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นางสาวอภิรดี จันทร์เพ็ญ

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

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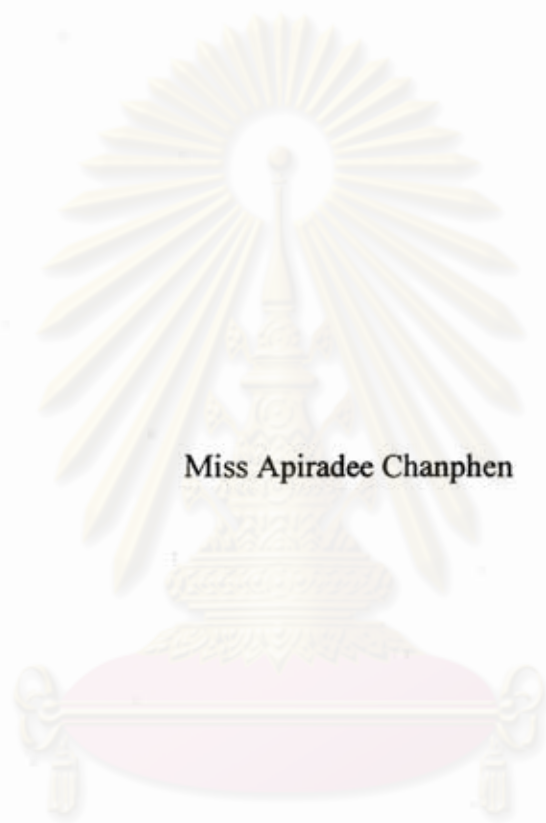
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SYNTHESIS AND POLYMERIZATION OF 3,4-DIALKOXY THIOPHENE



Miss Apiradee Chanphen

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

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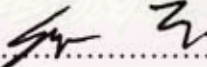
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Thesis Advisor         Assistant Professor Yongsak Sritana-anant, Ph.D.


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Accepted by the Faculty of Science, Chulalongkorn University in Partial  
Fulfillment of the Requirements for the Master's Degree


  
.....Dean of the Faculty of Science  
(Professor Supot Hannongbua, Dr.rer.nat.)

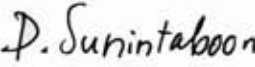
THESIS COMMITTEE

  
.....Chairman  
(Associate Professor Supawan Tantayanon, Ph.D.)

  
.....Thesis Advisor  
(Assistant Professor Yongsak Sritana-anant, Ph.D.)

  
.....Examiner  
(Assistant Professor Varawut Tangpasuthadol, Ph.D.)

  
.....Examiner  
(Assistant Professor Worawan Bhanthumnavin, Ph.D.)

  
.....External Examiner  
(Panya Sunintaboon, Ph.D.)

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พอลิ(3,4-เอทิลีนไดออกซีไทโอเฟน) มีสมบัติการนำไฟฟ้าที่ดี แต่ไม่ละลายในตัวทำละลายอินทรีย์ทั่วไป ทำให้เกิดข้อจำกัดในการนำไปแปรรูปเพื่อใช้งาน พยายามแก้ปัญหานี้โดยเตรียมมอนอเมอร์ชนิดใหม่ที่ปรับเปลี่ยนหมู่แทนที่บนวงไทโอเฟนเพื่อใช้ในการเตรียมพอลิไทโอเฟน ด้วยวิธีพอลิเมอไรเซชันโดยใช้สารเคมีหรือเทคนิคการให้ความร้อนในภาวะของแข็งหรือของเหลว จากปฏิกิริยาโบรมิเนชันของ 3,4-เอทิลีนไดออกซีไทโอเฟน 3,4-ไดเมทอกซีไทโอเฟน 2'-ไฮดรอกซีเมทิล-3,4-เอทิลีนไดออกซีไทโอเฟน (3) ได้ผลิตภัณฑ์ 2,5-ไดโบรโม-3,4-เอทิลีนไดออกซีไทโอเฟน 2,5-ไดโบรโม-3,4-ไดเมทอกซีไทโอเฟน 2'-ไฮดรอกซีเมทิล-2,5-ไดโบรโม-3,4-เอทิลีนไดออกซีไทโอเฟน เท่ากับ 85, 80 และ 72% ตามลำดับ จากปฏิกิริยาการแทนที่ด้วย 2-โบรโมเอทานอลในขั้นตอนต่อมาของ 2,5-ไดโบรโม-3,4-เอทิลีนไดออกซีไทโอเฟนสามารถสังเคราะห์ ได้ผลิตภัณฑ์เป็นอนุพันธ์คราวน์อีเทอร์ฟิวส์ไทโอเฟน (2) ในปริมาณ 22% เมื่อใช้ 3,4-ไดเมทอกซีไทโอเฟนได้เป็นสารตั้งต้นในปฏิกิริยาการแทนที่ในลักษณะอื่น ได้ผลิตภัณฑ์คือ 2'-ไฮดรอกซีเมทิล-3,4-เอทิลีนไดออกซีไทโอเฟน (3) และ 3,4-ไดเบนโซเอทไทโอเฟน (6) ในปริมาณ 20% ทั้ง 2 กรณี ปฏิกิริยาพอลิเมอไรเซชันด้วยสารเคมีของ 3,4-ไดไฮดรอกซีไทโอเฟน (5) ได้ผลิตภัณฑ์พอลิ(3,4-ไดไฮดรอกซีไทโอเฟน) (7) ในปริมาณเท่ากับ 98% ส่วนปฏิกิริยาพอลิเมอไรเซชันโดยใช้ความร้อนของ 2,5-ไดโบรโม-2'-ไฮดรอกซีเมทิล-3,4-เอทิลีนไดออกซีไทโอเฟน ได้ผลิตภัณฑ์พอลิ(2'-ไฮดรอกซีเมทิล-3,4-เอทิลีนไดออกซีไทโอเฟน) (8) เท่ากับ 54%

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา วิศวกรรมเคมีและวิทยาศาสตร์พอลิเมอร์ ภายมือชื่อนิติศ..... อภิรดี จันทร์เพ็ญ.....  
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 KEYWORDS: PEDOT, DIALKOXYTHIOPHENE, SOLID STATE  
 POLYMERIZATION

APIRADEE CHANPHEN: SYNTHESIS AND POLYMERIZATION OF 3,4-DIALKOXY THIOPHENE. THESIS ADVISOR: ASSIST. PROF. YONGSAK SRITANA-ANANT, Ph.D., 93 pp.

Poly(3,4-ethylenedioxythiophene) is acknowledged for its high electrical conductivity but insoluble in common organic solvents, leading to difficulties in fabrication process. In attempts to solve this problem, new monomers were synthesized by modifying the substituents on the thiophene rings. They were used to prepare polythiophene via chemical, thermal solid or liquid state polymerization techniques. Brominations of 3,4-ethylenedioxythiophene, 3,4-dimethoxythiophene, and 2'-hydroxymethyl-3,4-ethylenedioxythiophene provided 2,5-dibromo-3,4-ethylenedioxythiophene, 2,5-dibromo-3,4-dimethoxythiophene, and 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene in 85, 80 and 72% yields, respectively. Subsequent substitutions with 2-bromoethanol on 2,5-dibromo-3,4-ethylenedioxythiophene yielded the crown-ether fused thiophene derivative **2** in 22% yield. When, using 3,4-dimethoxythiophene as the precursor in other substitutions, 2'-hydroxymethyl-3,4-ethylenedioxythiophene **3** and 3,4-dibenzoyloxythiophene **6** could be obtained both in 20% yields. Finally, chemical polymerization of 3,4-dihydroxythiophene **5** and thermal polymerization of 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene provided their corresponding polymers in 98% and 54% yield, respectively.

Field of Study: Petrochemistry and Polymer Science Student's Signature: A. Chanphen  
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## LIST OF ABBREVIATIONS

$^{13}\text{C-NMR}$	: carbon-13 nuclear magnetic resonance spectroscopy
$^1\text{H-NMR}$	: proton nuclear magnetic resonance spectroscopy
$\text{AlCl}_3$	: anhydrous aluminum chloride
$\text{cm}^{-1}$	: unit of wavenumber (IR)
$\text{CH}_3\text{COOH}$	: acetic acid
d	: doublet (NMR), day (s)
DBEDOT	: 2,5-dibromo-3,4-ethylenedioxythiophene
DBHEDOT	: 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene
DBDMT	: 2,5-dibromo-3,4-dimethoxythiophene
DCDMT	: 2,5-dichloro-3,4-dimethoxythiophene
DMT	: 3,4-dimethoxythiophene
EDOT	: 3,4-ethylenedioxythiophene
HEDOT	: 2'-hydroxymethyl-3,4-ethylenedioxythiophene
DMF	: <i>N,N</i> -dimethylformamide
$\text{DMSO-}d_6$	: hexadeuterated dimethyl sulfoxide
eq	: equivalent (s)
EtOAc	: ethyl acetate
EtOH	: ethanol
eV	: electron volt
$\text{FeCl}_3$	: anhydrous ferric chloride
GPC	: gel permeation chromatography
g	: gram (s)
HH	: head to head
h	: hour (s)
HT	: head to tail
HCl	: hydrochloric acid
HOMO	: highest occupied molecular orbital
Hz	: hertz (s)

IR	: infrared spectroscopy
<i>J</i>	: coupling constant
LED	: light emitting diode
LiClO <sub>4</sub>	: lithium perchlorate
LUMO	: lowest unoccupied molecular orbital
M	: molar (s)
m	: multiplet (NMR)
MeOH	: methanol
min	: minute
mg	: milligram (s)
mL	: milliliter (s)
mmol	: millimole (s)
<i>M<sub>n</sub></i>	: number average molecular weight
mM	: millimolar
m.p.	: melting point
m/z	: mass per charge ratio (s)
MS	: mass spectrometry
MSA	: methanesulfonic acid
NaOH	: sodium hydroxide
NBS	: <i>N</i> -bromosuccinimide
NCS	: <i>N</i> -chlorosuccinimide
nm	: nanometer (s)
°C	: degree Celsius
ppm	: parts per million (unit of chemical shift)
PDHT	: poly(3,4-dihydroxythiophene)
PDMT	: poly(3,4-dimethoxythiophene)
PHEDOT	: poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene)
P3AT	: poly(3-alkylthiophene)
P3HT	: poly(3-hexylthiophene)
PT	: polythiophene
q	: quartet (NMR)
RT	: room temperature

s	: singlet (NMR)
st	: stretching vibration (IR)
S	: Siemen
SSP	: solid state polymerization
THF	: tetrahydrofuran
PTSA	: <i>p</i> -toluenesulfonic acid
TT	: tail to tail
t	: triplet (NMR)
TLC	: thin layer chromatography
UV	: ultra-violet
$\delta$	: chemical shift
$\lambda_{\max}$	: maximum wavelength



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# CHAPTER I

## INTRODUCTION

During the past three decades, research on functional  $\pi$ -conjugated systems has rapidly grown. The discovery of the metal-like conductivity in oxidized poly(acetylene) and later in polyaromatic systems such as poly(thiophene) or poly(pyrrole) in the late 1970s and early 1980s has progressively explored novel materials for various applications [1-4]. Organic electronics, or plastic electronics, is a moderately new multidisciplinary field of research that involves a series of conceptual, experimental, and modeling challenges concerning electronic devices made with carbon-based materials such as semi-conducting  $\pi$ -conjugated polymers and small organic molecules. It is different from conventional electronics that use inorganic materials such as silicon or gallium arsenide in many aspects. With the emergence of organic electronics or plastic electronics, it has generated a quite different view of the chemistry of functional  $\pi$ -conjugated systems to control and manipulate quantities such as absorption and emission spectra, oxidation and reduction potentials or luminescence efficiency as new priority targets. The development of organic devices allows the creative design of new architectures for electronic components. The quest for more powerful and smaller/thinner/flexible electronic devices requires novel materials with new and improved characteristics and new fabrication processes. Conducting polymers have unique properties that are interesting for this new technology [5]. They not only have the electronic properties of a semiconductor but also the mechanical flexibility and ease of production of plastics. Moreover, conjugated polymers are good materials to be employed in the fabrication of electronic devices because their properties, can be fine-tuned by external parameters during chemical synthesis within a certain band width. Another important motivation is the expected low cost of the end product. The intrinsic flexibility of the polymers enables new and low-cost manufacturing techniques of flexible roll-up displays, flexible sensors, large photovoltaic arrays and many others. In fact, the manufacturing processes that will eventually be chosen for making organic electronics

products are unknown. However, it appears that the economics prospect of organic electronics will be much more attractive and feasible than silicon manufacturing.

### 1.1 Applications of organic conducting polymers

According to the attractive and tunable properties of organic conducting polymers, this facilitates the use of conducting polymers in many applications such as:

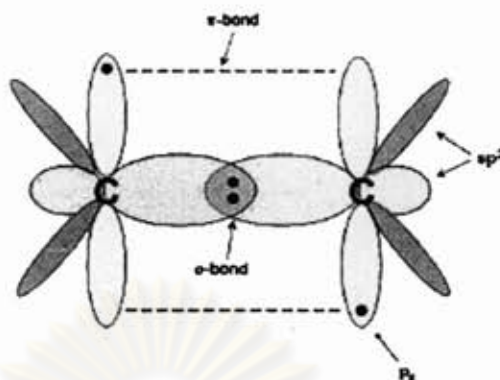
- **Applications utilizing the inherent conductivity of polymer**  
Antistatic coating (metal and polymer), microelectronic devices, stealth material for providing a minimum radar profile for military aircrafts and naval vessels
- **Electrochemical switching, energy storage and conversion**  
New rechargeable battery, redox supercapacitors
- **Polymer photovoltaics (light- induce charge separation)**
- **Display technologies**  
Light emitting diode (LED), flat panel displays
- **Electromechanical actuators**  
Artificial muscles, windows wipers in spacecrafts, rehabilitation gloves  
electronic Braille screen, bionic ears for deaf patients.
- **Separation technologies**  
Novel smart-membrane, selective molecular recognition
- **Cellular communication**  
Growth and control of biological cell cultures
- **Controlled release devices**  
Ideal host for the controlled release of chemical substances
- **Corrosion protection**  
New-generation Corrosion protective coatings

## 1.2 Electronic properties of conducting polymers

The field of organic electronics was established in 1970s when MacDiarmid, Heeger and Shirakawa discovered that the conductivity of polyacetylene films could be altered over several orders of magnitude by chemical doping [6]. For their breakthrough work in this area, they were awarded the Nobel Prize in Chemistry in the year 2000 [7-9].

Conducting and semiconducting organic materials with either electron (*n-type*) or hole transport (*p-type*) materials can be made. Since the pioneer work, many novel materials used in electronic applications have been rapidly developed and characterized. The particular bonding arrangement of the carbon atoms in the polymer backbone is the main reason for the characteristic electronic properties of tunable conductivity, electrochromism, electroluminescence and electroactivity [10].

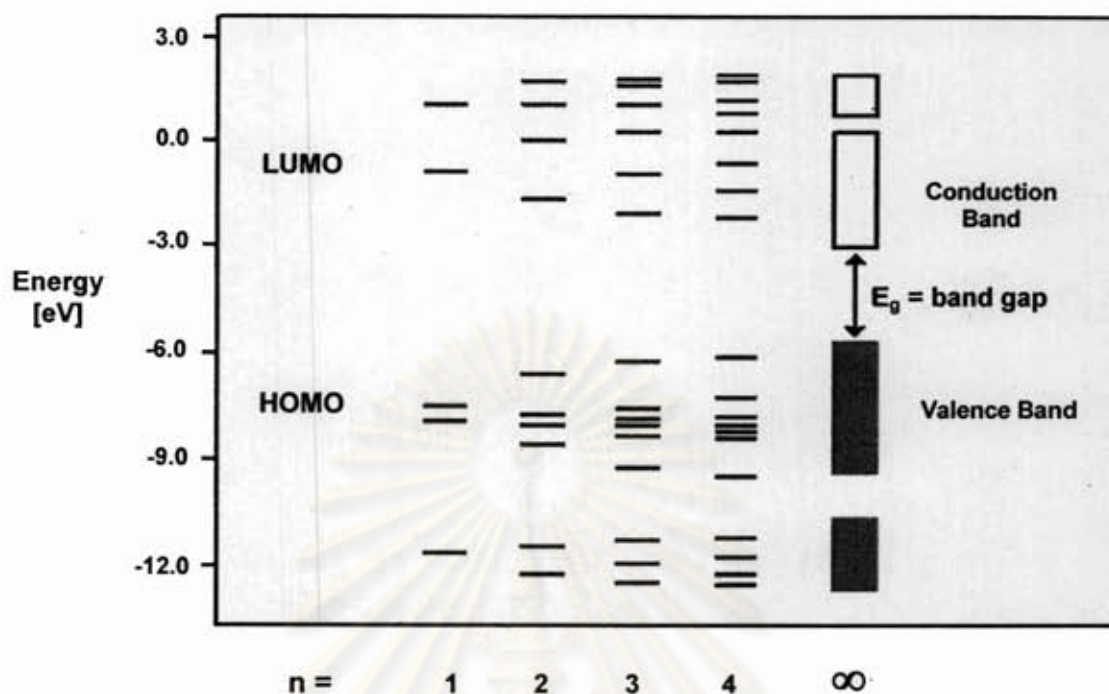
A general characteristic of conducting polymers is the presence of double bonds alternating with single bonds along the polymer chain, i.e. conjugated bonds. The electron configuration of the six electrons in a carbon atom (in its ground state) is  $1s^2 2s^2 2p^2$ . The electrons in the core orbital do not contribute to the chemical bonding. The s and p orbitals combine to form hybrid orbitals ( $sp^1$ ,  $sp^2$ , and  $sp^3$ ), depending upon the number of orbitals they combined), which result in triple, double, or single bond, respectively. In conjugated polymers, one 2s orbital pairs with the two 2p orbitals to form three  $sp^2$  hybrid orbitals, leaving one p orbital unhybridized. Two  $sp^2$  orbitals on each carbon atom form covalent bonds with neighboring carbon atoms; the remaining  $sp^2$  orbital normally forms a covalent bond with a hydrogen or side group. This is called  $\sigma$ -bond which is cylindrical symmetry around the internuclear axis [11]. The unhybridized  $p_z$  orbital side overlaps with the unhybridized  $p_z$  orbital on the neighboring carbon. This bond is called a  $\pi$ -bond, as is any bond which arises from electrons approaching side by side, off the internuclear axis shown in **Figure 1.1**.



**Figure 1.1** Bonding in conducting conjugated polymers. The  $sp^2$  hybrid orbitals are shown in light gray, and the unhybridized  $p_z$  orbitals in white. Electrons are represented by the dots. The two  $sp^2$  hybrid orbitals on the side extended in and out of the plane of the page [11].

The electrons in the  $\pi$ -bonds are weakly bound and readily delocalized. These delocalized  $\pi$ -electrons are conduction electrons in these materials. In summary, the  $sp^2$  hybridization in conducting polymers is important as it leaves one  $\pi$  electron per atom to form its own bond.

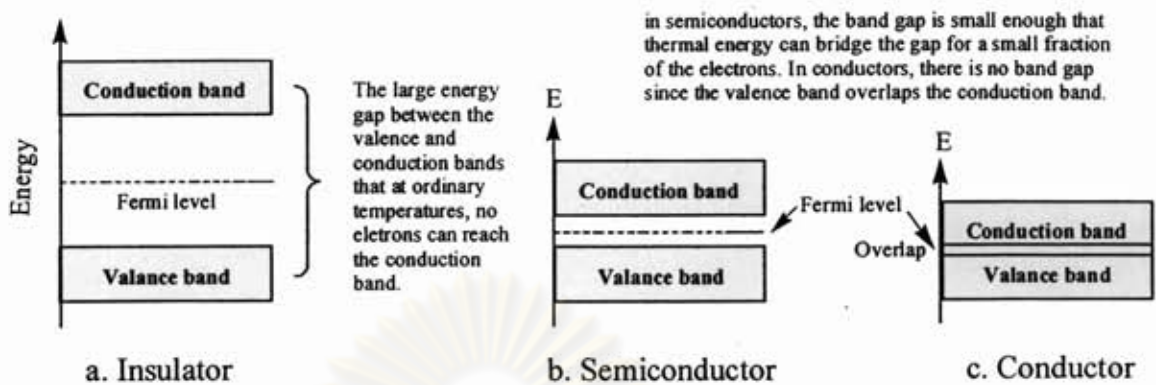
Both conjugated conducting polymers and inorganic semiconductor electronic structure are very similar in nature. They have their electrons organized in bands rather than in discrete levels and their ground state energy bands are either completely filled or completely empty. The band structure of a conjugated polymer originates from the interaction of the  $\pi$ -orbitals of the repeating units throughout the chain. This is illustrated in **Figure 1.2** where the calculated energy levels of oligothiophenes with  $n = 1-4$  and polythiophene are shown as a function of oligomer length. Addition of every new thiophene unit causes rehybridization of the energy levels yielding more and more sub levels until a point reached at which there are bands rather than discrete levels. Interaction between the  $\pi$ -electrons of neighboring molecules leads to a three-dimensional band structure.



