to the wide variety of interesting and important phenomena which define the field. The doping can be accomplished in a number of ways; chemically or electrochemically dope.

2.9 Theoretical Aspects of Charge Transfer [35]

Electron or charge transfer in conjugated polymers determines whether the polymer is conductive or insulating. How the charge is transported determines the performance of the devices fabricated from the polymer. Oxidation or reduction of a conjugated polymer leads to the introduction of positive or negative charges into the polymer chain, giving rise to an increased conductivity. The term *doping* can be misleading as what occurs is best viewed as a redox process. The insulating neutral polymer is converted into a salt consisting of a polycation (or polyanion) and counterions, which are the reduced forms of the oxidizing agent (or the oxidized forms of the reducing agent). From a chemical point of view, the "doped" polymers are actually new compounds – carbocations or carbanions of the original compound.

Using solid-state physics language, however, oxidation corresponds to *p*-type doping and reduction to *n*-type doping. *P*-doping occurs with a positive applied voltage, under which conditions the polymer chain is oxidized. Electrons move from the chain to the electrode giving rise to polarons (partially delocalized radical cations; see Figure 2.6) and bipolarons (polaron with a second electron removed) in the chain. Polarons and bipolarons may be viewed as electron holes, which can move along the chain to produce an electrical current. Anions become incorporated into the polymer matrix to compensate the positively charged polymer backbone. *N*-doping occurs when a negative applied potential is applied to the polymer, under which conditions negative charges are created in the chain as electrons move from the electrode to the polymer. Consequently, cations from the solution become incorporated into the polymer structure to compensate for the negatively charged polymer backbone. Electrons serve as charge carriers in this case.

ศูนย์วิทยทรัพยากร

จุฬาลงกรณ์มหาวิทยาลัย
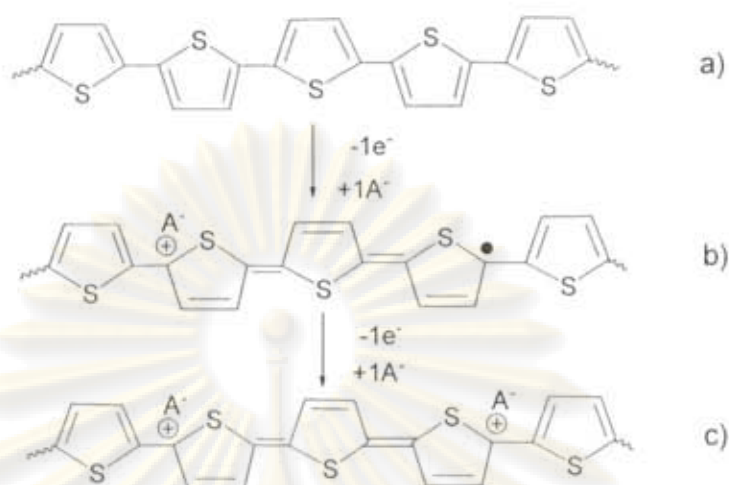
Figure 2.6 Depictions of a) neutral (undoped chain), b) polaron, and c) bipolaron

Overall conductivity in a polymer is determined by both its intramolecular and intermolecular conductivities. Chain length plays the most important role in intramolecular conductivity. The longer the conjugated π-system, the greater the conductivity will be. Intermolecular conductivity returns us to the electron/hopping discussion which first arose when making a distinction between redox and conjugated polymers. Intermolecular conductivity is due to the same phenomenon as one finds in redox polymers (hopping). Because conjugated polymers are normally constructed of layered planar conjugated molecules, the attractive interactions between π-electron clouds enhance electron hopping between layers. This has been labeled π-dimerization.

The *doping level* is a measure of to what degree the polymer is oxidized or reduced. The electrically conducting form is obtained when the polymer is doped. For example, the polymer polyacetylene exhibits a conductivity of $10^{-9}\ \Omega^{-1}\mathrm{cm}^{-1}$ in its undoped form while achieving conductivities of $10^{3}\ \Omega^{-1}\mathrm{cm}^{-1}$ and higher in the doped form. The electrical conductivity is strongly dependent upon the polymer's doping level. Polymers may be doped either chemically or electrochemically. The doping level is normally higher for electrochemically doped polymers than for chemically doped polymers. With chemical doping, electron acceptors (*p*-doping) or electron donors (*n*-doping) need to be added to the solution in order to make the doping reaction take place. Some examples are oxygen, I_2 and arsenic pentafluoride. A

polymer can be doped electrochemically by simply applying an appropriate potential across the film in the presence of counterions.

In Figure 2.7, UV-VIS spectroelectrochemical curves recorded for different electrode potential are shown for regioregular poly(3,4-ethylenedioxythiophene) prepared using the method of Kvarnstrom and coworkers [36]. Cyclic voltammograms of poly(3,4-ethylenedioxythiophene) unambiguously indicate that oxidative doping of this polymer is a two-step phenomenon since two overlapping redox couples are clearly seen. This two-step oxidation is also manifested in UV-vis spectroelectrochemical studies. The spectra recorded for increasing doping levels show gradual bleaching of the π-π^* transition with simultaneous growth of two peaks at 580 nm and 700 nm, usually ascribed to the formation of bipolaron sub-gap states.
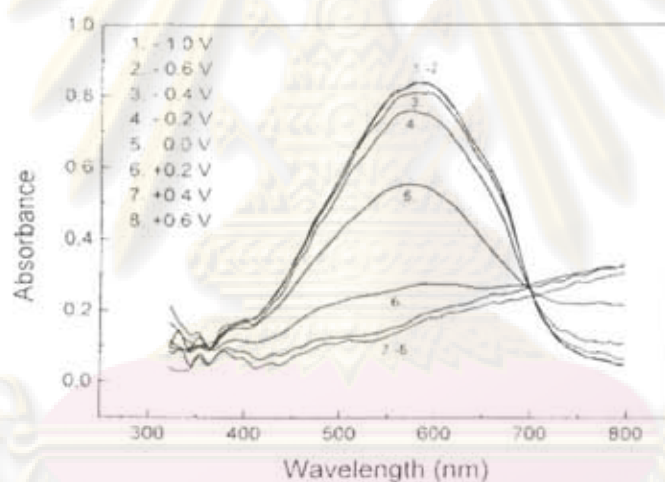
Figure 2.7 UV-VIS absorption spectra of PEDOT film on ITO during the oxidation process in 0.1 M TBAPF$_6$-acetonitrile. The potential range is -1.0-+0.6 V, scan rate 100 mV/s.

2.10 Effective conjugation length (ECL)

Ideally, a conducting polymer would have its π electrons in the unsaturated bonds conjugated throughout the whole chain. This requirement usually does not hold due to the following:

i)   Formation of defects in polymer

ii)   Twisting of plans structures out of conjugation in the polymer.

Examples of the two reasons above are shown in Figure 2.8. Formation of a defect in polyacetylene as a saturated sp^3-hybridized methylene caused the disruptive effect in the flow of electrons on polymer chain. In another case, the steric incumbent between adjacent R groups on HH thienyl units in irregular poly(3-alkylthiophene) brought about the twisting of the thienyl ring planes out of coplanarity, causing an increase in the energy needed to allow the flow of electrons through the polymer chain, hence making the polymer chain less conductive.

Polyacetylene   Poly(3-alkylthiophene)

Figure 2.8 A defect in polyacetylene and steric-induced structure twisting in poly(3-alkylthiphene)

Another possible reason would be the twisting of polymer chain, which occurs randomly at the single bonds and divided the polymer into separated sections with their own co planarity (Figure 2.9). Twisting of polymer chain would also cause the reduction of conjugation in the polymer.
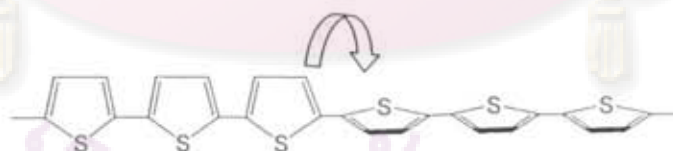
Figure 2.9 Twisting of polythiophene

2.11 Conductivity measurement by four point probe technique [37]

The four point probe, as depicted schematically in Figure 2.10, contains four thin collinear tungsten wires which are made to contact the sample under test. Current I is made to flow between the outer probes, and voltage V is measured between the two inner probes, ideally without drawing any current. If the sample is of semi-

infinite volume and if the interprobe spacings are $s_1 = s_2 = s_3 = s$, then it can be shown that the resistivity of the semi-infinite volume is given by

$$\rho_0 = 2\pi s \,(V/I) \tag{2.1}$$
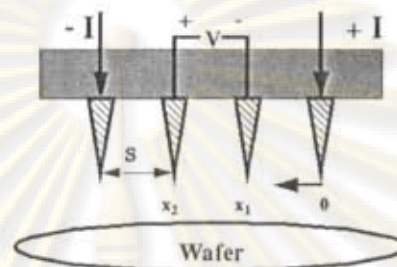
Figure 2.10 Schematic representation of 4-point probe configuration

The subscript 0 in the preceding equation indicates the measured value of the resistivity and is equal to the actual value, ρ, only if the sample is of semi-infinite volume. Practical samples, of course, are of finite size. Hence, in general, ρ *is not equal to* ρ_0. Correction factors for six different boundary configurations have been derived by Valdes[1]. These show that in general if l, the distance from any probe to the nearest boundary, is at least 5s, no correction is required. For the cases when the sample thickness is $<= 5s$, we can compute the true resistivity from

$$\rho_0 = 2a\pi s \,(V/I) = a\rho_0 \tag{2.2}$$

where a is the thickness correction factor which is plotted on page GT-2. From an examination of the plot, we see that for values of $t/s >= 5$ the corresponding value of a is unity. Thus, for samples whose thickness is at least 5 times the probe spacing, no correction factor is needed. Typical probe spacings are 25-60 mils and the wafers used in most cases are only 10-20 mils thick, so unfortunately we cannot ignore the correction factor. Looking again at the plot, however, we see that the curve is a straight line for values of $t/s <= 0.5$. Since it is a log-log plot the equation for the line must be of the form

$$a = K \, (t/s)^m \qquad (2.3)$$

where K is the value of a at $(t/s) = 1$, and m is the slope. Inspection of the plot shows that in this case $m = 1$. K is determined to be 0.72 by extrapolating the linear region up to the value at $(t/s) - 1$. (The exact value can be shown to be $1/(2\ln2)$.) Hence for slices equal to or less than one half the probe spacing

$$a = 0.72 \, (t/s) \qquad (2.4)$$

When substituted into the basic equation we get:

$$\rho_0 = 2a\pi s \, (V/I) = 4.53 \, (V/I) \text{ for } t/s <= 0.5 \qquad (2.5)$$

