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นายพรชัย ลุยะพันธุ์

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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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PLASMA POLYMERIZATION AND IODINE DOPING OF THIOPHENE DERIVATIVES

Mr. Pornchai Luyaphand

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พรชัย ลูยะพันธุ์: พลาสมาพอลิเมอไรเซชันและการโดปด้วยไอโอดีนของอนุพันธ์ไทโอฟีน (PLASMA POLYMERIZATION AND IODINE DOPING OF THIOPHENE DERIVATIVES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.บุญโชติ เผ่าสวัสดิ์ยรรยง, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร.วรวรรณ พันธุ์นาวัน, 64 หน้า.

งานวิจัยนี้ได้สังเคราะห์พอลิ 2-เมทิลไทโอฟีนและพอลิ 3-เมทิลไทโอฟีนด้วยวิธีพลาสมาพอลิเมอไรเซชัน ในการสังเคราะห์ใช้กำลังไมโครเวฟในช่วง 350-450 วัตต์ และใช้เวลาในการสังเคราะห์ 2 นาที จากนั้นนำมาวิเคราะห์ด้วยเทคนิคสเปกโทรโฟโตเมตรี การวิเคราะห์หมู่ฟังก์ชันของโครงสร้างฟิล์มพอลิไทโอฟีนด้วยเทคนิคอินฟราเรดสเปกโทรสโคปี พบว่าพอลิ 2-เมทิลไทโอฟีนและพอลิ 3-เมทิลไทโอฟีนที่สังเคราะห์ด้วยวิธีพลาสมามีหมู่ฟังก์ชันสอดคล้องกับสารละลายมอนอเมอร์ ในการวิเคราะห์องค์ประกอบของฟิล์มด้วยเทคนิคเอนเนอร์จิสเปกโทรสโกปีเอกซเรย์สเปกโทรโฟโตเมตรี พบว่าพอลิ 2-เมทิลไทโอฟีนที่สังเคราะห์ด้วยวิธีพลาสมามีค่าอัตราส่วนของปริมาณคาร์บอนต่อซัลเฟอร์ต่ำกว่าทางทฤษฎี ส่วนพอลิ 3-เมทิลไทโอฟีนที่สังเคราะห์ด้วยวิธีพลาสมามีค่าปริมาณคาร์บอนต่อซัลเฟอร์ใกล้เคียงหรือสูงกว่าทางทฤษฎี ค่าการนำไฟฟ้าของฟิล์มพอลิ 2-เมทิลไทโอฟีนและพอลิ 3-เมทิลไทโอฟีนไทโอฟีนที่ยังไม่โดปมีค่า 1.04×10^{-8} ถึง 1.20×10^{-7} และ 1.05×10^{-7} ถึง 2.01×10^{-7} ซีเมนต่อเซนติเมตร ตามลำดับ ส่วนโดปพอลิ 2-เมทิลไทโอฟีนและพอลิ 3-เมทิลไทโอฟีนด้วยวิธีอินสิทู่ (2.29×10^{-5} และ 1.85×10^{-5} ซีเมนต่อเซนติเมตร ตามลำดับ) มีค่าการนำไฟฟ้าในตอนเริ่มต้นต่ำกว่าการโดปด้วยวิธีทั่วไป อย่างไรก็ตามค่าการนำไฟฟ้าของวัสดุที่โดปด้วยวิธีทั่วไปนั้นจะลดลงอย่างรวดเร็ว (ใน 24 ชั่วโมง) จนมีค่าใกล้เคียงกับตอนที่ยังไม่โดป ส่วนการโดปแบบอินสิทู่ นั้นค่าการนำไฟฟ้าจะลดลงในช่วงแรก และเมื่อเวลาผ่านไปนานขึ้นค่าการนำไฟฟ้าค่อนข้างคงที่ (นานกว่า 160 ชั่วโมง)

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BOONCHOAT PAOSAWATYAN YONG, Ph.D., CO-ADVISOR: ASST.
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Plasma polymerization of poly(2-methylthiophene) and poly(3-methylthiophene) thin films have been synthesized. Plasma polymerization parameters were studied. Microwave power in the range of 350-450 W was employed for 2 minutes. Plasma-polymerized poly(2-methylthiophene) and plasma-polymerized poly(3-methylthiophene) films were characterized by various spectrophotometric methods. Infrared analyses showed absorption frequencies of important functional groups mostly similarly observed in the case of monomer. Results from Energy-dispersive X-ray spectroscopy analysis were suggestive of partial fragmentation of the films. The C/S ratio of plasma-polymerized poly(2-methylthiophene) is lower than the theoretical value. For the plasma-polymerized poly(3-methylthiophene), the C/S ratio is equal to or higher than theoretical value. Electrical conductive measurements revealed that the plasma-polymerized poly(2-methylthiophene) and the plasma-polymerized poly(3-methylthiophene) films exhibit conductivities 1.04×10^{-8} to 1.20×10^{-7} and 1.05×10^{-7} to 2.01×10^{-7} S/cm, respectively. As for the doped plasma-polymerized poly(2-methylthiophene) and plasma-polymerized poly(3-methylthiophene) materials, initial conductivities (2.29×10^{-5} and 1.85×10^{-5} S/cm, respectively) were lower than the plasma-polymerized films which were doped with the conventional method. However, it was found that conductivity of the latter decreased more rapidly and reached an undoped value in a short time (24 hours). In contrary, the decaying rate of conductivity of *in situ* doped material could be sustained for a longer period of time (more than 160 hours).

Field of Study: Petrochemistry and polymer science. Student's Signature

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Co-advisor's Signature

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LIST OF ABBREVIATIONS

A	=	ammeter
ATR	=	Attenuated Total Reflection
cm	=	centimeter
DC	=	Direct Current
EDS	=	Energy-dispersive X-ray spectroscopy
eV	=	electron volt
FTIR	=	Fourier Transform Infrared
HH	=	head-to-head
HT	=	head-to-tail
I	=	current
min	=	minute
mL	=	milliliter
mm ³	=	cubic millimeter
mmol	=	millimole
nm	=	nanometer
OES	=	Optical Emission Spectroscopy
S	=	siemen
sccm	=	Standard Cubic Centimeters per Minute
SEM	=	Scanning Electron Microscope
TT	=	tail-to-tail
UV	=	Ultraviolet
V	=	voltage
W	=	watt
μm	=	micrometer

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Polymers have long emerged as one of the most important materials in everyday life. The use of polymers moved from primarily materials such as coatings and containers to active materials with useful optical, electronic, and mechanical properties. Conducting polymers have been studied intensively since the 1970s. The first conducting polymer was synthesized in doped polyacetylene by the group of Alan J. Heeger, Alan G. Macdiarmid, and Hideki Shirakawa [1]. Conducting polymers were developed by using conjugated polyvinylenes, polyarylenes, and polyheterocycles such as polyaniline, polypyrrole, polythiophene, and poly(p-phenylene). Among conducting polymers, polythiophene displays good stability and high electrical conductivity when doped with strong acceptors or donors [2]. Polythiophene has attractive properties such as light weight and flexibility. They are widely used in several applications such as solar cells, light-emitting diode, and polymeric batteries [3, 4]. These polymers have been generally synthesized by two methods namely, electrochemical and chemical polymerization. However, both methods have considerable disadvantages. By the chemical technique, an insoluble powdered polymer is synthesized, which requires further purification for the removal of oxidants and surfactants [5]. With the electrochemical technique, a precise current density control is required to produce films, and the obtained films are rather fragile restricted [6]. Plasma polymerization is a solvent-free process. The films of plasma polymerization have high degree of branching and cross-linking [7]. In addition, the films have a high thermal stability and resistance to organic solvents [5]. Moreover, plasma polymerized films can be grown on almost any surface [8].

In previous research, the effect of conjugation length of polythiophene was demonstrated in such way that the conductivity of oligothiophenes increases with

expanding conjugation length of up to 6-11 monomer units, after which the conductivity becomes constant [9, 10]. Recently, we found that plasma polymerization of polythiophene thin film leads to partial fragmentation of the aromatic thiophene rings [7] and the structure of the thiophene monomer with electron-donating groups has been proposed to be used to reduce fragmentation [11]. Hence, to obtain thin films with a high conductivity, the conjugated structure of the monomer should be retained in the film. Therefore, it is desirable to find a system in which fragmentation of the ring upon plasma polymerization would be decreased. In order to improve the conductivity, doping after polymerization (*ex situ* doping) is usually carried out. It was found that the conductivity of the *ex situ* doping rapidly decreased to more or less that of the undoped material [12]. On the other hand, the *in situ* doping has more sustained electrical conductivity than that obtained from its *ex situ* counterparts [13]. Since the discovery of conducting polymers, the development of conducting polymers has huge research interest due to their excellent electrical properties. Polythiophene is a polymer of high environmental stability and can also be used in electronic devices such as diode. In this work, electrical measurement performed on polythiophene based Schottky diodes is used to investigate the electronic properties of the polymer.

In this research, plasma polymerization of thiophene derivatives, 2-methylthiophene and 3-methylthiophene, with electron-donating methyl group are described. The film was characterized by attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR), UV-visible spectroscopy, scanning electron microscopy (SEM), and electrical conductivity measurement.

1.2 Objectives

The goal of this research is focused on an efficient method to fabricate the polythiophene films synthesized by using thiophene with 2-methyl and 3-methyl substituents utilizing a well-assembled MW plasma system and to improve electrical conductivity by *in situ* doping with iodine. In addition, the fabrication of Schottky diodes based on polythiophene, the current-voltage characteristics are reported.

CHAPTER II

THEORY AND LITTERATURE REVIEW

2.1 Conducting polymers

2.1.1 Introduction to conducting polymers

Polymers were mainly regarded as good insulating materials. However, in the 1970s the discovery of conducting polymer in doped polyacetylene was revealed by the group of Alan J. Heeger, Alan G. Macdiarmid and Hideki Shirakawa [1]. The structural requirement for a conducting polymer is a π -conjugated electron system constituting the polymer backbone. A conjugated system is a system of connected p-orbitals with delocalized electrons in compounds with alternating single and multiple bonds, which in general may lower the overall energy of the molecule and increase stability. Conjugation is the overlap of one p-orbital with another across an intervening sigma bond as shown in **Figure 2.1**.

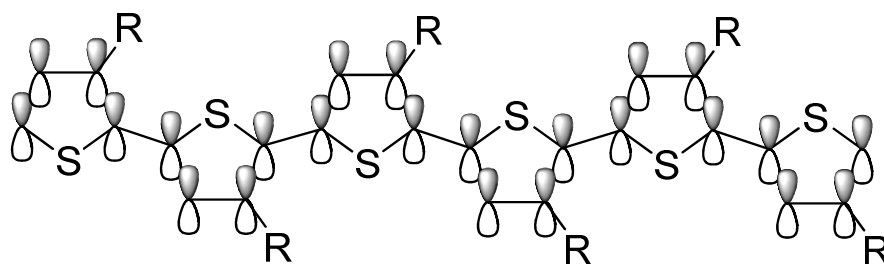


Figure 2.1 Conjugated structure of poly(alkylthiophene).

A conjugated polymer may be cyclic, acyclic, linear, or mixed. A simple classification of conjugated polymer is shown in **Figure 2.2**.

2.1.2 Classification of conducting polymers

All materials can be divided into three main groups according to conductivity: insulators, semiconductors and conductors. Conducting polymers are generally

classified in semiconductors as indicated in **Figure 2.3**. Because of the instability of polyacetylene in the environment, the potential of using other types of conjugated molecules were studied to be used as a substitute. So conducting polymers that have been developed, those based on polyanilines, polypyrroles, polythiophenes, polyphenylenes and poly(*p*-phenylene vinylene)s have attracted the most attention. In order to make them electronically conductive, it is necessary to introduce mobile carriers into the conjugated system; this is achieved by oxidation or reduction reactions and the insertion of counterions (called ‘doping’).

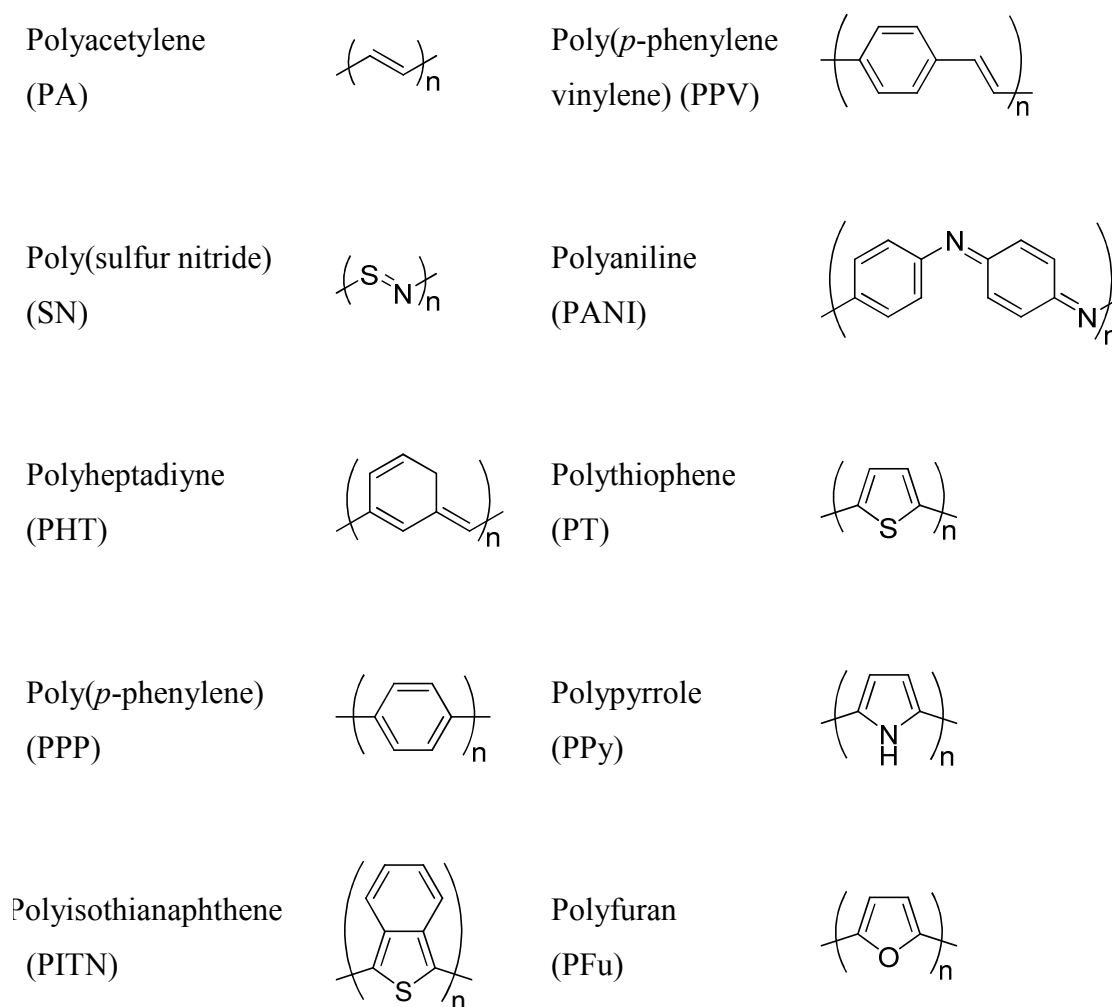


Figure 2.2 Molecular structures of some conjugated polymers.

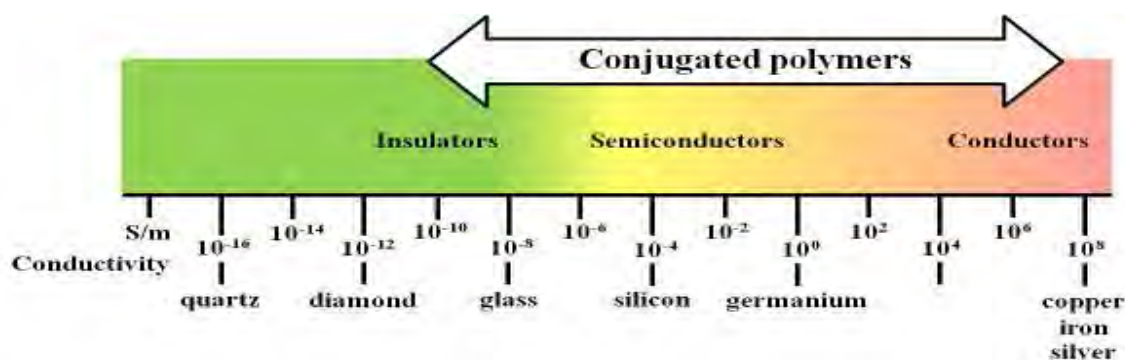


Figure 2.3 Conductivity of different materials [14].

Polyvinylenes, polyarylenes, and polyheterocycles are the major classes of conducting polymers. Polyvinylenes are well known polymers, which have good thermal stabilities and high electrical conductivities [15]. Poly(*p*-phenylene), polyazulene, and poly(*p*-phenylene vinylene) belong to the family of polyarylenes or polyaromatics. Poly(*p*-phenylene) was the first non-acetylenic hydrocarbon polymer that showed high conductivity on doping which was demonstrated in 1980 [16]. This triggered further research for finding other conducting polymers. Many polyheterocyclics also could be added to the list of organic conducting polymers such as polypyrrole, polythiophene, and polyfuran, all having a five membered ring structure with one heteroatom like oxygen or nitrogen or sulfur [17]. A simple classification of conducting polymers on the basis of chain composition is shown in **Figure 2.4**.