**Figure 1.2** Calculated (frontier) energy levels of oligothiophenes with  $n = 1-4$  and of polythiophene ( $E_g =$  band gap energy) [12].

Analogous to semiconductors, the highest occupied band is called the valence band, while the lowest unoccupied band 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 possess delocalized electrons in  $\pi$ -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.

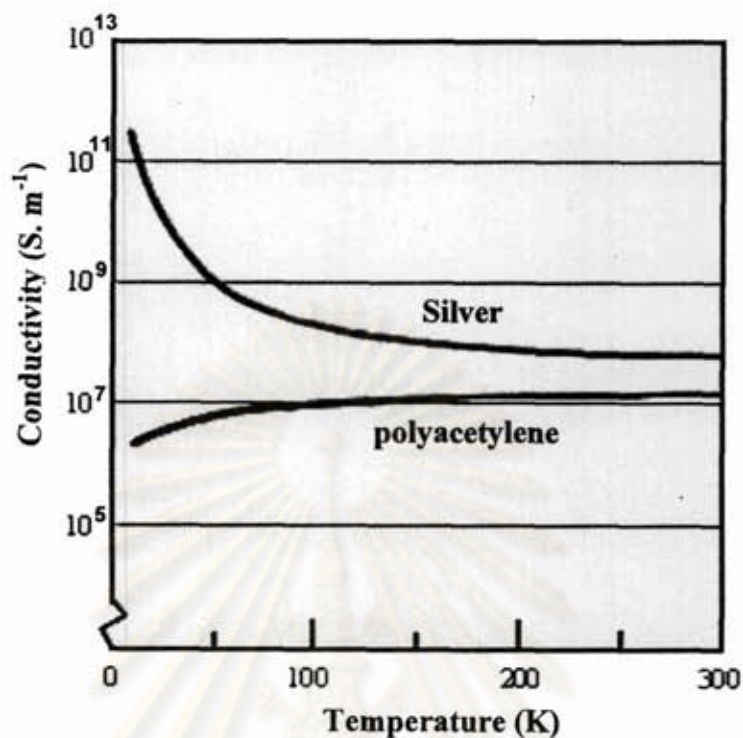
The difference between  $\pi$ -conjugated polymers and metals is that in metals, the orbitals of the atoms overlap with the equivalent orbitals of their neighboring atoms in all directions to form molecular orbitals similar to those of isolated molecules. With  $N$  numbers of interacting atomic orbitals, there would be  $N$  molecular orbitals. In the metals or any continuous solid-state structures,  $N$  will be a very large number (typically  $10^{22}$  for a  $1 \text{ cm}^3$  metal piece). With so many molecular orbitals spaced together in a given range of energies, they form an apparently continuous band of energies (Figure 1.3).



**Figure 1.3** Simple band picture explaining the difference between an insulator, a semiconductor, and a metal [12].

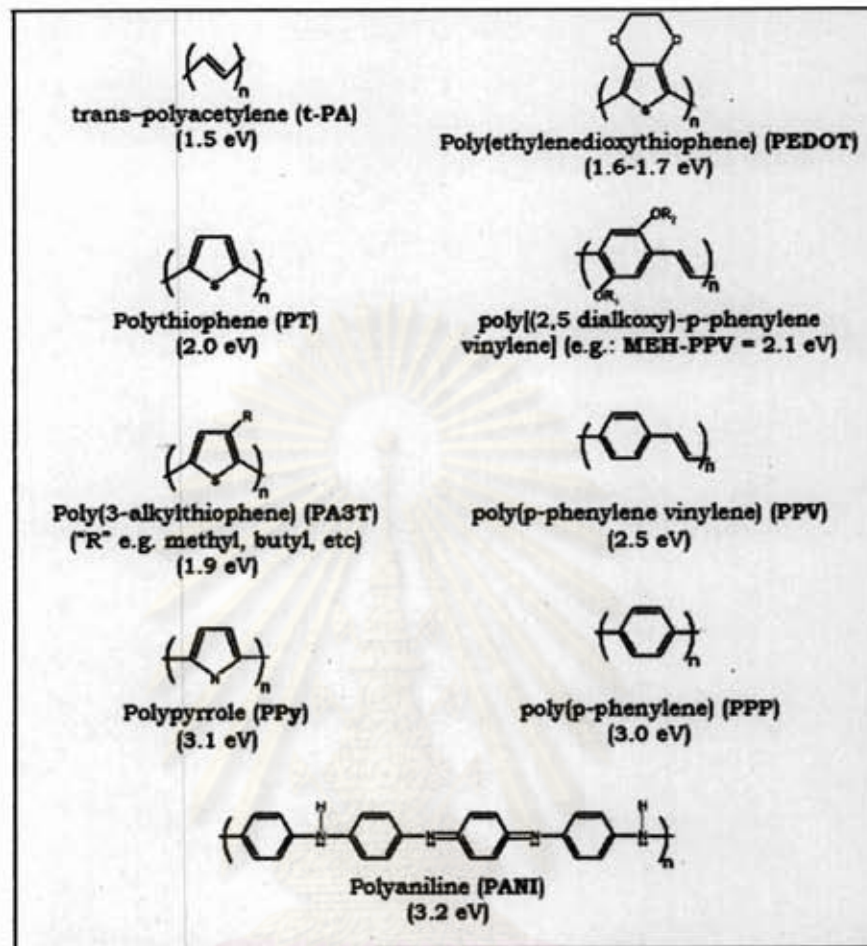
In insulators, the electrons in the valence band are separated by a large gap from the conduction band. However, in conductors like metals, the valence band overlaps with the conduction band. In addition, in semiconductors, there is a small enough gap between the valence and conduction bands that thermal or 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.

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 “holes” at lower energy. Metals and conducting polymers exhibit opposite directions of conducting behavior as a function of temperature as shown in **Figure 1.4**. Conductivity generally increases with decreasing 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.



**Figure 1.4** The conductivity of conducting polymers decreases with falling temperature in contrast to that of metals [12].

Since  $\pi$ -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 to its desired electrical and optical properties. Reduction of the band gap to approximately zero is expected to afford an intrinsic conductor like metals. Example of them  $\pi$ -conjugated polymers being intensively studied are shown in **Figure 1.5**.



**Figure 1.5** Chemical structures of few  $\pi$ -conjugated polymers and their band gap Energy [5].

### 1.3 Effect of doping [12]

The doping process is an addition of a doping agent into the polymer expecting to enhance the conductivity of the polymer. The modification of electrical conductivity of conducting polymers from insulator to metal can be accomplished either by chemical doping or by electrochemical doping. Both *n-type* (electron donating) and *p-type* (electron accepting) dopants have been used to induce an insulator-to-conductor transition in electronic polymers. Familiar to inorganic semiconductors, these dopants remove or add charges to the polymers. However, unlike substitutional doping that occurs in conventional semiconductors, the dopant atomic or molecular ions are interstitially positioned between  $\pi$ -conjugated polymers chain, and donate charges to or accept charges from the polymer backbone. In this



case, the counter ion is not covalently bound to the polymer, but only attracted to it by the Coulombic force. In self-doping cases, these dopants are covalently bound to the polymer backbone [11]. Initially added charges during doping process do not simply start to fill the conduction band to have metallic behavior immediately. The strong coupling between electrons and phonons near the doped charges causes distortions of the bond lengths. For degenerate ground state polymers such as trans-polyacetylene, doped charges at low doping levels are stored in charged solitons whereas nondegenerate systems they are stored as charged polarons or bipolarons [13-16]. High doping for the non-degenerate polymers results in polarons interacting to form a polaron lattice or electrically conducting partially filled energy band [17-18]. Bipolarons or the pairs of polarons are formed in less ordered regions of doped polymers [19].

Simultaneous with the doping, the electrochemical potential (the Fermi level) (**Figure 1.3**) 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. The electrical conductivity results from the existence of charge carriers through charge doping and from the ability of those charge carriers to move along the  $\pi$ -bonds; however, disorder restricts the carrier mobility and limits the electrical conductivity in the metallic state. Accordingly, electrical conductivity of doped conjugated polymers is improved due to two reasons:

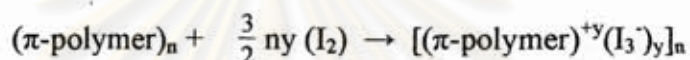
1. Doping process introduces carriers into the electronic structure. Since every repeating unit is a potential redox site, conjugated polymers can be doped *n*-type (reduced) or *p*-type (oxidized) to a relatively high density of charge carriers.
2. The attraction of an electron in one unit to the nuclei in the neighboring units leads to carrier delocalization along the polymer chain and to charge carrier mobility, which is extended into three dimensions through inter-chain electron transfer.

Charge injection or “doping” onto conjugated conducting polymers leads to the wide variety of interesting and important phenomena which define the field. The doping can be accomplished in a number of ways:

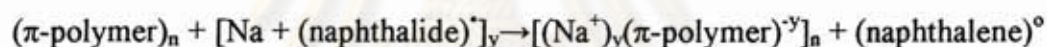
### 1.3.1 Chemical doping by charge transfer

The first discovery of the ability to dope conjugated polymers involved charge transfer redox chemistry; oxidation (*p*-type doping) or reduction (*n*-type doping), as demonstrated with the following examples:

1. *p*-type



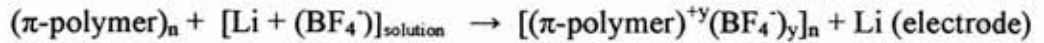
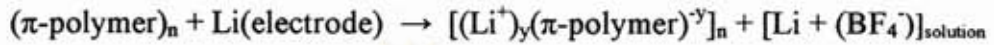
2. *n*-type



When the doping level is sufficiently high, the electronic structure of conjugated polymers approached to that of a metal.

### 1.3.2 Electrochemical doping

Although chemical (charge transfer) doping is an efficient and straightforward process, it is normally difficult to control. Complete doping to the highest concentrations yields reasonably high quality materials; however, attempts to obtain intermediate doping levels often result in inhomogeneous doping. Electrochemical doping was originated to solve this problem. In electrochemical doping, the electrode supplies the redox charge to the conducting polymer, while ions diffuse into (or out of) the polymer structure from the nearby electrolyte to compensate the electronic charge. The doping level is determined by the voltage between the conducting polymer and the counter-electrode; at electrochemical equilibrium the doping level can be achieved by setting the electrochemical cell at a fixed applied voltage and simply waiting as long as necessary for the system to come to electrochemical equilibrium as indicated by the current through the cell going to Zero. Electrochemical doping is illustrated by the following examples:

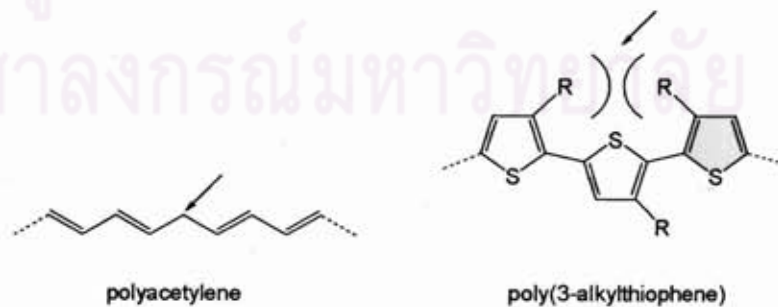
1. *p*-type2. *n*-type

## 1.4 Effective conjugation length (ECL)

Ideal conducting polymers should have its  $\pi$  electrons in the conjugated unsaturated bonds even by distributing throughout the whole chain. This requirement usually does not hold due to the following:

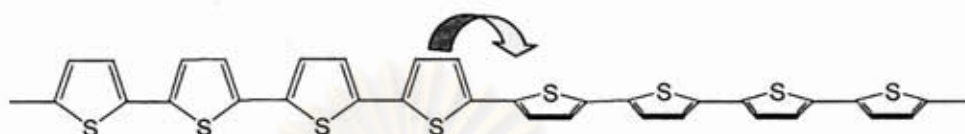
- i) Formation of defects in polymer
- ii) Twisting of planar structure out of conjugation in the polymer.

Examples of the two reasons above are exemplified in **Figure 1.9**. 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.



**Figure 1.6** A defect in polyacetylene and 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 (**Figure 1.10**). Twisting of polymer chain would also cause the reduction of conjugation in the polymer.



**Figure 1.7** Twisting of polythiophene.

### 1.5 Structural basis of functionalization

Among the various possible strategies for modification of conducting polymers, the polymerization of monomer modified by covalent grafting of functional groups represents the most straightforward method to achieve a molecular level control of the structure, electronic and electrochemical properties of functional conducting polymers. However, despite its elegant simplicity, this approach poses several complex problems. As a matter of fact, the synthesis of the modified conducting polymers in which a specific function will be coupled to the conjugated  $\pi$  system requires that the modification of the monomer structure remain compatible with both the polymerization and the conservation of an extensively conjugated system in the resulting polymer in order to preserve its relevant electronic, optical, and electrochemical properties. Consequently, the synthesis of functional conducting polymers from a substituted monomer in respect of the above prerequisites implies a detailed comprehension of the structural effects of substitution (inductive, mesomeric and steric) of the monomer at the various stages of organization of the material [20], i.e.

- Molecular
  - reactivity of the monomer
  - propagation of the polymerization
- Macromolecular
  - planarity of the conjugated system (effective conjugation length)

- Macroscopic
  - crystallinity, morphology
  - mechanical properties
  - macroscopic conductivity

## 1.6 Polythiophene

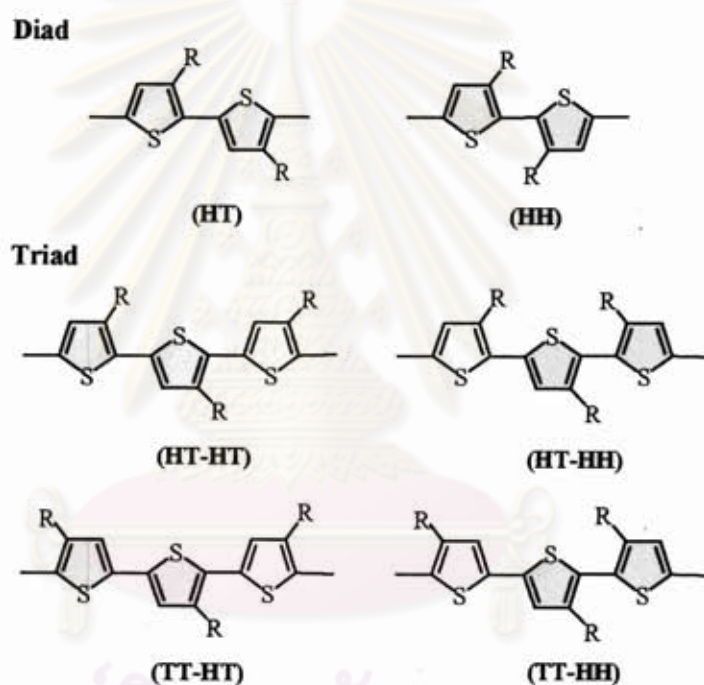
Polythiophene is composed of repeating five-membered heterocyclic monomeric unit. It is also considered one of the promising classes of conducting polymers for technological used [21]. This is attributed to its good environmental stability in neutral form, its structural versatility which allows their electronic and electrochemical properties to be modified by chemical means and its characteristics of having non-degenerate ground state for the two limiting structures of polythiophene aromatic ground state and quinoidal ground state [22,23]. For these reasons, polythiophene has been used in many applications such as:

- The electrical properties of the doped conducting state, for example antistatic and EMI shielding, gas sensors, radiation detector, and corrosion protective films.
- The electrical properties of the natural semiconducting state such as photovoltaic cell and non-linear optics.
- The electrochemical reversibility of the transition between the doped and the undoped states, for instance, new rechargeable battery, display devices, electrochemical sensor, and modified electrode [20].

Polythiophene with an ideal extended  $\pi$ -conjugation is possible only in polymers with perfectly 2,5-linked repeating units. However, 2,4- and 2,3-couplings as well as hydrogenated thiophene units can also be found in the polymers.

The two main disadvantages of polythiophene are its infusibility and insolubility which results from strong interchain stacking and relative chain rigidity. The standard procedure of attaching long, flexible chains to the conjugated backbone can often have deleterious effects on the electrical conductivity of polymers in their conducting state. A significant discovery demonstrated that polythiophene belongs to

one of few cases in which substitution of hydrogen at the 3-position by alkyl chain or electron donating group with flexible chain does not affect polymer conductivity of the polymer, whereas impart solubility and consequently enhance processibility. The substituted thienyl was polymerized by a number of chemical and electrochemical methods to yield poly(3-alkylthiophene) [25,26]. The flexible substituents solubilized the polythiophene chains by this disruption of their interchain stacking [26]. This in turn facilitated the processibility of these polymers [27].



**Figure 1.8** Regioisomers of the poly(3-alkylthiophene)s.

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 in turn result in four triad regioisomers in the polymer chain, *i.e.* HT-HT, HT-HH, TT-HT, and TT-HH (Figure 1.11). Although HT coupling is generally favored, since the less repulsive force of HT coupling is expected about 15-20% of HH coupling is also observed.

## 1.7 Synthesis of polythiophene

According to many intensive research efforts, polythiophene is generally prepared by means of two main routes which are the electrochemical and the chemical syntheses.



**Figure 1.9** The synthesis of Polythiophene and derivatives.

### 1.7.1 Electrochemical polymerization

Initially, polythiophene was obtained by electrochemical polymerization of thiophene monomers [26]. Even a polymer film was produced at the anode surface after electropolymerization, the obtained polymers are not easily processible further. This method is appropriate for the preparation of polymers such as polythiophene and poly(3-methylthiophene). The yield of polymers prepared from electrochemical polymerization is moderate to low, and their structures are not well-defined.

Compared to other chemical and electrochemical syntheses of conducting polymers, the anodic electropolymerization of the monomer shows several advantages such as absence of catalysts, direct grafting of the doped conducting polymer onto the electrode surface (which is of particular interest for electrochemical applications), easy control of the film thickness by deposition charge, and possibility to carry out in situ characterization of the growing process or of the polymer by electrochemical and/or spectroscopic techniques.

The electrochemical formation of conducting polymers is a unique process. Although it displays some similarities with the electrodeposition of metals since it proceeds via a nucleation and phase-growth mechanism, the major difference is that charged species precursors of the deposited material must be initially produced by oxidation of the neutral monomer at the anode surface. The consequence is that

various electrochemical and chemical follow-up reactions are possible, making a difficult problem for the elucidation of the electropolymerization mechanism [1].

As discussed, electrochemical polymerization is very useful method for preparing polymers such as polythiophene, poly(3-methylthiophene), and poly(3-phenylthiophene) (**Figure 1.9**), which are insoluble and infusible. When these polymers are obtained in the form of powder they cannot be processed into a film or other useful forms [27].

Polythiophene is not stable at the potentials used for the electrochemical polymerization of thiophene, so polythiophene deposited on the anode at the earlier stage of the polymerization is overoxidized and has been damaged, while electrochemical polymerization produces new polymer.

#### **1.7.2 Oxidative coupling polymerization with iron (III) chloride**

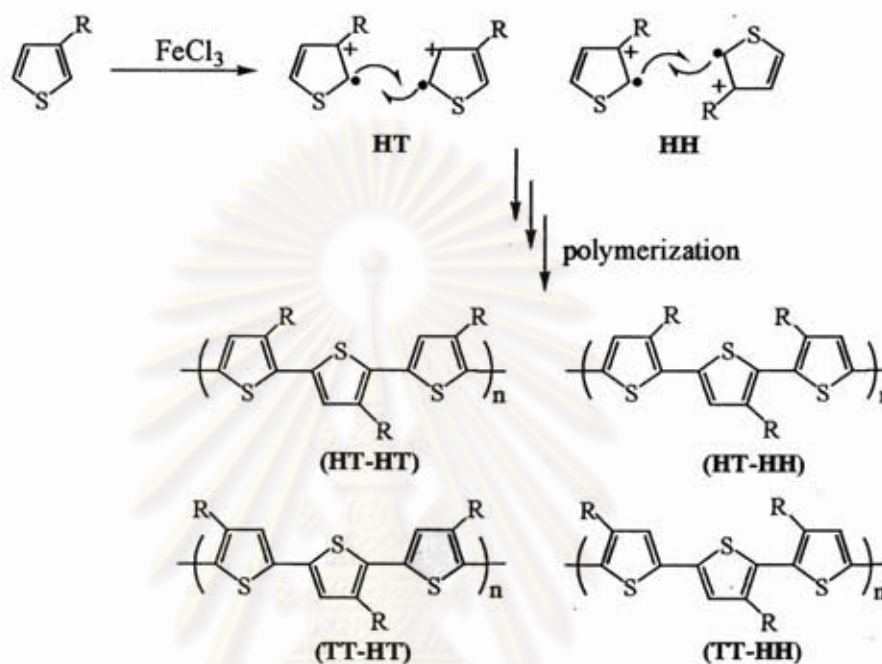
In contrast to electrochemical polymerization, the yield of polythiophene prepared from the oxidative polymerization with iron (III) chloride is relatively high. Moreover, the molecular weight of polymer synthesized by this method is sufficiently high to be cast into a film. Another chemical route, the Grignard coupling, is very essential for the preparation of polymers with a well-defined structure because no substituent migration occurs during coupling reaction. The drawback of this method is the conductivity of polymers prepared from this method is lower than those obtained by other methods.