All samples used in the lab satisfy the one-half relationship so the above formula can be used to determine ρ. Resistivity measurements will be performed on the starting material for each experiment. The value of ρ obtained will be referred to as the bulk resistivity, and the units are Ω-cm. If both sides of Equation (2.5) are divided by t we get

$$R_s = \rho/t = 4.53 \, (V/I) \quad \text{for } t/s <= 0.5 \qquad (2.6)$$

which we refer to as sheet resistance. When the thickness t is very small, as would be the case for a diffused layer, this is the preferred measurement quantity. Note that Rs is independent of any geometrical dimension and is therefore a function of the material alone. The significance of the sheet resistance can be more easily seen if we refer to the end-to-end resistance of a rectangular sample.

Therefore, R_s may be interpreted as the resistance of a square sample, and for this reason the units of R_s are taken to be Ohms per square or Ω/sq. Dimensionally, this is the same as Ω, but this notation serves as a convenient reminder of the geometrical significance of sheet resistance.

CHAPTER III

EXPERIMENTAL

3.1 Materials

All reagents and materials were analytical grade and used without further purification

1.	Acetone	: Merck
2.	Acetic acid glacial	: Merck
3.	Chloroform	: Fluka
4.	Dichloromethane	: Fluka
5.	2,3-dihydrothieno[3,4-b]-1,4-dioxin	: Aldrich
6.	1,4-dioxane	: Merck
7.	Ethanol	: Merck
8.	Hexane	: Fluka
9.	N-bromosuccinimide	: Merck
10.	n-butanol	: Lab-scan
11.	Sodium hydrogen carbonate	: Lab-scan
12.	Toluene	: Merck
13.	Polystyrene (Mw= 3×10^5)	: Dow Chemical
14.	Polybutadiene (Mw= 4×10^4)	: Dow Chemical

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance (NMR) Spectrometer

All spectra were collected by NMR model Varian Mercury plus 400. Sample was dissolved in $CDCl_3$ and operated at 399.84 MHz for ^{1}H and 100.54 MHz for ^{13}C nuclei.

3.2.2 UV-visible Spectrophotometer

UV-visible spectrophotometer model UV-2550 SHIMADZU was used to investigate surface absorption spectrum of PEDOT/polymer composite film and extracted PEDOT powder.

3.2.3 Mass Spectrometry (MS)

Molecular weight of DBEDOT was analyzed by Mass spectrometry (Micromass Quattro micro API) using chloroform as the solvent. The instrument was operated by using CP-sil 8 column (30m × 0.25mm), injection volumn = 1 μL., split ratio = 200, column flow = 2 mL min^{-1} and column oven = 250 °C at 10 °C min^{-1}.

3.2.4 Fourier-Transform Infrared Spectrophotometer (FT-IR)

IR spectra of a standard PEDOT and PEDOT extracted from the PEDOT/polymer composite film were analyzed by FT-IR model Nicolet Impact 410.

3.2.5 Four-Point Probe Conductometer

The conductivity values of PEDOT/polymer composite films were determined by a four-point probe conductometer model KEITHLEY Semiconductor Characterization System 4200. The reported conductivity is an average value measured from four different areas when 100 measurements for each area were performed.

3.2.6 X-ray Diffractometer (XRD)

Diffractograms of standard PEDOT and extracted from the PEDOT/polymer composite film by XRD model Rigaku D5000 using a scan range of 5.00-50.00 degree, a scan speed of 5.00 deg min^{-1} and a sample width of 0.020 degree.

3.2.7 Thermogravimetric Analysis (TGA)

The combustion stage and melting point were investigated by a Mettler Toledo thermo gravimetric analyser model TGA/SDTA 851. PEDOT/polymer composite film was analyzed by heating from 30 °C to 600 °C using 20 °C min^{-1} heating rate under ambient atmosphere.

3.2.8 Optical Microscopy (OM)

The surface morphology of PEDOT/polymer composite film was visualized at a magnification of ×40 by reflection mode of Optical Microscopy model National DC4-156-S with sunlight lamp.

3.3 Methods

3.3.1 Synthesis of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)
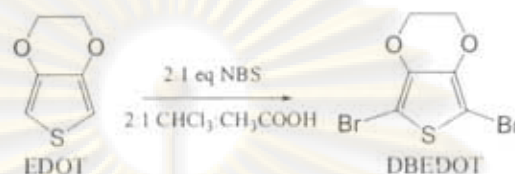
Scheme 3.1 Bromination of EDOT

To a stirred solution of 3,4-ethylenedioxythiophene (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 °C under a nitrogen atmosphere for 8 h. Then the mixture was quenched and washed with 1.5% sodium hydrogen carbonate solution (100 mL × 3 times). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined chloroform extract was dried with anhydrous magnesium sulfate. During the solvent removal by rotary evaporator, 3 mL of ethanol were 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 PEDOT/polymer composite film

A toluene solution of 0.075 g of DBEDOT and 0.025 g of polystyrene or polybutadiene was sonicated in an ultrasonic bath for 15 min. The 0.5 mL solution was drop-cast on a glass slide to form a thin film of 2.5 inches in diameter. The solvent was removed under reduced pressure for 30 min. The glass substrate covered with a thin film of polymer containing DBEDOT was put in a closed vial and then heated in an oven (at 50 or 70 °C) for a desired period of time. The resulting PEDOT/polymer composite film was then characterized by OM, TGA, UV-Visible spectroscopy. Conductivity of the PEDOT/polymer composite film was determined by a four-point probe conductometer. The average percentage yield of the PEDOT

formed in the PEDOT/polymer composite film was calculated from the weight of the PEDOT obtained after the polymer matrix was removed by soxhlet extraction with toluene overnight (×3 times).
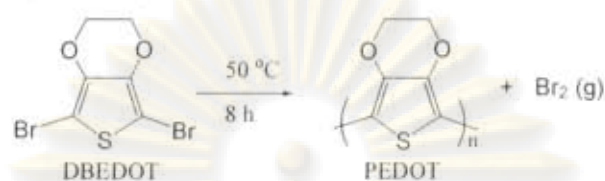
Scheme 3.2 Solid state polymerization of DBEDOT

3.3.3 Doping with Iodine

After being kept in a closed vial for 1 month in a dessicator, a PEDOT/polymer composite film was placed in an iodine chamber for 2 h. The conductivity of the composite film was then measured by four-point probe conductometer.

CHAPTER IV

RESULTS AND DISCUSSION

The aim of this work is to form polymer composites containing 3,4-polyethylenedioxythiophene (PEDOT) by solid state polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in the matrix of commercially available polymer i.e. polystyrene (PS) or polybutadiene (PB). 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 the preparation of PEDOT/polymer composite films. Several parameters that can affect physical properties and conductivity of the composite films were investigated including polymer matrix (PS vs PB), DBEDOT:polymer weight ratio, DBEDOT concentration, time and temperature used in the step of solid state polymerization (SSP). The last part investigates the effect of storage on the conductivity of the composite film and the potential of re-doping by iodine.

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. DBEDOT can be synthesized by bromination of EDOT as shown in Scheme 4.1.
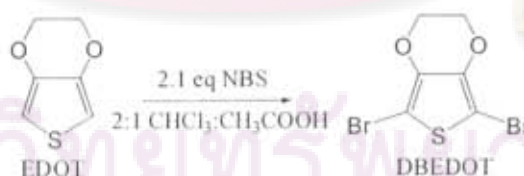
Scheme 4.1 Bromination of EDOT

The mechanism of bromination on EDOT was purposed into 2 possible path ways
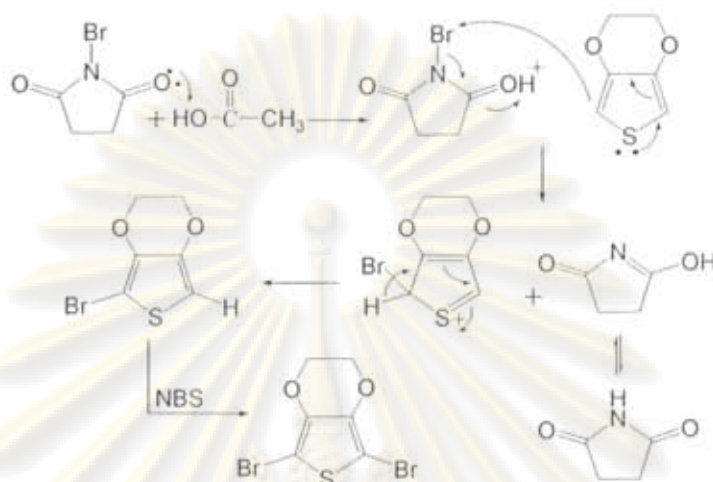
Scheme 4.2 Bromination mechanism through electrophilic aromatic substitution
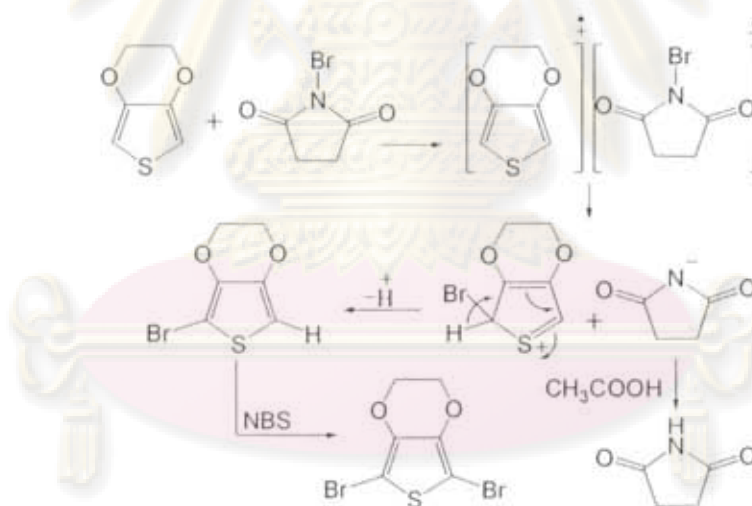
Scheme 4.3 Bromination mechanism through radical-based single electron transfer followed by aromatic substitution.