2.1.3 Application of conducting polymers

Conducting polymers have been used in a range of electronic devices. Many of the applications are based on the fundamental principles of physics. One of the first applications of these materials was in rechargeable batteries. A potential use for conducting polymers such as polyaniline, polyfuran, and polythiophene are as gas sensing devices. Thin-film polyaniline-based gas sensing elements are inexpensive, and have been shown to sensitive to gases such as CO, NH₃, HCl and HCN. Polyfuran and polythiophene have been considered as humidity sensors, radiation detectors, and gas sensors [18].

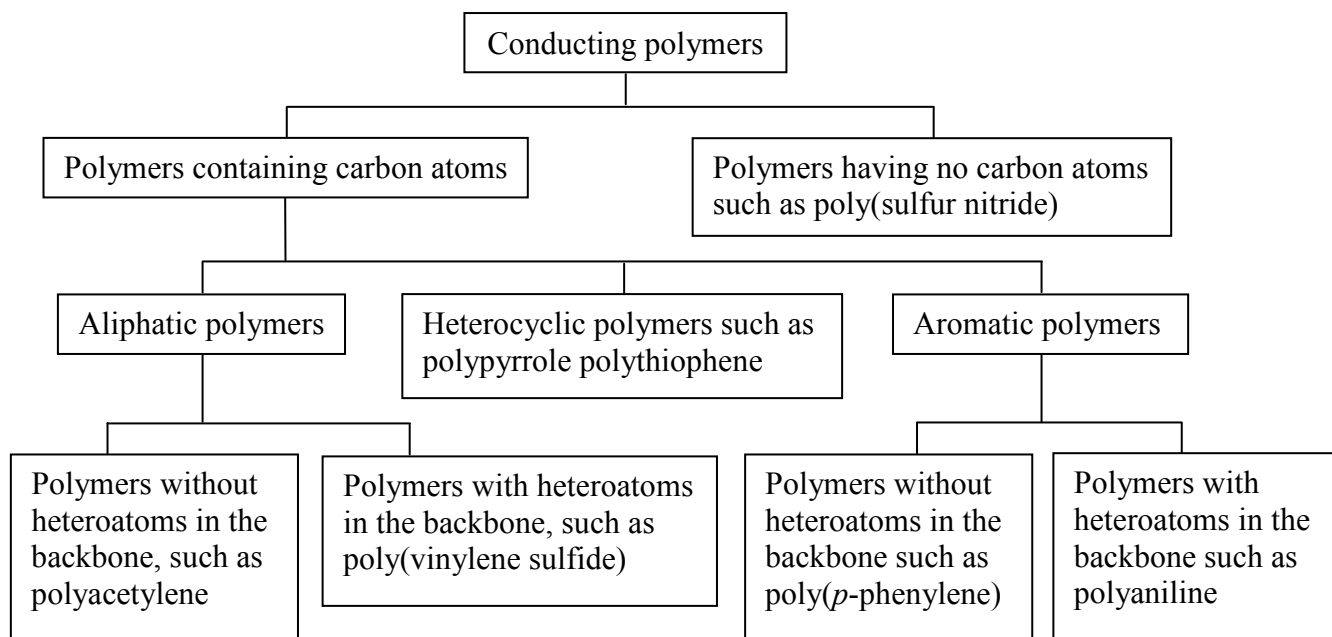


Figure 2.4 Classification of conducting polymers.

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes their electroactivity, as shown in **Table 2.1**.

Table 2.1 Application of conducting polymers [19].

Group 1	Group 2
electrostatic materials	molecular electronics
conducting adhesives	electrical displays
electromagnetic shielding	chemical biochemical and thermal sensors
printed circuit boards	rechargeable batteries and solid electrolytes
artificial nerves	drug release systems
antistatic clothing	optical computers
piezoceramics	ion exchange membranes
active electrons (diodes, transistors)	electromechanical actuators
aircraft structure	smart structures

2.2 Mechanism of conductivity [20]

The conductivity of a material depends on its electronic energy level structure (Figure 2.5). The energy difference between the highest occupied band (valence band) and lowest unoccupied band (conduction band) is called the band gap. Conduction occurs when an electron is promoted from the valence band to the conduction band. If the band gap is a small, thermal excitation of electron from the valence band to the conduction band give rise to conductivity. This is what happens in conventional semiconductors. When the band gap is wide, thermal energy is insufficient to excite electrons across the gap and the solid is an insulator. In conductors, there is no band gap since the valence band overlaps with the conduction band and hence their high conductivity.

Conducting polymers are different in that they do not conduct electrons *via* the same mechanisms used to describe conventional semiconductors. The electronic ground state of conducting polymer is an insulator. The electronic conductivity of conducting polymers results from mobile charge carriers introduced into the conjugated π -system through doping.

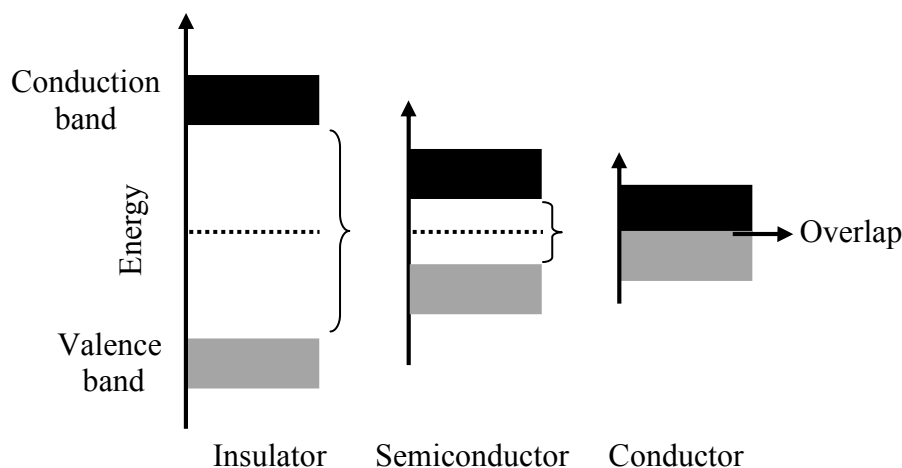


Figure 2.5 Energy band in solid.

2.3 Effect of doping [19, 20]

Doping of a conducting polymer involves oxidation or reduction of the polymer backbone. Oxidation removes electrons and produces a positively charged

polymer and is described as p-doping. Reduction produces a negatively charged backbone and is known as n-doping. In these p-doping and n-doping processes, the positive and negative charges on polymer remain delocalized and are balanced by the incorporation of counterions (anions or cations) which are referred to as dopants. The chemical and electrochemical doping of conjugated polymer are shown in **Figure 2.6**.

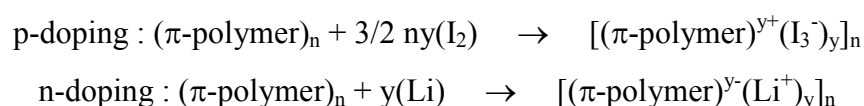


Figure 2.6 Chemical and electrochemical doping of conjugated polymer.

To explain the electronic phenomena in these organic conducting polymers, concept including solitons, polarons, and bipolarons have been proposed by solid-state physicists. The π -conjugated systems based on aromatic rings, such as polythiophene, polypyrrole and their derivatives have nondegenerate ground states. In these polymers, the ground state degeneracy is weakly lifted so that polarons and bipolarons are important and dominant charge storage configurations. Polythiophene and derivatives were often doped by an oxidative doping because they are electron rich and favor to lose electron. For example, the oxidative doping of polythiophene is shown in **Figure 2.7**.

The removal of one electron from the π -conjugated system of thiophene results in the formation of a radical cation. In solid-state physics, a radical cation that is partially delocalized over a segment of the polymer is called a polaron. It is stabilized through the polarization of the surrounding medium, hence the name. Since it is really a radical cation, a polaron has spin $1/2$. The radical and cation are coupled to each other *via* local resonance of the charge and the radical. The presence of a polaron induces the creation of a domain of quinone-type bond sequence within the polythiophene chain exhibiting an aromatic bond sequence. The lattice distortion produced by this is of higher energy than the remaining portion of the chain. The creation and separation of these defects cost energy, which limits the number of quinoid-like rings that can link these two species, *i.e.*, radical and cation, together. In the case of polythiophene it is believed that the distortion extends over four thiophene

rings. Upon further oxidation the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. This is of lower energy than the creation of two distinct polarons; therefore, at higher doping levels it becomes possible for two polarons to combine to form a bipolaron, thereby replacing polarons with bipolarons.

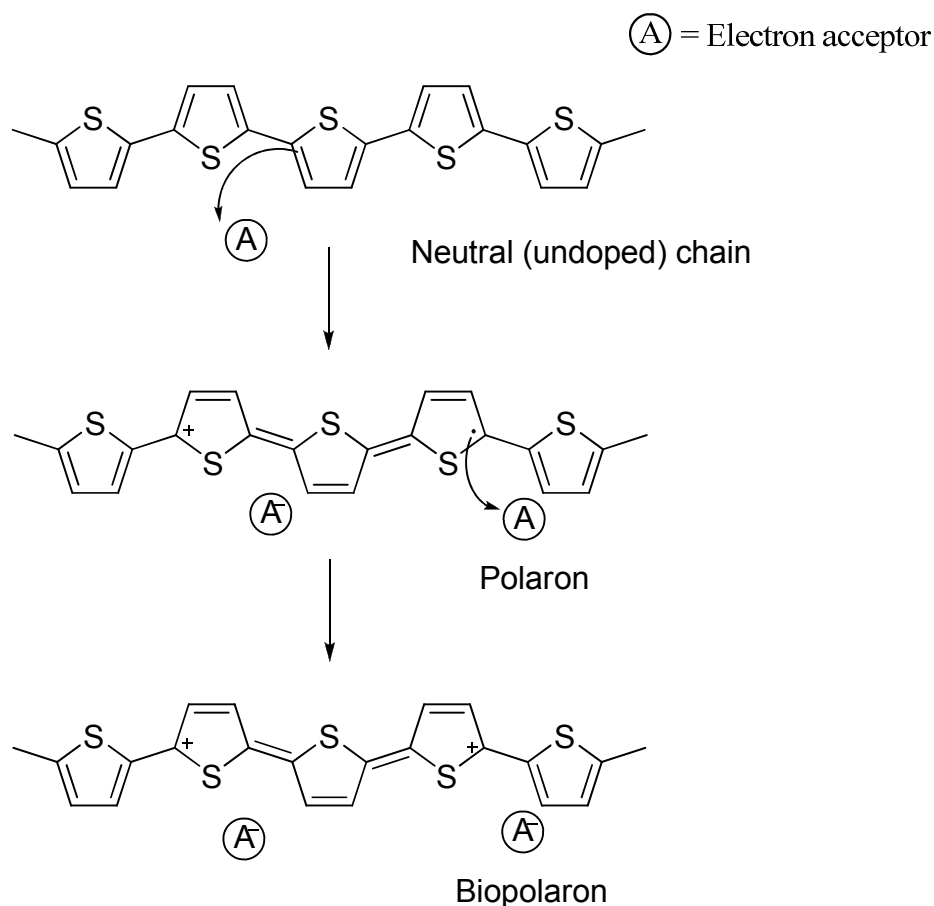


Figure 2.7 Polaron and bipolaron in polythiophene.

2.4 Polythiophene and derivatives

Polythiophene is a polymer composed of five membered a sulfur heterocyclic monomeric units. It is environmentally stable and highly resistant to heat. Polythiophene attracted much attention as a conducting polymer due to ease of synthesis, high stability, and structural versatility. Polythiophenes and their derivatives have been studied intensively and utilized in various applications such as solar cells, light-emitting diode and polymeric batteries [3, 4].

A significant discovery demonstrated that polythiophene belongs to one of a few cases in which substitution of hydrogen at the 3-position by an alkyl chain does not affect the conductivity of the polymer, which impart solubility and consequently enhance processibility. The 3- substituent can be incorporated into the polymer chain with two different regioregularities: head-to-tail (HT) and head-to-head (HH) orientations which can result in four triad regioisomers in the polymer chain, *i.e.* HT-HT, HT-HH, TT-HT and TT-HH (**Figure 2.8**).

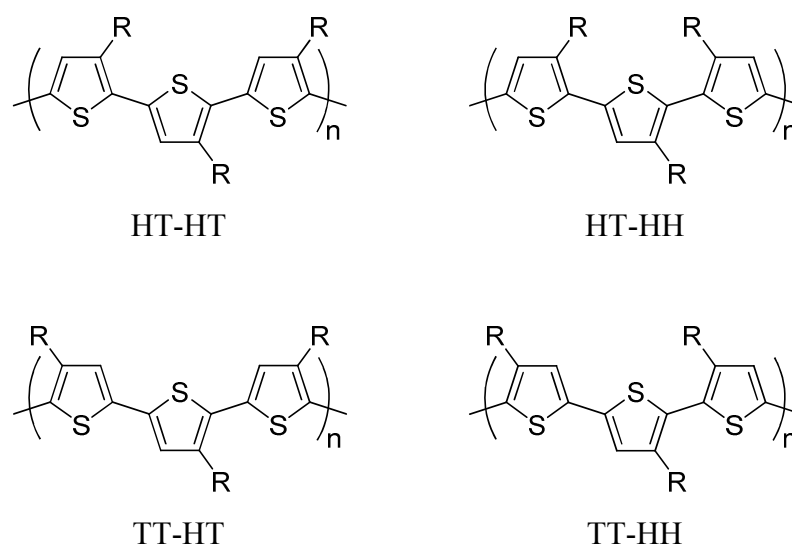


Figure 2.8 Regioisomers of the poly(3-alkylthiophene).

2.5 Synthesis of polythiophene and derivatives

Polythiophene has been prepared for the first time by electrochemical polymerization. Since a film is produced on the anode during polymerization, this method is suitable for the preparation of polymers such as polythiophene and poly(3-methylthiophene), which is not processible after polymers are formed. However, in electrochemical polymerization, the yield of polymers is low and the polymers often do not have a well-defined structure. On the other hand, since facile oxidative polymerization with iron (III) chloride produces polythiophene in a high yield, this method is suitable for processing polythiophenes such as poly(3-methylthiophene).

The molecular weight of polymer obtained by this method is sufficiently high for a film to be cast.

2.5.1 Chemical polymerization of thiophene and derivatives

The oxidative polymerization of thiophene using ferric chloride described by Sugimoto can be performed at room temperature [21]. This method is easily accessible to almost all scientists who wish to obtain poly(3-alkylthiophene) and will provide sufficient amounts of the polymer for laboratory use. The resulting polymers are soluble in common organic solvents and their film can be formed by simply casting its solution on a substrate. In addition, 3-alkylthiophenes are commercially available (**Figure 2.9**).

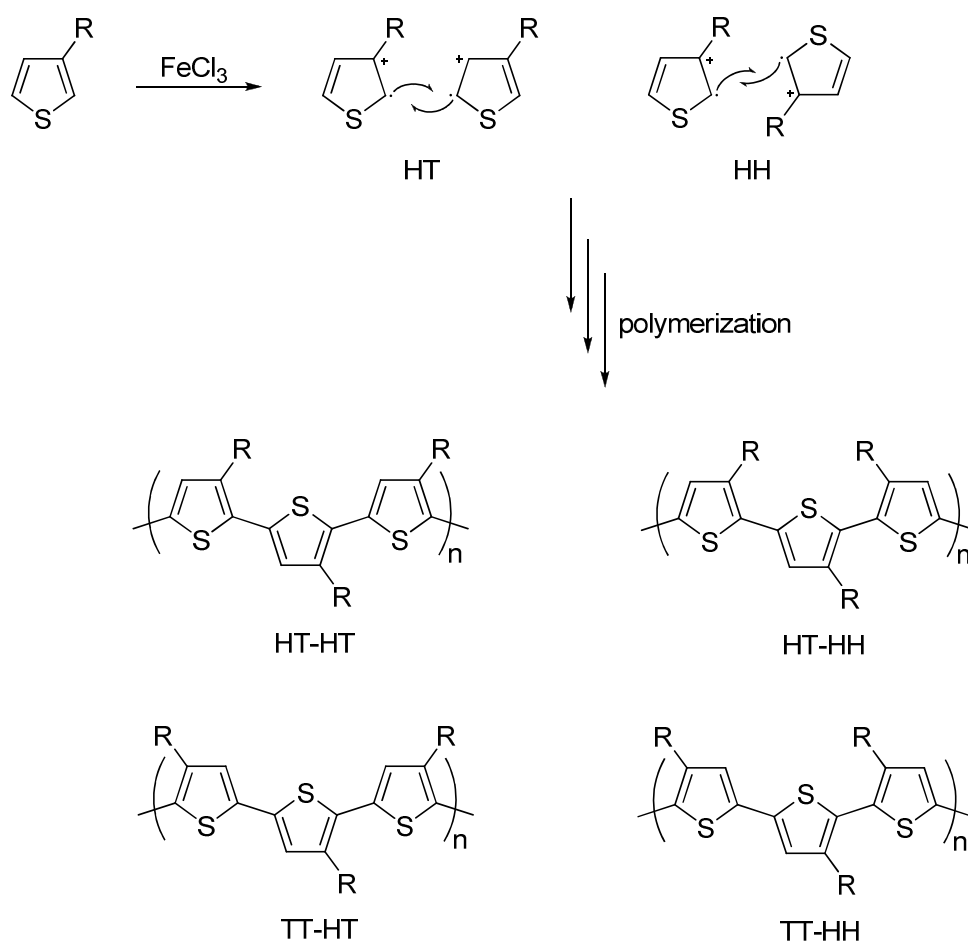


Figure 2.9 The oxidative coupling reaction of 3-alkylthiophene by FeCl_3 .