Polymers obtained from this method are soluble in common organic solvents and their films can be formed by simply casting its solution on a solid substrate. In addition, many 3-alkylthiophenes are commercially prepared by this method.

Sugimoto and coworker [28] elaborated transition metal halides as oxidizing agent for polymerization of 3-hexylthiophene and found that iron (III) chlorides were the effective one (**Figure 1.10**). The films was fabricated by casting a solution of the resulting poly(3-hexylthiophene) on substrate and the results showed similar characteristics to those prepared by the electrochemical method.



Poly(3-alkylthiophene) was undoped from trace of  $\text{FeCl}_3$  by extraction with methanol, but this polymer remained in partially doped states. Completely undoped polymer was obtained by reduction with an aqueous solution of hydrazine.



**Figure 1.10** The oxidative coupling reaction of 3-alkylthiophene by  $\text{FeCl}_3$  [28].

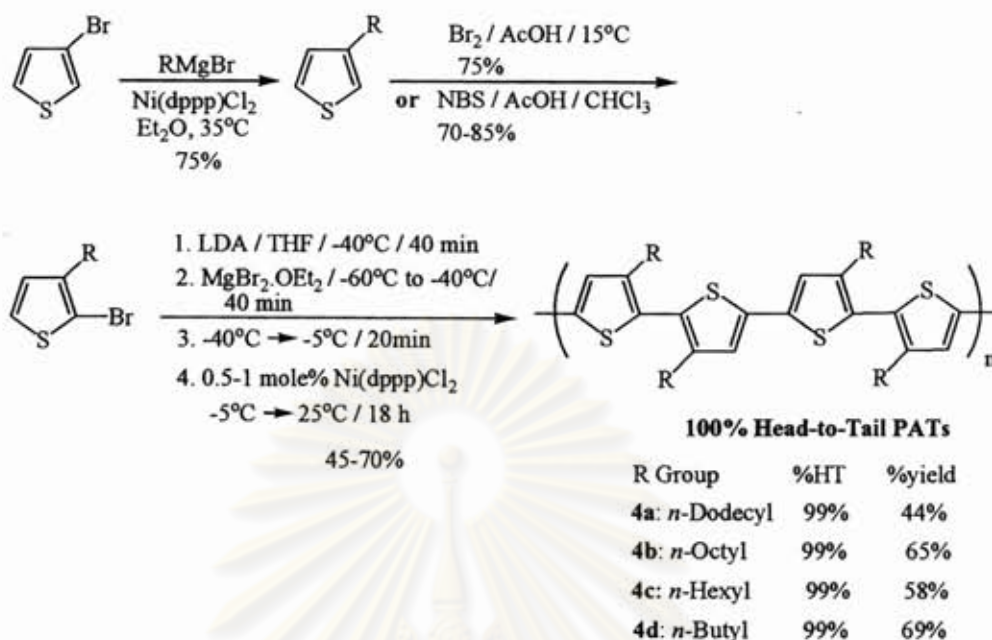
Amou [29] studied the polymerization mechanism and polymerization conditions, and found that a lower temperature and concentration were effective for increasing the HT coupling. Niemi [30] performed a detailed study on the polymerization mechanism of 3-alkylthiophene with iron (III) chloride. The results showed that only solid iron (III) chloride was active as an oxidative polymerization agent for 3-alkylthiophene while the soluble part of iron (III) chloride was inert. The solubility of iron (III) chloride in chloroform and the consuming effect of evolved hydrogen chloride gas explained the extra amount of iron (III) chloride that was initially necessary to obtain high conversion in polymerization. A plausible polymerization mechanism of 3-alkylthiophene was proposed to proceed through a radical mechanism, developed on the basis of the crystal structure of iron (III) chloride and quantum chemical computations of thiophene derivatives.

### 1.7.3 Grignard coupling and other chemical polymerizations

Polymerization using a metal-catalyzed cross-coupling technique has been extensively investigated [31,32]. The reaction is supposed to proceed by an oxidative addition of an organic halide with a metal catalyst and then transmetalation between the catalyst complex and a reactive Grignard or other organometallic reagent (or disproportionation) generates a diorganometallic complex. The last step involves reductive elimination of the coupled product with regeneration of the metal catalyst. Numerous organometallic species (including organomagnesium, organozinc, organoboron, organoaluminum, and organotin) have been demonstrated to be used in cross-coupling reactions with organic halides.

The synthesis of regioregular HT-P3AT was reported by McCullough and coworkers [33] in early 1992 (Figure 1.11). This synthetic method [34-38] regiospecifically generated 2-bromo-5-(bromomagnesio)-3-alkylthiophene which was polymerized with catalytic amounts of Ni(dppp)Cl<sub>2</sub> using Kumada cross-coupling methods [39] to give P3ATs with 98-100% HT-HT couplings. In this approach, HT-P3ATs were prepared in yields of 44-69 % in a one-pot, multistep procedure. Molecular weights of HT-P3ATs are typically in the range of  $(20-40) \times 10^3$  (PDI  $\approx$  1.4). A prepared sample of HT-poly(dodecylthiophene) had  $M_n = 130,000$  (PDI = 2.1).

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**Figure 1.11** The McCullough method for the regiospecific synthesis of poly(3-alkylthiophene)s [33].

### 1.8 Poly(3,4-dialkoxythiophene)

Substitution of polythiophene ring at  $\beta$  position with flexible alkyl or alkyl containing one or more ether groups results in the conducting polymers with unusual properties such as processability and stereoselectivity [40]. In addition, introducing electron donating substituent such as alkoxy group into thiophene ring also decrease polymerization potential and significantly enhance polymer electroactivity in the solution, compared to that of poly(3-alkylthiophene) analogues. Oxygen directly attached to the ring was further substantially stabilized the conducting p-type of polymers by stabilization of the positive charge in the polymer backbone [41].

Incorporation of the second alkoxy substituent into the thiophene ring or cyclization between 3- and 4- positions of the thiophene ring is a convenient way for preparing the perfectly stereoregular, long conjugated polymers (high effective conjugation length) by elimination 2,4' or  $\alpha,\beta$  couplings [42].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is the prime example. Owing to its excellent electronic properties (electrical conductivity, electrochromic properties,

etc.) and high stability, PEDOT is one of the most industrially important conjugated polymers. Due to a stereoregularity of the only possible polymer structure, it has a very high conductivity (up to 550 S/cm in the electrochemical doped state). The remarkable stability of PEDOT in its doped state, compared with other conducting polymers, allows a number of potential applications [42]. Prepared by oxidative chemical and electrochemical polymerization method, PEDOT is found relatively insoluble in conventional organic solvents leading to the difficulties in fabrication process. Nevertheless, there is an anticipation that the increase of the alkyl chain length in the alkoxy group could lead to a soluble polymers in organic solvents.

The substituted EDOT derivatives (EDOT-CH<sub>3</sub>, EDOT-C<sub>6</sub>H<sub>13</sub> and EDOT-C<sub>10</sub>H<sub>21</sub>) are developed by Jonas and coworkers [43]. Chemical and electrochemical polymerization of these monomers resulted in insoluble polymers with comparable conducting properties as PEDOT.

Groenendaal and coworkers synthesized alkylated 3,4-ethylenedioxythiophenes (EDOT-C<sub>n</sub>H<sub>2n-1</sub>: n = 1,6,10,14) and polymerized by electropolymerization in acetonitrile [44]. The increasing alkyl chain length increased coplanar disposition of the thiophene rings. The conductivity of the polymers initially was decreased and then increased again. The tetradecyl-substituted polymer has an exceptionally high conductivity.

Roncali and coworkers synthesized EDOT derivatives with hydroxymethyl and oligo(oxyethylene) groups covalently attached at the ethylenedioxy bridge [45]. The hydroxymethyl group significantly enhanced the ability of EDOT to electropolymerization in water. The electrochemical and optical properties of the oligo(oxyethylene)-substituted polymer exhibited a negative shift of oxidation potential and a considerable increase of effective conjugation length with a 0.10 eV decrease of the bandgap.

Zuo and coworkers performed the addition reaction of perfluorohydroxyethylene into ethylene bridge of EDOT via Mitsunobu reaction of perfluorohexylated diol and diethyl 3,4-dihydroxythiophenedicarboxylate, and

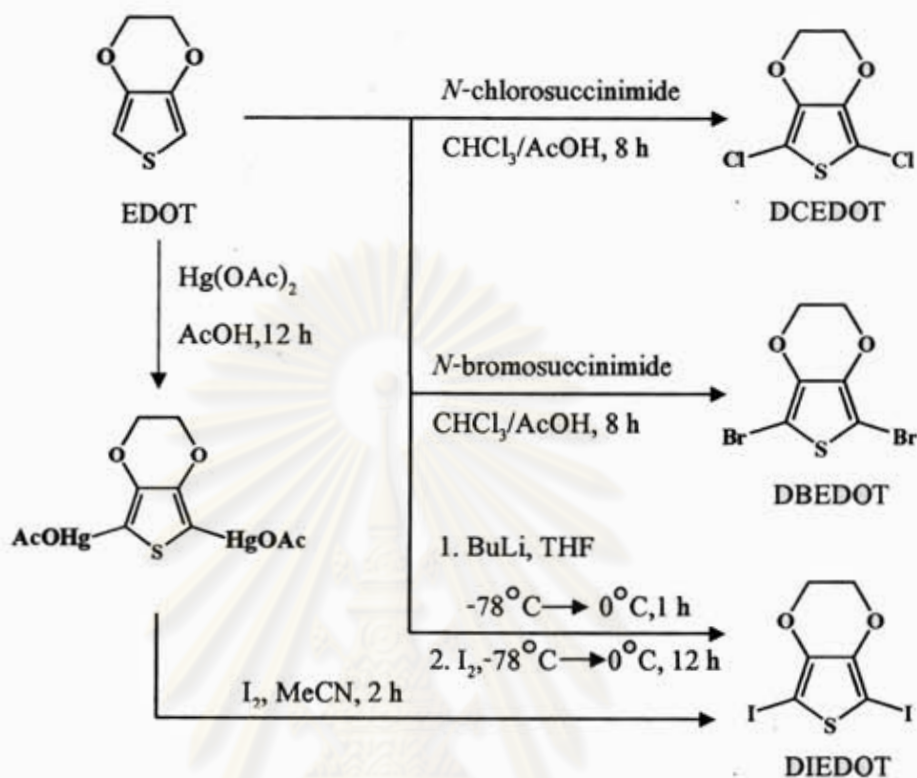
followed by decarboxylation reaction. The synthesized monomer was then polymerized using both oxidative chemical and electrochemical polymerization techniques [46]. In undoped state, resultant polymers (PEDOT-C<sub>6</sub>F<sub>13</sub>) slightly dissolved in chloroform. The measured conductivity of undoped polymers was slightly higher than that of PEDOT ( $3.0 \times 10^{-6}$  S/cm and  $1.2 \times 10^{-6}$  S/cm, respectively).

### 1.9 Solid state synthesis of PEDOT

Polymerization of PEDOT by traditional oxidative polymerization with FeCl<sub>3</sub> 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.

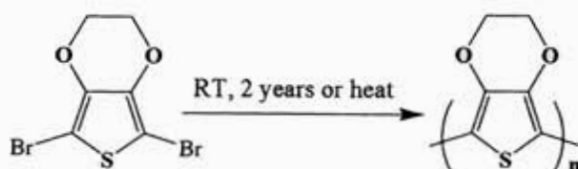
The advantages of solid-state polymerization including low operating temperatures, which restrain side reactions and thermal degradation of production, while requiring inexpensive equipment, and uncomplicated and environmentally sound procedures. However, at solid-state polymerization low temperatures, rate of the reactions are slow compared to polymerization in the melt phase because of the reduce mobility of the reacting species, and the slow diffusion of the by-products [47].

In addition, Meng and coworkers studied solid state polymerization (SSP) of the dihalogen-substituted 3,4-ethylenedioxythiophene (EDOT) (Figure 1.12), whose halogen atoms are Cl, Br or I, respectively. The polymerization results indicated that DBEDOT was the most reactive monomer, and polymerization reaction occurred via radical cationic polymerization which electron donating group (3,4-ethylenedioxy group) enhanced the stability of cation intermediate. They also suggested that the distance between bromine atoms of each DBEDOT was less than the summation of Van der Waal radius, confirmed by single-crystal X-ray technique, may be another factor that facilitates the solid state polymerization [48].



**Figure 1.12** Synthesis of dihalo-EDOT monomers [48].

Meng and coworkers [49] discovered that the solid-state polymerization (SSP) of DBEDOT was discovered by chance as a result of prolonged storage (2 years) at room temperature or heated ( $50\text{--}80^\circ\text{C}$ ) of the monomer (**Figure 1.13**). The colorless crystalline DBEDOT transformed into a black blue material while retaining the morphology. Surprisingly, the conductivity of this decomposition product appeared to be very high (up to  $80\text{ S/cm}$ ) for an organic solid. Indeed, the most likely explanation for the observed transformation was polymerization with formation of bromine-doped PEDOT.



**Figure 1.13** Solid state polymerization of DBEDOT.

The conductivity of different SSP-PEDOT samples was measured by the four point probe method at room temperature (Table 1.1). 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<sub>3</sub>-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.

**Table 1.1** Conductivity data of PEDOT polymers [49].

	Conductivity( $\sigma$ ); S.cm <sup>-1</sup>				
	SSP-PEDOT <sup>a</sup>				FeCl <sub>3</sub> -PEDOT <sup>b</sup>
Reaction temperature( °C)	20	60	80	120	0-5
Reaction time	2 years	24 h	4 h	24 h	24 h
1. Crystal	80	33	20	- <sup>c</sup>	- <sup>c</sup>
2. Pellets as synthesized	30	18	16	0.1	- <sup>d</sup>
3. Pellets after I <sub>2</sub> doping	53	30	27	5.8	7.6

<sup>a</sup> Prepared from solid state polymerization

<sup>b</sup> Prepared from oxidative coupling polymerization by FeCl<sub>3</sub>

<sup>c</sup> cannot be obtained

<sup>d</sup> very small value

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

As a unique derivative of polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT), possesses several advantageous properties compared with unsubstituted polythiophene and polythiophene derivatives. PEDOT had received considerable

interests attributable to its low band gap, high electrical conductivity, good stability, and excellent optical transparency in the visible region. Even ether groups at  $\beta, \beta'$  positions of thiophene ring in PEDOT avoided the formation of  $\alpha\text{-}\beta'$  linkages defect during polymerization. Thus derivatization of thiophene ring by other substituents such as alkoxy or polyether groups at the  $\beta$  positions could lead to higher solubility and improved physical and chemical properties. Solid state polymerization (SSP) of their new structurally pre-organized crystalline monomers could also result in another well-defined polymer structures with high conductivity. Moreover, this method was uncomplicated, less side reactions and environmentally sound procedures. This research will aim at functionalization of thiophene derivatives carrying alkoxy and other functional groups, and then the synthesis of new polythiophene derivatives will be attempted from these monomers through solid state polymerization (SSP) or other polymerization methods.

### 1.10 Objectives

The goal of this research focused on making poly(3,4-dialkoxythiophene) derivatives from new 3,4-dialkoxythiophene monomers and study their physical, electrical and chemical properties.

### 1.11 Scope of the investigation

The sequential investigation was carried out as follows.

1. Literature survey on related research
2. Preparation of 2,5-dibromo-3,4-dialkoxythiophene by direct bromination of
  - a. 3,4-ethylenedioxythiophene (EDOT)
  - b. 3,4-dimethoxythiophene (DMT)
  - c. 3,4-dialkoxythiophene monomer



3. Synthesis of 3,4-dialkoxythiophene by ether exchange reaction of 2,5-Dibromo-3,4-ethylenedioxythiophene and 3,4-dimethoxythiophene
4. Synthesize poly(3,4-dialkoxythiophene) derivatives from 3,4-dialkoxythiophene monomers by
  - a. Oxidative coupling polymerization
  - b. Solid state polymerization (SSP)
5. Study and compare the conductivity of poly(3,4-dialkoxythiophene) derivatives from oxidative coupling polymerization with ferric chloride ( $\text{FeCl}_3$ ) from 4a and solid state polymerization (SSP) process from 5b.
6. Data analysis



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## CHAPTER II

### EXPERIMENTS

#### 2.1 Instruments and equipments

Melting points were determined with a Stuart Scientific Melting Point SMP1 (Bibby Sterlin Ltd., Staffordshire, UK). The FT-IR spectra were recorded on a Perkin-Elmer FT-IR spectroscopy, spectrum RXI spectrometer (Perkin Elmer Instruments LLC., Shelton., U.S.A.). Solid samples were incorporated into a pellet of potassium bromide while liquid samples were analyzed as neat. The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were obtained in deuterated chloroform ( $\text{CDCl}_3$ ), deuterated dimethylsulfoxide ( $\text{DMSO-}d_6$ ) or deuterated acetone ( $\text{Acetone-}d_6$ ) using Varian Mercury NMR spectrometer operated at 400.00 MHz for  $^1\text{H}$  and 100.00 MHz for  $^{13}\text{C}$  nuclei (Varian Company, USA). The mass spectra were recorded on Mass Spectrometer: Waters Micromass Quattro micro API ESCi (Waters, USA). Samples were dissolved in EtOAc and directly injected 50  $\mu\text{L}$  into the Mass Spectrometer in. The absorption spectra were recorded on UV-VISIBLE Spectrometer: UV-2550 (Shimadzu Corporation, Kyoto, Japan).

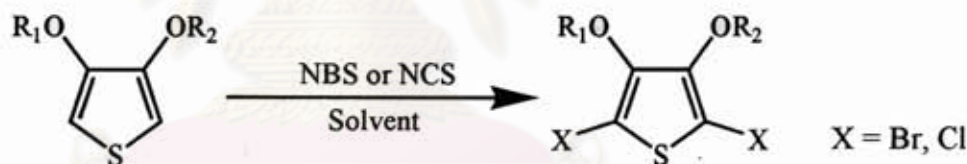
#### 2.2 Chemicals

Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck Kieselgel 60 F<sub>254</sub>) (Merck KgaA, Darmstadt, Germany). Column chromatography was performed using silica gel 0.06-0.2 mm or 70-230 mesh ASTM (Merck Kieselgel 60 G, Merck KgaA, Darmstadt, Germany or Scharlau Chemie S. A., Barcelona, Spain). Solvents used in synthesis were reagent or analytical grades. Solvents used in column chromatography were distilled from commercial grade prior to use. Other reagents were purchased from the following vendors:

- Labscan (Bangkok, Thailand): chloroform, concentrated hydrochloric acid, toluene, tetrahydrofuran, dimethylsulfoxide, acetonitrile, acetic acid

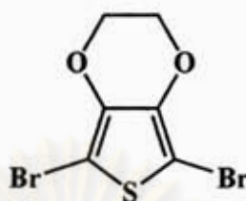
- Acrös Organic (USA): *N*-bromosuccinimide, *N*-chlorosuccinimide, Lithium perchlorate, 2-bromoethanol, *p*-toluenesulfonic acid
- Carlo Erba Reagent (Milan, Italy): benzoyl chloride, ferric chloride
- Fluka Chemical Company (Buchs, Switzerland): glycerol
- Merck Co. Ltd. (Darmstadt, Germany): ethanol, anhydrous sodium hydrogen carbonate, sodium hydroxide, anhydrous sodium sulfate, acetone, acetonitrile
- Riedel-de Haën: anhydrous aluminum (III) chloride
- Aldrich : 3,4-ethylenedioxythiophene (EDOT), 3,4-dimethoxythiophene (DMT)
- Wilmad (New Jersey, USA): deuterated chloroform, deuterated dimethylsulfoxide

### 2.3 Halogenations of thiophene derivatives (X = Br, Cl)



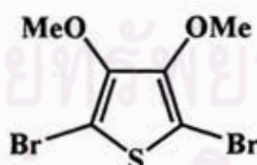
General procedure : In a two-neck 50 mL round bottom flask filled with 9 mL of a 2:1 solvent mixture of chloroform (CHCl<sub>3</sub>) (6 mL) and acetic acid (CH<sub>3</sub>COOH) (3 mL), a thiophene precursor (1 mmol) was added. Then the solution was slowly added 2.5 equivalents of *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) at 0-5 °C under inert atmosphere. The reaction mixture was stirred at ambient temperature. After completion, The reaction mixture was quenched by adding saturated sodium hydrogen carbonate solution. The organic layer was separated, and water layer was extracted with chloroform three times. The combination between organic layer and chloroform extract was washed with water. After drying over anhydrous sodium sulfate, the solution was evaporated using rotary evaporator. The obtained solution was then purified by column chromatography. The corresponding dihalothiophene derivatives were obtained.