Unlike the method described by Meng and coworkers [31], 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 with 1.5% NaHCO$_3$ solution (100 mL × 3 times). The crystallization of

DBEDOT product was then induced by an 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 a rotary evaporator. White needle-like crystals with 80% yield were 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.

^{1}H-NMR spectra of the synthesized DBEDOT and EDOT were 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 3 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 and two carbons at –C-S position, respectively.
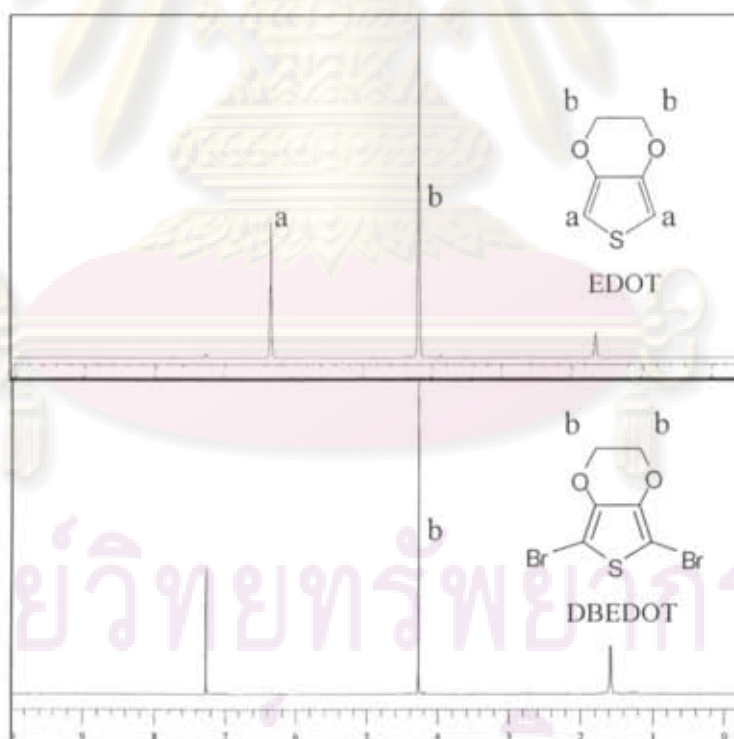
Figure 4.1 ^{1}H-NMR spectra of EDOT and DBEDOT
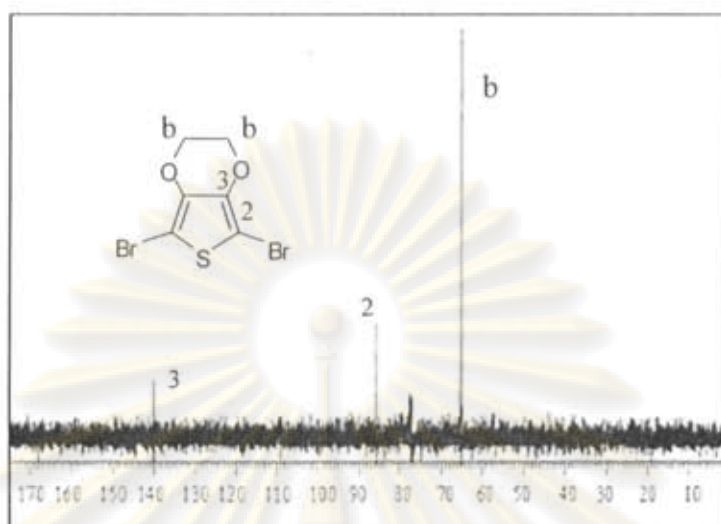
Figure 4.2 ^{13}C-NMR spectrum of DBEDOT

MS spectrum of the synthesized DBEDOT is shown 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.
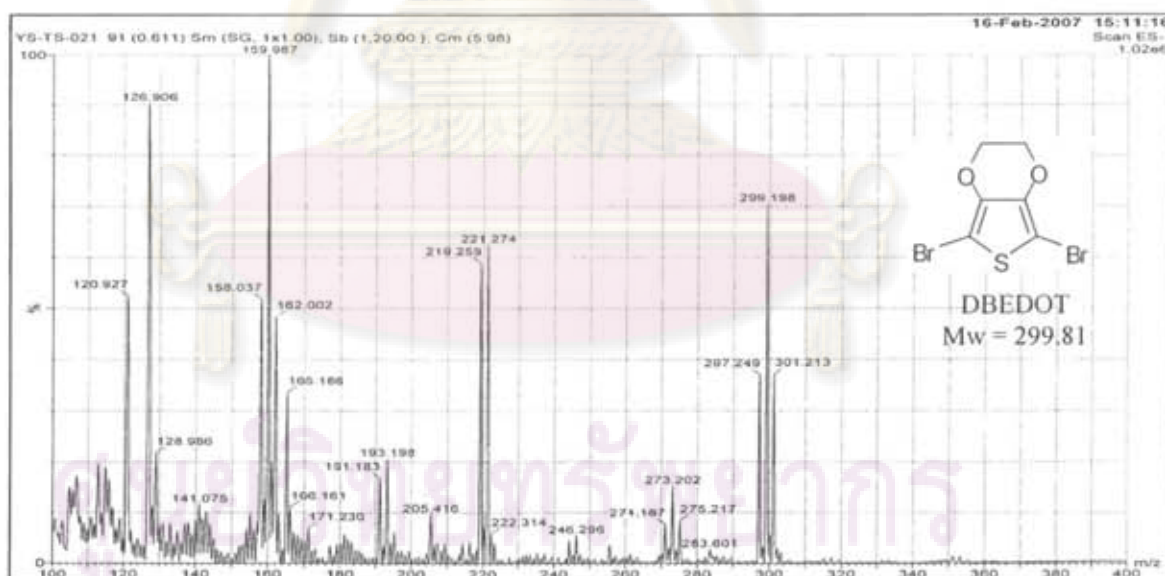
Figure 4.3 MS spectrum of DBEDOT

4.2 Solubility tests of DBEDOT

It was found that DBEDOT was highly soluble in all common organic solvents tested. The result is shown in Table 4.1 and its solution was stable when heated above solvent boiling point. DBEDOT melting temperature is 105-106°C.

Table 4.1 Solubility of DBEDOT

Solvent	Solubility test
Ethanol	Soluble
1,4-Dioxane	Soluble
Chloroform	Soluble
Butanol	Soluble (slow)
Dichloromethane	Soluble
Toluene	Soluble
Hexane	Soluble (with slightly heat)

4.3 Preparation of PEDOT/polymer composite film

The preparation of polymer composite film containing 3,4-polyethylenedioxy thiophene (PEDOT) was performed by solid state polymerization (SSP) of DBEDOT (Scheme 4.4) in the matrix of commercially available polymers which are polystyrene (PS) or polybutadiene (PB). PS was selected as a representative of semi-crystalline polymer having a glass transition temperature (T_g) above room temperature which is 100 °C. PB was chosen as an amorphous polymer having a T_g well below room temperature which is -100 °C.
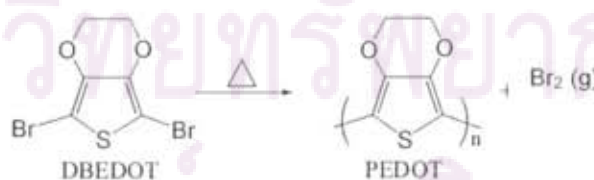
Scheme 4.4 Solid state polymerization of DBEDOT

The mechanism of SSP of DBEDOT has been proposed by Meng and *et al.* [30]. 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 will go through the propagation step and eventually forms PEDOT. The presence of bromine in the reaction, in fact, facilitates polymerization in the initiation step.
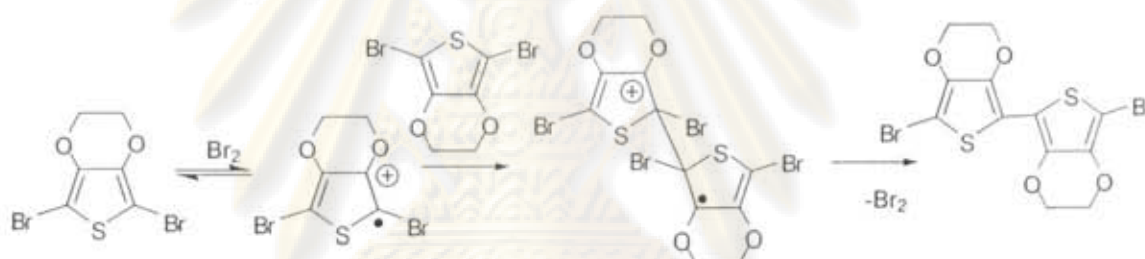
Scheme 4.5 Mechanism of solid state polymerization of DBEDOT

In order to prove whether the SSP of DBEDOT proceeds and PEDOT can be formed in the matrix of other polymer, we first conducted an experiment by using PS as a matrix and toluene as a solvent for dissolving PS. Toluene was chosen for several important reasons: (1) it can readily dissolve both DBEDOT and the polymer matrix (PS and PB), (2) its boiling point is not too high so the removal after the film formation is not too difficult, and (3) it is an aprotic, non-polar solvent so there should be no concern about the interaction between DBEDOT and the solvent that might interfere with the polymerization process. The SSP was performed at 50 °C for 7 h using the DBEDOT/PS weight ratio of 3:1 and the concentration of DBEDOT of 0.225 mg m/L. The physical appearance of the resulting PEDOT/PS composite film was characterized. The PEDOT extracted from PEDOT/PS composite film was also characterized by UV-Visible spectroscopy and FT-IR spectroscopy.