2.5.2 Electrochemical polymerization of thiophene and derivatives

A polymeric film can also be obtained by electrochemical polymerization. This is a very useful method for preparing polymers such as polythiophene, poly(3-methylthiophene) and poly(3-phenylthiophene) (**Figure 2.10**), which are insoluble and infusible. When these polymers are obtained in the form of powder we cannot process them into the film or other useful forms. Polythiophene is not stable at potentials used for electrochemical polymerization of thiophene. Thus, polythiophene deposited on the anode at the earlier stages of the polymerization is overoxidized and has deteriorated, while electrochemical polymerization produces new polymer.

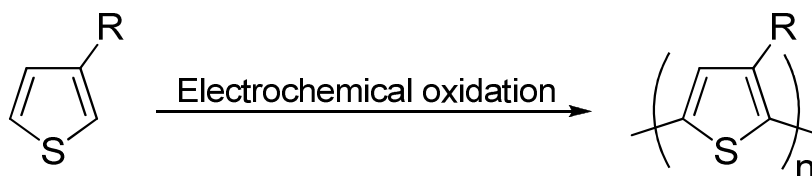


Figure 2.10 The electropolymerization method for the synthesis of poly(3-alkylthiophene) (R= H, Me, Ph)

An alternative method, plasma polymerization, makes use of molecules occurring in various plasma environments. This technique results in very thin but uniform polymeric layers that strongly adhere to a desired substrate. It has been found that the plasma polymerized films are usually highly cross-linked and are resistant to higher temperatures and chemicals. The disadvantage is the poor predictability of the chemical structure of the resulting plasma polymerized layer. Several monomers have been plasma polymerized with the objective to obtain conductive surfaces. Success in synthesizing processible conducting polymer has promised their potential application in electronic devices [22].

2.6 Plasma

The fourth state of matter is plasma. Plasma may be defined as an ionized gas containing both charged and neutral species, including free electrons, positive and/or negative ions, atom, and molecules. The differences between the four states of matter, can be explained by the energy and interactions of molecules as shown in **Figure**

2.11. Between molecules, a strong attraction force exists. To overcome these forces, a certain amount of energy is necessary. Because the energy of the molecules is too low to cause free movement in solids, molecules are ordered in regular patterns. When enough energy is added, it becomes liquid. Now, molecules possess the energy to break the rigid pattern, but they cannot move out of the attraction field of each other. Addition of even more energy causes matter to turn into a gas. Molecules then no longer have intermolecular interactions and can move freely. In these three conditions, molecules do not possess a charge because the positive charge of the nucleus of an atom is always compensated by the charge of the surrounding electron cloud. When enough energy is added to a gas, electrons are able to escape from the electric field, created by the nucleus. Plasma can be found easily in the universe, including solar coronas, lightning bolts, and nuclear fusion. Plasma also appears in man-made devices such as fluorescent lamps, neon tubes, welding arcs, and gas lasers.

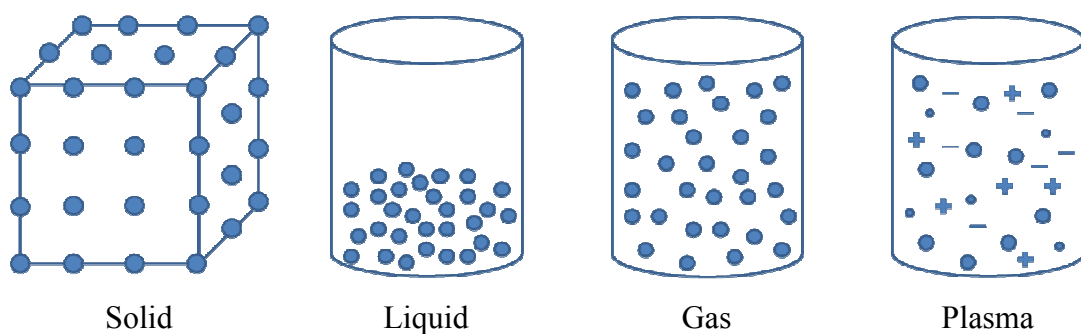


Figure 2.11 The four states of matter.

Plasma may be classified as “hot” or “cold”. Plasma temperature is expressed in units of electronvolts (eV). Cold or non-thermal plasma contains very hot free electrons of several eV, which generate high chemical reactivity while neutrals and ions remain near room temperature. Cold plasma is also partially-ionized with a low fractional ionization. On the other hand, hot or thermal equilibrium plasma contains constituents, which are all at approximately the same temperature so that the heat content, and therefore overall temperature, is high and they are close to maximal.

2.7 Plasma polymerization

Plasma processes are a growing technology in different domains. A lot of technological applications could only be made possible with plasma assisted methods. Examples of industrial plasma processes are surface modification, pollution control, sterilization, cleaning, and etching. Plasma can also be found in a lot of well known applications, such as lamps, and plasma screens [23]. Recently, synthesis of thin polymer films by use of plasma polymerization has emerged as an interesting new approach. Plasma polymerization is a 'dry' technique that doesn't require the use of solvents. From an ecological and economical point of view, the absence of solvents and solvent waste offers a lot of advantages.

In the plasma polymerization process, the ionization of a molecule by collision with an accelerated electron is an essential process for creating plasma of a monomer. The ionization of a molecule is first elementary step of plasma polymerization and is far more complex than the ionization of an atom. Conventional polymerization is highly dependent on the structure of the monomer. However, in plasma polymerization, monomers and any organic compound without a polymerizable structure such as a double bond can polymerize. Plasma polymerization takes place through several reaction steps [24]. In the initiation stage, free radicals and atoms are produced by collisions of electrons and ions with monomer molecules, or by dissociation of monomers adsorbed on the surface of the sample. Secondly, propagation of the reaction is the actual formation of the polymeric chain. This can take place both in the gas phase and on the substrate film. Finally, termination can also take place in the gas phase or at the polymer surface, by similar processes as in the propagation step, but ending either with the final product or with a closed polymer chain.

Plasma polymerization is frequently used to deposit thin films. The advantages of plasma polymer films include excellent coating adhesion on almost all substrates [25, 26], chemical [27], mechanical [28] and thermal stability [29]. As doped polythiophene is known for its high and stable conductivity, thiophene and their derivatives are often used as a monomer in plasma polymerization. For example, conducting films of polythiophene have been prepared by radio frequency (RF) plasma polymerization. These films displayed a conductivity of 1.8×10^{-4} S/cm after

doping with iodine by exposing the films to iodine vapor in a sealed container overnight at room temperature [30]. Highly crosslinked and amorphous polythiophene films have been prepared by Bhat and coworker. The electrical conductivity of the films was found in the range of 10^{-15} – 10^{-10} S/cm which was rather low as compared to other methods of preparation [31]. Groenewoud and coworkers have demonstrated that the conductivity of synthesized polythiophene of pulsed plasma polymerization was higher when deposition pressure (from 0.06 to 0.3 mbar) was higher [12]. Decrease in band gap of poly(3-methylthiophene) from 2.69 to 1.86 eV has been observed, with increasing the RF plasma power from 30 to 120 W [32]. The thickness 200 nm of poly(3-methylthiophene) film was prepared successfully by RF plasma polymerization and the optical band gap has been estimated to be 2.14 eV [33]. Poly(3-methylthiophene) has been synthesized by plasma polymerization under atmospheric pressure, and the films prepared are highly crosslinked [4]. Thin films (100 nm) of poly(3-octylthiophene) conducting polymer has been prepared by plasma polymerization using 30 W RF power supply. These films are morphologically uniform, highly reproducible, semi-crystalline, and environmentally stable [34].

Under plasma conditions non-specific and very complex chemical reactions occur. It was found that plasma polymerization thin film lead to partial fragmentation of the aromatic thiophene rings. Hence, to obtain the thin films with a high conductivity, the conjugated structure of the monomer should be retained in the thin film. Therefore, fragmentation of plasma polymerization should be decreased. In an earlier study, it was found that the monomer structure has an influence on the fragmentation of thiophene during deposition [11]. It was observed that fragmentation during deposition was enhanced by substitution of thiophene with electron-withdrawing substituents, whereas it was suppressed by electron-donating substituents.

In order to improve the conductivity, doping after polymerization (*ex situ* doping) is usually carried out. It was found that the conductivity of the *ex situ* doping rapidly decreased to more or less that of undoped material [12]. Whereas the *in situ* doping has more sustained electrical conductivity than doping method after film growth [13].

In recent years, considerable attention was given to the fabrication and characterization of the films and Schottky diodes using conducting polymers as active materials. Conducting polymers consisting of a π -conjugated backbone are attractive because of their unique electronic properties.

2.8 Schottky diode

A diode is a semiconductor device that has two electrodes (anode and cathode). The most common function of a diode is to allow an electric current to pass in one direction (called the diode's forward direction) while blocking current in the opposite direction (the reverse direction). Thus, diodes are used especially as rectifiers which change alternating current into direct current and to vary the amplitude of a signal in proportion to the voltage in a circuit, as in a radio or television receiver. The behavior of a diode is investigated by current-voltage characteristic which exhibit non-linear as shown in **Figure 2.12**.

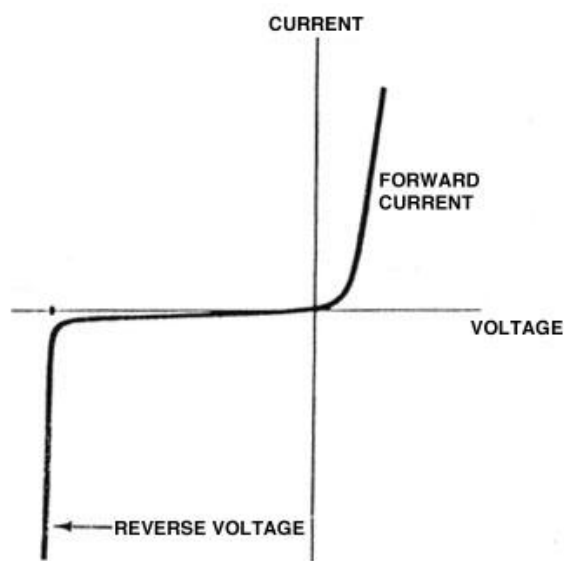


Figure 2.12 Current-voltage characteristics for diode.

Since the discovery of conducting polymers, the development of conducting polymers has gained huge research interest due to their excellent electrical, magnetic, optical, and mechanical properties [35]. The electrical properties of conjugated polymers have been intensively studied because of their utilization in electronic devices such as energy storages, sensors, and Schottky diodes [36-38].

Schottky diodes are constructed from a metal to semiconductor contact. Recently, metal/organic semiconductor Schottky junction as an alternate to the metal/inorganic semiconductor junction has been developed. There are a lot of polymers and they can be used for the fabrication of microelectronic devices. The first report example of Schottky diode made with a conductive polymer was based on polyacetylene [39]. Polythiophene and its derivatives have been the subject of many investigations in Schottky diode [38, 40]. It is well known that polythiophene is stable against the oxidation. In this work, electrical measurement performed on plasma-polymerized polythiophene based Schottky diode is used to investigate the electronic properties of the polymer.

The aforementioned reports showed that plasma polymerization proves to be an excellent alternative to conventional polymerization of conducting films and the structure of the thiophene monomer with electron-donating groups has been proposed to be used to reduce fragmentation in thiophene ring. The *in situ* doping has more sustained electrical conductivity than that obtained from its *ex situ* counterparts. Polythiophene is a polymer of high environmental stability and can also be used in electronic devices such as diode.

The aim of this study is to fabricate the plasma-polymerized poly(2-methylthiophene) and plasma-polymerized poly(3-methylthiophene) films. An *in situ* doping of plasma-polymerized poly(2-methylthiophene) and plasma-polymerized poly(3-methylthiophene) with iodine will also be investigated to increase electrical conductivity of the films. In addition, the fabrication of Schottky diodes based on polythiophene, the current-voltage characteristics are reported.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The following chemicals were obtained from Sigma-Aldrich, Fluka, Carlo Erba, RCI Labscan and TIG and used without further purification: thiophene (99 %, Sigma-Aldrich), 2-methylthiophene (98%, Fluka), 3-methylthiophene (98%, Sigma-Aldrich), iodine (AR grade, Carlo Erba), acetone (AR grade, RCI Labscan), methanol (AR grade, RCI Labscan) and Argon gas (TIG).

3.2 Equipment

Fabricated poly(2-methylthiophene) and poly(3-methylthiophene) films were analyzed with the following equipment. Characterization details are described in **section 3.6**.

- 3.2.1 Attenuated total reflection-fourier transform infrared (ATR-FTIR) spectroscopy: Nicolet iS10 FT-IR spectrometer
- 3.2.2 UV-visible spectroscopy: P.G. instrument Ltd., T90 + UV-Vis spectrometer
- 3.2.3 Scanning electron microscopy (SEM): JEOL, JSM-6480LV
- 3.2.4 Energy-dispersive X-ray spectroscopy (EDS): OXFORD, INCAX-sight 7573
- 3.2.5 Electrical conductivity measurements: HP 4140B pA meter/DC voltage source

3.3 Chemical synthesis of poly(3-methylthiophene) [41]

The chemical synthesis of poly(3-methylthiophene) was performed as follows. A solution of 3-methylthiophene monomer 0.29 g (3 mmol) in 5 mL of dichloromethane was slowly added to a stirred suspension of 0.65 g (4 mmol) of

anhydrous ferric chloride in 5 mL of dichloromethane. When the addition was complete, the mixture was stirred for an additional 6 hours at 0°C. After that the reaction mixture was allowed to warm to room temperature and stirred overnight for 18 hours, the precipitate was filtered off and rinsed with methanol until the washed solution was colorless. Filtration of the precipitate gave a brown powder in 92% yield (0.27 g). The remaining ferric chloride in the precipitate was extracted out by soxhlet extraction with methanol for 24 hours. ATR-FTIR : aromatic C-H stretching around 3119 cm^{-1} , aliphatic C-H stretching around 2917 cm^{-1} , aromatic C=C stretching around 1439 and 1377 cm^{-1} , C-C stretching around 1204 cm^{-1} , C-H aromatic bending around 1166 cm^{-1} and C-S stretching around 819 cm^{-1} .

3.4 Plasma polymerization of 2-methylthiophene and 3-methylthiophene

Before the plasma polymerization process, glass substrates ($1.2 \times 2.5 \text{ cm}^2$) were first ultrasonically cleaned in acetone, methanol and deionized water for 5 minutes, respectively. Then the glass substrates are dried at 100°C for 5 minutes then transferred to be stored in a desiccator ready for use [42].

Glass substrates which will be used in a fabrication process where electrical conductivity of the film would be measured are required to be treated by the following method prior to film fabrication. In order for the electrical conductivity of plasma polymerized thin films on glass substrates to be determined by two-point probe measurement, these had two copper electrodes on glass substrates. These electrodes were deposited using a DC sputtering method operating at 0.006 torr, 15 W, and 15 minutes to afford coated copper with the size of $0.6 \times 1.2 \text{ cm}^2$. A substrate is illustrated in **Figure 3.1**.

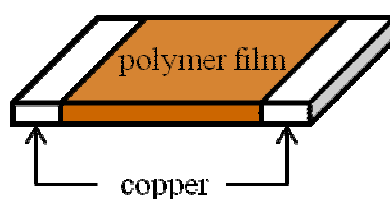


Figure 3.1 The substrate preparation for measurement of electrical conductivity.

All plasma-polymerized poly(2-methylthiophene) and poly(3-methylthiophene) films used in present research were prepared by microwave plasma polymerization [42]. The microwave plasma assembly was displayed in **Figure 3.2** and **Figure 3.3**. At first clean glass substrates were placed in the chamber and the reactor was evacuated to the base pressure 0.03-0.05 torr. The chamber were pre-treated with an argon plasma for 1 min, after which the reactor was again evacuated to base pressure. In this treatment with an argon plasma, the flow rate of argon gas was fixed at 5 sccm, the pressure at 0.75 torr and the microwave power at 350 W. In the polymerization process, argon was used as a carrier gas to transport the monomer vapor into the chamber. The argon gas flow rate and pressure of the system were kept at the same conditions in all experiments. Plasma-polymerized films were fabricated under various microwave power (350, 400, and 450 W) while a constant pressure of 2.5 torr was used. The polymerization time was 2 min, which start to reckon time as long as the plasma polymerization was generated.



Figure 3.2 The photograph of microwave plasma system.