**2.3.1 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT; R<sub>1</sub>-R<sub>2</sub> = CH<sub>2</sub>CH<sub>2</sub>)**



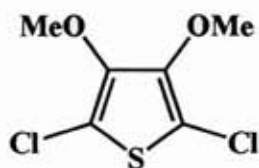
The compound was obtained via bromination of 3,4-ethylenedioxythiophene (EDOT) by slowly adding NBS (0.4450 g, 2.5 mmol) to a stirred solution of EDOT (0.1421 g, 1 mmol) dissolved in a 2:1 solvent mixture of chloroform (CHCl<sub>3</sub>) (6 mL) and acetic acid (CH<sub>3</sub>COOH) (3 mL) at 0-5 °C under inert atmosphere. The crude mixture was purified by passing through a silica gel column, and eluted with 8:2 mixtures of hexane and dichloromethane to get a white crystalline solid. It was recrystallized using methanol to produce a white needle like crystals (0.4832 g, 85%), mp 96-97 °C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 4.26 (s, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-) (Figure A.1, Appendix A); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 64.9, 85.5, 139.7 (Figure A.2, Appendix A). MS-H (EtOAc): m/z 299.1 (Figure A.3, Appendix A).

**2.3.2 2,5-dibromo-3,4-dimethoxythiophene (DBDMT; R<sub>1</sub>= R<sub>2</sub> = CH<sub>3</sub>)**



The compound was prepared from a reaction of 3,4-dimethoxythiophene (DMT) (0.1442 g, 1 mmol) and NBS (0.4450 g, 2.5 mmol) in 2:1 solvent mixture of chloroform (CHCl<sub>3</sub>) (6 mL) and acetic acid (CH<sub>3</sub>COOH) (3 mL). The crude mixture was purified by column chromatography, and eluted with 8:2 mixtures of hexane and dichloromethane to get a pale yellow oil (0.2583 g, 80%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 3.90 (s, 6H, Ar-OCH<sub>3</sub>) (Figure A.4, Appendix A); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 61.2, 95.0 148.2 (Figure A.5, Appendix A). MS-H (EtOAc): m/z 301.9 (Figure A.6, Appendix A).

### 2.3.3 2,5-dichloro-3,4-dimethoxythiophene (DCDMT; $R_1 = R_2 = \text{CH}_3$ )

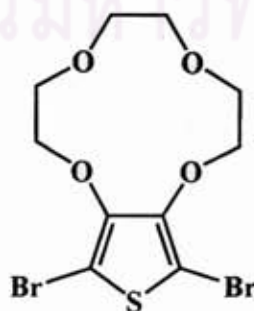


The compound was prepared from a reaction of 3,4-dimethoxythiophene (DMT) (0.1442 g, 1 mmol) and NCS (0.3338 g, 2.5 mmol) in 2:1 solvent mixture of chloroform ( $\text{CHCl}_3$ ) (6 mL) and acetic acid ( $\text{CH}_3\text{COOH}$ ) (3 mL). The crude mixture was purified by column chromatography, and eluted with hexane to get a pale yellow oil (0.1725 g, 80%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 3.90 (s, 6H, Ar-O $\text{CH}_3$ ) (Figure A.7, Appendix A);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 60.8, 108.6, 145.3 (Figure A.8, Appendix A). MS- $\text{H}^+$  (EtOAc):  $m/z$  212.1 (Figure A.9, Appendix A).

### 2.4 Ether exchange of 3,4-dialkoxythiophene

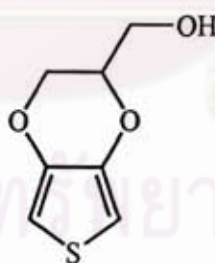


#### 2.4.1 Synthesis of 2',5'-dibromothiopheno-12-crown-4 ( $R_3-R_4 = -\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ ) 2



The crown ether derivative was synthesized by introducing DBEDOT (0.4498 g, 1.5 mmol) into 2-bromoethanol (3.5 mL, 50 mmol) in the presence of *p*-toluenesulfonic acid (PTSA) (0.5706 g, 3 mmol). The mixture was allowed to heat at 80 °C for 2 hour and then quenched with saturated sodium hydrogen carbonate solution. The organic layer was separated, and water layer was extracted with dichloromethane three times. The combination between organic layer and dichloromethane extract was rinsed with distilled water and dried with anhydrous sodium sulfate. The solution was concentrated by evaporating solvent using rotary evaporator. The crude mixture was then purified by passing through a silica gel column, and eluted with 8:2 mixtures of dichloromethane and hexane. The product was obtained as pale-yellow liquid (0.1725 g, 11%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 3.50 (t, 2H, Ar-OCH<sub>2</sub>-) 4.2 (s, 2H, Ar-OCH<sub>2</sub>CH<sub>2</sub>-), 4.5 (t, 2H, -OCH<sub>2</sub>CH<sub>2</sub>O-) (Figure A.10, Appendix A); <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 27.7, 64.7, 64.9, 133.8, 161.7 (Figure A.11, Appendix A). MS-H<sup>+</sup> (EtOAc): m/z 389.0 (Figure A.12, Appendix A).

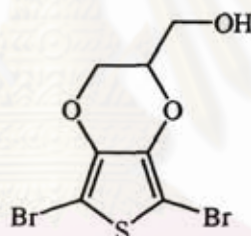
#### 2.4.2 Synthesis of 2'-hydroxymethyl-3,4-ethylenedioxythiophene (HEDOT; R<sub>3</sub>-R<sub>4</sub>= CH<sub>2</sub>CH(CH<sub>2</sub>OH)) 3



2'-hydroxymethyl-3,4-ethylenedioxythiophene was prepared from 3,4-dimethoxythiophene. Ether exchange was done using 3,4-dimethoxythiophene (0.1442 g, 1 mmol), glycerol (3.0 mL, 40 mmol) and *p*-toluenesulfonic acid (PTSA) (0.1902 g, 1 mmol). The mixture was heated at 80 °C for 5 hours and then quenched with saturated sodium hydrogen carbonate solution. The organic layer was separated, and water layer was extracted with ethylacetate three times. The combination between organic layer and ethylacetate extracts was rinsed with distilled water and dried with anhydrous sodium sulfate. The solution was concentrated by evaporating solvent

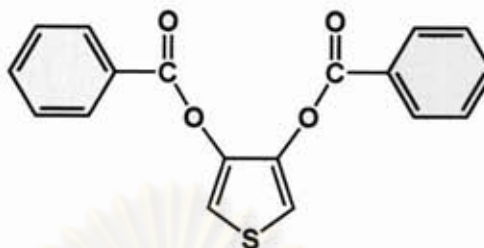
using rotary evaporator. The product was purified by passing through a silica gel column, and eluted with 1:1 mixtures of dichloromethane and hexane. The product was obtained as pale yellow liquid (0.1725 g, 20%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 2.28 (s, 1H, OH), 3.72-3.81 (m, 2H,  $\text{OCHCH}_2\text{-OH}$ ), 4.00-4.03 (m, 1H,  $\text{OCHCH}_2\text{-OH}$ ), 4.14-4.16 (m, 2H, Ar- $\text{OCH}_2\text{CHO}$ -), 6.27 (s, 2H, Ar-H) (**Figure A.13, Appendix A**);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 61.5, 65.7, 74.0, 99.8, 99.9, 141.3 (**Figure A.14, Appendix A**). IR (KBr,  $\text{cm}^{-1}$ ): 3411 (O-H st), 1489 (C=C st) (**Figure A.15, Appendix A**).

#### 2.4.2.1 Synthesis of 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene (DBHEDOT; $\text{R}_1\text{-R}_2 = \text{CH}_2\text{CH}(\text{CH}_2\text{OH})$ )



To the solution of 2'-hydroxymethyl-3,4-ethylenedioxythiophene (HEDOT) (0.1720 g, 1 mmol) in a 2:1 solvent mixture of chloroform (6 mL) and acetic acid (3 mL) at 0-5 °C under inert atmosphere was slowly added *N*-bromosuccinimide (NBS) (0.4450 g, 2.5 mmol). The solution was purified by passing through a silica gel column, and eluted with pure dichloromethane to get a pale-yellow liquid product (0.4450 g, 72%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 2.28 (s, 1H, OH), 3.78-3.89 (m, 2H,  $\text{CH}_2\text{-OH}$ ), 4.09-4.11 (m, 1H,  $\text{OCHCH}_2\text{-OH}$ ), 4.21-4.28 (m, 2H, Ar- $\text{OCH}_2\text{CHO}$ ) (**Figure A.16, Appendix A**);  $^{13}\text{C-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 61.8, 65.8, 74.5, 85.5, 85.6, 139.4, 139.5 (**Figure A.17, Appendix A**). MS-H (EtOAc):  $m/z$  329.1 (**Figure A.18, Appendix A**).

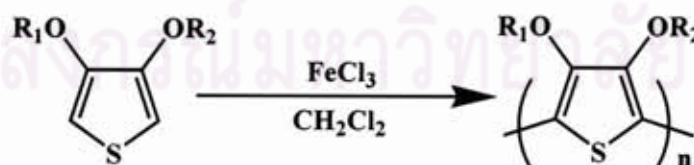
## 2.5 Synthesis of 3,4-dibenzoyloxythiophene ( $R_3, R_4 = \text{OCOC}_6\text{H}_5$ ) 6



A solution of 3,4-dimethoxythiophene (0.1442 g, 1 mmol) in toluene (5 mL) was heated for 2 hours at 60 °C with anhydrous aluminum chloride (0.3334 g, 2.5 mmol) under an atmosphere of nitrogen. The resulting solution was poured into dilute hydrochloric acid (20 mL). The acid solution was extracted with ether and the dihydroxythiophene was extracted from the ether-toluene solution with sodium hydroxide. Treatment of the alkaline solution with a excess of benzoyl chloride (0.35 mL, 3 mmol) gave the product (0.0648 g, 20%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.36 (s, 2H), 7.44 (t, 1H), 7.60 (t, 2H), 8.11 (d, 2H) (**Figure A.19, Appendix A**);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 110.7, 128.6, 128.8, 130.4, 133.8, 138.4, 163.5 (**Figure A.20, Appendix A**). MS- $[\text{M}+\text{Na}]^+$  (MeOH):  $m/z$  347.0 (**Figure A.21, Appendix A**).

## 2.6 Polymerization

### 2.6.1 Oxidative coupling polymerization

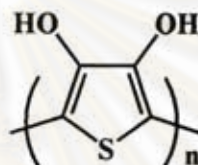


General procedure: To a two-necked 50 mL flask equipped with a magnetic stirrer was added the thiophene monomer and dichloromethane (4 mL) under nitrogen atmosphere. The solution was slowly added into a stirred suspension of three equivalents of anhydrous ferric chloride in dichloromethane (4 mL). When the addition was completed, the mixture was stirred for an additional 24 h at room



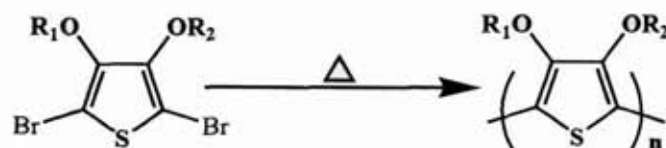
temperature. After the polymerization, the reaction mixture was poured into methanol to recover the product followed by washing with methanol several times. The solution was filtered and purified by a Soxhlet extraction with methanol until the solution was colorless. The resulting polymer was then dried to give the corresponding polythiophene derivatives.

#### 2.6.1.1 Synthesis of poly(3,4-dihydroxythiophene) (PDHT; $R_1, R_2 = OH$ ) 7

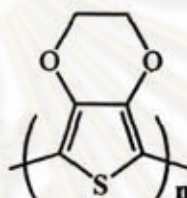


A solution of 3,4-dimethoxythiophene (0.1442 g, 1 mmol) in toluene (5 mL) was heated for 2 hour at 60 °C with anhydrous aluminum chloride (0.3334 g, 2.5 mmol) under an atmosphere of nitrogen. The resulting solution was poured into dilute hydrochloric acid. The acid solution was extracted with  $CH_2Cl_2$  and collected the solution of dihydroxythiophene to polymerize with anhydrous ferric chloride (0.4055 g, 2.5 mmol) following the general procedure above. After the polymerization, methanol was poured into the reaction mixture to recover the product followed by washing the product precipitate with methanol several times until the washed solution was colorless. The resulting polymer was then dried to give the corresponding polythiophene derivatives as dark solid (0.1160 g, 98%). It was partially soluble in methanol, acetone, tetrahydrofuran, *N,N*-dimethylformamide, dimethylsulfoxide but completely soluble in 0.5 M sodium hydroxide.  $^1H$ -NMR (400 MHz, NaOH/ $D_2O$ ): no signal;  $^{13}C$ -NMR (100 MHz, NaOH/ $D_2O$ ):  $\delta$  (ppm) 168.2, 172.9 (Figure A.22, Appendix A). IR of the soluble part (KBr,  $cm^{-1}$ ): 3428 (O-H st), 1642 (C=C st) (Figure A.23, Appendix A); IR of the insoluble part (direct probe on surface,  $cm^{-1}$ ): 3369 (O-H st), 1631 (C=C st) (Figure A.24, Appendix A).

## 2.6.2 Thermal polymerization of 2,5-dibromothiophene derivatives

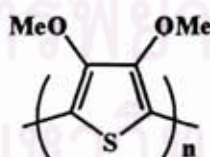


### 2.6.2.1 Poly(3,4-ethylenedioxythiophene) (PEDOT; $R_1=R_2 = \text{CH}_2\text{CH}_2$ )



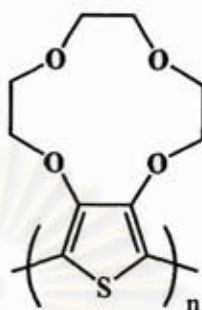
The compound was prepared from an incubation of crystallized 2,5-dibromo-3,4-ethylenedioxythiophene at 70 °C for 24 h. The color of the crystals changed from white to dark blue with brown vapor appeared. The product was insoluble in all organic solvents.

### 2.6.2.2 Poly(3,4-dimethoxythiophene) (PDMT; $R_1=R_2 = \text{CH}_3$ )



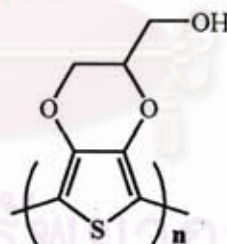
2,5-dibromo-3,4-dimethoxythiophene monomer, as starting material was incubated at 80 °C to 160 °C in a closed round-bottomed flask. Unfortunately, no physical change indicating an occurrence of polymerization was observed. The liquid only evaporized and recondensed back to its original state.

**2.6.2.3 Poly(thiopheno-12-crown-4) ( $R_3-R_4 =$   
 $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ )**



Compound 2, as starting material was incubated at 80 °C to 160 °C in a closed round-bottomed flask. Unfortunately, no physical change indicating an occurrence of polymerization was observed.

**2.6.2.4 Poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene)  
(PHEDOT;  $R_1-R_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ) 8**



The liquid film of 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene from section 2.3.4 (0.0396 g, 0.12 mmol) was incubated at 100 °C in a closed round-bottomed flask for 15 minute. The liquid changed from pale yellow to dark blue with brown vapor appeared. The resulting polymer was then dried to give the corresponding polythiophene derivatives. The resulting polymer was then dried to give the dark solid (0.0214 g, 54%) as product. It was slightly soluble in methanol, acetone, tetrahydrofuran, dimethylsulfoxide and chloroform.  $^1\text{H-NMR}$  of the soluble part (400 MHz, Acetone- $d_6$ ):  $\delta$  (ppm) 3.35-4.60 (broad m,  $\text{CH}_2\text{CHCH}_2$ ), 4.80 (broad s, OH) (Figure A.25, Appendix A). IR of the soluble part (KBr,  $\text{cm}^{-1}$ ): 3439 (O-H st),

1639 (C=C st) (**Figure A.26, Appendix A**); IR of the insoluble part (direct probe on surface,  $\text{cm}^{-1}$ ): 3323 (O-H st), 1683 (C=C st) (**Figure A.27, Appendix A**).

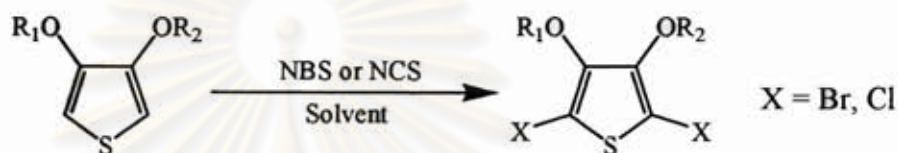


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## CHAPTER III

### RESULTS AND DISCUSSION

#### 3.1 Halogenation of thiophene derivatives

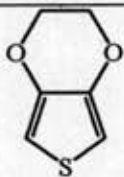
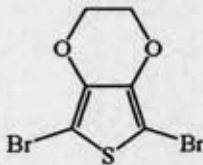
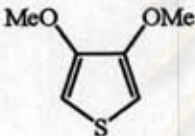
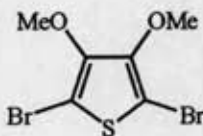
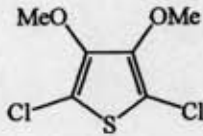
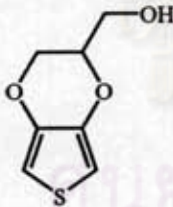



**Figure 3.1** Synthesis of 2,5-dihalo-3,4-dialkoxythiophene derivatives.

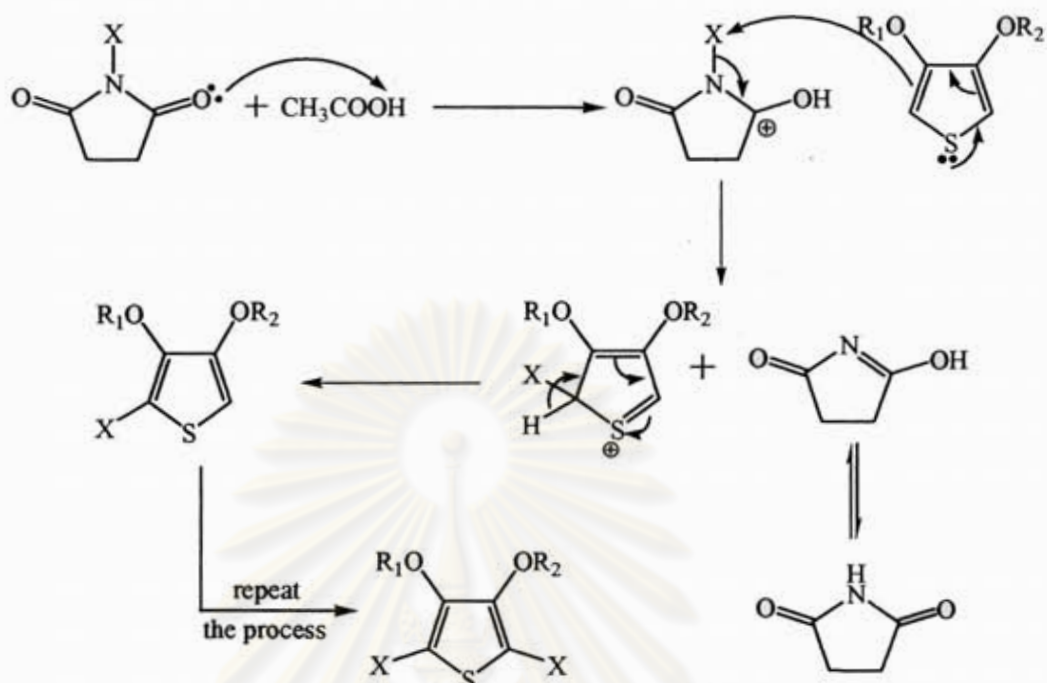
Since  $\alpha$ -position of thiophene ring is generally very reactive towards electrophiles or radicals. Substitution  $\alpha$ -hydrogens by halogenation reaction of EDOT prior to carrying out reactions at the ethylene-bridge may be necessary to prevent side-reactions [50]. Following the bromination procedure by Kellogg and coworkers [51], thiophene was brominated by using *N*-bromosuccinimide (NBS), and provided moderately pure 2,5-dibromothiophene in 60% yield.