As illustrated in Figure 4.4, upon heating, the color of the composite film cast from the mixture of PS and DBEDOT on a glass substrate gradually changed from colorless to dark green and completely turned dark blue within 7 h. The blue color can be used as an indication of the transformation of DBEDOT to PEDOT. If the SSP was performed in a closed vial, brown gas and liquid of bromine can also be observed.
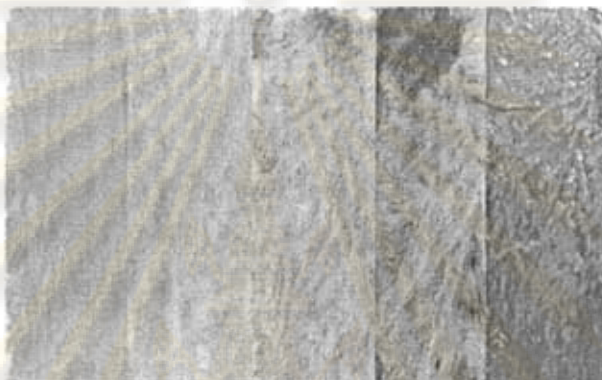
Figure 4.4 Physical appearance of the composite film cast from the mixture of PS and DBEDOT (DBEDOT/PS weight ratio = 3:1) upon heating at 50 °C for up to 7 h.

FT-IR spectra of PEDOT prepared by SSP of DBEDOT in the absence of the polymer matrix, which will be called "controlled PEDOT" (a) and PEDOT extracted from PEDOT/polymer composite film which will be called "extracted PEDOT" (b) are displayed in Figure 4.5. The fact that the FT-IR spectrum of the extracted PEDOT exhibits the same fingerprints as those of the controlled PEDOT confirms the success of SSP in the PS matrix. The peak assignments of PEDOT based on the literatures are given as follows [38]. The peaks at 1510.9 and 1410.0 cm^{-1} originate from the asymmetric stretching of C=C and symmetric stretching of C=C, respectively. The peak at 1355.7 cm^{-1} is assigned to C–C inter-ring stretching. The peak from C–C antisymmetric stretching can be seen at 978.6 cm^{-1}. The peak at 901.1 cm^{-1} corresponds to the ethylenedioxy ring deformation. The peaks at 1079.3 and 746.1 cm^{-1} are assigned to the =C–O stretching and C–S–C bending, respectively.
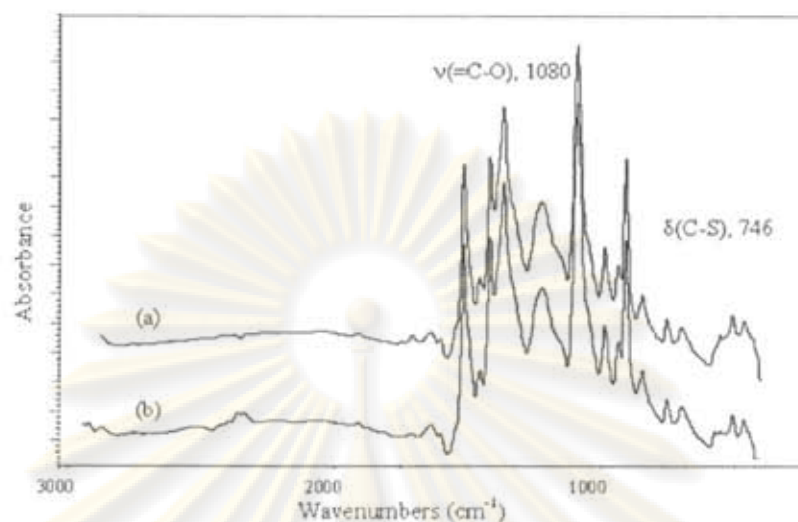
Figure 4.5 FT-IR spectra of (a) controlled PEDOT and (b) extracted PEDOT.

To confirm the coexistence of PEDOT and PS in the composite films, the characterization by TGA was performed. Figure 4.6 displays TGA chromatograms of PEDOT/PS composite films (2 DBEDOT/PS weight ratios: 1:1 and 3:1), PS and controlled PEDOT. There are three distinct stages of weight loss in the PS/PEDOT composite films. The weight loss at ~120 $^{\circ}$C corresponds to the removal of bromine gas while those at ~200 °C and ~ 400 °C can be assigned to the loss of fragments of PEDOT and PS, respectively. The magnitude of weight loss at ~200 °C is proportional to the composition of PEDOT in the composite, meaning the greater the weight loss, the higher the amount of PEDOT in the composite film.
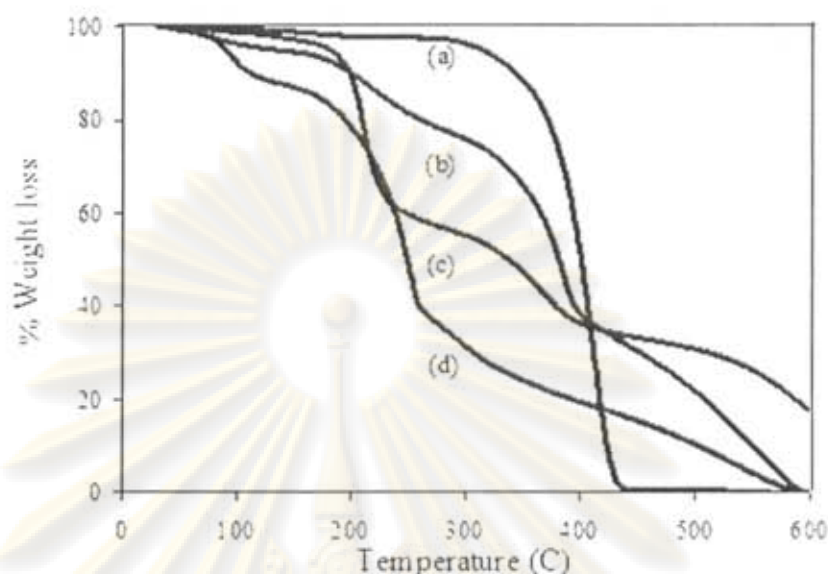
Figure 4.6 TGA thermograms of (a) PS, PS/PEDOT composite film prepared using DBEDOT/PS weight ratio of (b) 1:1, (c) 3:1, and (d) controlled PEDOT

UV–Vis spectra recorded at solid state of PEDOT/PS composite film, the extracted PEDOT, and the controlled PEDOT are shown in Figure 4.7. The extracted PEDOT and the PEDOT/PS composite film exhibit one absorption band with a maximum at ~350 nm, corresponding to the π-π^* transition of the conjugated main chain, at neutral state (undoped), and the other one which is weaker and broader at 550 nm, corresponding to the π-π^* transition of conjugate main chain with inter-chain interaction and π-stacking. The latter band usually appears during the doping process of conjugated polymers and is ascribed to polaron type carriers [39]. The controlled PEDOT (b), on the other hand, shows only the broad absorption band at 580 nm indicating that the PEDOT is only in the doped state. The red shift of this band (from 550 nm) implies that there is more order and π-stacking of PEDOT molecules when they were polymerized in solid state in the absence of the polymer matrix. In the presence of polymer matrix, SSP was evidently less efficient resulting in the PEDOT with less degree of order. The appearance of the absorption band due to the neutral state suggests that a part of the PEDOT in the extracted PEDOT and the PEDOT/PS composite film was undoped. This can be explained as a result of bromine (acts as dopants) loss during extraction process in the case of the extracted PEDOT. The

toluene solution which became slightly yellow implies that there was bromine extracted out with the polymer. The same loss was also observed during SSP of DBEDOT in the matrix of PS, as described earlier.
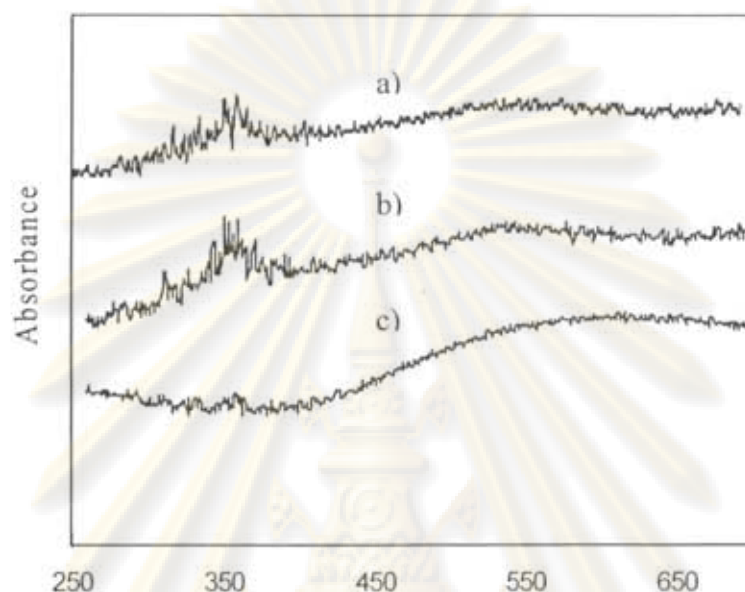
Figure 4.7 UV-Visible spectra of (a) extracted PEDOT, (b) PEDOT/PS composite film, and (c) controlled PEDOT