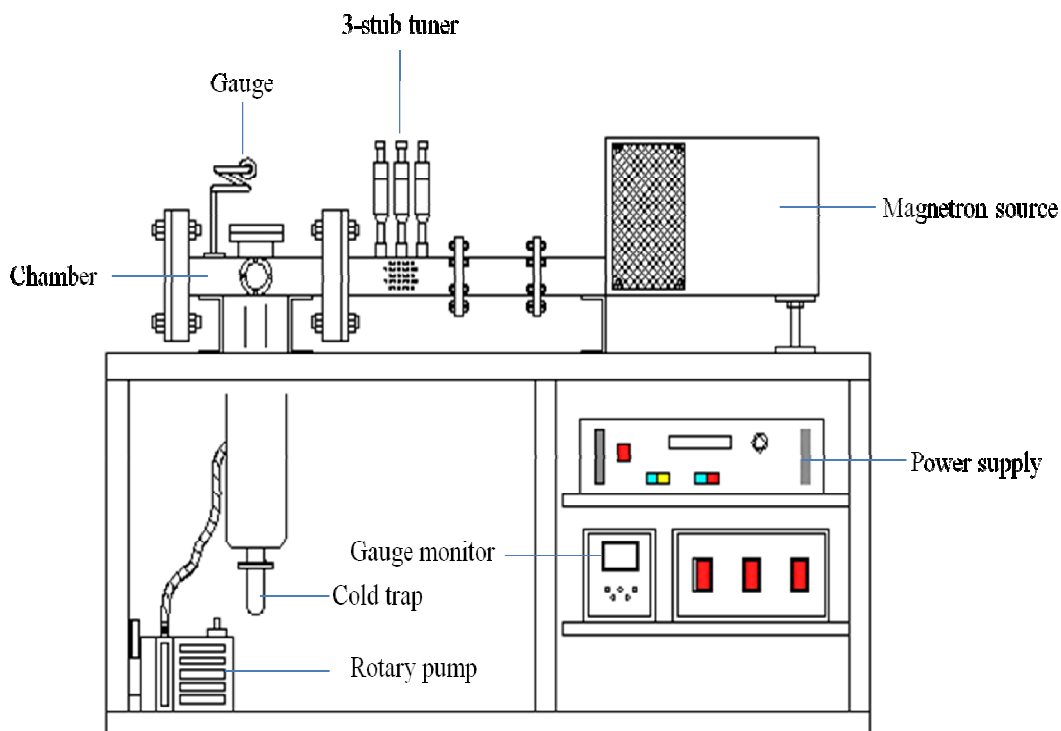


Figure 3.3 The schematic diagram of microwave plasma system.

3.5 Preparation of *in situ* iodine-doped plasma polymerized poly(2-methylthiophene) and poly(3-methylthiophene)

In the doping method [42], the iodine crystals were placed on a glass slide and then placed into the chamber and the chamber was subsequently evacuated. The sublimation of iodine resulted in a purple vapor throughout the chamber. Then argon gas was bubbled through a monomer to apply monomer into the chamber. Subsequently, microwave discharge was applied to generate plasma. During this process, optical emission spectroscopy technique was carried out to analyze the plasma phase to give significant information on iodine species present. The measuring probe was placed at the outside glass window of the chamber at which the plasma discharge can be seen as shown in **Figure 3.4**. The plasma polymerized films were produced at the microwave power of 450 W, the polymerization time was 2 minutes the chamber pressure during film growing was maintained at approximately 3.5 torr.

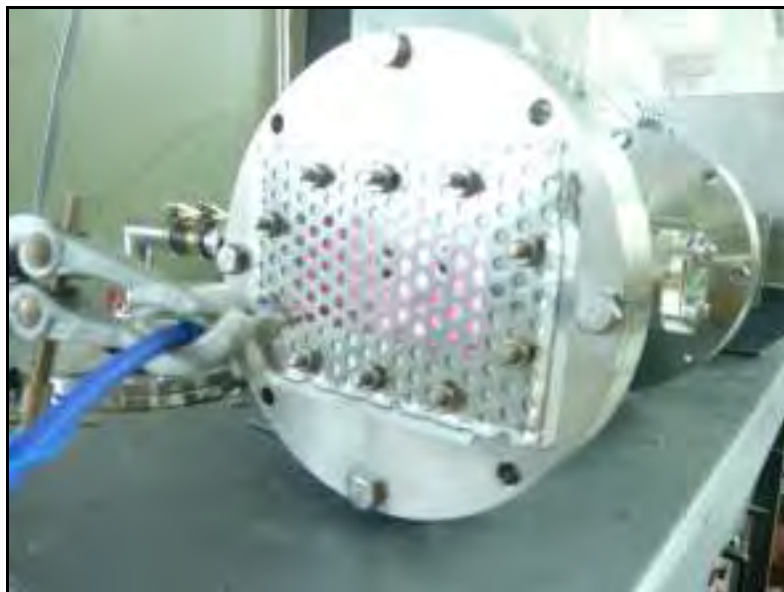


Figure 3.4 Position of OES probe during plasma temperature measurement.

3.6 Characterization of plasma polymerized poly(2-methylthiophene) and poly(3-methylthiophene)

The plasma polymerized films were characterized by the following methods:

3.6.1 Attenuated total reflection-Fourier transform infrared (ATR-FTIR)

The functional groups of the samples was studied with infrared spectroscopy. The spectra of films deposited on glass substrate were investigated by using a Nicolet iS10 FT-IR spectrometer in the range of $750\text{-}4000\text{ cm}^{-1}$.

3.6.2 UV-Visible spectroscopy

To study the surface absorption of polymer film, the UV-visible absorption spectra of the films were obtained using a P.G. instrument Ltd., T90 + UV-Vis spectrometer in the wavelength range of 190-900 nm.

3.6.3 Scanning electron microscopy (SEM)

The morphology and film thickness of the polymer films were observed by JEOL, JSM-6480LV electron microscope. A cross sectional technique was used to determine the film thickness.

3.6.4 Energy-dispersive X-ray spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample. In this research, it was performed on an OXFORD, INCAX-sight 7573 spectrometer.

3.6.5 Electrical conductivity

The current voltage characteristics was measured by a two-point probe at room temperature. The sample current was measured at applied voltage from 0 to 100 V with a HP 4140B pA meter/DC voltage source, including Lab View program.

3.7 Schottky diode

Schottky diodes, the most widely used contact in electronic devices and controlled mainly by its interface properties, made by introducing organic layer on semiconductors have been shown to exhibit promising characteristics for diode applications. Schottky diodes require one ohmic contact and one rectifying contact. In this research, schottky diodes are fabricated in a sandwich structure with the polymer film between an ohmic contact and a rectifying contact as shown in **Figure 3.5**. The Schottky diode was fabricated with the structure of Al at the bottom on a glass substrate, plasma-polymerized polythiophene in the middle and Al at the top as defined by Al/plasma-polymerized polythiophene/Al.

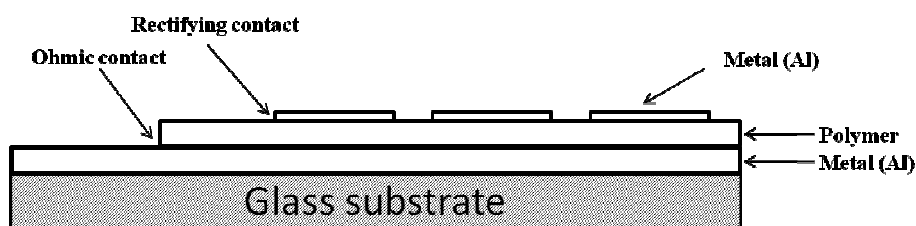


Figure 3.5 Cross-section view of a polymer schottky diode structure.

In order to produce a schottky diode, a glass substrate ($1.2 \times 2.5 \text{ cm}^2$ dimension) was cleaned by method in described **section 3.4**. Al ohmic contact of the fabricated diode was deposited by the DC sputtering system under the deposition

condition as follows: sputtering power of 45 W, sputtering pressure of 2.9×10^{-3} torr, and sputtering time of 90 minutes. The thickness of the Al layer was controlled by the deposition rate of approximately 1.5 nm/s. Growth of polythiophene film was achieved with the deposition conditions in described **section 3.4**. Finally, the aluminum was sputtered to complete the rectifying contact on the polythiophene film surface through a shadow mask as shown in **Figure 3.6**.

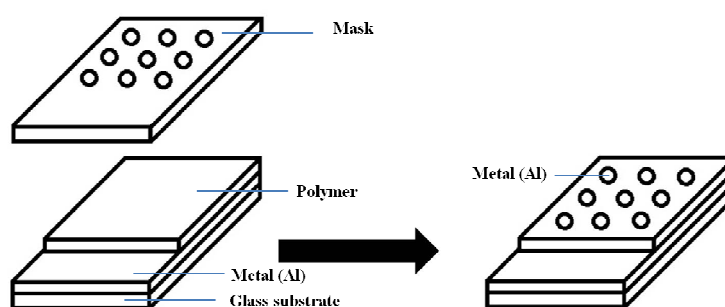


Figure 3.6 Front view of a polymer schottky diode structure with shadow mask.

A Hewlett Packard pA meter model 4140B was used to measure the DC current-voltage characteristic of the schottky diodes. A diagram of DC measurement setup is illustrated in **Figure 3.7**.

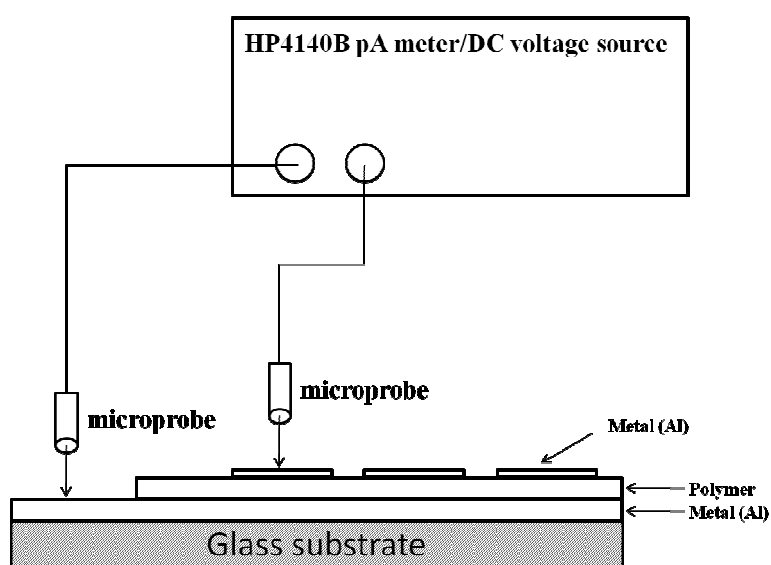


Figure 3.7 Schematic diagram of DC measurement setup.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Chemical synthesis of poly(3-methylthiophene) (P3MeTh)

The synthesis of poly(3-methylthiophene) by oxidation polymerization using ferric chloride was performed following the method used by Tepveera [41]. Poly(3-methylthiophene) was obtained in 92% yield in the form of brown powder that cannot be dissolved in all organic solvents. Poly(3-methylthiophene) can be conventionally prepared, while poly(2-methylthiophene) cannot be chemically synthesized, because the α -position of the thiophene ring has the methyl group.

4.2 Plasma polymerization of 2-methylthiophene and 3-methylthiophene thin films

The color of the plasma-polymerized poly(2-methylthiophene) (P2MeTh) and poly(3-methylthiophene) (P3MeTh) films were light-brown to dark-brown on the glass slide substrates (**Figure 4.1**). It was found that the color of the films became more intense in color when an increasing microwave power. During optimization to investigate appropriate microwave power, it was found that the suitable power in the comparison are 350, 400, and 450 W at 2 minutes.



Figure 4.1 Examples of plasma-polymerized films by microwave plasma polymerization at different microwave power (a) poly(2-methylthiophene) and (b) poly(3-methylthiophene).

4.2.1 Film characterization

4.2.1.1 Functional groups and chemical characteristics

The functional groups of the P3MeTh were investigated by ATR-FTIR. The spectra of films obtained using 350, 400, and 450 W are shown in **Figure 4.2**. The spectra of plasma-polymerized films are broader than chemical synthesis and monomer because of branching and cross-linking of the films. This is consistent with amorphous structure of plasma-polymerized materials. Since the plasma process involves high energy, there are a number of reactive species such as radicals, ions, *etc.* present in the process [31]. A spectrum from chemically-synthesized P3MeTh obtained by conventional solution polymerization was also included for comparison. The transmittance spectra of 3-methylthiophene monomer, chemically-synthesized, and plasma-polymerized P3MeTh exhibits the following characteristic peaks: aromatic stretching at 3084 cm^{-1} ; alkene C-H stretching at 2962 ; alkane C-H stretching at 2923 cm^{-1} ; symmetric C=C stretching mode at 1439 cm^{-1} ; C=C stretching of the thiophene rings at 1369 cm^{-1} ; =C-H bending at 1030 cm^{-1} and C-S stretching at 828 cm^{-1} . The data are summarized again in **Table 4.1**.

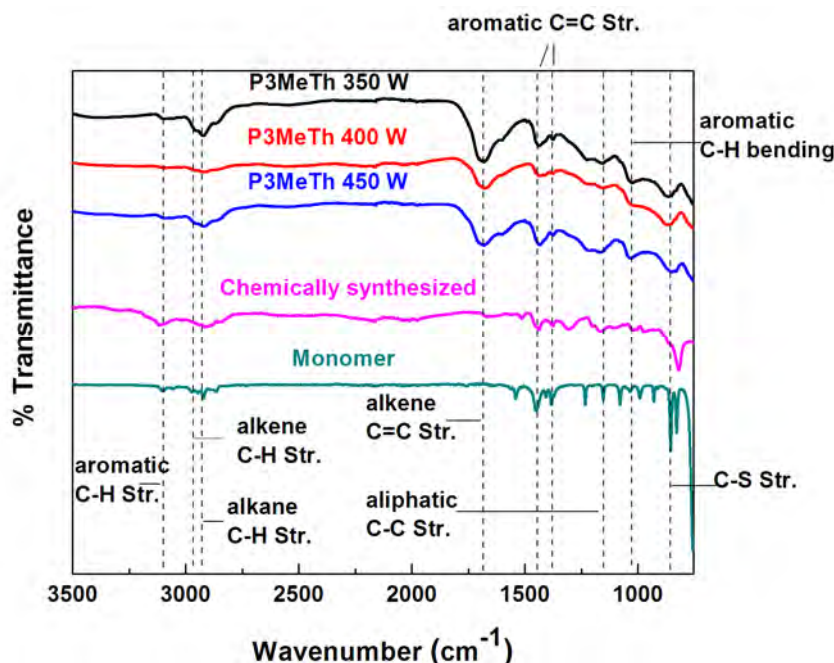


Figure 4.2 ATR-FTIR spectra of 3-methylthiophene monomer, chemically-synthesized P3MeTh and P3MeTh prepared from plasma polymerization at different MW power.

Table 4.1 ATR-FTIR spectra of monomer, chemically synthesized P3MeTh and P3MeTh prepared from plasma polymerization at different MW power.

Assignments	Wavenumber (cm ⁻¹)		
	3-methylthiophene monomer	chemically synthesized P3MeTh	plasma-polymerized P3MeTh
aromatic C-H stretching	3103	3119	3104
alkene C-H stretching	-	-	2962
alkane C-H stretching	2922	2917	2917
alkene C=C stretching	-	-	1682
C=C ring stretching	1451, 1384	1439, 1377	1435, 1378
C-C stretching	1234	1166	1169
C-H aromatic bending	1079	1024	1033
C-S stretching	856	819	849

It is not surprising to observe that in the spectra of plasma P3MeTh aromatic C-H stretching of the thiophene ring around 3104 cm⁻¹ are weakened or in some cases almost disappeared. In general, signals for *sp*²-C-H bond are already rather weak in nature. Amorphous structure of the plasma-polymerized P3MeTh resulting from myriad structural differences would no doubt result in really weak signals. The previously non-existing wavenumber at 1682 and 2962 cm⁻¹ (representing alkene C=C stretching and alkene C-H stretching, respectively) in the spectrum of the plasma-polymerized P3MeTh are somewhat suggestive of fragmentation of the thiophene ring. The most distinct feature in plasma P3MeTh spectra is the weakened band at 849 cm⁻¹ assigned to the C-S stretching. This result also suggests a certain degree of thiophene ring fragmentation which is in good agreement with literature report [45]. Despite of some evidence for ring fragmentation, aromatic C=C stretching around 1435 and 1378 cm⁻¹ confirm existence of cyclic structure. In addition, spectra in the fingerprint region still show relatively well maintained characteristics of the thiophene rings. When comparing IR absorption frequencies between the spectra of plasma-polymerized polythiophene [13] and plasma-polymerized P3MeTh, it is exhibited that peaks of both polymers similarly show major absorptions. It seems that

IR spectra cannot be used to compare the fragmentation. However, the comparison of fragmentation was confirmed by EDS analysis with the detail of which will be discussed later.

Poly(2-methylthiophene) cannot be chemically synthesized, because the α - position of the thiophene ring has the methyl group. However, plasma polymerization is a promising solution to this problem. The advantage of plasma polymerization is the ability of it to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions. The spectra of plasma-polymerized P2MeTh obtained using 350, 400, and 450 W of microwave power, as well as the monomer spectrum, are presented in **Figure 4.3**. The spectra of plasma-polymerized P2MeTh films are broader than monomer because of the branching and cross-linking. A detailed peak assignment is presented in **Table 4.2**. The bands at 1438 and 1374 cm^{-1} representing the C=C ring stretching to indicate the thiophene ring is mostly preserved during plasma polymerization. However, the peak at 1672 and 2960 cm^{-1} (representing alkene C=C stretching and alkene C-H stretching, respectively) were observed and the weakened C-S stretching at 848 cm^{-1} also support that partial fragmentation has also occurred.

The spectra of plasma-polymerized P2MeTh films show nearly similar change as of plasma-polymerized P3MeTh. Both spectra, plasma-polymerized P2MeTh and plasma-polymerized P3MeTh show peaks around 1430 and 1370 cm^{-1} which are characteristic of the C=C ring stretching. This means that at least a part of the original monomer structure is still present in the plasma-polymerized films. Both spectra also show an absorption peak around 3100 cm^{-1} , which comes from the aromatic C-H stretching. This proves that the plasma-polymerized film still contains double bonds. Certain absorptions in the infrared region that are not present in the monomer spectrum suggest fragmentation of the monomer structure. Evidence for alkene structure can be found in the C-H stretching vibrations at 2960 cm^{-1} . Around 1680 cm^{-1} , the C=C stretching can be seen.