Likewise, the bromination at room temperature of EDOT, DMT and HEDOT, utilizing *N*-bromosuccinimide (NBS) as the brominating reagent gave products with different percent yields depending on the  $\beta$ -substituents on the thiophene ring as depicted in **Table 3.1**. The original standard procedure using  $\text{CHCl}_3/\text{CH}_3\text{COOH}$  mixture with long reaction time still seemed to give better results. Nevertheless, brief reaction in  $\text{CH}_2\text{Cl}_2$  could provide a reasonable amount of product or even better in some cases such as that of 2'-hydroxymethyl-3,4-ethylenethiophene (Entries 6,7; Table 3.1). Moreover, *N*-chlorosuccinimide (NCS) was used as chlorinating agent for DMT to give the dichloro derivative. The peak in  $^1\text{H-NMR}$  spectrum at  $\delta \sim 6.3$  ppm which corresponds to  $\alpha$ -hydrogen signal on thiophene ring was disappeared after either bromination or chlorination.

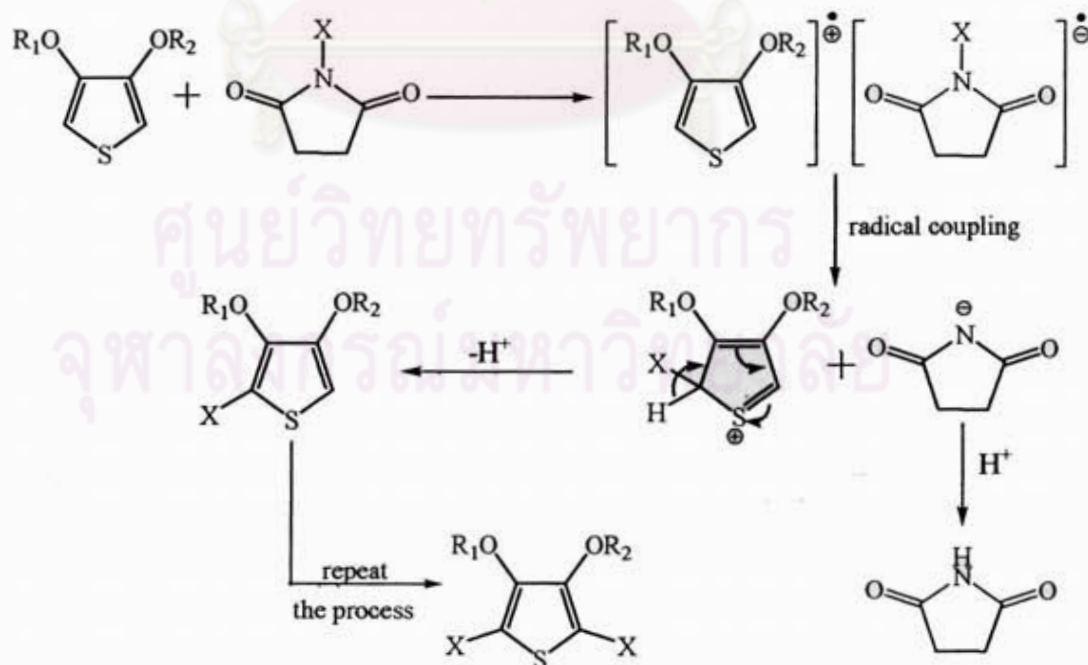
**Table 3.1** Synthesis of 2,5-dihalo-3,4-dialkoxythiophene derivatives

Entry	Substrate	Reagent	Solvent	Time	Product	Yield
1		NBS	2:1 CHCl <sub>3</sub> :CH <sub>3</sub> COOH	5 h		85%
2		NBS	2:1 CHCl <sub>3</sub> :CH <sub>3</sub> COOH	2 h		80%
3			CH <sub>2</sub> Cl <sub>2</sub>	10 min		73%
4		NCS	2:1 CHCl <sub>3</sub> :CH <sub>3</sub> COOH	2 h		81%
5	CH <sub>2</sub> Cl <sub>2</sub>		69 h	75%		
6		NBS	2:1 CHCl <sub>3</sub> :CH <sub>3</sub> COOH	1 h		72%
7			CH <sub>2</sub> Cl <sub>2</sub>	10 min		82%

Two different pathways of bromination mechanism of thiophene ring were plausibly proposed [51,52]. The likely mechanism is illustrated in **Scheme 3.1**. It suggested that the bromination reaction was occurred via acid-catalyzed electrophilic aromatic substitution in polar solvent. Another mechanism was proposed that the reaction was taken place through radical-based single electron transfer followed by aromatic radical substitution as shown in **Scheme 3.2**. The chlorination mechanism is likely to be similar to that of bromination.

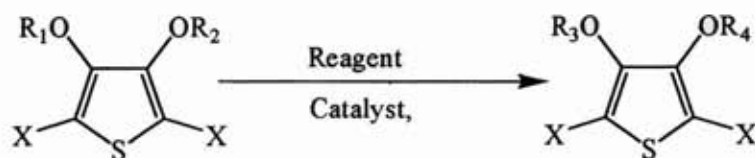


**Scheme 3.1** Bromination mechanism through electrophilic aromatic substitution.



**Scheme 3.2** Bromination mechanism through radical-based single electron transfer followed by aromatic substitution.

### 3.2 Synthesis of 3,4-dialkoxythiophene derivatives



DBEDOT: X = Br; R<sub>1</sub>-R<sub>2</sub> = -CH<sub>2</sub>CH<sub>2</sub>-

DBDMT: X = Br, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>

DCDMT: X = Cl, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>

DMT: X = H, R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>

**Figure 3.2** Synthesis of 3,4-dialkoxythiophene derivatives.

**Table 3.2** Synthesis of 3,4-dialkoxythiophene derivatives

Entry	Substrate	Reagent	Condition	Time	Product (yield)
1	DBEDOT	paraformaldehyde	PTSA, Toluene/ 80 °C	31 h	dark solid
2	DBEDOT	paraformaldehyde	PTSA, DMF/ 80 °C	5 h	dark solid
3	DBEDOT	paraformaldehyde	AlCl <sub>3</sub> , 1,2-dichloroethane / reflux	24 h	dark solid
4	DBEDOT	paraformaldehyde	H <sub>2</sub> SO <sub>4</sub> , EtOH/ reflux	24 h	dark solid
5	DBEDOT	formalin 37%	AlCl <sub>3</sub> , 1,2-dichloroethane / reflux	24 h	dark solid
6	DBEDOT	2,2-dimethoxypropane	PTSA, toluene/ reflux	6 h	dark solid
7	DBDMT	paraformaldehyde	PTSA, toluene/ reflux	1 h	dark solid



Table 3.2 Synthesis of 3,4-dialkoxythiophene derivatives (continued)

Entry	Substrate	Reagent	Condition	Time	Product (yield)
8	DBDMT	paraformaldehyde	PTSA, DMF/ reflux	24 h	dark solid
9	DBDMT	paraformaldehyde	AlCl <sub>3</sub> , 1,2-dichloroethane / reflux	3 h	dark solid
10	DBDMT	formalin 37%	PTSA, toluene/ reflux	2 h	dark solid
11	DBDMT	butyraldehyde	PTSA, 1,2-dichloroethane / reflux	2 h	dark solid
12	DBDMT	benzyl bromide	K <sub>2</sub> CO <sub>3</sub> , DMF / 90 °C	7 d	- <sup>a</sup>
13	DBDMT	benzyl bromide	TMAI, KI, DMF/ 90 °C	2 d	- <sup>a</sup>
14	DBDMT	benzyl bromide	TEA DMF/ 90 °C	30 h	- <sup>a</sup>
15	DBDMT	trimethylsilyl chloride	KI/ reflux	3 h	- <sup>a</sup>
16	DBDMT	trimethylsilyl chloride	TBAI, NaI ACN/ reflux	20 h	- <sup>a</sup>
17	DBDMT	trimethylsilyl chloride	TEA DMF/ 90 °C	30 h	- <sup>a</sup>
18	DCDMT	paraformaldehyde	PTSA, toluene/ reflux	2 d	NR
19	DCDMT	paraformaldehyde	PTSA, DMF/ 90 °C	2 d	NR

**Table 3.2** Synthesis of 3,4-dialkoxythiophene derivatives (continued)

Entry	Substrate	Reagent	Condition	Time	Product (yield)
20	DCDMT	2,2-dimethoxypropane	PTSA, DMF/ 90 °C	2 d	NR
21	DCDMT	benzyl bromide	K <sub>2</sub> CO <sub>3</sub> , DMF/ 90 °C	2 d	NR
22	DCDMT	trimethylsilyl chloride	KI/ RT	3 d 20 h	- <sup>b</sup>
23	DCDMT	trimethylsilyl chloride	NaI, ACN/ RT	4 d	- <sup>b</sup>
24	DCDMT	dichlorodimethylsilane	TBAI, KI/ RT	2 d	- <sup>b</sup>
25	DCDMT	tert-butyl dimethylsilyl chloride	TBAI, KI, CH <sub>2</sub> Cl <sub>2</sub> / RT	3 d 19 h	- <sup>b</sup>
26	DCDMT	benzaldehyde	PTSA, Chlorobenzene / reflux	2 d	- <sup>b</sup>
27	DMT	hexamethylene-tetramine	PTSA, DMF/ 90 °C	3 d	NR
28	DMT	benzyl bromide	K <sub>2</sub> CO <sub>3</sub> , DMF/ 90 °C	3 d 22 h	NR
29	DMT	trimethylsilyl chloride	TBAI, KI / reflux	1 d 9 h	NR
30	DBEDOT	2-bromoethanol	PTSA/ 80 °C	2 h	liquid (11%)
31	DBEDOT	2-bromoethanol	MSA, LiClO <sub>4</sub> /80°C	2 h	liquid (22%)

**Table 3.2** Synthesis of 3,4-dialkoxythiophene derivatives (continued)

Entry	Substrat	Reagent	Condition	Time	Product (yield)
32	DMT	glycerol	PTSA, 80 °C	3 h	liquid (18%)
33	DMT	glycerol	PTSA, 80 °C	5 h	liquid (20%)
34	DMT	glycerol	PTSA, 80 °C	24 h	liquid (11%)

NR = No reaction

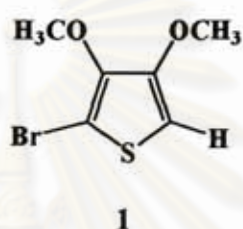
<sup>a</sup> debromination

<sup>b</sup> dechlorination

From **Table 3.2**, entries 1-6, 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) obtained from bromination reaction was initially used as the precursor to carry out ether exchange reaction utilizing different catalysts and conditions aiming towards the methylene-bridged dioxythiophene derivative in which the bromo groups were put in place to prevent premature polymerization. However, it was found that all products were obtained in dark solid form which were anticipated to be poly(3,4-ethylenedioxythiophene) (PEDOT) since they could not be dissolved in any organic solvents. These evidences suggested that the intended ether exchange reaction to replace the ethylene bridge in DBEDOT was not successful due to the facile debrominations followed immediately by the polymerization reaction to produce dark solid polymer that could not be characterized by usual solution-based methods.

Next, DBDMT was selected as the precursor as a substitute for DBEDOT expecting that the methyl groups might be removed were easily than the ethylene bridge. The ether exchange reactions employing PTSA as a catalyst for entries 7-11 also gave the similar insoluble dark solid products which were expected to be poly(3,4-ethylenedioxythiophene) (PDMT) insolubility of solid product in organic solvent [40].

The results of entries 12-17 demonstrated that the desired nucleophilic substitutions did not occur. Instead, out of the bromine atoms was found to detach from the thiophene ring. The obtained product was BDMT (1), confirmed by the presence of two signals the desymmetrized CH<sub>3</sub> groups and a singlet signal of the  $\alpha$ -position of the thiophene ring from <sup>1</sup>H spectrum (Figure A.29, Appendix A). Two methyl peak from <sup>13</sup>C NMR spectrum (Figure A.30, Appendix A) additionally confirmed this interpretation.



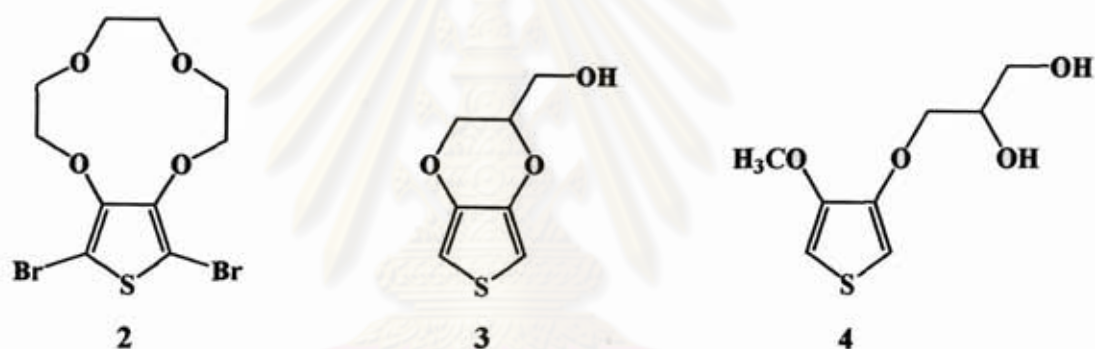
**Figure 3.3** 2-Bromo-3,4-dimethoxythiophene (BDMT).

The results above implied that the bromine atom were susceptible to be easily detached from DBDMT, hence allowed the polymerization to occur faster than the substitutions at the dioxy groups. To avoid this problem, the dichloro derivative was made in which the chlorine atoms were expected to be DCDMT was chosen as a precursor for entries 18-26 to carry out substitution reaction of  $\alpha$ -hydrogen of thiophene ring. Nevertheless, the substitution of entries 18-21 did not occur but dechlorination reaction did not observe. Opposite to prior entries, dechlorination of entries 22-26 was observed.

Non-halogenated DMT was picked as a precursor for entries 27, 28, and 29 to perform nucleophilic substitution, however, again, substitution reaction did not take place. Only starting material was recovered.

Fortunately, as shown in entries 30 and 31, it was found that the substitution of the ethylene bridge in DBEDOT was occurred upon the reaction with the 2-bromoethanol in the presence of *p*-toluenesulfonic acid (PTSA) at 80 °C. The thiophene crown ether product (2) (Figure 3.4) was obtained as pale yellow liquid in 11% yield. <sup>1</sup>H-NMR (Figure A.10, Appendix A) demonstrated triplets signal at  $\delta$  3.5, 4.5 ppm and singlet signal at 4.2 ppm which corresponded to the signals of

hydrogen atoms on the crown ether.  $^{13}\text{C}$ -NMR spectrum (**Figure A.11, Appendix A**) of the crown ether product correctly revealed 5 different types of carbon that substantiated the crown ether structure. To increase the yield, methane sulfonic acid (MSA) in the presence of lithium perchlorate ( $\text{LiClO}_4$ ) was used as the catalyst. Lithium ion is believed to be a template to help binding four oxygen atoms to form crown ether ring and enhance the amount of product. The resulting yield (22%, entry 31) was partly improved in comparison to that from PTSA-based catalyst. The inferior yield could be attributed to the competition between from other ether exchange reactions and polymerization reaction in which some dark solid precipitate suspected to be PEDOT was observed.

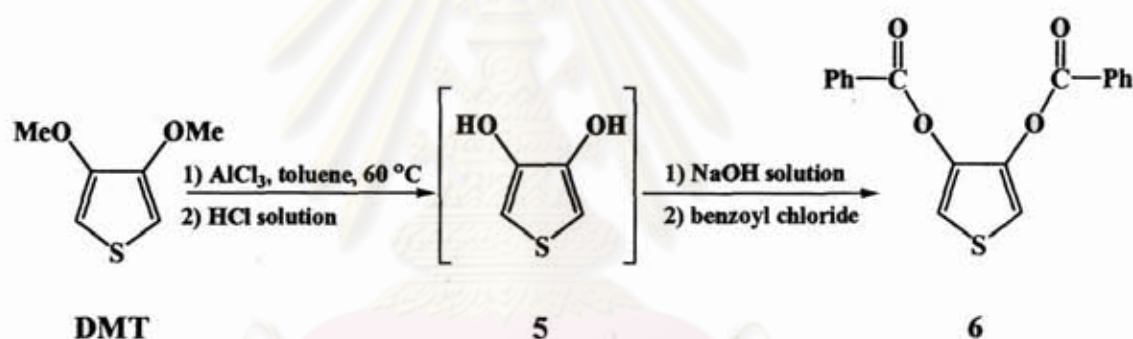


**Figure 3.4** The products from the ether exchange reactions (entries 30-34, **Table 3.2**).

Moreover, DMT was utilized as the precursor for entries 32, 33 and 34 to perform ether exchange reaction with glycerol. Reaction mixture was heated at  $80^\circ\text{C}$  for three hours and gave the product **3** in 18% yield. However, it was found that the reaction was not completed and 13% yield of the by-product **4** could be isolated (**Figure 3.4**). This by-product was the intermediate arose from incomplete substitution of glycerol replacing only one methoxy group of DMT. Characterizations by  $^1\text{H}$ -NMR (**Figure A.31, Appendix A**) and  $^{13}\text{C}$ -NMR (**Figure A.32, Appendix A**) confirmed the structure of the intermediate **4**. When the reaction mixture was repeated and continued for 5 hours and 24 hours, only 20% and 11% yields of the product **3** (**Figure 3.4**) were obtained respectively. This means that longer reaction time might

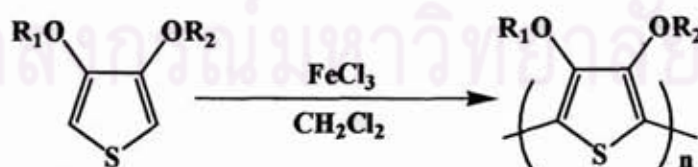
not the competitive ether exchange side reaction and polymerization could also be applied in this case.

Fager and coworker [53] have reported an alternative method to functionalize at the 3,4-dioxy position of DMT by simply removed the methyl groups and quickly trapped the unstable dihydroxy intermediate **5** with benzoyl chloride to give dibenzoate **6** (Scheme 3.3). The compound of interest, 3,4-dihydroxythiophene (**5**), was not isolated due to its excessive instability toward oxygen. To confirm the existence of compound **5**, this process was reproduced in which the dibenzoate **6** could be synthesized in 20% yield as confirmed by  $^1\text{H-NMR}$  (Figure A.19, Appendix A) and  $^{13}\text{C-NMR}$  spectrum (Figure A.20, Appendix A).



**Scheme 3.3** The synthesis of dibenzoate of 3,4-dioxythiophene reported by Fager [53].

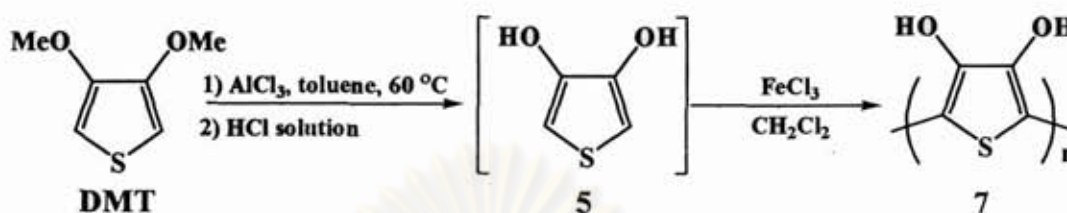
### 3.3 Oxidative coupling polymerization of 3,4-dihydroxythiophene



**Figure 3.5** Synthesis of 3,4-dialkoxythiophene derivatives by oxidative coupling polymerization.

The synthesis of polythiophene derivative by oxidative coupling polymerization using ferric chloride was adapted from that reported by Tepveera [54]. Together with the process using previously mentioned, the Fager's procedure, 3,4-

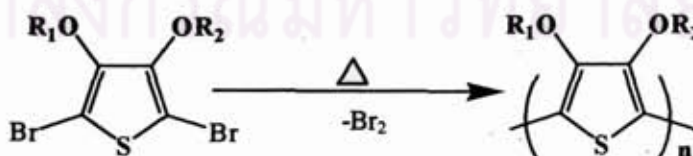
dihydroxythiophene was first synthesized and was further polymerized by oxidative coupling technique using  $\text{FeCl}_3$  as the oxidizing agent (Scheme 3.4).



**Scheme 3.4** The synthesis of poly(3,4-dihydroxythiophene)

Poly(3,4-dihydroxythiophene) (PDHT) (7) was obtained as dark blue solid in 98% yield. It was partially soluble in methanol, dimethyl sulfoxide, *N,N*-dimethylformamide, tetrahydrofuran, acetone, but could be completely soluble in 0.5 M NaOH solution, indicating the acidic property of phenolic-like moieties. The  $^1\text{H-NMR}$  spectrum of the solution in NaOH/ $\text{D}_2\text{O}$  showed no signal (Figure A.22, Appendix A).  $^{13}\text{C-NMR}$  spectrum of the same solution appeared two signals at  $\delta \sim 168.2$  and  $172.9$  ppm which could correspond to  $\alpha$  and  $\beta$ -carbons on the thiophene ring. IR spectrum of PDHT (Figure A.24, Appendix A) showed very strong O-H stretching ( $3200\text{-}3400\text{ cm}^{-1}$ ) and C=C stretching ( $1695\text{ cm}^{-1}$ ) characteristic bands. The molecular weight measurement by GPC of the fraction that dissolved in THF gave approximated  $M_n$  of only 373, corresponding to about 4 monomer unit.