X-ray diffraction patterns shown in Figure 4.8 reveal the crystalline structure of the extracted PEDOT from PEDOT/PS and PEDOT/PB composite films in comparison with the controlled PEDOT. Similar to the XRD pattern of PEDOT previously reported by others [40], the diffraction peaks of the PEDOT appearing at scattering angle $2\theta \sim 6.1°$, $12.1°$ and $25.8°$ can be assigned to the (100), (200), and (020) of the orthorhombic crystal structure. The fact that the peaks of the composite films are less intense and broader than those of the controlled PEDOT suggests that the structure of controlled PEDOT is more ordered and its crystallinity is higher in comparison with the extracted PEDOT. This implication is in accordance with the UV-Vis data.
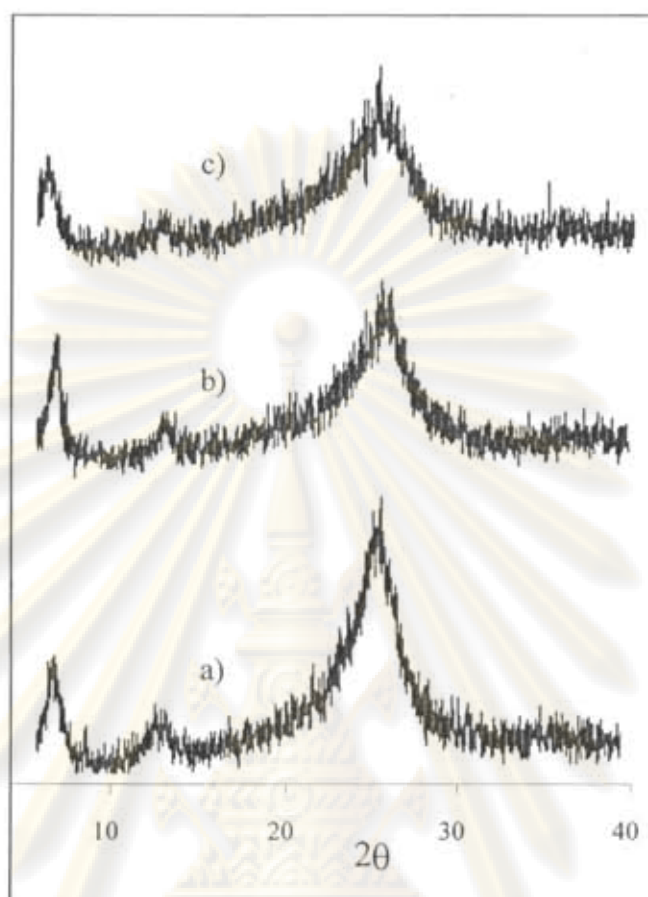
Figure 4.8 XRD spectra of (a) controlled PEDOT, extracted PEDOT from (b) PEDOT/PS composite film, and (c) PEDOT/PB composite film.

4.4 Parameters affecting percentage yield and conductivity of the PEDOT/ polymer composite films

This section describes the effects of some parameters on physical properties and conductivities of the composite films.

4.4.1 DBEDOT/polymer weight ratio

By fixing the weight of polymer matrix (PS or PB) at 0.025 g and toluene of 0.3 ml (DBEDOT concentration = 0.225 g m/L), DBEDOT/polymer weight ratio was varied. Figure 4.10 displays the percentage yield of PEDOT extracted from the PEDOT/polymer composite film as a function of DBEDOT/polymer weight ratio. The yield higher than 80% can be obtained in both PEDOT/PS and PEDOT/PB composite films when the ratio of 3:1 and 4:1 were used. In the case of low DBEDOT/polymer weight ratio, especially 1:1 of which DBEDOT quantity is the lowest, the DBEDOT

crystals were so far apart that they cannot lead to efficient SSP. The extremely low %yield (~3%) of PEDOT was obtained using the ratio of 1:1. Heterogenous distribution of PEDOT throughout the composite films can be easily observed. The composite films were not entirely dark blue. Some area was translucent. Although the ratio of 4:1 gave the high %yield of PEDOT, the physical and mechanical integrity of the composite films are inferior to those obtained from the 3:1 ratio. Extensive agglomeration and excess quantity of dark blue PEDOT were observed on the surface of the composite films. The composite film was also brittle, especially in the case of PEDOT/PS composite film.

Figure 4.9 Percentage yield of extracted PEDOT from PEDOT/PS and PEDOT/PB composite films as a function of DBEDOT/polymer weight ratio. The SSP was conducted at 50 °C for 8 h.

The conductivity data shown in Figure 4.10 evidently are in good agreement with the physical properties and %yield of the composite films. The 3:1 PEDOT/PS composite film exhibited the highest conductivity of 12 S/cm. Apparently, the composite films with low %yield and inhomogeneous distribution of PEDOT in the matrix were low in conductivity. Unlikely, the conductivity of the PEDOT/PB film seems to increase with the DBEDOT/PB weight ratio. The highest conductivity of ~ 3 S/cm was detected on the 4:1 PEDOT/PB composite film. Despite their similar %yield of PEDOT in the 3:1 composite film (~80%), the PEDOT/PS composite film possesses significantly higher conductivity than that of the PEDOT/PB composite

film. It is suspected that the physical properties of the polymer matrix (T_g, surface morphology) may play a role in the structure of PEDOT and conductivity. This issue will later be addressed. Due to the fact that the 3:1 DBEDOT/polymer weight ratio gives PEDOT/polymer composite films with reasonably good physical and mechanical properties as well as conductivity, it was chosen as the optimal ratio for further studies.
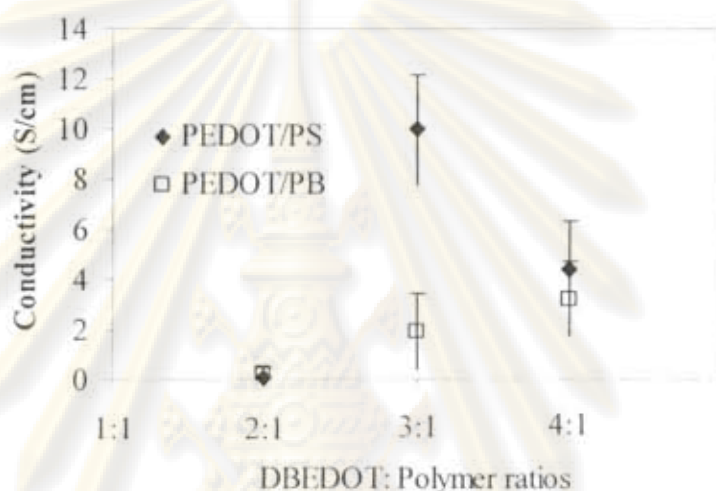
Figure 4.10 Conductivity of PEDOT/PS and PEDOT/PB composite films as a function of DBEDOT/polymer weight ratio. The SSP was conducted at 50 °C for 8 h.

4.4.2 DBEDOT concentration

Figure 4.11 illustrates the percentage yield of PEDOT extracted from the PEDOT/polymer composite film as a function of DBEDOT concentration. By using the DBEDOT/polymer weight ratio of 3:1, the concentration of DBEDOT was changed by varying the amount of solvent added. A slight increase of %yield of PEDOT (4-5%) was obtained upon the increase of concentration from 0.075 g/mL to 0.225 g/mL (3 times higher). It should be noted that the concentration cannot be raised any further because the DBEDOT and polymer mixture became insoluble above the concentration of 0.225 g/mL. The explanation that was used to describe the effect of the DBEDOT:polymer weight ratio on the SSP efficiency can also be applied here. The greater the quantity of DBEDOT in the mixture, the closer the DBEDOT molecules. This gives DBEDOT more chance to polymerize. The suitable distribution

and arrangement of DBEDOT in the polymer matrix is very critical to the success of SSP because DBEDOT is not allowed to move in the solid state.

The conductivity of the PEDOT/PS composite film (shown in Figure 4.12) increases as a function of DBEDOT concentration. The non-linear increase can be ascribed to the inhomogeneous distribution of PEDOT in PS matrix at low DBEDOT concentration. It seems that a good conductivity can be obtained only when a suitable arrangement and distribution of DBEDOT, which can be varied as a function of DBEDOT/PS weight ratio and DBEDOT concentration, was employed. The same effect is, however, not so strong in the case of PEDOT/PB composite. The conductivity cannot be elevated anymore even though the DBEDOT concentration was raised from 0.150 to 0.225 g/mL. Once again, this should have something to do with the physical properties of the matrix.
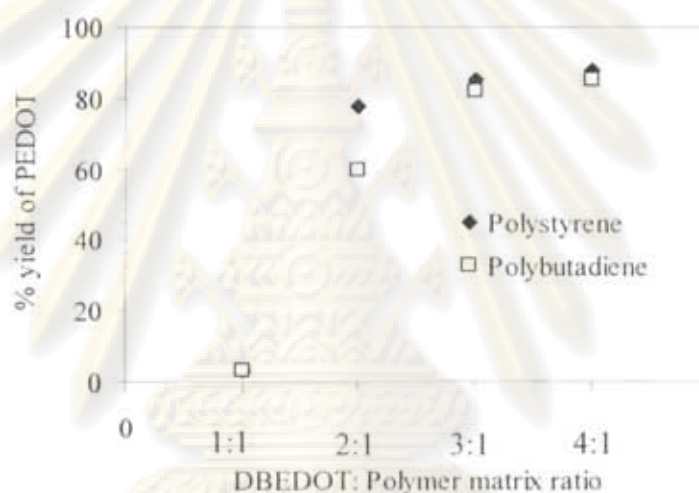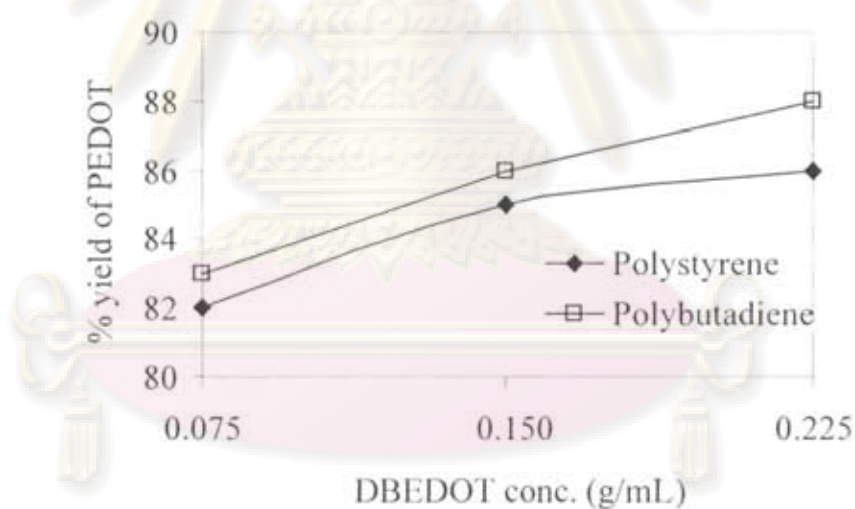