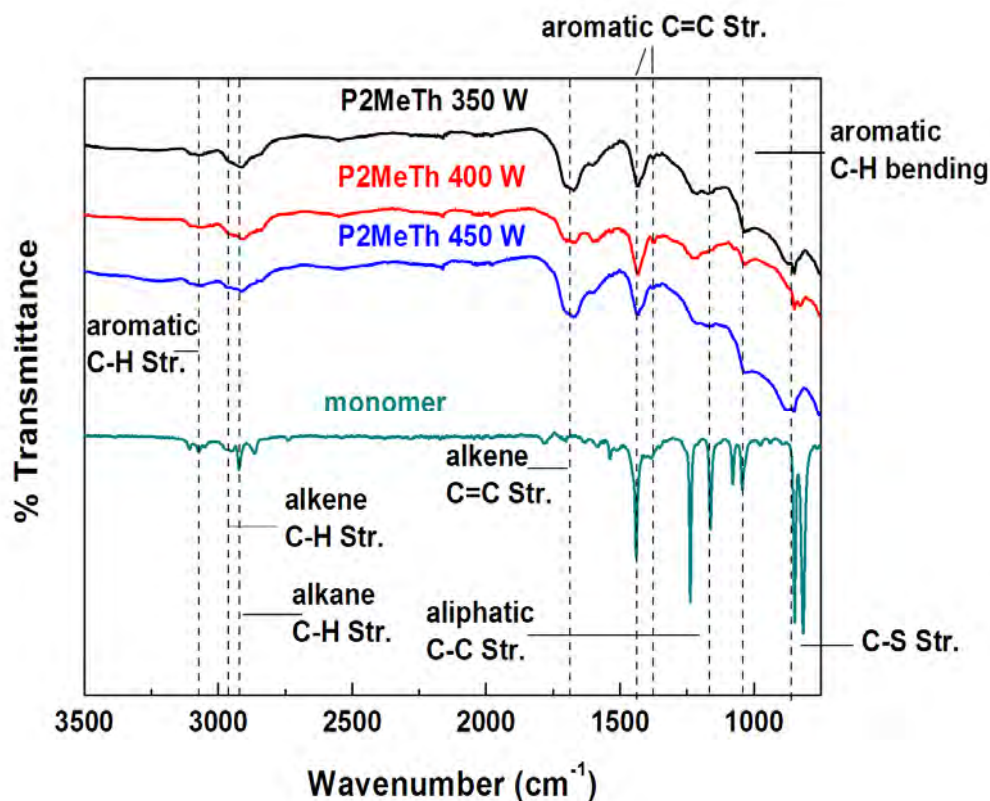


Figure 4.3 ATR-FTIR spectra of 2-methylthiophene monomer, chemically-synthesized and plasma-polymerized P2MeTh at different MW power.

Table 4.2 ATR-FTIR spectra of monomer and P2MeTh prepared from plasma polymerization at different MW power.

Assignments	Wavenumber (cm ⁻¹)	
	2-methylthiophene monomer	plasma- polymerized P2MeTh
aromatic C-H stretching	3073	3072
alkene C-H stretching	-	2960
alkane C-H stretching	2921	2921
C=C stretching	-	1672
C=C ring stretching	1440, 1381	1438, 1374
C-C stretching	1237	1162
C-H aromatic bending	1043	1042
C-S stretching	815	848

In conclusion, plasma deposition of P2MeTh and P3MeTh leads to many defects such as unintended cross-linking and degradation of the monomer structure with the formation of alkene functions. This is consistent with the results obtained in the literature report which is prepared by plasma-polymerized of thiophene and 3-methylthiophene [4].

4.2.1.2 Elemental composition

EDS analysis was performed to determine the chemical composition of the films as shown in **Table 4.3**. In this study, the elemental compositions of plasma-polymerized films were compared with the theoretical value of monomer (from the atomic ratio of carbon to sulfur (C/S)). In this case, a C/S ratio close to the theoretical value of that of the monomer (5/1) would indicate that the plasma-polymerized films was not much damaged. The C/S ratios of plasma-polymerized P3MeTh prepared at 350 and 400 W are equal to the theoretical values. The C/S ratio of plasma-polymerized P3MeTh is higher than theoretical value when microwave power is increase to 450 W. This is suggestive of a decrease in sulfur content from the main structure. It is noteworthy that as the microwave power increased, the C/S ratio is higher. This is highly possible since a more energetic plasma environment may be experienced by the existing film. Moreover, C-C and C=C bonds are stronger (290 and 720 kJ mol⁻¹, respectively) than the C-S bond (272 kJ mol⁻¹). Therefore, the C-S bond is relatively more easily broken. The effect of the microwave power employed on the C/S ratio may be explained by the increase in electron density with increasing power input. At higher power input more electrons with adequate energy to break the C-S bond attack the already deposited poly(3-methylthiophene) layer which resulted in a higher C/S ratio. This indicates that the partial fragmentation occurred in the thiophene ring. The effect of the microwave power employed on the C/S ratio is explained by the increase in electron density and the number of collisions between electrons and other plasma species [12]. However, when compared to the case of the unsubstituted polythiophene, the degree of fragmentation is lower [13]. It can be implied that, the 3-methylthiophene monomer is thiophene derivative with electron-donating group, it can be achieved with good retention of the C/S ratio of the monomer.

Table 4.3 The elemental composition of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh.

MW Power (W)	C/S in	
	plasma-polymerized P2MeTh	plasma-polymerized P3MeTh
350	4.2	5.0
400	3.9	5.1
450	4.6	6.8

In contrast, the C/S ratio of plasma-polymerized P2MeTh (3.9-4.6) is lower than the theoretical value (5/1). This is indicative of a decrease in carbon content from the main structure. This may result in 2-methylthiophene lost their methyl group with formation of thenyl fragments which stabilize mainly to thiophene as shown in **Figure 4.4** [43].

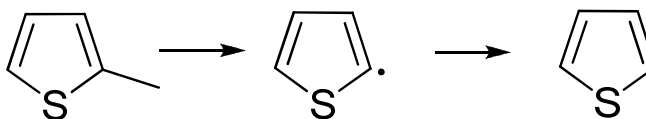


Figure 4.4 Elimination of the alkyl group with formation of thenyl fragments which stabilize mainly to thiophene [43].

In this case, a C/S ratio is similar to the theoretical value of the thiophene monomer (4/1) which corresponds to the ratio of plasma-polymerized P2MeTh at MW power of 350 and 400 W. But at MW power 450 W, the C/S ratio of plasma-polymerized P2MeTh is higher than the C/S ratio of thiophene monomer. This means that thiophene ring is broken during plasma polymerization. The effect of plasma polymerization maybe has C-S bond broken and the increase in electron density may result in an increase in the number of collisions between electrons and other plasma species.

Because of the reactive species (radicals, ions, and electrons) present in the plasma, it is difficult to predict the chemical structure of a surface deposited *via* plasma polymerization technique. For plasma-polymerized P3MeTh, the C/S ratio is equal to or higher than theoretical value (5/1), while for the plasma-polymerized P2MeTh the C/S ratio is lower than expected from theory.

4.2.1.3 Film morphology

Surface morphology and film thickness were observed by Scanning Electron Microscope (SEM). The plasma-polymerized P2MeTh and plasma-polymerized P3MeTh films have worm structure as shown in **Figure 4.5**. In the plasma-polymerized P2MeTh, the size of the worm structure increase with the higher MW power. As the microwave power increased in plasma-polymerized P3MeTh, the uniform surface increasing. Fabricated plasma-polymerized P2MeTh and plasma-polymerized P3MeTh films were formed in the 2.48-3.67 and 2.67-3.08 μm thickness range, respectively. The thickness of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh films are significantly affected by microwave power. The deposition rate is increased with microwave power increasing as shown in **Table 4.4**.

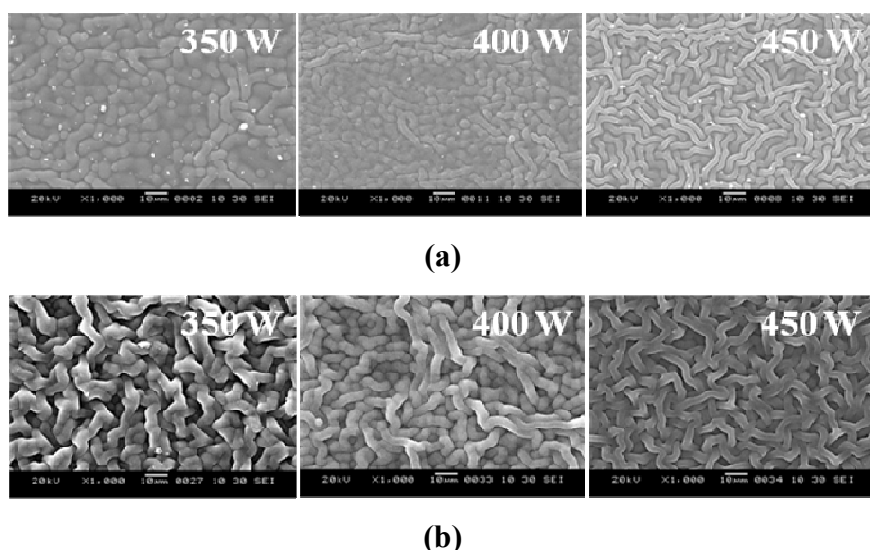


Figure 4.5 The surface morphology of plasma-polymerized films on the glass substrate at various MW power (a) plasma-polymerized P2MeTh and (b) plasma-polymerized P3MeTh.

Table 4.4 The film thickness of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh at various MW power.

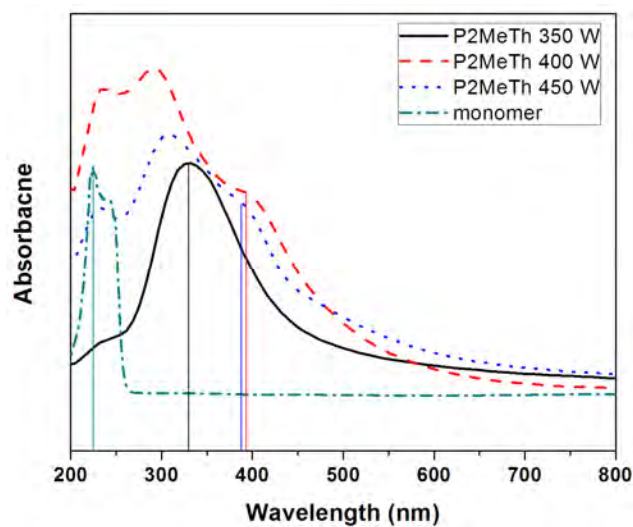
MW power (W)	Thickness (μm)	
	plasma-polymerized P2MeTh	plasma-polymerized P3MeTh
350	2.48	2.68
400	2.84	2.67
450	3.67	3.08

4.2.1.4 Optical characteristics

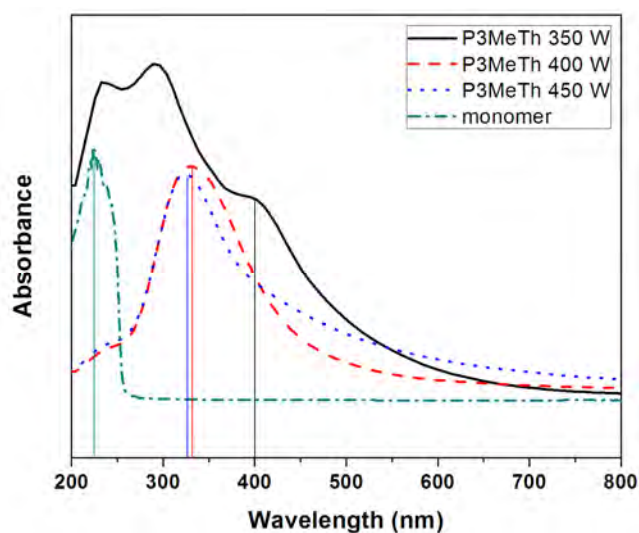
The UV-Vis maximum absorption (λ_{max}) of 2-methylthiophene monomer, plasma-polymerized P2MeTh, 3-methylthiophene monomer and plasma-polymerized P3MeTh films are shown in **Figure 4.6** and summarized in **Table 4.5**. The maxima absorption of the 2-methylthiophene monomer and 3-methylthiophene monomer which are attributed to π - π^* transition are observed at around 224 and 225 nm, respectively and the λ_{max} of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh are around 329-388 and 326-400 nm, respectively. The λ_{max} of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh are higher than those of the monomer. This is suggestive of a longer π -electron conjugation length in the plasma-polymerized P2MeTh and plasma-polymerized P3MeTh films which resulted in a red shift. The λ_{max} of plasma-polymerized P3MeTh has been shown here that as microwave power decreased, an absorption was observed at relatively longer wavelength. In the plasma-polymerized P2MeTh, the microwave power can affect λ_{max} . The higher the microwave power, the higher the λ_{max} .

Table 4.5 λ_{max} of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh.

MW power (W)	λ_{max} (nm)	
	plasma-polymerized P2MeTh	plasma-polymerized P3MeTh
350	329	400
400	388	332
450	380	326



(a)

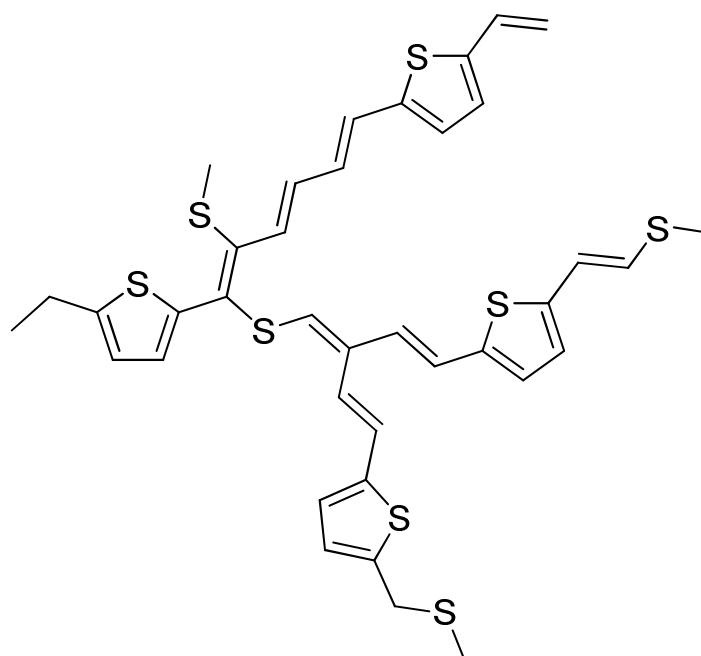


(b)

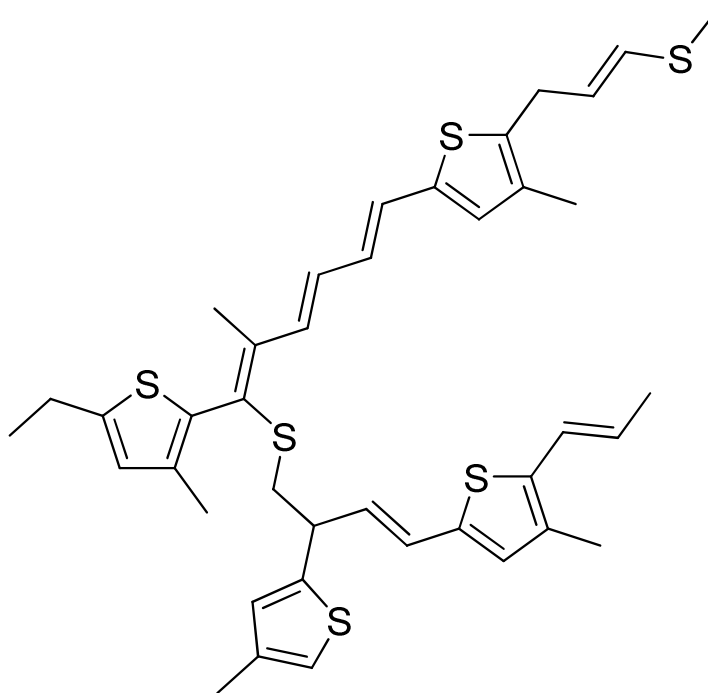
Figure 4.6 The UV-Vis absorbance spectra of; (a) 2-methylthiophene monomer and plasma-polymerized P2MeTh, (b) 3-methylthiophene monomer and plasma-polymerized P3MeTh.

From ATR-FTIR spectra and EDS, it is possible that a small degree of the thiophene ring might have been decomposed to some extension in the plasma-polymerized films. Summarizing these results, **Figure 4.7** shows a structure model of

plasma-polymerized P2MeTh and plasma-polymerized P3MeTh estimated from ATR-FTIR spectra and EDS analysis data.



(a)



(b)

Figure 4.7 Proposed structures of (a) plasma-polymerized P2MeTh and (b) plasma polymerized P3MeTh.

4.2.1.5 Electrical conductivity

The conductivity of the plasma-polymerized films deposited on glass slide were measured using a two-probe method. The I - V characteristics were measured between 0 to 100 V. The typical plot for current versus voltage is depicted in **Figure 4.8**.