### 3.4 Thermal polymerization of 2,5-dibromothiophene derivatives



**Figure 3.6** Synthesis route of 3,4-dialkoxythiophene derivatives by thermal polymerization.

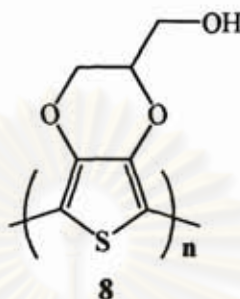
The synthesis procedure of polythiophene derivatives by thermal polymerization was adapted from the solid state polymerization (SSP) used by Meng and coworkers [48,49]. The solid state polymerization was suggested to spontaneously occur and give readily-doped PEDOT by simple heating of the corresponding dibromo derivatives of EDOT monomer. The stacking congested structure of the DBEDOT in the crystal form and halogen-halogen closed-contact force the debromination with in situ C-C bonds formation resulting in solid state polymerization of these compounds. The procedure was repeated to verify and optimize the process. The result showed that, PEDOT could be obtained as insoluble dark blue crystal by incubation of the colorless crystalline DBEDOT at 80 °C for 4 h. During the reaction, significant amount of red-brown bromine vapor was observed over the crystal pad suggested that debromination reaction had proceeded.

Next, other 2,5-dibromothiophene derivatives: the dibromo derivatives of DMT, HEDOT and compound 2 were used as the monomers instead of DBEDOT. Upon the heating the liquid DBDMT and compound 2 between 80 °C to 160 °C in closed containers, no physical change was observed in both cases. This might be because intermolecular distance among the monomers of these two compounds may not be short enough to induce the polymerization.

However, upon heating at 100 °C for 15 minutes, polymerization reaction of the dibromo derivatives of compound 3 took place with a change from pale yellow liquid to dark blue solid state in closed container. This polymer **8** (Figure 3.5) was partially soluble in methanol, dimethyl sulfoxide, tetrahydrofuran, and acetone. From its <sup>1</sup>H-NMR characterization, (Figure A.25, Appendix A) a singlet signal at 5.23 ppm was assumed to be the protons of the hydroxyl groups on ethylene bridge. The other protons were shown as multiplet signal at 3.35-4.60 ppm. The optical properties of polymer **8** was analyzed by UV-Vis spectroscopy using partially dissolved portion of the polymers in methanol. This blue solution showed a relatively large value maximum wavelength absorption ( $\lambda_{\text{max}}$ ) at 610 nm (Figure A.28, Appendix A). The molecular weight measurement by GPC of the fraction that dissolved in THF gave approximated  $M_n$  of only 598, corresponding to about 3 monomer unit. In IR



spectrum, the polymer **8** showed very strong O-H stretching ( $3100\text{-}3600\text{ cm}^{-1}$ ) and C=C stretching ( $1683\text{ cm}^{-1}$ ) characteristic bands (**Figure A.27, Appendix A**).



**Figure 3.7** Structure of poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene) (PHEDOT) from thermal polymerization of 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene (DBHEDOT).

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

## CHAPTER IV

### CONCLUSION

The new 3,4-dialkoxythiophene derivatives were successfully synthesized by the ether exchange reactions using *p*-toluenesulfonic acid (PTSA) as the catalyst. The reaction of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) with 2-bromoethanol give compound **2** in 22% yield. In another case, the reaction of 3,4-dimethoxythiophene with glycerol give compound **3** in 20% yield. Up to 20% yield of dibenzoate of 3,4-dihydroxythiophene has been obtained through demethylation of 3,4-dimethoxythiophene with anhydrous aluminum chloride and subsequently trapping of the intermediate by benzoylation with benzoyl chloride.

The synthesis of poly(3,4-dihydroxythiophene) (PDHT) in 98% yield was made by directly demethylation of 3,4-dimethoxythiophene with anhydrous aluminum chloride followed by oxidative coupling polymerization of the resulting intermediate using anhydrous ferric chloride as the oxidative coupling agent. The solid state polymerization (SSP) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) to poly(3,4-ethylenedioxythiophene) (PEDOT) was successfully repeated. The procedure was applied to the thermal polymerization of 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene to give poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene) (**8**) in 54% yield while similar attempts with 2,5-dibromo-3,4-dimethoxythiophene (DBDMT) and compound **2** were not yet successful.

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ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย



**APPENDIX**

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

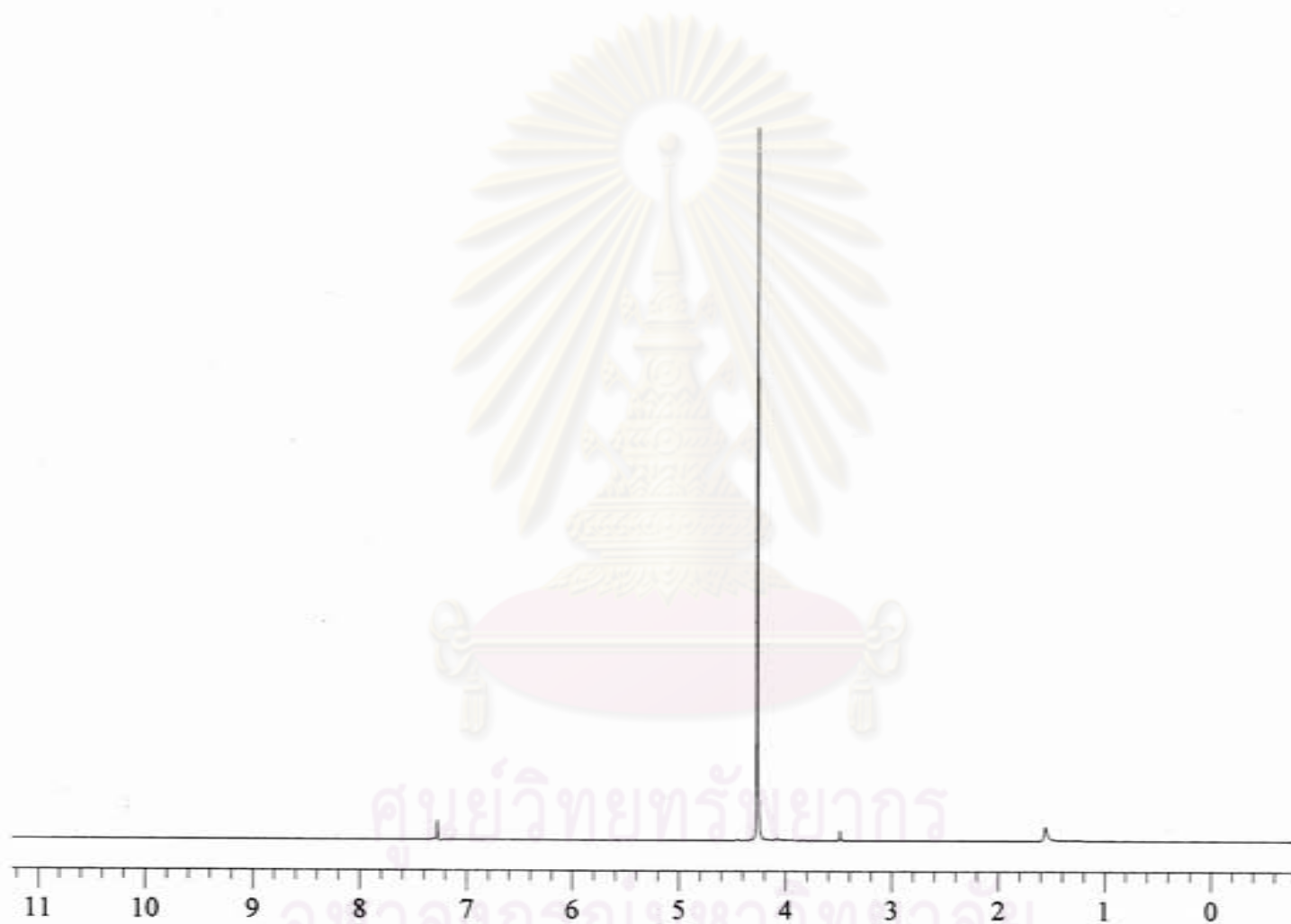


Figure A.1  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)

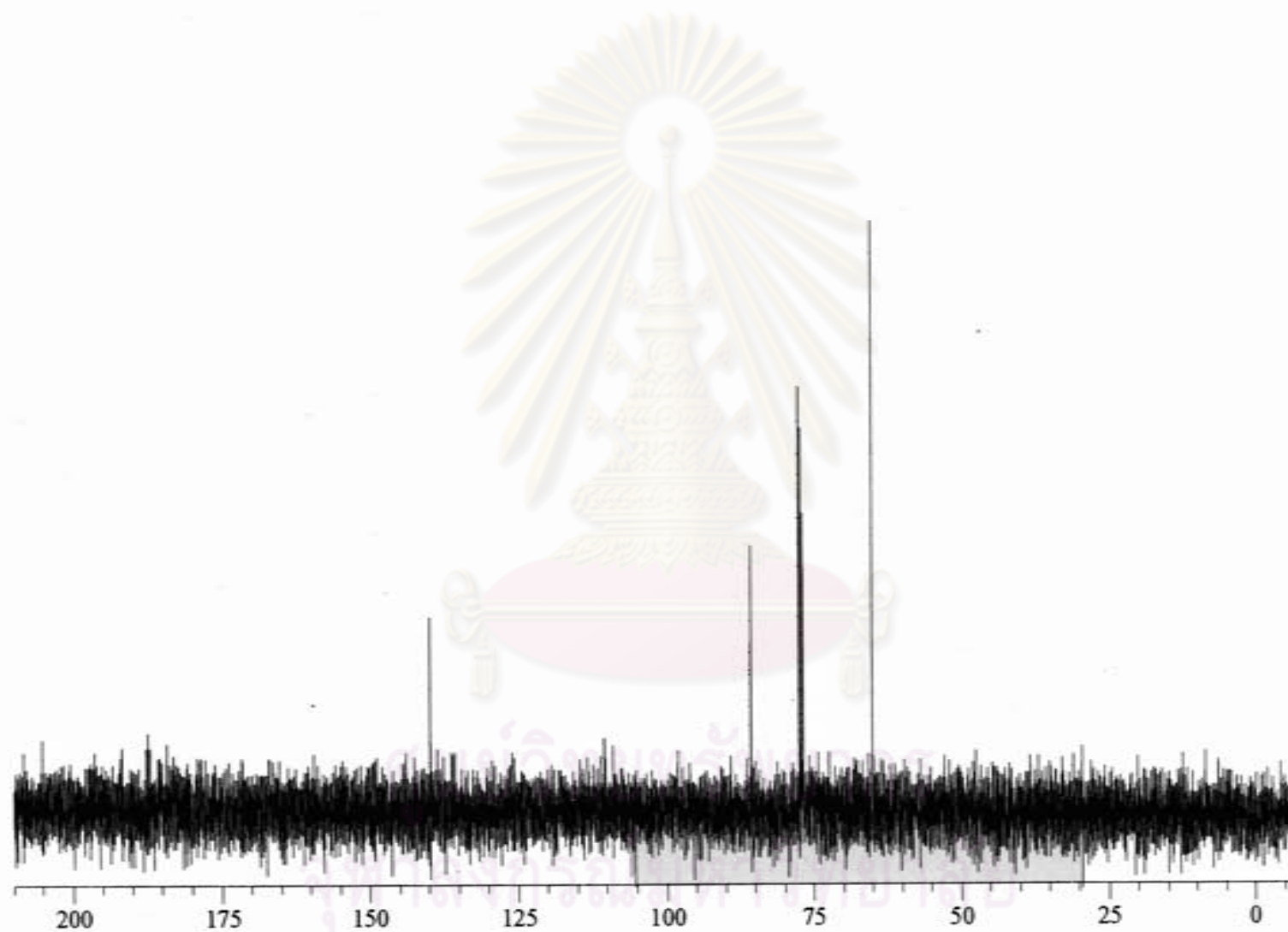


Figure A.2  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)

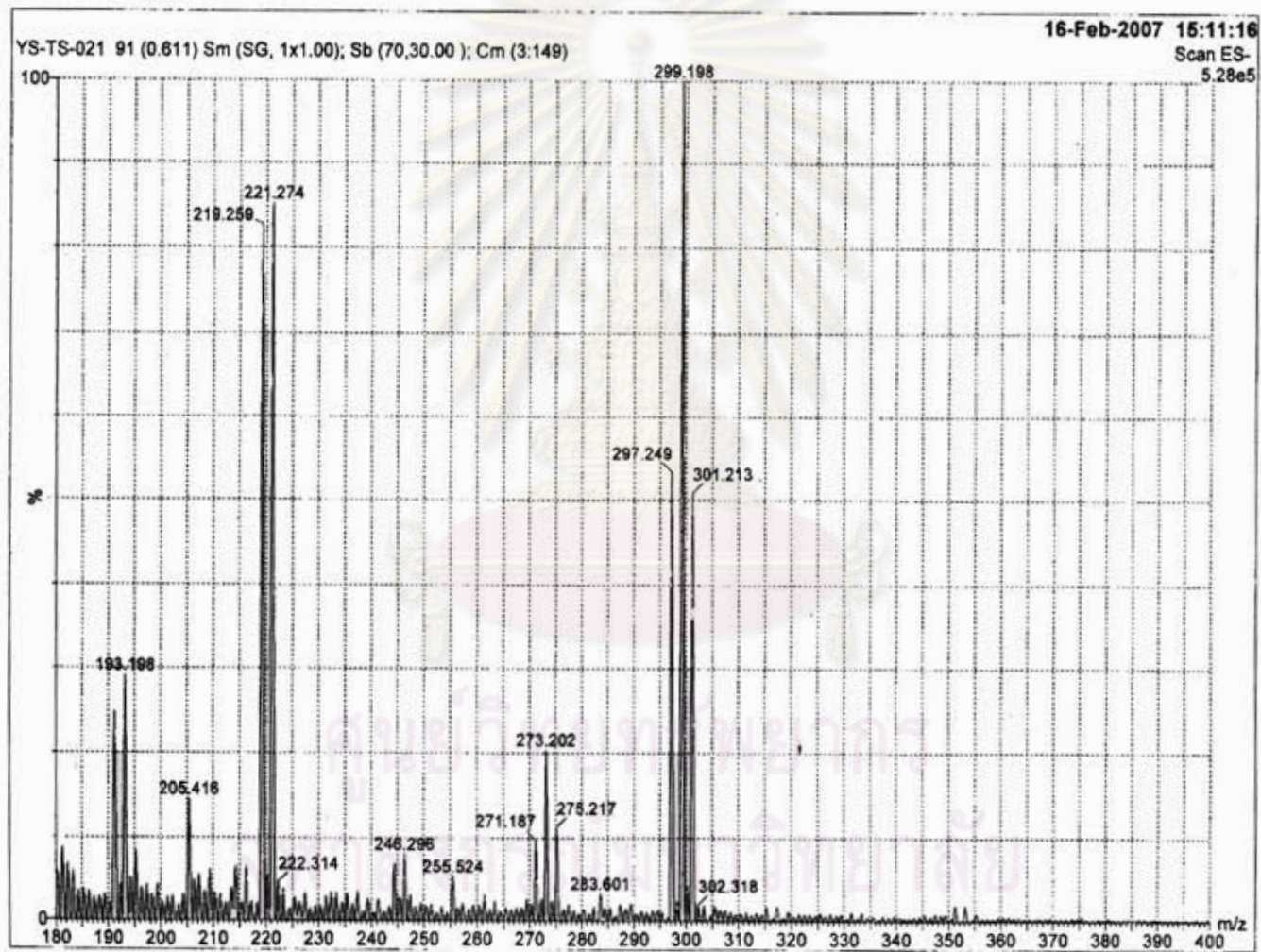
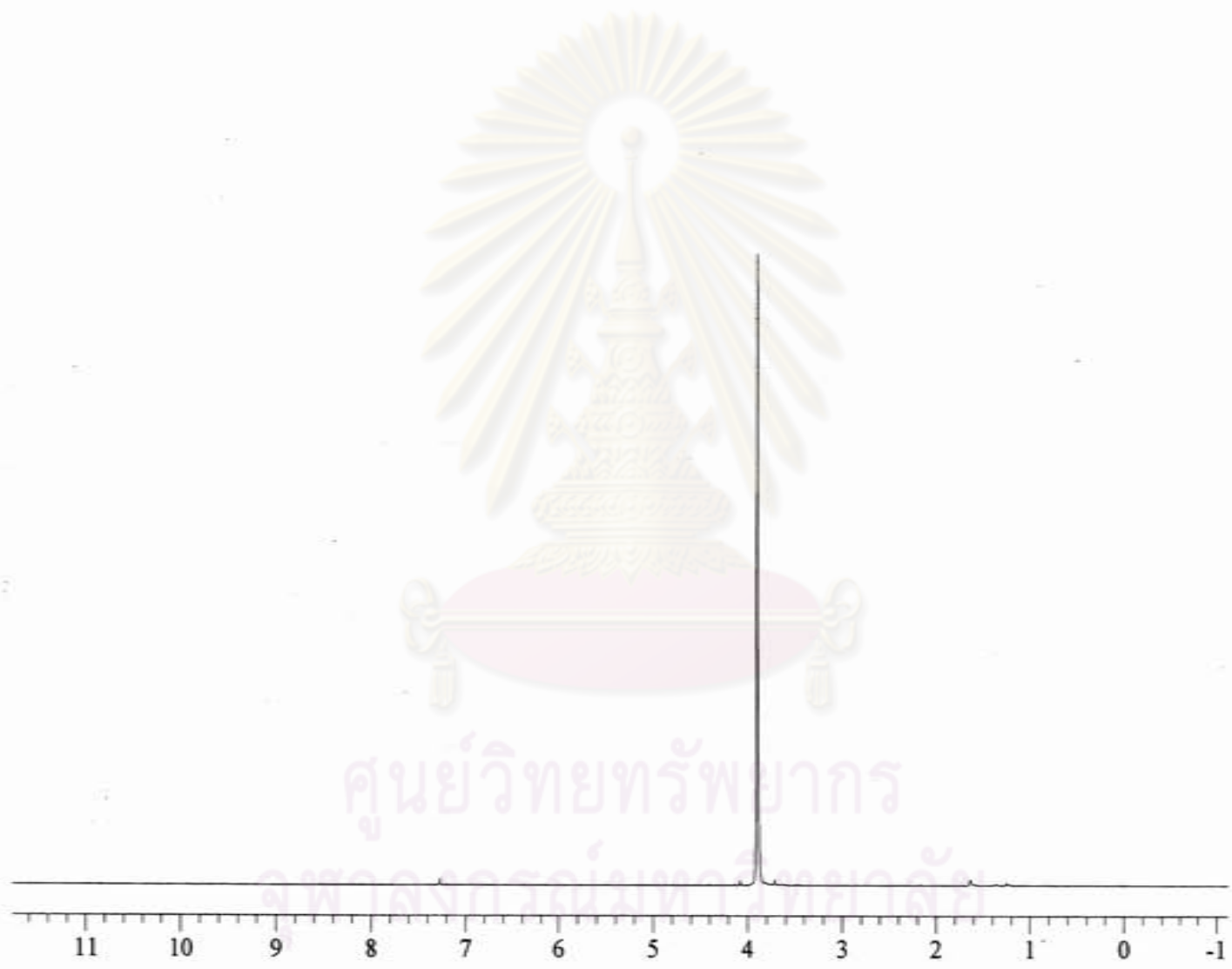


Figure A.3 Mass spectrum of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)