Figure 4.11 Percentage yield of extracted PEDOT from 3:1 PEDOT/PS and PEDOT/PB composite films as a function of DBEDOT concentration. The SSP was conducted at 50 °C for 8 h.
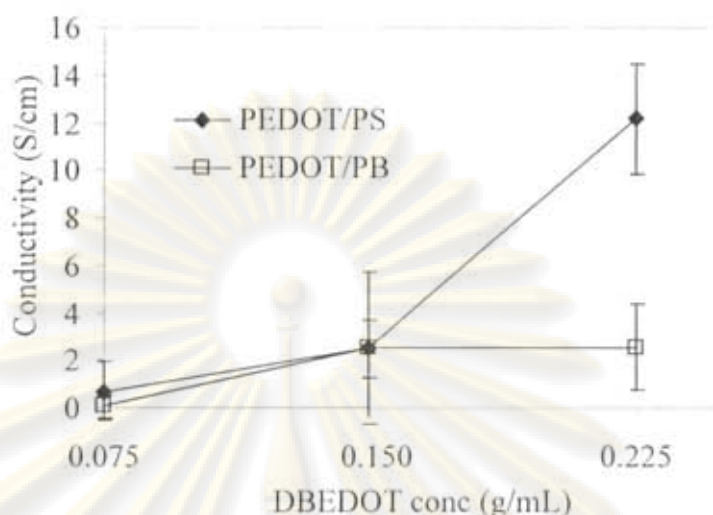
Figure 4.12 Conductivity of PEDOT/PS and PEDOT/PB composite film as a function of DBEDOT concentration, using 3:1 DBEDOT/polymer weight ratio. The SSP was conducted at 50 °C for 8 h.

4.4.3 Effect of temperature and reaction time used for SSP

Originally, a temperature range of 50-100 °C was chosen to be used for SSP mainly because it is below melting temperature of PS (T_m of PS = 350 °C, T_m of PB = 50 °C) and DBEDOT (T_m = 105 °C) However, it was found that heating above 80 °C for more than 1 h made the composite film turned dark brown and black. This outcome suggests that DBEDOT was decomposed instead of undergoing SSP. For this reason, the highest temperature used for the following investigation was 70°C. It should be noted that all SSP experiments described previously were performed at 50°C.

It was found that at least 6 h of heat treatment is required for the SSP so that enough quantity of PEDOT is formed and the conductivity of the composite film becomes measurable. It is also obvious that it is this same 6 h that the composite film began to turn dark blue. The conductivity data shown in Figure 4.13 suggest that the highest conductivity was achieved after 8 h of reaction. Evidently, 50°C seems to give the composite films with higher conductivity than 70°C both in the case of PEDOT/PS and PEDOT/PB composites. We proposed 2 possible explanations for this outcome: (1) the higher temperature allows the polymer matrix to vibrate much more

especially in the case of PS whose T_g is about 100^oC. The higher the temperature, the closer to the T_g. For this reason, the PEDOT conformation may slightly be changed. This causes adverse effect on the packing of the PEDOT chain as well as the conjugation length. Since T_g of PB is below room temperature ($T_g \sim$ -20 °C), the PB can move much more freely than the PS, the ordered packing of the PEDOT in the PB matrix is much less efficient. The conjugation length should be quite short. This is probably the reason why the conductivity of PEDOT/PB is always low regardless of the content of the PEDOT in the composite film (see %yield of extracted PEDOT). (2) The residual toluene that may exist in the PEDOT/polymer composite film may start to vaporize upon heating. This may dissolve some of the DBEDOT during SSP process. Thus, the polymerization is no longer in the solid state and yields PEDOT with less ordered structure.

Another reason that makes the PEDOT/PS composite more conductive than the PEDOT/PB may be due to better inter-chain interactions between PS and PEDOT than those between PB and PEDOT. π–Stacking between aromatic ring of PS and thiophene ring of DBEDOT together with the rigidity of PS may help locking the DBEDOT in place during SSP and yield PEDOT with extended conformation and well-packed chain. Having the extended conformation, the neighboring thiophene rings in the PEDOT chains are oriented almost in the same plane so that the conjugated π-electrons could be delocalized over the whole chain which leads to high charge-carrier mobility or high conductive PEDOT. It is also possible that these same effects prevent conformational change of PEDOT upon storage. This can be realize

In the case of PEDOT/PB composite film of which conductivity is much lower than that of PEDOT/PS composite film, it is believed that PB became almost liquid-like especially upon heating ($T_g \sim$ -20 °C), allowing DBEDOT as well as short PEDOT chain to move and rotate freely during polymerization. This movement presumably yields PEDOT with less ordered coil conformation. In the coil conformation, the plan of a thiophene ring on the PEDOT chain deviates greatly from the plan of its neighboring thiophene ring, so that the C_α- C_α bond between the two thiophene ring is more like a σ bond and has a low density of conjugated π-electrons

The electrons are not completely delocalized over the whole PEDOT chain resulting in low conductivity.

This speculation agrees well with the XRD data. In general, the system becomes more conducting as the crystallinity increases. If the molecular order of the polymer chains is reduced, then the charge transport is interrupted by the conjugation defects, leading to a drastic decrease in the conductivity as is the case for the extracted PEDOT from PEDOT/PB composite film whose XRD patterns are broader and lower in intensity in comparison with the extracted PEDOT from PEDOT/PS composite film and the controlled PEDOT.
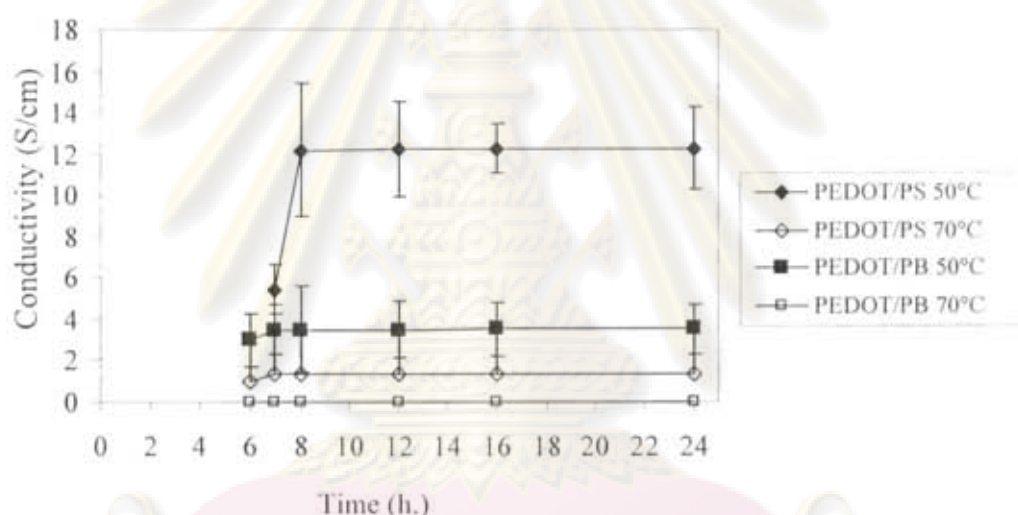
Figure 4.13 Conductivity of PEDOT/PS and PEDOT/PB composite films as a function of reaction time and temperature, using 3:1 DBEDOT/polymer weight ratio.

4.4.4 Surface roughness of PEDOT/polymer composite film

To our surprise, it was found that the conductivity of PEDOT/PS composite film can reach as high as 58 S/cm if it was measured on the bottom side (in contact with glass) of the film which is much smoother than the top side (in contact with air). The trend is opposite in the case of PEDOT/PB composite film. The top side is smoother than the bottom one. The surface morphologies of the composite films visualized under optical microscope are shown in Figure 4.14. This suggests that the surface roughness has a strong influence on the measured conductivity value.

(a) (b)

(c) (d)
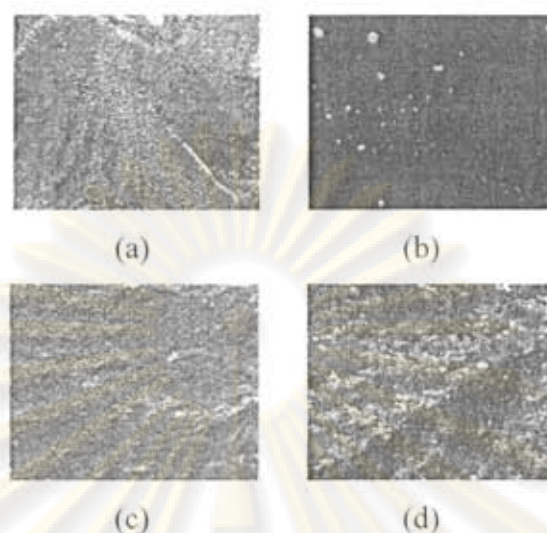
Figure 4.14 Surface morphologies of (a) PEDOT/PS composite film, top side, (b) PEDOT/PS composite film, bottom side, (c) PEDOT/PB composite film, top side, (d) PEDOT/PB composite film, bottom side.