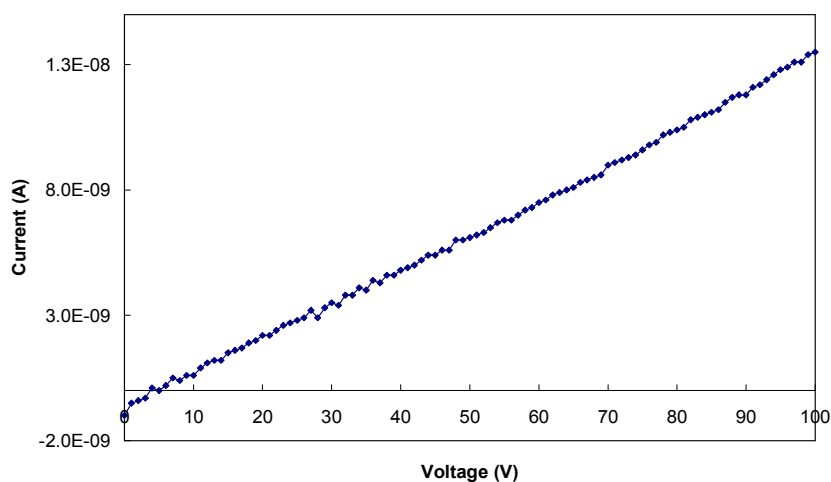


Figure 4.8 The plot of current versus voltage at room temperature.

In this study I - V characteristic shows linearity which obeys Ohmic's law. The conductivity of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh are in range 1.04×10^{-8} to 1.20×10^{-7} S/cm and 1.05×10^{-7} to 2.01×10^{-7} S/cm, respectively as summarized in **Table 4.6**.

Table 4.6 Electrical conductivity of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh.

MW Power (W)	Conductivity (S/cm)	
	plasma-polymerized P2MeTh	plasma-polymerized P3MeTh
350	1.20×10^{-7}	2.01×10^{-7}
400	1.04×10^{-8}	2.00×10^{-7}
450	3.71×10^{-8}	1.05×10^{-7}

The conductivity of plasma-polymerized P3MeTh are higher than plasma-polymerized P2MeTh in all MW power. However, it seems that the relation of MW power, C/S ratio, and λ_{\max} cannot be used to predict the conductivity of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh. This shows that other effects impaired by the substituents also have an effect on the conductivity such as coplanarity of thiophene rings. Example of this reason is shown in **Figure 4.9**. The steric incumbent between adjacent R groups on thienyl units 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.

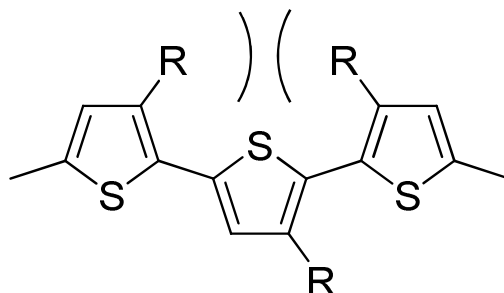


Figure 4.9 Steric induced structural twisting in poly(3-alkylthiophene).

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 coplanarity as shown in **Figure 4.10**. Twisting of polymer chain would also cause the reduction of conjugation in the polymer.

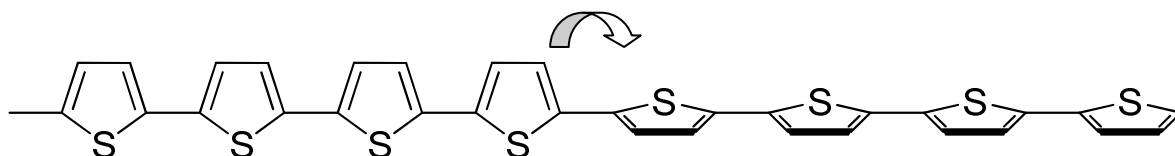


Figure 4.10 Twisting of polythiophene.

For comparison purposes, reported electrical conductivity values of conventional chemically-synthesized, electrochemically-synthesized poly(3-

methylthiophene) and other plasma-polymerized poly(3-methylthiophene) are tabulated and shown in **Table 4.7**.

Table 4.7 Compare the electrical conductivity of poly(3-methylthiophene) by different plasma polymerization methods.

Polymerization process	Conductivity (S/cm)	Ref
MW plasma	1.05×10^{-7} to 2.01×10^{-7}	
AF plasma	1.78×10^{-7}	[45]
RF plasma	7.89×10^{-10}	[45]
Electrochemical	9.1×10^{-5}	[45]
Chemical	1×10^{-9}	[30]

4.3 Preparation of *in situ* iodine-doped plasma polymerized poly(2-methylthiophene) and poly(3-methylthiophene)

The color of the *in situ* iodine-doped plasma-polymerized poly(2-methylthiophene) (P2MeTh/I₂) and *in situ* iodine-doped plasma-polymerized poly(3-methylthiophene) (P3MeTh/I₂) films were resulted in dark-brown films on the glass slide substrates (**Figure 4.11**). The films were synthesized only at MW power 450 W. This was accounted for by the fact that while iodine was introduced in the chamber, the pressure of the system increased. As a result, higher microwave power must be applied in order to generate plasma.

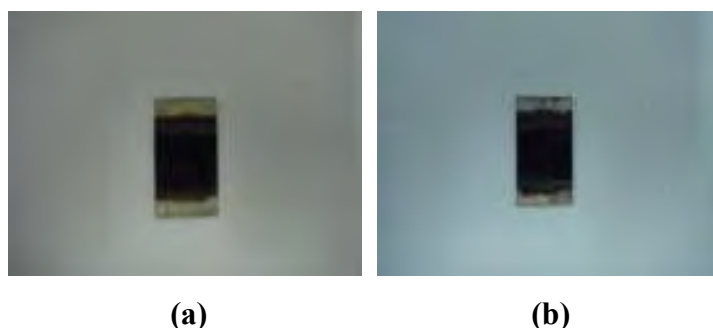


Figure 4.11 Examples of *in situ* iodine-doped plasma-polymerized films by microwave plasma polymerization (a) poly(2-methylthiophene) and (b) poly(3-methylthiophene).

OES technique was carried out to analyze the plasma phase to verify that iodine species were present. OES spectra taken at 450 W during the fabrication of P2MeTh/I₂ and P3MeTh/I₂ are as shown in **Figure 4.12** and the position of iodine peaks were observed at 804.34, 885.64, 890.09, 902.18, 905.88, 911.30, 933.67 and 973.33 [13].

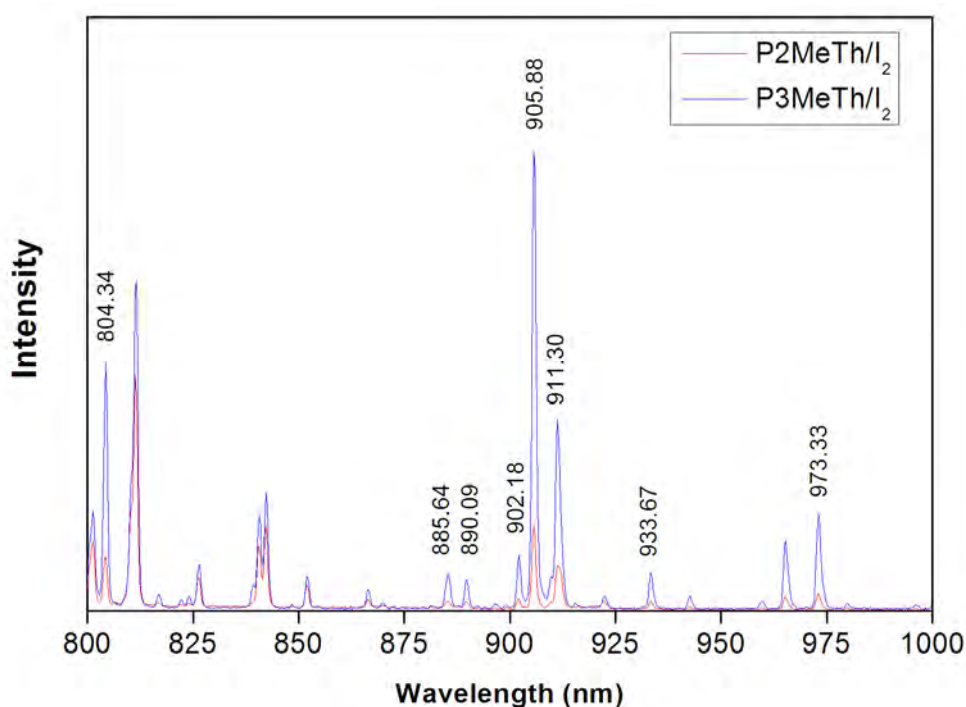


Figure 4.12 OES spectra of P2MeTh/I₂ and P3MeTh/I₂.

4.3.1 Film characterization

4.3.1.1 Functional groups and chemical characteristics

The P2MeTh/I₂ and P3MeTh/I₂ were compared in **Figure 4.13**. Many reactions with iodine may occur during the *in situ* doping process. This may also result in an even more amorphous structure of the films. The spectra of the P2MeTh/I₂ and P3MeTh/I₂ films shows nearly similar to undoped films. Consequently, the ATR-FTIR spectra are broad. However, attempts are made here to identify some transmittance which might be suggestive of certain structural features related to incorporation of iodine in the films. For instance, the new transmittance band around 1540-1590 cm⁻¹ may be described as -CH₂I or -CI=CH₂ groups.

In the plasma process, numerous different fragments, for instance radicals ions, *etc.* could be generated. Therefore, complex chemical structures of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh are not totally unforeseen. Moreover, many reactions with iodine may occur during the *in situ* doping process. Iodine probably reacted with iodine residual radicals in the plasma-polymerized P2MeTh and plasma-polymerized P3MeTh films. In addition, iodine radicals may be able to remove hydrogen atom from thiophene structures because the aromatic structure can stabilize the resulting radical.

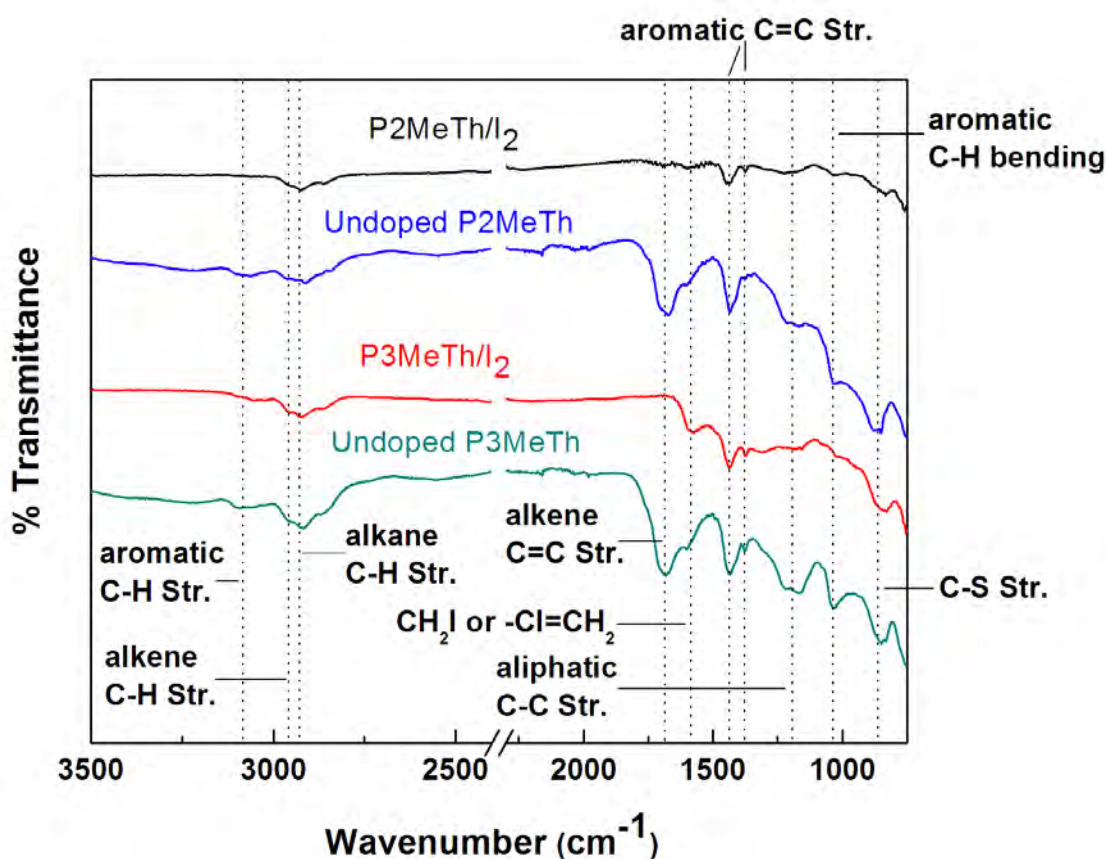
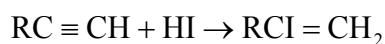
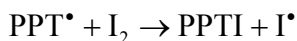


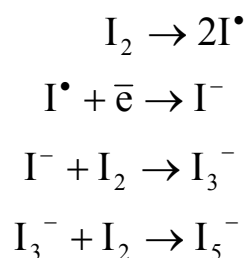
Figure 4.13 ATR-FTIR spectra of P2MeTh/I₂ and P3MeTh/I₂ at 450 W.

Subsequently, the so-formed HI can react with C≡C as evident from a report by Groenewoud as shown in equations below. The radical on the thiophene structure can in its react with other iodine radicals to form mono-substituted thiophene, *etc.* [7].



4.3.1.2 Elemental composition

EDS indicates the presence of iodine in the *in situ* doping. The atomic percentage of iodine in P2MeTh/I₂ and P3MeTh/I₂ are 1.53 and 0.62, respectively as shown in **Table 4.8**. It was proposed by Groenewoud [7] that when the iodine vapor suffers the plasma, many reactions with iodine may occur such as iodine radical. An iodine radical can then capture an electron from plasma environment resulting in the formation of monoiodine ion (I⁻). Even with the detection of the I⁻ ion, it was found that I₃⁻ and I₅⁻ are the most important forms.



This is a good correspond with the ATR-FTIR result that the iodine partly makes chemical bonding with film.

Table 4.8 The elemental composition of P2MeTh/I₂ and P3MeTh/I₂.

MW Power (W)	C/S in		Iodine content (%)	
	P2MeTh/I ₂	P3MeTh/I ₂	P2MeTh/I ₂	P3MeTh/I ₂
450	4.4	5.5	1.53	0.62
450 (undoped)	4.6	6.8	-	-

Lower C/S elemental compositions were found in the case of *in situ* iodine-doped plasma-polymerized poly(2-methylthiophene) and *in situ* iodine-doped plasma-polymerized poly(3-methylthiophene) compared those of undoped plasma-polymerized P2MeTh (4.6) and plasma-polymerized P3MeTh (6.8). It is proposed that the decrease is a result of an impact of a large iodine atom on some of the thiophene ring in the gas phase during plasma polymerization.

4.3.1.3 Film morphology

The P2MeTh/I₂ and P3MeTh/I₂ films were found to be 0.93 and 1.04 μm, respectively by SEM analysis. P2MeTh/I₂ and P3MeTh/I₂ films were obtained as thinner film and smoother surface (**Figure 4.14**) compared to undoped films. This may be attributed to be the result of iodine impact upon the polymer chains.

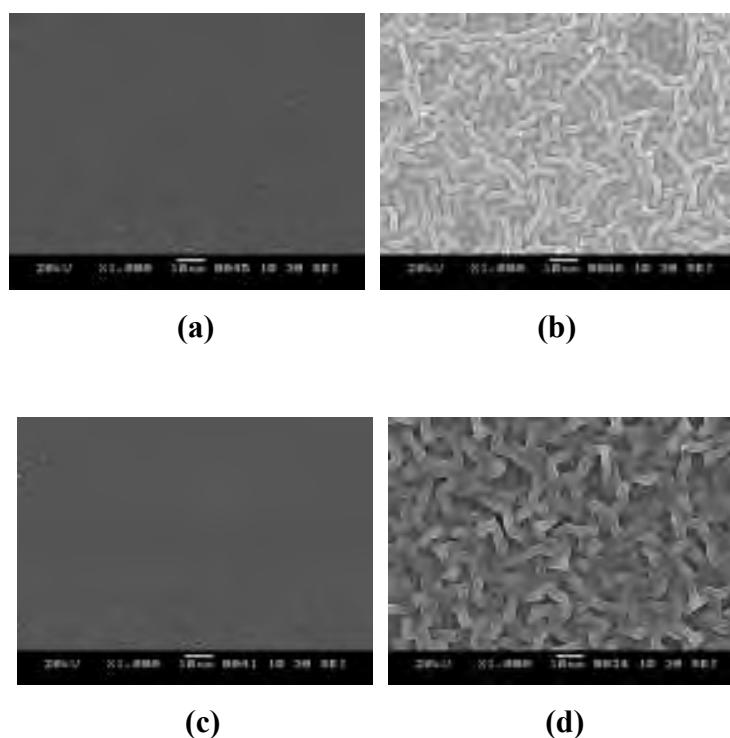


Figure 4.14 Morphology of *in situ* iodine-doped plasma-polymerized films and undoped plasma-polymerized films at 450 W (a) P2MeTh/I₂, (b) P2MeTh, (c) P3MeTh/I₂, and (d) P3MeTh.

4.3.1.4 Optical characteristics

The maximum absorption of P2MeTh/I₂ and P3MeTh/I₂ at 450 W were observed at 395 and 544 nm, respectively as shown in **Figure 4.15**. The λ_{\max} of P2MeTh/I₂ and P3MeTh/I₂ were shifted to higher wavelength than monomer and undoped films.