**Figure A.4**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of 2,5-dibromo-3,4-dimethoxythiophene (DBDMT)

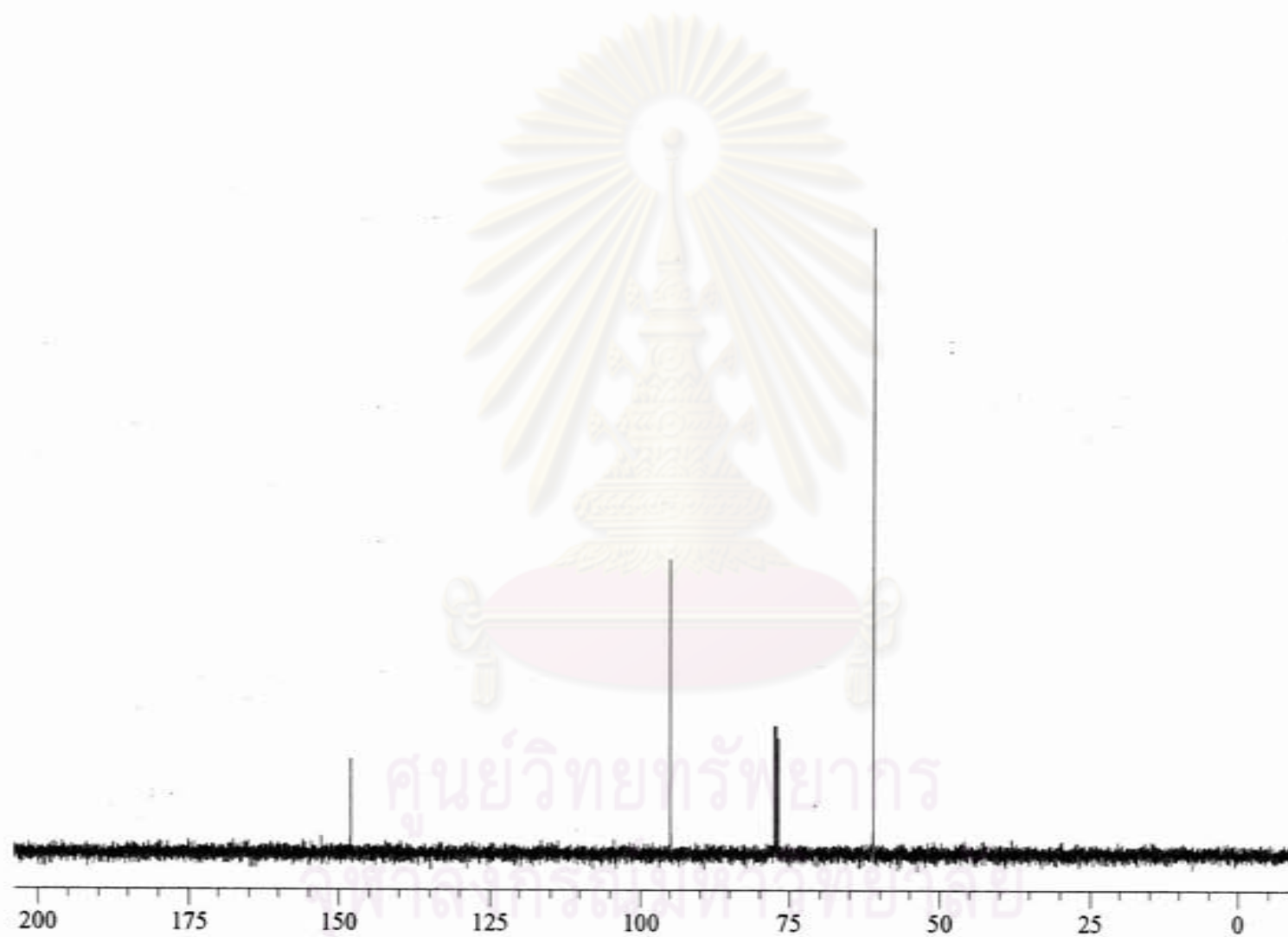


Figure A.5  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of 2,5-dibromo-3,4-dimethoxythiophene (DBDMT)

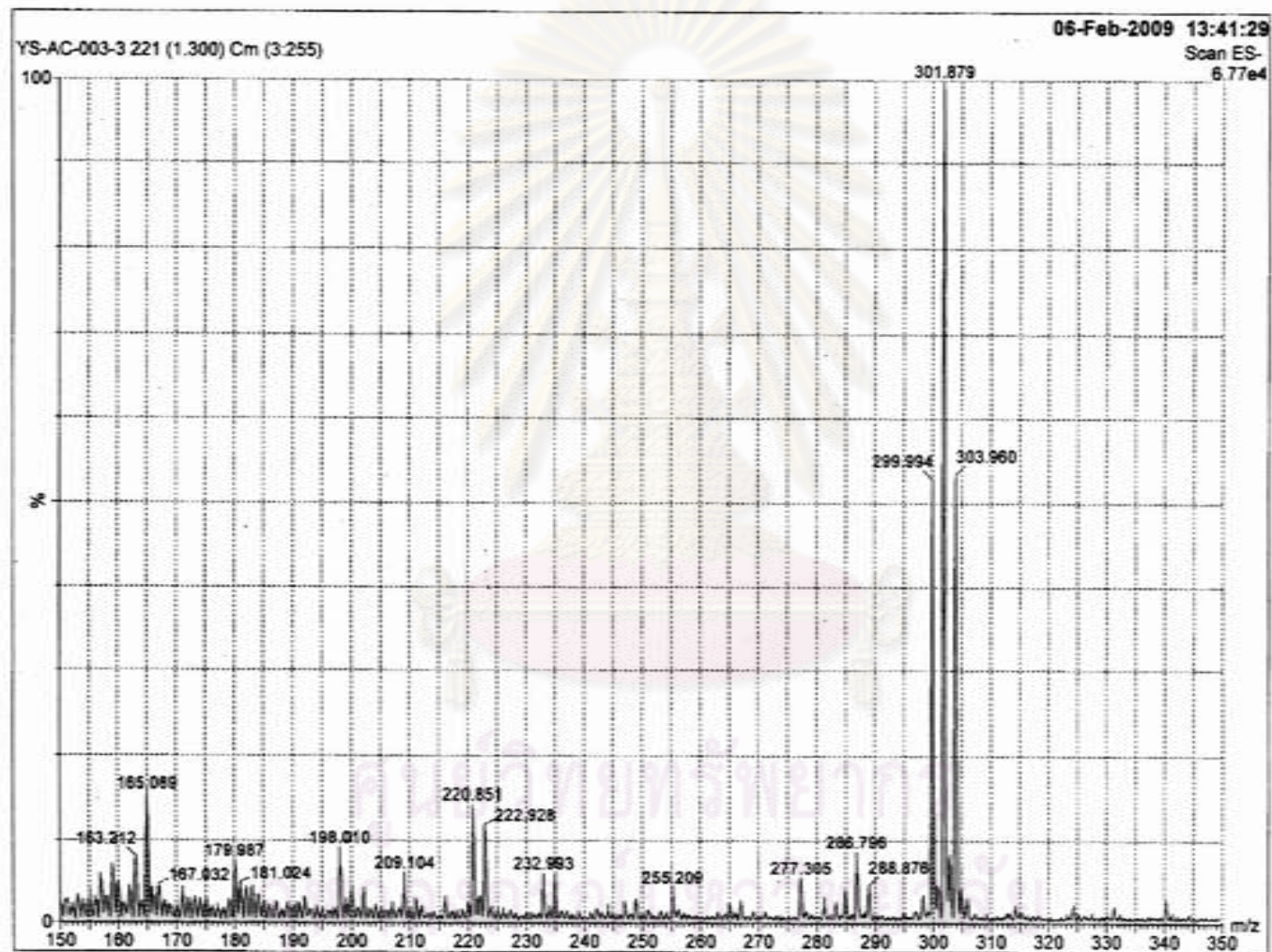


Figure A.6 Mass spectrum of 2,5-dibromo-3,4-dimethoxythiophene (DBDMT)



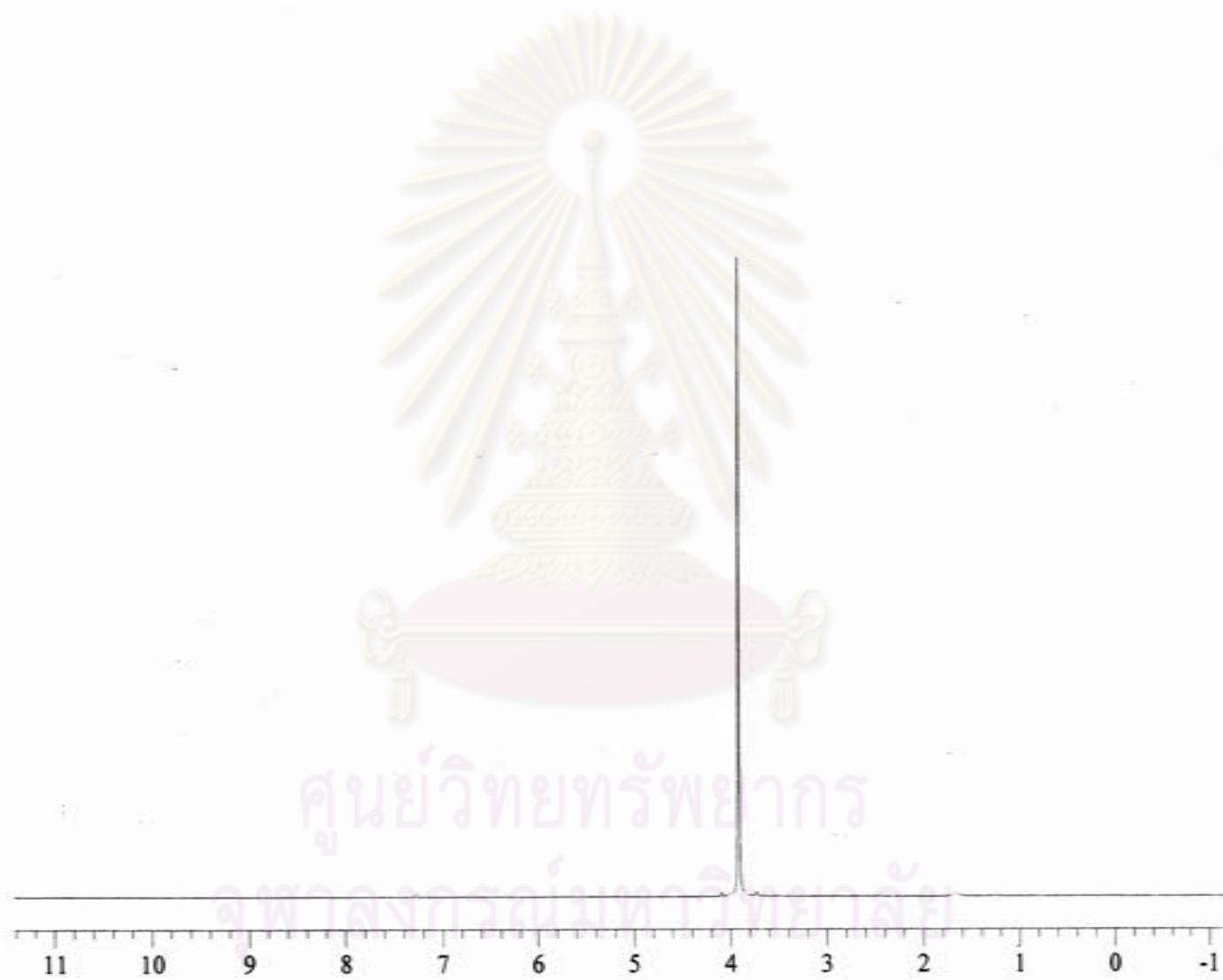


Figure A.7  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of 2,5-dichloro-3,4-dimethoxythiophene (DCDMT)

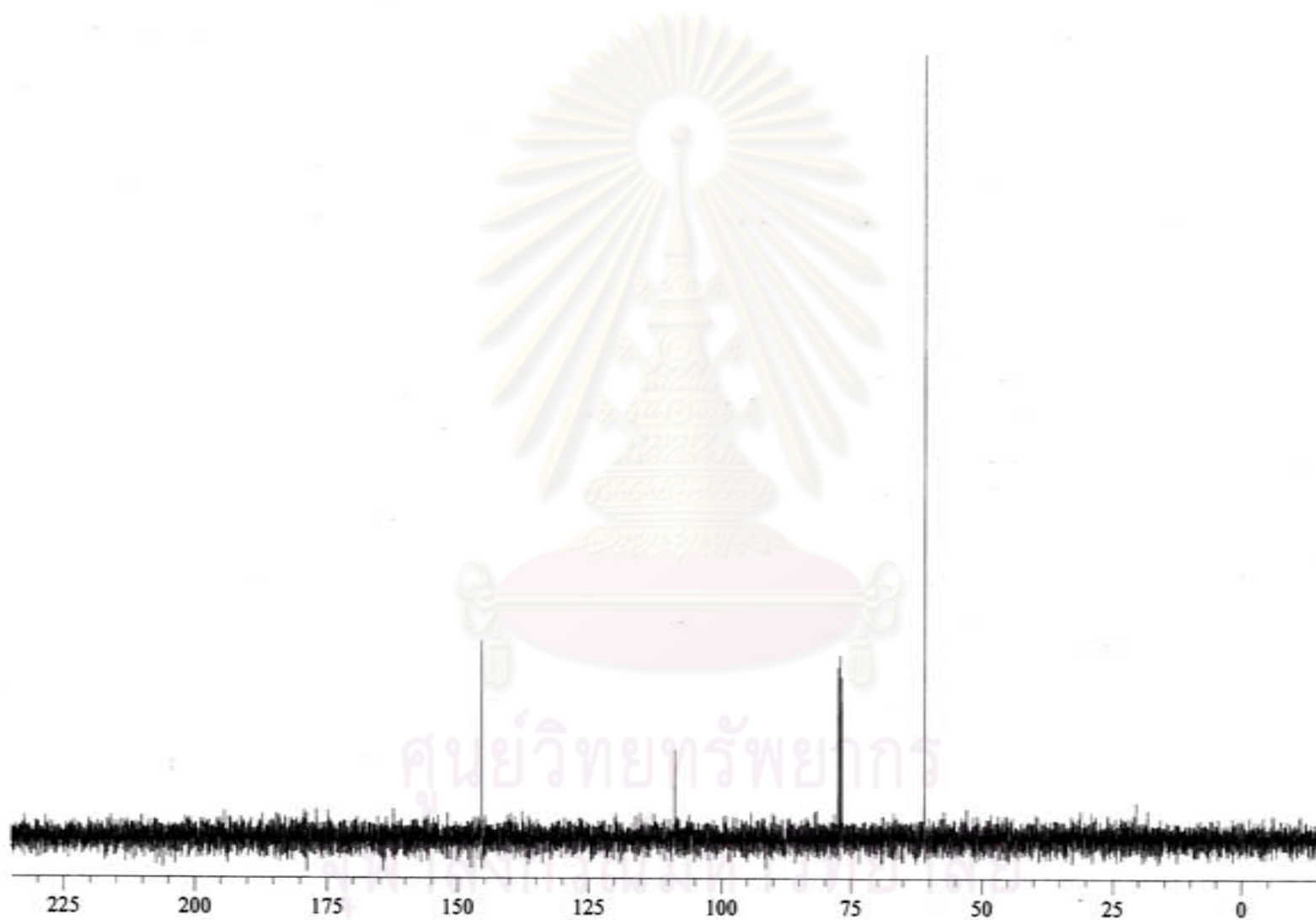


Figure A.8  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of 2,5-dichloro-3,4-dimethoxythiophene (DCDMT)

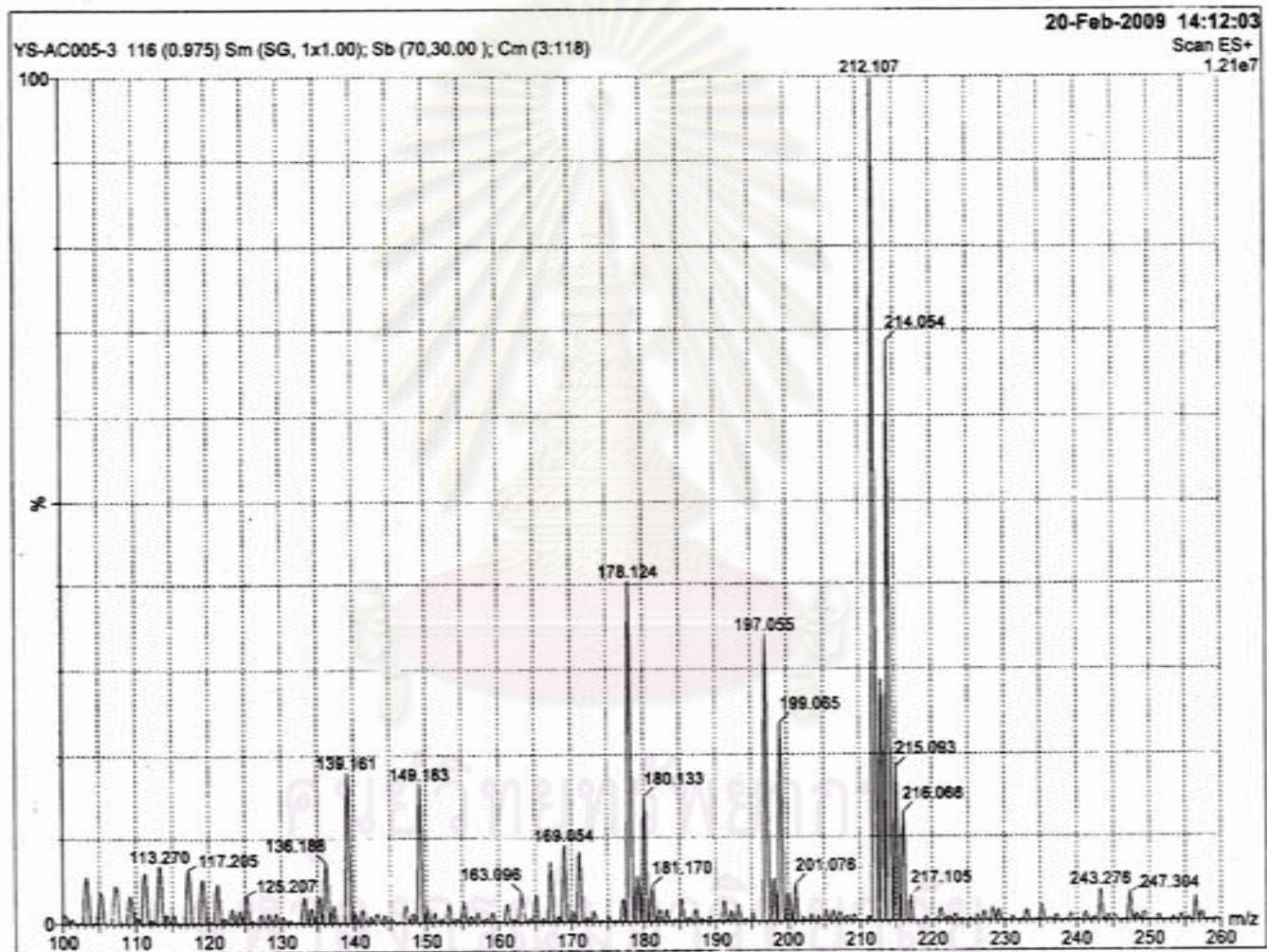


Figure A.9 Mass spectrum of 2,5-dichloro-3,4-dimethoxythiophene (DCDMT)