The data shown in Figure 4.15 indicate that the conductivity of PEDOT/PS composite films on the bottom side were about 40 S/cm greater than the top side at both 50 °C and 70 °C. That is not the case for the PEDOT/PB composite films. The conductivity on the bottom side (0.01 S/cm) which is rougher was much lower than the top side. The smoother side of the PEDOT/polymer composite film, apparently, results in higher conductivity. This phenomenon can be explained based on the method of four-point probe technique. On a smooth surface, the four probes of the conductometer can be in good contact with the surface of the composite film (see Figure 4.16). In principle, the distance between the probes and the surface should be equal and results in a linear relationship between current and voltage. The resistance which is inversely proportional to the conductivity can be directly and accurately determined from the slope of the I&V curve shown on the right hand side of Figure 4.17. On the other hand, the distance between each probe and the surface cannot possibly be equivalent in the case of a rough surface (Figure 4.16, left hand side). As a result, the slope of the I&V curve is not exactly linear. The resistance can only be estimated from the initial part of the slope which is presumably linear. Evidently, the value does not well represent the actual resistivity of the composite film.
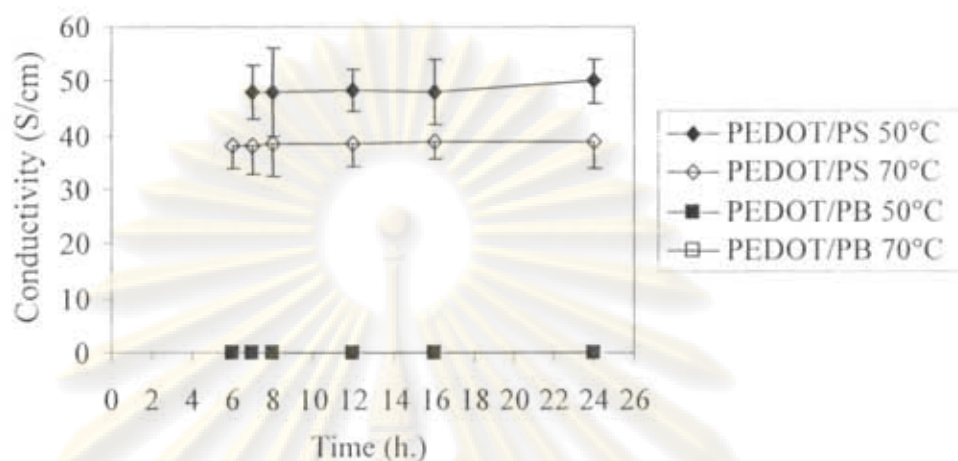
Figure 4.15 Conductivity of PEDOT/PS and PEDOT/PB composite films, measured on the bottom side, as a function of reaction time and temperature, using 3:1 DBEDOT/polymer weight ratio.
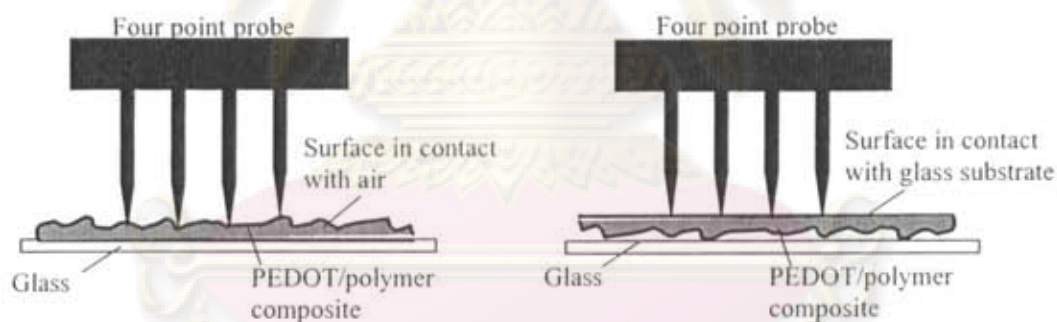
Figure 4.16 Schematic representation of four point probe in contact with smooth and rough surface.

(a)   (b)

Figure 4.17 I&V curve of PEDOT/PS composite film (a) on the surface side and (b) on the bottom side.

4.5 Effect of storage on conductivity

PEDOT/polymer composite films were kept in closed vials under nitrogen atmosphere and stored in a dessicator for 1 month. The conductivity values of PEDOT/PS and PEDOT/PB composite films both before and after storage are displayed in Table 4.2 and 4.3 respectively. Obviously, the conductivities of all composite films decrease after 1-month storage. This can be explained as a result of Br_2 loss during the storage.

Table 4.2 Conductivity of PEDOT/PS composite films before and after 1 month storage

Temperature (°C)	DBEDOT conc. (g/mL)	Conductivity (S/cm)			
		Before storage		After storage	
		Top side	Bottom side	Top side	Bottom side
50 °C	0.150	2.49	35.56	5.08×10^{-3}	16.17
	0.225	12.19	48.30	6.24×10^{-2}	17.68
70 °C	0.225	3.52	38.30	5.36×10^{-3}	16.54

Table 4.3 Conductivity of PEDOT/PB composite films before and after 1 month storage

Temperature (°C)	DBEDOT conc. (g/mL)	Conductivity (S/cm)			
		Before storage		After storage	
		Top side	Bottom side	Top side	Bottom side
50 °C	0.150	2.21	7.10×10^{-3}	3.21×10^{-3}	N/A
	0.225	3.50	9.23×10^{-2}	5.08×10^{-3}	N/A
70 °C	0.225	5.70×10^{-3}	6.42×10^{-2}	6.24×10^{-2}	N/A

N/A = Not available

4.6 Doping with I_2

It is obvious that the conductivities of all PEDOT/PS composite films can be completely recovered. The conductivities on re-doped film are closely resemble those of the freshly prepared films initially having Br_2 as dopants. This outcome also implies that there were no significant comformation changes of PEDOT in the PS matrix during storage. In contrast, the conductivities of all PEDOT/PB composite films cannot be recovered suggesting that there must be some conformation changes of PEDOT in the PB matrix upon storage. This change is no doubt induced by the consistent movement of PB chains whose T_g is below ambient temperature.

Table 4.4 Conductivity of PEDOT/PB and PEDOT/PS composite films after doping with I_2

Temperature (°C)	DBEDOT conc. (g/mL)	Conductivity (S/cm)			
		PEDOT/PS		PEDOT/PB	
		Top side	Bottom side	Top side	Bottom side
50 °C	0.150	14.19	35.25	7.45×10^{-3}	N/A
	0.225	17.67	43.45	9.33×10^{-3}	N/A
70 °C	0.225	16.17	40.50	2.09×10^{-1}	N/A

N/A = Not available

CHAPTER V

CONCLUSION AND SUGGESTION

Conducting polymer composite films containing poly(3,4-ethylenedioxythiophene) (PEDOT) was successfully prepared through solid state polymerization (SSP) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in the presence of either polystyrene (PS) or polybutadiene (PB) matrix. The percentage yield of up to 85 % of the PEDOT could be obtained. The fact that FT-IR and XRD spectra of the extracted PEDOT exhibit the same fingerprints as those of the controlled PEDOT confirms the success of SSP. The coexistence of PEDOT and PS in the composite films was verified by TGA analysis. The appearance of two absorption bands in UV-Vis spectra of the PEDOT/PS composite suggests that the PEDOT exist in both doped and undoped states and implying that the Br_2 released during SSP can act as dopants.

The PEDOT/PS composite films possess significantly higher conductivities than the PEDOT/PB composite films. This can be ascribed to the better inter-chain interactions between PS and PEDOT and the rigidity of the PS allowing the more ordered and extended PEDOT to be formed. As opposed to PS, PB does not have any specific interactions with either DBEDOT or PEDOT. Its low T_g also leads to chain movement during SSP of DBEDOT. The formed PEDOT conformation should be less ordered than that of the PEDOT formed in the PS matrix. The optimal condition to obtain the highest conductivity of the PEDOT/PS composite was to use 3:1 DBEDOT:PS weight ratio, 0.225 g/mL of DBEDOT and conducting the SSP at $50^{\circ}C$ for 7 h

The conductivity of the PEDOT composite films was found to decrease upon storage due to the loss of Br_2. The conductivity can be completely recovered after re-doping with I_2 in the case of PEDOT/PS composite films. The recovery was not possible for the PEDOT/PB composite films suggesting that there was some

irreversible conformational change of PEDOT chains in the PB matrix whose chains consistently moved as a result of T_g being lower than ambient temperature.

It is interesting to investigate the effects of polymer matrix molecular weight as well as %crystallinity on the physical properties and the conductivity of PEDOT polymer composite. It should be possible to use the method of SSP for making conducting polymer composite from other DBEDOT derivatives. Using spin casting instead of drop casting may help improving the composite film uniformity and smoothness which have strong influence on the conductivity of the composite film. All of these issues can be proposed as future direction of this research work.

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APPENDIX

Percentage yield extraction of SSP PEDOT

Table A-1 Percentage yield of PEDOT recovered from PEDOT/PS and PEDOT/PB composite films obtained after solvent extraction as a function of DBEDOT: polymer weight ratio. The SSP was conducted at 50 °C for 8 h.

DBEDOT : Polymer	PEDOT/PS (% yield)	PEDOT/PB (% yield)
1:1	3	3
2:1	60	78
3:1	82	85
4:1	85	88

Table A-2 Percentage yield of PEDOT recovered from 3:1 PEDOT/PS and PEDOT/PB composite films obtained after solvent extraction as a function of DBEDOT concentration. The SSP was conducted at 50 °C for 8 h.