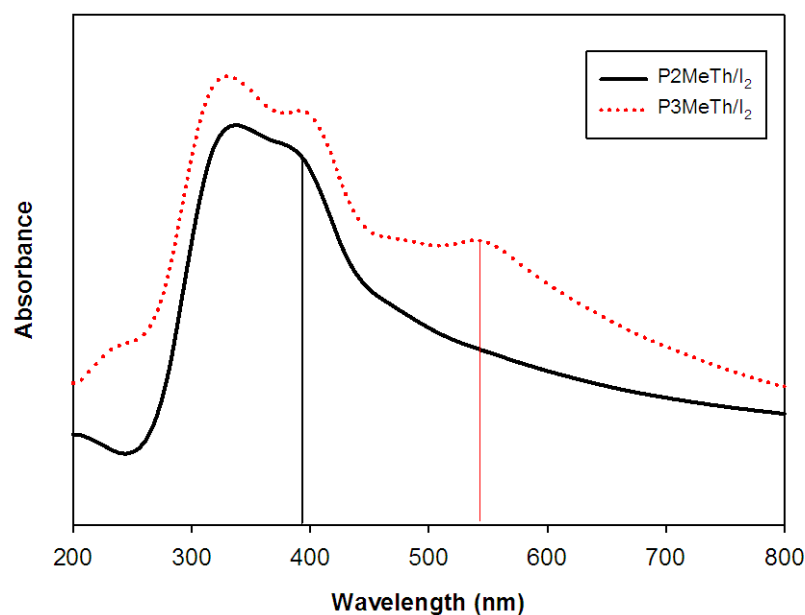


Figure 4.15 The UV-Vis absorption spectra of P2MeTh/I₂ and P3MeTh/I₂.

A red shift to a longer wavelength than those of undoped plasma-polymerized P2MeTh and plasma-polymerized P3MeTh (329-388 and 326-400 nm, respectively) were evident. This confirms the incorporation of iodine in the films. The shift of UV absorption is strongly suggestive of the formation of the (PPT)⁺I⁻ charge-transfer complex. Consequently, an enhanced electrical conductivity was also observed (*vide infra*).

4.3.1.5 Electrical conductivity

The conductivity values of P2MeTh/I₂ is 2.29×10^{-5} S/cm which is up to three orders of magnitude higher than that of plasma-polymerized P2MeTh (3.71×10^{-8} S/cm) and the conductivity values of P3MeTh/I₂ is 1.85×10^{-5} S/cm which is up to two orders of magnitude higher than that of plasma-polymerized P3MeTh (1.05×10^{-7} S/cm). This result indicated that the *in situ* doping can improve the electrical conductivity of the films. The comparative data of semiconducting polymers prepared by several techniques are summarized in **Table 4.9** and **Table 4.10**.

Table 4.9 Compare the electrical conductivity of iodine-doped poly(3-methylthiophene) by conventional and different plasma polymerization methods.

Polymerization process	Doping method (Doping period)	Conductivity		Ref
		Undoped	Doped	
MW plasma	I ₂ , <i>in situ</i> doping, 2 min	1.05×10^{-7}	1.85×10^{-5}	
Pulsed RF plasma	I ₂ , <i>ex situ</i> doping, 5 min	unspecified	5.6×10^{-4}	[11]
AC plasma	I ₂ , <i>ex situ</i> doping, unspecified	$< 1 \times 10^{-5}$	$< 1 \times 10^{-5}$	[4]
AF plasma	I ₂ , <i>ex situ</i> doping, 5 h	1.78×10^{-7}	1.02×10^{-3}	[45]
RF plasma	I ₂ , <i>ex situ</i> doping, 5 h	7.89×10^{-10}	2.79×10^{-4}	[45]
Electrochemical	I ₂ , <i>ex situ</i> doping unspecified	9.1×10^{-5}	1.02×10^2	[45]
Chemical	I ₂ , <i>ex situ</i> doping, unspecified	1×10^{-9}	1.4×10^1	[30]

Table 4.10 Compare the electrical conductivity of iodine-doped poly(2-methylthiophene) by different plasma polymerization methods.

Polymerization process	Doping method (Doping period)	Conductivity		Ref
		Undoped	Doped	
MW plasma	I ₂ , <i>in situ</i> doping, 2 min	3.71×10^{-8}	2.29×10^{-5}	
Pulsed RF plasma	I ₂ , <i>ex situ</i> doping, 5 min	unspecified	3.16×10^{-4}	[11]

From the literature reports, most of the doping processes were carried out after the synthesis of the films by exposing the films to an iodine vapor in a sealed container at various lengths time [4, 11, 45]. It is obvious that the conductivity of the *ex situ* doping films higher *in situ* doping films. In general it can be seen that in the case of *ex situ* doping, after being doped initial electrical conductivity were exhibited. However, over a period of time, conductivities were reported to decrease to more or less a value of an undoped material [7, 13, 46].

In order to study and compare the difference in the lifetime of doped state of poly(2-methylthiophene) and poly(3-methylthiophene) obtained from different methods, comparison of the conductivity of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh between *in situ* and *ex situ* doping were carried out. For

the *ex situ* doping method, film of P2MeTh and P3MeTh prepared by plasma polymerization at 450 W for 2 minutes were doped by placing them in a sealed container containing iodine crystals for 24 h. A relationship between standing time and conductivity was plotted as depicted in **Figure 4.16**. Conductivity of the films was measured at intervals of time to determine the decreasing rate of conductivity. After the doping process, conductivity of both methods were decreased. It was found that conductivity of the film (*ex situ* doping) rapidly decreased to more or less that of undoped material in approximately 24 h. The decrease in conductivity of *ex situ* doping method is consistent with that diffusion of the adsorbed iodine can occur over time. In the *in situ* doping method the conductivity was decrease in a longer period of time compared to the results obtained from the *ex situ* doping. Therefore, the *in situ* doping had presumably evenly distributed iodine dopant all over the entire bulk of the films. It can be proven that *in situ* doping provides the increased conductivity and high stability for a long time.

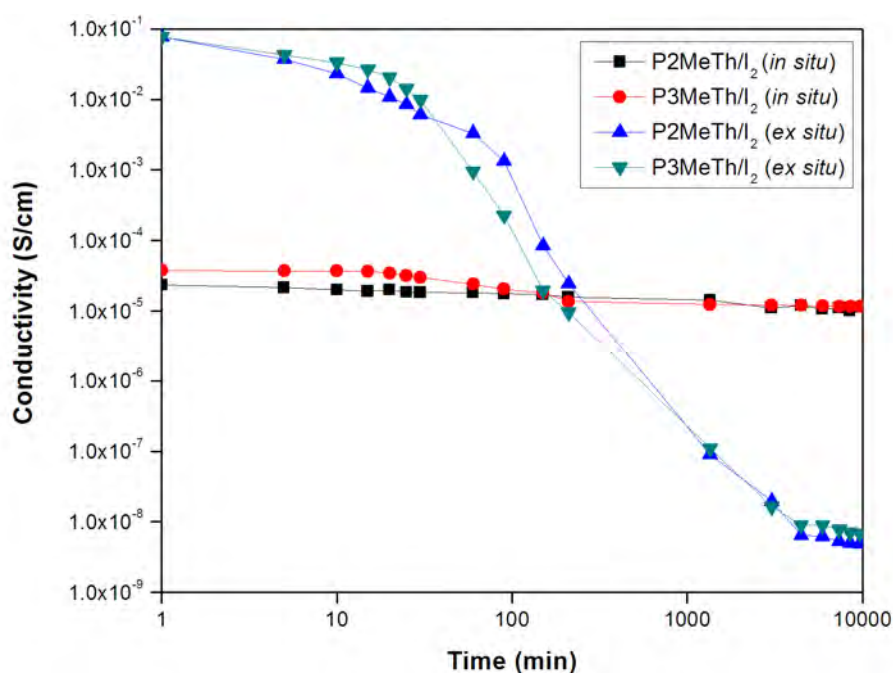


Figure 4.16 A relationship between time and conductivity of the *in situ*- and the *ex situ*- doped films.

4.4 Schottky diode

Polythiophene is a polymer of high environmental stability and can also be used in electronic devices such as diode. In this work, electrical measurement performed on polythiophene based Schottky diodes is used to investigate the electronic properties of the polymer. The I - V characteristics of the prepared Al/plasma-polymerized polythiophene/Al device is shown in **Figure 4.17**. This characteristic is nonlinear, asymmetric, and shows a rectifying behavior. This indicates that polythiophene films prepared from microwave plasma polymerization exhibit properties as Schottky diode.

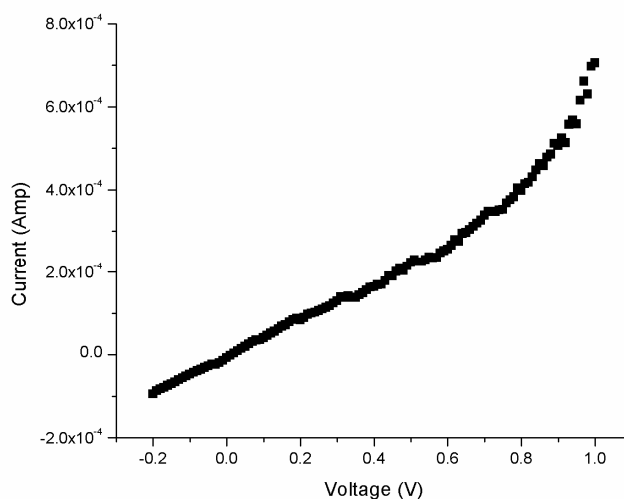


Figure 4.17 Current-voltage characteristics of Al/plasma-polymerized polythiophene/Al.

CHAPTER V

CONCLUSIONS

The syntheses of poly(2-methylthiophene) and poly(3-methylthiophene) were varied the condition of microwave power (350, 400, and 450 W). The effect of microwave power on chemical structure, elemental composition, and electrical conductivity are summarized. The transmittance ATR-FTIR spectra of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh around 3100 cm^{-1} are absent which represent an aromatic =C-H stretching and weaken the band around 850 cm^{-1} assigned to the C-S stretching. This result clearly indicates that the thiophene ring is destructed by plasma polymerization. The elemental compositions of plasma-polymerized P3MeTh have C/S ratio in the range 5.0 to 6.8 which higher than 3-methylthiophene monomer (5.0). For plasma-polymerized P2MeTh, the C/S ratio is in the range 3.9 to 4.6 which lower than expected to 2-methylthiophene monomer (5.0). This may result in 2-methylthiophene lost their methyl group with formation of thenyl fragments which stabilize mainly to thiophene. UV-Vis spectra of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh showed an absorption maximum around 329-388 and 326-400 nm, respectively. The electrical conductivity of are range of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh are in range 1.04×10^{-8} to 1.20×10^{-7} S/cm and 1.05×10^{-7} to 2.01×10^{-7} S/cm, respectively. However, it seems that the relation of MW power, C/S ratio, and λ_{max} cannot be used to predict the conductivity of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh. This shows that other effects impaired by the substituents also have an effect on the conductivity such as coplanarity of thiophene rings.

The *in situ* doping with iodine is a method to increase the electrical conductivity. Firstly, this iodine vapor, initially in the crystal form, and monomer vapor were added into the vacuum chamber. After that, the microwave power was applied in order to generate plasma. Then, the iodine-doped poly(2-methylthiophene)

and poly(3-methylthiophene) film were deposited on a glass substrate. The results from ATR-FTIR and EDS experiments indicated that iodine exists on the poly(2-methylthiophene) and poly(3-methylthiophene) films because of the appearance of $-\text{CH}_2\text{I}$ or $-\text{CI}=\text{CH}_2$ around $1540\text{-}1590\text{ cm}^{-1}$. Moreover, the atomic percentage of iodine in *in situ* iodine-doped plasma-polymerized P2MeTh and plasma-polymerized P3MeTh films are 1.53 and 0.62%, respectively. The *in situ* iodine-doped P2MeTh and *in situ* iodine-doped P3MeTh by microwave plasma polymerization gave products that showed λ_{max} around 395 and 544 nm, respectively. This *in situ* doping is successful at increasing the conductivity. The conductivity of the iodine-doped poly(2-methylthiophene) and iodine-doped poly(3-methylthiophene) films were 2.29×10^{-5} and 1.85×10^{-5} S/cm, respectively.

Moreover, the *in situ* and *ex situ* doping methods were compared to check how stable of the conductivity. The conductivity of *in situ* doped films were lower than of *ex situ* doped films. However, after 24 hours, the conductivity of the product from *ex situ* doping method was almost totally lost whereas the one from *in situ* method still has high conductivity. This result has revealed that the *in situ* doping method is more stable than conventional doping method.

The *I-V* characteristics of Al/plasma-polymerized polythiophene/Al diode demonstrated nonlinear behavior. This indicates that polythiophene films prepared from microwave plasma polymerization exhibit properties as Schottky diode.

In the future, the process of microwave plasma polymerization could be optimized by varying some parameters, such as pressure, reaction time, flow rate of feed gas, and so on since these parameters might affect the elemental composition of material and fragmentation during deposition. In the doping step, the starting materials (dopant) and the method for doping could be also optimized in order to obtain the highest electrical conductivity. From the literature report, the use of plasma treatment technique after the doping process (*ex situ*) was investigated and results showed that this technique improve both the conductivity and stability of iodine doped films [47]. This suggests that in the future the plasma treatment technique could be performed to keep the films' conductivity as high and long as possible.

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APPENDICES

APPENDIX A
Elemental composition of samples determined by
Energy-Dispersive X-Ray Spectroscopy (EDS)

Table A.1 The elemental composition of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh.

Condition	Carbon content (%)			Sulfur content (%)			C/S
	Set 1	Set 2	Average	Set 1	Set 2	Average	
Power							
Monomer							
	(W)						
350	80.26	81.14	80.70	19.74	18.86	19.30	4.07 4.30 4.2
400	80.84	77.87	79.36	19.16	22.13	20.56	4.22 3.52 3.9
450	81.56	82.26	81.91	18.44	16.93	17.68	4.42 4.86 4.6
350	83.58	82.82	83.20	16.42	17.18	16.80	5.09 4.82 5.0
400	84.62	82.52	83.57	15.38	17.48	16.43	5.50 4.72 5.1
450	88.98	84.51	86.74	11.02	15.49	12.83	8.07 5.46 6.8

Data was obtained using an OXFORD, INCA X-sight 7573 spectrometer.

Table A.2 The elemental composition of *in situ* iodine-doped plasma-polymerized P2MeTh and *in situ* iodine-doped plasma-polymerized P3MeTh.

Condition	Carbon content (%)			Sulfur content (%)			C/S			Iodine content (%)			
	Monomer	Set 1	Set 2	Average	Set 1	Set 2	Average	Set 1	Set 2	Average	Set 1	Set 2	Average
2-MeTh	450	80.72	79.20	80.12	17.06	19.96	18.20	4.73	3.97	4.4	2.22	0.84	1.53
3-MeTh	450	81.21	86.22	83.72	18.08	13.26	15.22	4.49	6.50	5.5	0.71	0.52	0.62

Data was obtained using an OXFORD, INCA X-sight 7573 spectrometer.

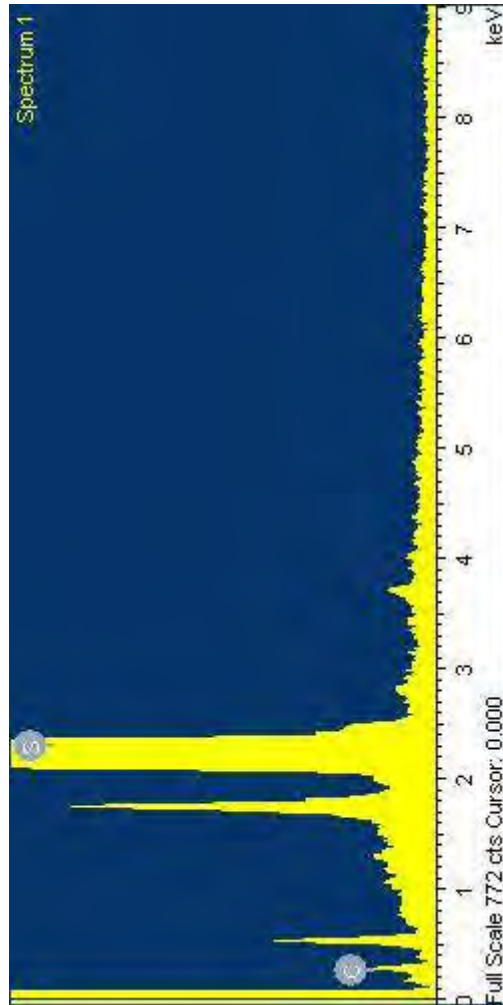


Figure A.1 EDS spectra of plasma-polymerized P2MeTh at 450 W.

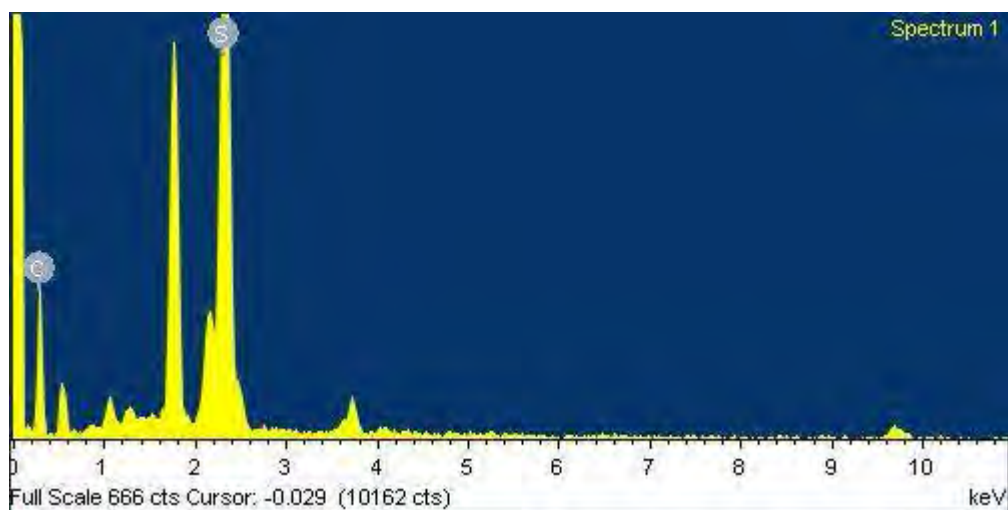


Figure A.2 EDS spectra of plasma-polymerized P3MeTh at 450 W.

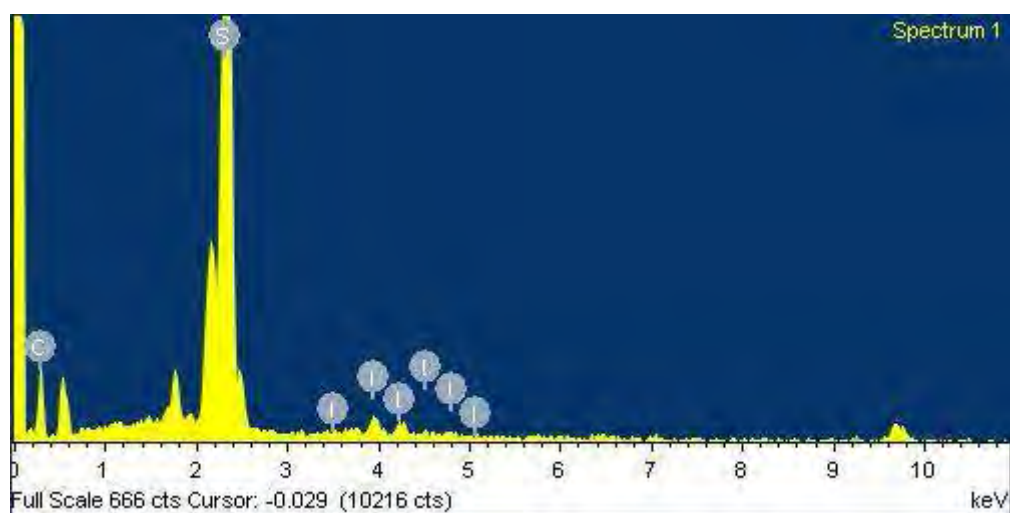


Figure A.3 EDS spectra of I₂ doped plasma-polymerized P2MeTh at 450 W

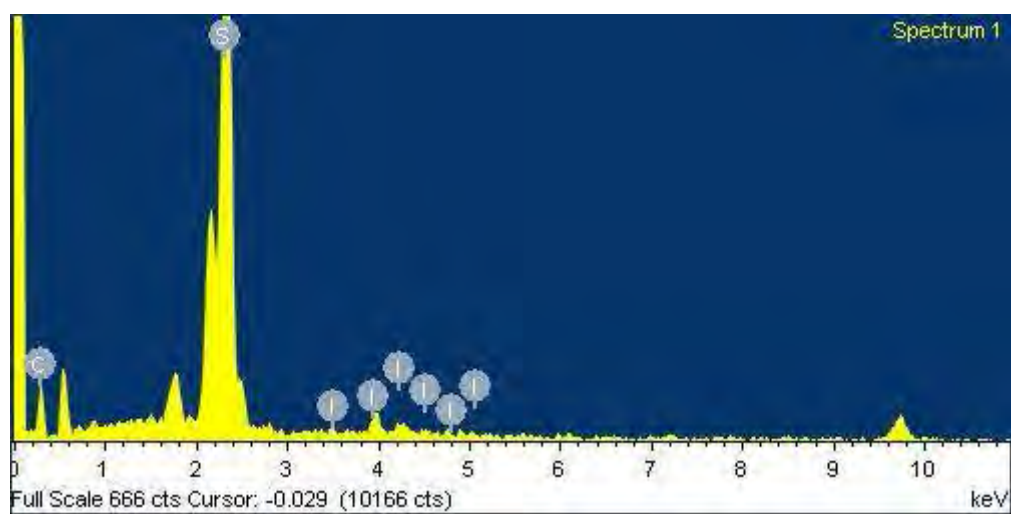


Figure A.4 EDS spectra of I₂ doped plasma-polymerized P3MeTh at 450 W.

APPENDIX B

Electrical Conductivity of Samples

Table B.1 Electrical conductivity of plasma-polymerized P2MeTh and plasma-polymerized P3MeTh.

Condition		Resistivity ($\Omega\cdot\text{cm}$)		Conductivity (S/cm)		
Monomer	Power (W)	Set 1	Set 2	Set 1	Set 2	Average
2-MeTh	350	7.04×10^6	1.02×10^7	1.42×10^{-7}	9.83×10^{-8}	1.20×10^{-7}
	400	8.70×10^7	1.08×10^8	1.15×10^{-8}	9.27×10^{-9}	1.04×10^{-8}
	450	1.40×10^7	3.45×10^8	7.14×10^{-8}	2.90×10^{-9}	3.71×10^{-8}
3-MeTh	350	6.80×10^6	3.92×10^6	1.47×10^{-7}	2.55×10^{-7}	2.01×10^{-7}
	400	7.09×10^6	3.86×10^6	1.41×10^{-7}	2.59×10^{-7}	2.00×10^{-7}
	450	7.35×10^6	1.33×10^7	1.36×10^{-7}	7.51×10^{-8}	1.05×10^{-7}

Table B.2 Electrical conductivity of iodine-doped plasma-polymerized P2MeTh and iodine-doped plasma-polymerized P3MeTh (*in situ* doping).

Condition		Resistivity ($\Omega\cdot\text{cm}$)		Conductivity (S/cm)		
Monomer	Power (W)	Set 1	Set 2	Set 1	Set 2	Average
2-MeTh	450	5.52×10^4	5.26×10^4	1.81×10^{-5}	1.90×10^{-5}	1.85×10^{-5}
3-MeTh	450	4.46×10^4	4.26×10^4	2.24×10^{-5}	2.35×10^{-5}	2.29×10^{-5}

Table B.3 Electrical conductivity of iodine-doped plasma-polymerized P2MeTh (*in situ* doping) at 450 W for 2 minutes.

Time (min)	Resistivity ($\Omega\cdot\text{cm}$)		Conductivity (S/cm)		
	Set 1	Set 2	Set 1	Set 2	Average
0	4.33×10^4	4.22×10^4	2.31×10^{-5}	2.37×10^{-5}	2.34×10^{-5}
5	4.59×10^4	4.76×10^4	2.18×10^{-5}	2.10×10^{-5}	2.14×10^{-5}
10	5.21×10^4	4.81×10^4	1.92×10^{-5}	2.08×10^{-5}	2.00×10^{-5}
15	5.35×10^4	5.18×10^4	1.87×10^{-5}	1.93×10^{-5}	1.90×10^{-5}
20	5.13×10^4	4.98×10^4	1.95×10^{-5}	2.01×10^{-5}	1.98×10^{-5}
25	5.52×10^4	5.29×10^4	1.81×10^{-5}	1.89×10^{-5}	1.85×10^{-5}
30	5.55×10^4	5.38×10^4	1.80×10^{-5}	1.86×10^{-5}	1.83×10^{-5}
60	5.62×10^4	5.49×10^4	1.78×10^{-5}	1.82×10^{-5}	1.80×10^{-5}
90	5.78×10^4	5.59×10^4	1.73×10^{-5}	1.79×10^{-5}	1.76×10^{-5}
150	5.81×10^4	5.75×10^4	1.72×10^{-5}	1.74×10^{-5}	1.70×10^{-5}
210	6.54×10^4	6.13×10^4	1.53×10^{-5}	1.63×10^{-5}	1.58×10^{-5}
1350	7.14×10^4	6.85×10^4	1.40×10^{-5}	1.46×10^{-5}	1.43×10^{-5}
3030	8.77×10^4	7.94×10^4	1.14×10^{-5}	1.26×10^{-5}	1.20×10^{-5}
4470	9.26×10^4	8.77×10^4	1.08×10^{-5}	1.14×10^{-5}	1.11×10^{-5}
5910	9.80×10^4	9.09×10^4	1.02×10^{-5}	1.10×10^{-5}	1.06×10^{-5}
7350	9.26×10^4	8.93×10^4	1.08×10^{-5}	1.12×10^{-5}	1.10×10^{-5}
8490	1.02×10^5	9.80×10^4	9.80×10^{-6}	1.02×10^{-5}	1.00×10^{-5}
9630	9.17×10^4	8.70×10^4	1.09×10^{-5}	1.15×10^{-5}	1.12×10^{-5}

Table B.4 Electrical conductivity of iodine-doped plasma-polymerized P3MeTh (*in situ* doping) at 450 W for 2 minutes.

Time (min)	Resistivity ($\Omega\cdot\text{cm}$)		Conductivity (S/cm)		
	Set 1	Set 2	Set 1	Set 2	Average
0	2.67×10^4	2.63×10^4	3.74×10^{-5}	3.80×10^{-5}	3.77×10^{-5}
5	2.73×10^4	2.67×10^4	3.66×10^{-5}	3.74×10^{-5}	3.70×10^{-5}
10	2.75×10^4	2.69×10^4	3.64×10^{-5}	3.72×10^{-5}	3.68×10^{-5}
15	2.75×10^4	2.74×10^4	3.63×10^{-5}	3.65×10^{-5}	3.64×10^{-5}
20	2.94×10^4	2.89×10^4	3.40×10^{-5}	3.46×10^{-5}	3.43×10^{-5}
25	3.16×10^4	3.09×10^4	3.16×10^{-5}	3.24×10^{-5}	3.20×10^{-5}
30	3.39×10^4	3.28×10^4	2.95×10^{-5}	3.05×10^{-5}	3.00×10^{-5}
60	4.22×10^4	4.15×10^4	2.37×10^{-5}	2.41×10^{-5}	2.39×10^{-5}
90	5.05×10^4	4.76×10^4	1.98×10^{-5}	2.10×10^{-5}	2.04×10^{-5}
150	5.65×10^4	5.41×10^4	1.77×10^{-5}	1.85×10^{-5}	1.81×10^{-5}
210	7.41×10^4	7.30×10^4	1.35×10^{-5}	1.37×10^{-5}	1.36×10^{-5}
1350	8.33×10^4	7.81×10^4	1.20×10^{-5}	1.28×10^{-5}	1.24×10^{-5}
3030	8.55×10^4	8.00×10^4	1.17×10^{-5}	1.25×10^{-5}	1.21×10^{-5}
4470	8.62×10^4	8.06×10^4	1.16×10^{-5}	1.24×10^{-5}	1.20×10^{-5}
5910	8.70×10^4	8.26×10^4	1.15×10^{-5}	1.21×10^{-5}	1.18×10^{-5}
7350	8.77×10^4	8.47×10^4	1.14×10^{-5}	1.18×10^{-5}	1.16×10^{-5}
8490	8.62×10^4	8.47×10^4	1.16×10^{-5}	1.18×10^{-5}	1.17×10^{-5}
9630	8.77×10^4	8.62×10^4	1.14×10^{-5}	1.16×10^{-5}	1.15×10^{-5}

Table B.5 Electrical conductivity of plasma-polymerized P2MeTh at 450 W for 2 minutes and iodine *ex situ* doping for 24 hours.

Time (min)	Resistivity ($\Omega\cdot\text{cm}$)		Conductivity (S/cm)		
	Set 1	Set 2	Set 1	Set 2	Average
0	1.30×10^1	1.29×10^1	7.70×10^{-2}	7.76×10^{-2}	7.73×10^{-2}
5	2.75×10^1	2.67×10^1	3.64×10^{-2}	3.74×10^{-2}	3.69×10^{-2}
10	4.41×10^1	4.29×10^1	2.27×10^{-2}	2.33×10^{-2}	2.30×10^{-2}
15	7.14×10^1	6.67×10^1	1.40×10^{-2}	1.50×10^{-2}	1.45×10^{-2}
20	9.43×10^1	9.09×10^1	1.06×10^{-2}	1.10×10^{-2}	1.08×10^{-2}
25	1.19×10^2	1.18×10^2	8.41×10^{-3}	8.51×10^{-3}	8.46×10^{-3}
30	1.65×10^2	1.64×10^2	6.05×10^{-3}	6.09×10^{-3}	6.07×10^{-3}
60	3.05×10^2	2.99×10^2	3.28×10^{-3}	3.34×10^{-3}	3.31×10^{-3}
90	7.69×10^2	7.35×10^2	1.30×10^{-3}	1.36×10^{-3}	1.33×10^{-3}
150	1.20×10^4	1.18×10^4	8.36×10^{-5}	8.44×10^{-5}	8.40×10^{-5}
210	4.24×10^4	4.07×10^4	2.36×10^{-5}	2.46×10^{-5}	2.41×10^{-5}
1350	1.11×10^7	1.10×10^7	9.01×10^{-8}	9.11×10^{-8}	9.06×10^{-8}
3030	5.21×10^7	5.05×10^7	1.92×10^{-8}	1.98×10^{-8}	1.95×10^{-8}
4470	1.54×10^8	1.53×10^8	6.48×10^{-9}	6.54×10^{-9}	6.51×10^{-9}
5910	1.62×10^8	1.60×10^8	6.17×10^{-9}	6.25×10^{-9}	6.21×10^{-9}
7350	1.89×10^8	1.85×10^8	5.28×10^{-9}	5.40×10^{-9}	5.34×10^{-9}
8490	2.02×10^8	1.98×10^8	4.96×10^{-9}	5.04×10^{-9}	5.00×10^{-9}
9630	2.05×10^8	2.03×10^8	4.87×10^{-9}	4.93×10^{-9}	4.90×10^{-9}

Table B.6 Electrical conductivity of plasma-polymerized P3MeTh at 450 W for 2 minutes and iodine *ex situ* doping for 24 hours.

Time (min)	Resistivity ($\Omega\cdot\text{cm}$)		Conductivity (S/cm)		
	Set 1	Set 2	Set 1	Set 2	Average
0	1.32×10^1	1.31×10^1	7.58×10^{-2}	7.66×10^{-2}	7.62×10^{-2}
5	2.36×10^1	2.33×10^1	4.24×10^{-2}	4.30×10^{-2}	4.27×10^{-2}
10	3.04×10^1	2.99×10^1	3.29×10^{-2}	3.35×10^{-2}	3.32×10^{-2}
15	3.83×10^1	3.69×10^1	2.61×10^{-2}	2.71×10^{-2}	2.66×10^{-2}
20	5.05×10^1	4.76×10^1	1.98×10^{-2}	2.10×10^{-2}	2.04×10^{-2}
25	7.19×10^1	6.99×10^1	1.39×10^{-2}	1.43×10^{-2}	1.41×10^{-2}
30	1.03×10^2	1.02×10^2	9.74×10^{-3}	9.82×10^{-3}	9.78×10^{-3}
60	1.05×10^3	1.04×10^3	9.49×10^{-4}	9.57×10^{-4}	9.53×10^{-4}
90	4.55×10^3	4.31×10^3	2.20×10^{-4}	2.32×10^{-4}	2.26×10^{-4}
150	5.21×10^4	5.00×10^4	1.92×10^{-5}	2.00×10^{-5}	1.96×10^{-5}
210	1.05×10^5	1.04×10^5	9.55×10^{-6}	9.59×10^{-6}	9.57×10^{-6}
1350	9.43×10^6	8.77×10^6	1.06×10^{-7}	1.14×10^{-7}	1.10×10^{-7}
3030	6.13×10^7	6.06×10^7	1.63×10^{-8}	1.65×10^{-8}	1.64×10^{-8}
4470	1.12×10^8	1.11×10^8	8.93×10^{-9}	9.01×10^{-9}	8.97×10^{-9}
5910	1.13×10^8	1.12×10^8	8.87×10^{-9}	8.95×10^{-9}	8.91×10^{-9}
7350	1.29×10^8	1.28×10^8	7.77×10^{-9}	7.83×10^{-9}	7.80×10^{-9}
8490	1.44×10^8	1.42×10^8	6.96×10^{-9}	7.04×10^{-9}	7.00×10^{-9}
9630	1.48×10^8	1.46×10^8	6.75×10^{-9}	6.85×10^{-9}	6.80×10^{-9}

VITA

Mr. Pornchai Luyaphand was born on Sunday 21st October, 1984 in Bangkok, Thailand. He finished high school education from Watsuthiwararam School, concentration in Mathematic and Science in 2002. He entered the Department of Chemistry, Faculty of Science, Chulalongkorn University and received a Bachelor of Science Degree in Chemistry in 2006. After graduation, he continued his graduate study at the same university in Petrochemistry and Polymer Science Program, focusing on the plasma polymerization. He will complete his Master of Science Degree in 2011. His current address is 546/41 Soi Sathupradit 40, Sathupradit Road, Bangpongpan, Yannawa, Bangkok, 10120.

Presentation in Conference:

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|----------------|---|
| September 2009 | The 7 th Asian-European International Conference On Plasma Surface Engineering (AEPSE), BEXCO Convention Center, Busan, Korea. |
| March 2010 | Siam Physics Congress, River Kwai village Hotel, Kanchanaburi, Thailand. |
| January 2011 | Pure and Applied Chemistry International Conference (PACCON), Bangkok, Thailand. |