DBEDOT conc. (g/mL)	PEDOT/PS (% yield)	PEDOT/PB (% yield)
0.075	82	83
0.150	85	86
0.225	86	88

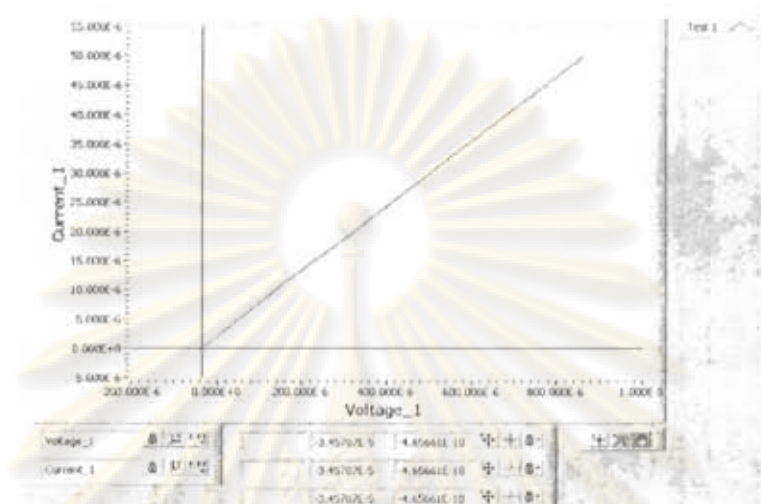## Conductivity measured by Four point probe technique

Figure A-1 I&V curve of PEDOT composite polymer by four point probe technique

$$V = IR \qquad (A\text{-}1)$$

$$\text{Resistivity } (\rho) = 4.53 \times R \times \text{film thickness } (0.001 \text{ cm}) \qquad (A\text{-}2)$$

$$\text{Conductivity } (S/cm) = 1/\rho \qquad (A\text{-}3)$$

Table A-3 Conductivity of PEDOT/PS and PEDOT/PB composite films measured on the front side as function of DBEDOT:polymer weight ratio. The SSP was conducted at 50 °C for 8 h.

DBEDOT : Polymer	PEDOT/PS Conductivity (S cm^{-1})	PEDOT/PB Conductivity (S cm^{-1})
1:1	N/A	N/A
2:1	0.09 ± 0.02	0.34 ± 0.20
3:1	12.19 ± 2.21	2.55 ± 1.50
4:1	6.32 ± 4.41	3.31 ± 1.50

N/A= Not available

Table A-4 Conductivity of PEDOT/PS and PEDOT/PB composite films measured on the front side as function of DBEDOT concentration (g/mL), using 3:1 DBEDOT: polymer weight ratio. The SSP was conducted at 50°C for 8 h.

DBEDOT conc. (g/mL)	PEDOT/PS Conductivity (S cm^{-1})	PEDOT/PB Conductivity (S cm^{-1})
0.075	0.70 ± 1.23	0.05 ± 0.50
0.150	2.49 ± 3.21	2.49 ± 1.20
0.225	12.19 ± 2.30	2.55 ± 1.80

Table A-5 Conductivity of PEDOT/PS and PEDOT/PB composites measured on the front side as a function of time and temperature used for the SSP, using 3:1 DBEDOT: polymer weight ratio and the DBEDOT concentration of 0.225 g/mL.

Reaction time	PEDOT/PS Conductivity (S cm^{-1})		PEDOT/PB Conductivity (S cm^{-1})	
	50°C	70°C	50°C	70°C
4	N/A	N/A	N/A	N/A
6	N/A	1.00 ± 1.56	3.0 ± 1.30	$5.4 \times 10^{-3} \pm 2 \times 10^{-3}$
7	5.42 ± 1.20	1.30 ± 1.26	3.50 ± 1.20	$5.6 \times 10^{-3} \pm 5 \times 10^{-3}$
8	12.19 ± 3.20	1.30 ± 2.22	3.50 ± 2.10	$5.6 \times 10^{-3} \pm 9 \times 10^{-3}$
12	12.21 ± 2.30	1.30 ± 1.34	3.50 ± 1.40	$5.6 \times 10^{-3} \pm 3 \times 10^{-3}$
16	12.27 ± 1.20	1.31 ± 1.28	3.52 ± 1.30	$5.7 \times 10^{-3} \pm 2 \times 10^{-3}$
24	12.26 ± 2.0	1.34 ± 1.32	3.52 ± 1.20	$5.7 \times 10^{-3} \pm 4 \times 10^{-3}$

N/A = Not available

Table A-6 Conductivity of PEDOT/PS composite films measured on the back side (in contact with glass substrate), using 3:1 DBEDOT: polymer weight ratio and the DBEDOT concentration of 0.225 g/mL. The SSP was conducted at 50 °C for 8 h.

Reaction time	PEDOT/PS Conductivity (S cm^{-1})		PEDOT/PB Conductivity (S cm^{-1})	
	50°C	70°C	50°C	70°C
4	N/A	N/A	N/A	N/A
6	N/A	38.42 ± 4.65	0.09 ± 0.07	0.06 ± 0.05
7	48.47 ± 5.89	38.02 ± 5.32	0.09 ± 0.07	0.06 ± 0.02
8	48.65 ± 8.74	38.38 ± 6.11	0.09 ± 0.05	0.06 ± 0.07
12	48.21 ± 4.56	38.50 ± 4.01	0.09 ± 0.10	0.07 ± 0.04
16	48.44 ± 6.84	38.65 ± 3.25	0.10 ± 0.02	0.07 ± 0.02
24	50.14 ± 4.41	39.21 ± 5.66	0.10 ± 0.03	0.07 ± 0.04

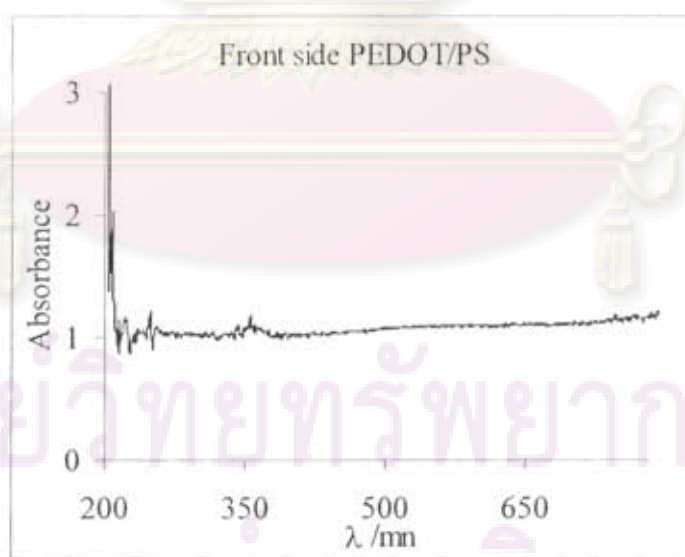N/A = Not available

UV-VIS absorption

Figure A-2 UV-Visible spectrum of the front side of the PEDOT/PS composite film on glass slide.
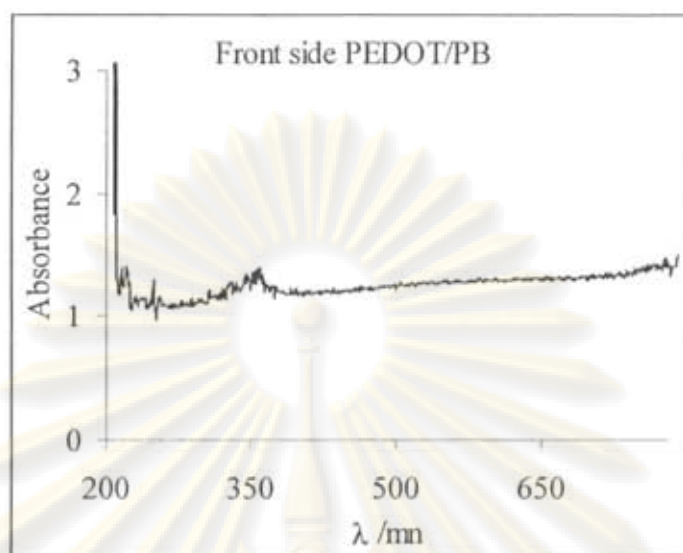
Figure A-3 UV-Visible spectrum of the front side of the PEDOT/PB composite film on glass slide.
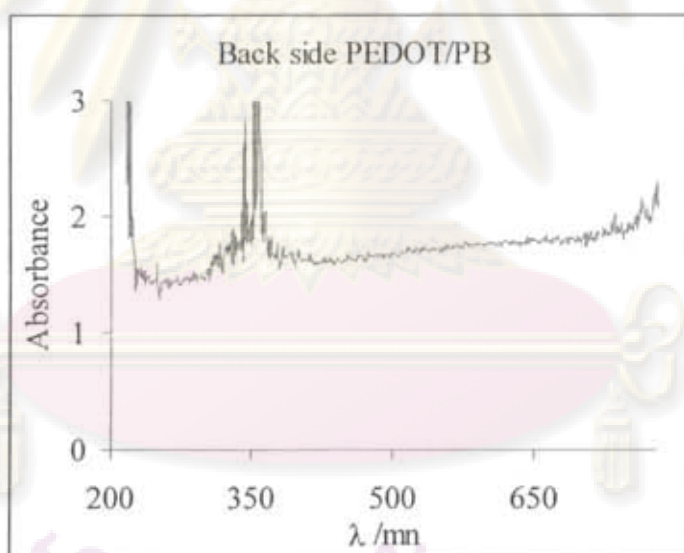

Figure A-4 UV-Visible spectrum of the back side of the PEDOT/PB composite film on glass slide.

VITAE

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