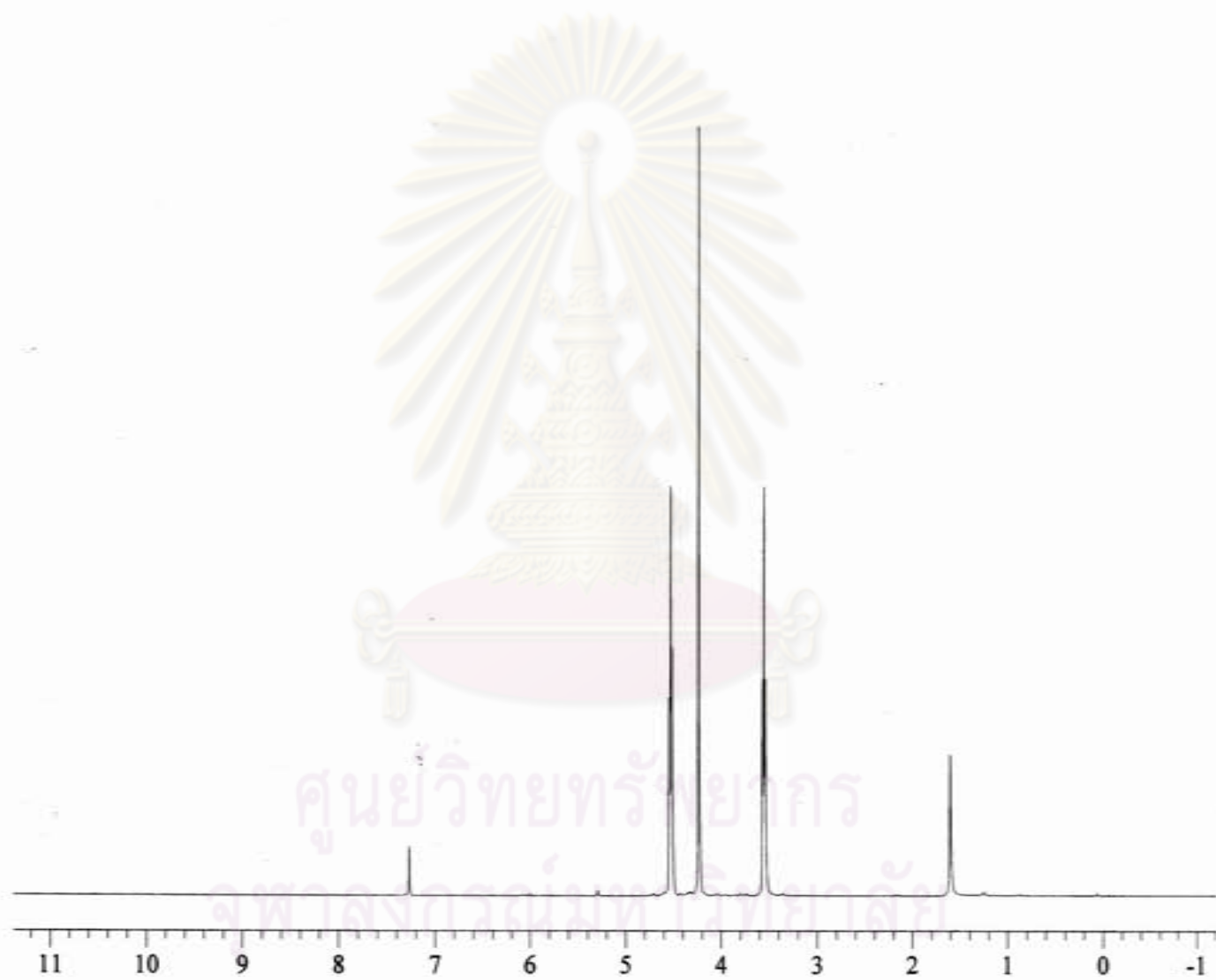
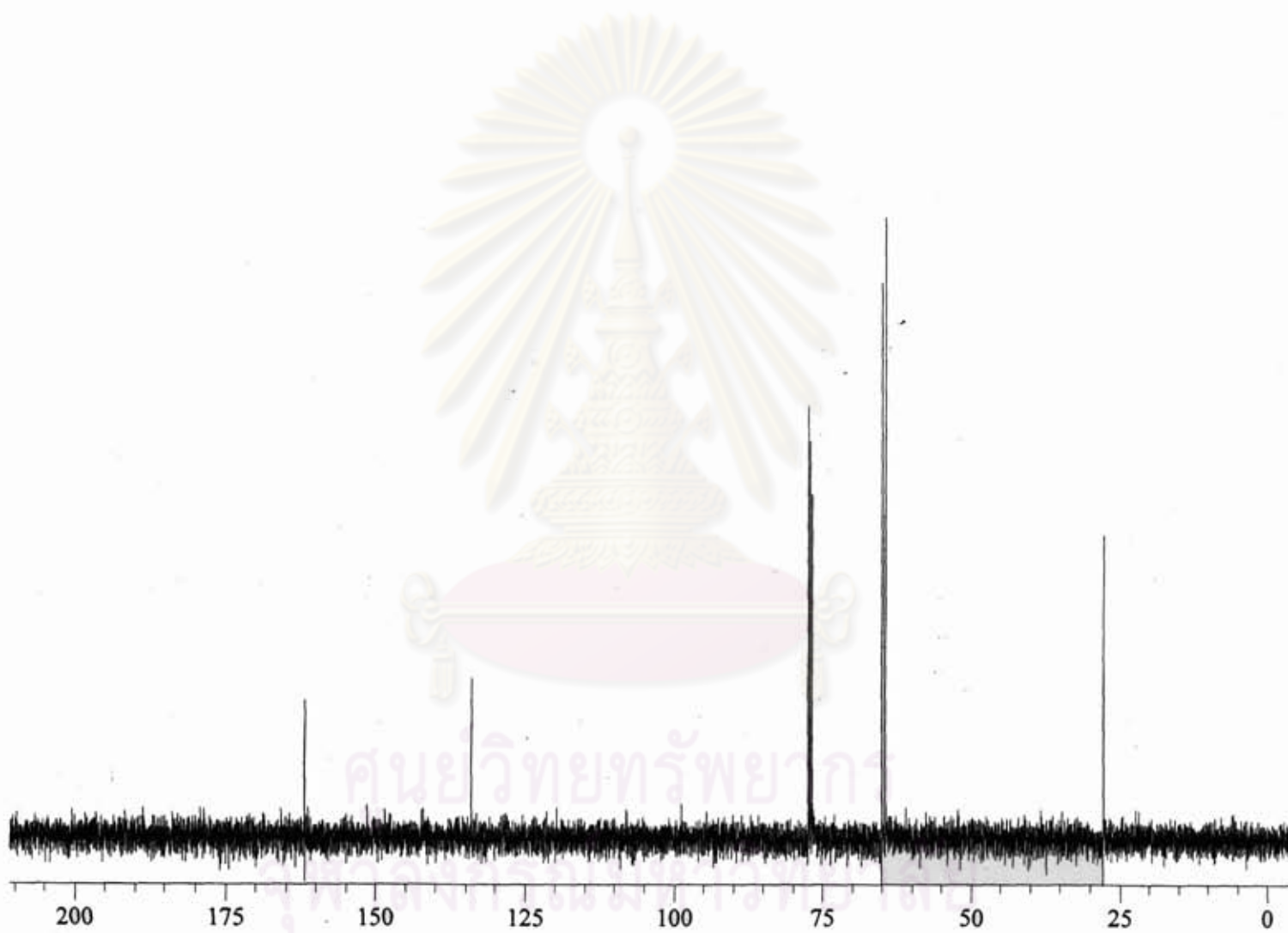


Figure A.10  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of 2',5'-dibromothiopheno-12-crown-4 2



**Figure A.11**  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of 2',5'-dibromothiopheno-12-crown-4 2

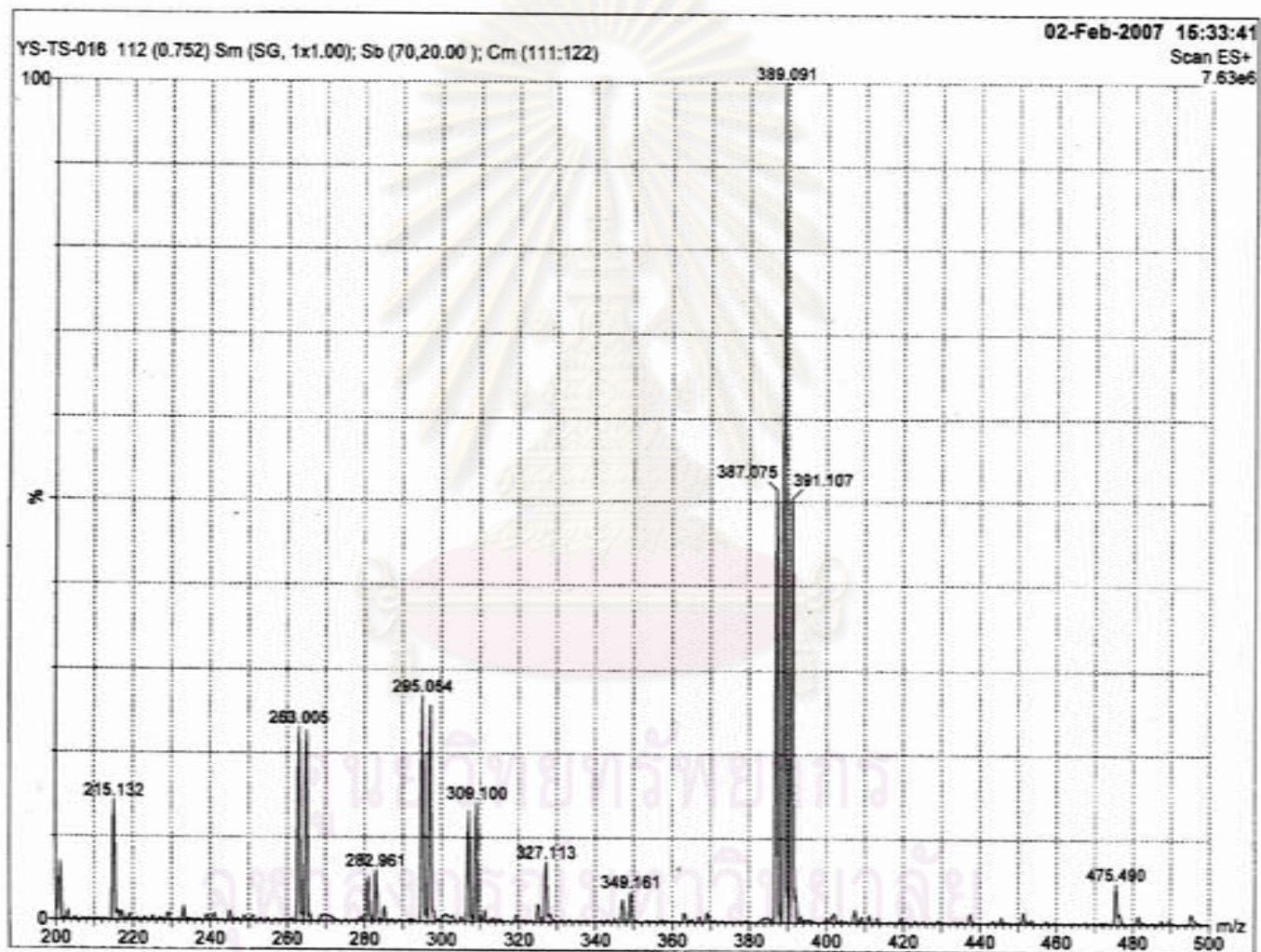


Figure A.12 Mass spectrum of 2',5'-dibromothiopheno-12-crown-4 2

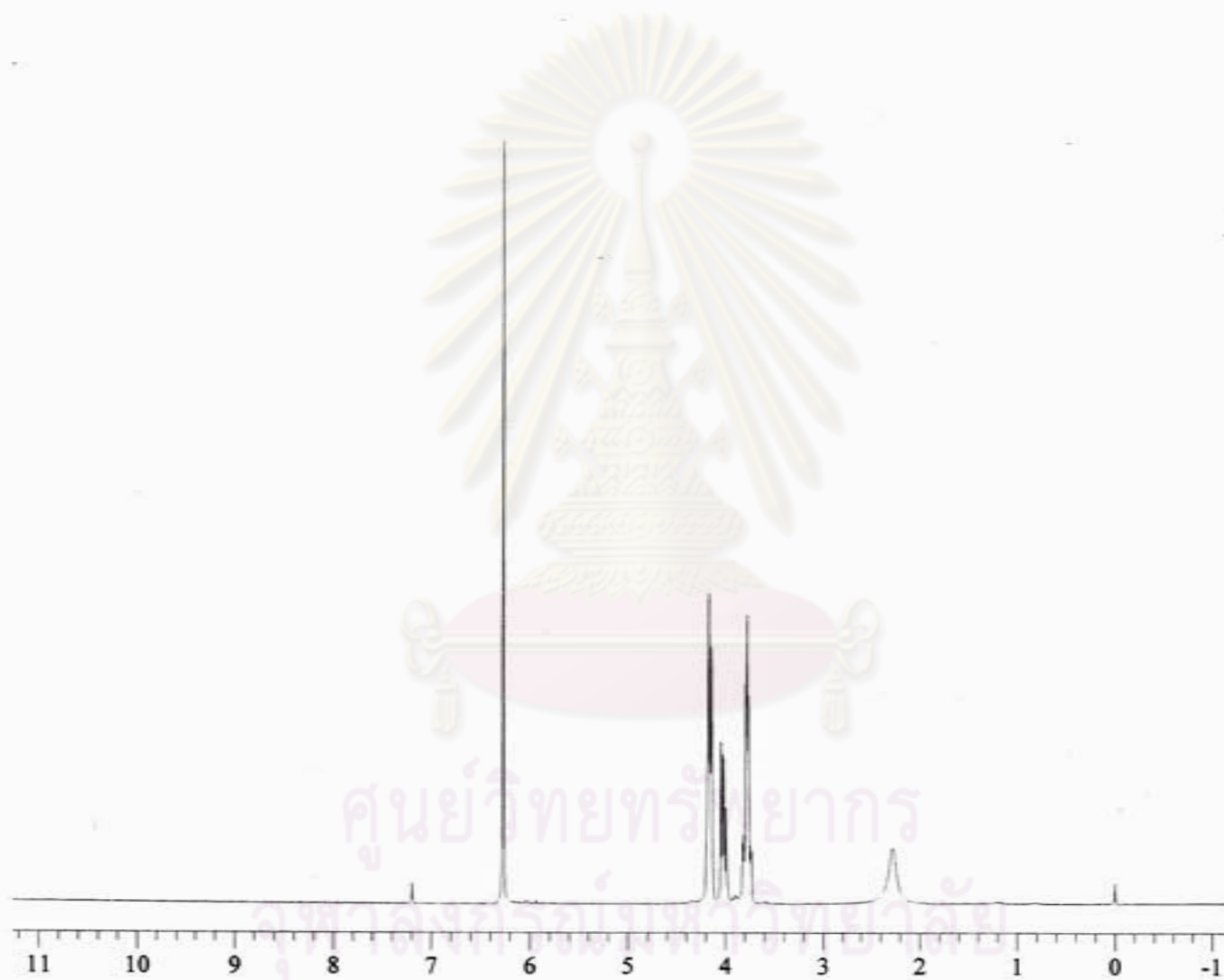


Figure A.13  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of 2'-hydroxymethyl-3,4-ethylenedioxythiophene (HEDOT)

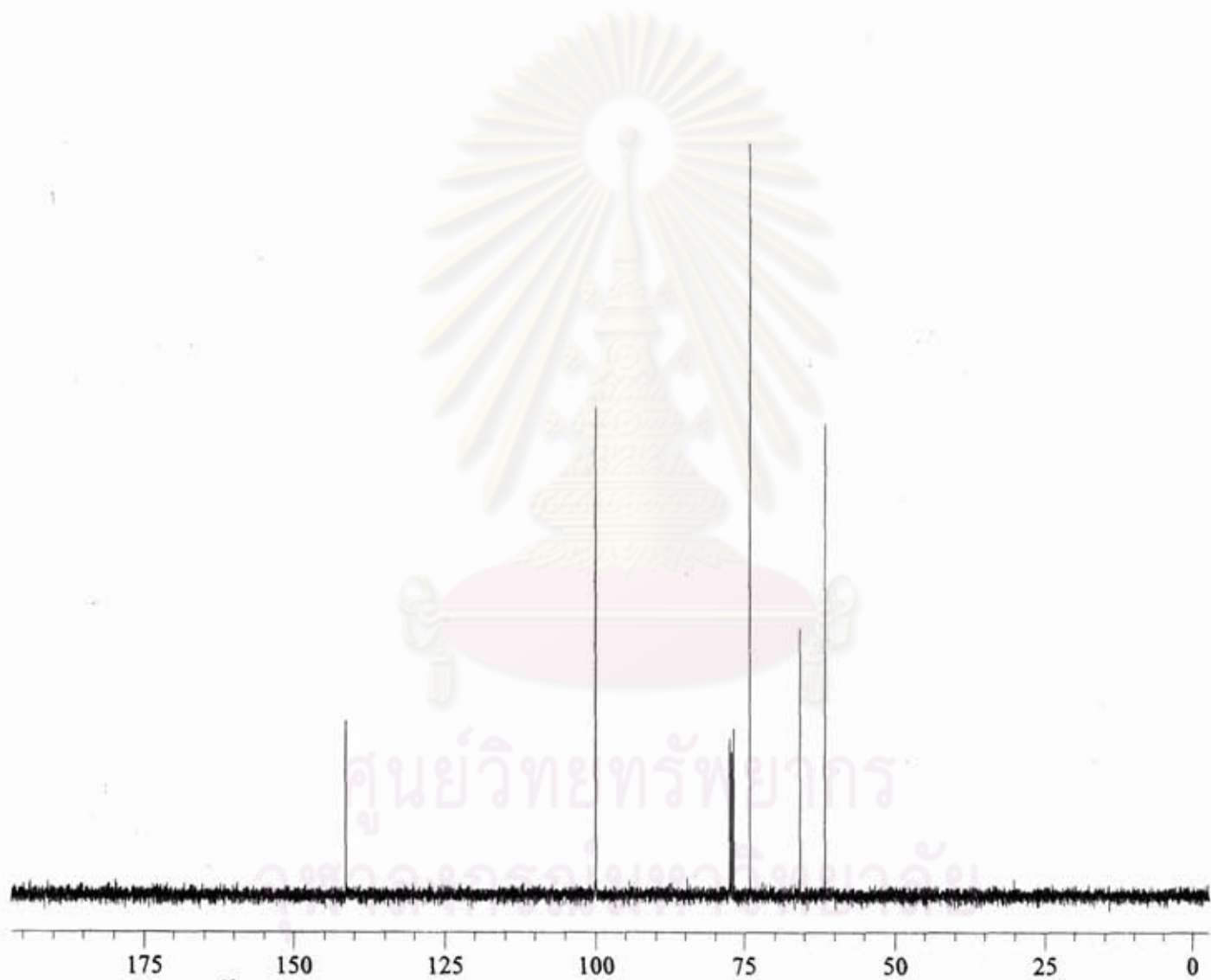


Figure A.14  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of 2'-hydroxymethyl-3,4-ethylenedioxythiophene (HEDOT)



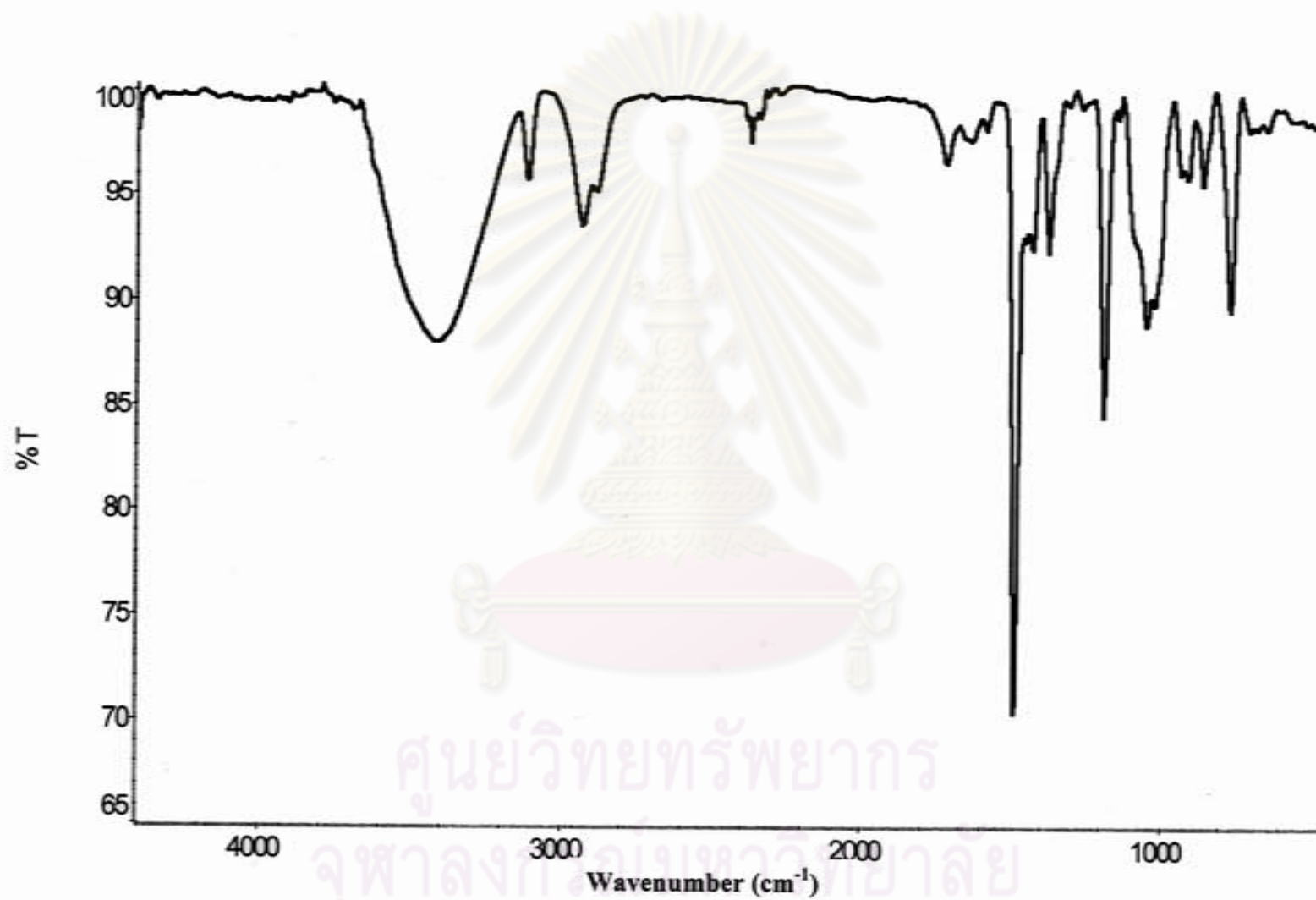


Figure A.15 IR spectrum of 2'-hydroxymethyl-3,4-ethylenedioxythiophene (HEDOT)

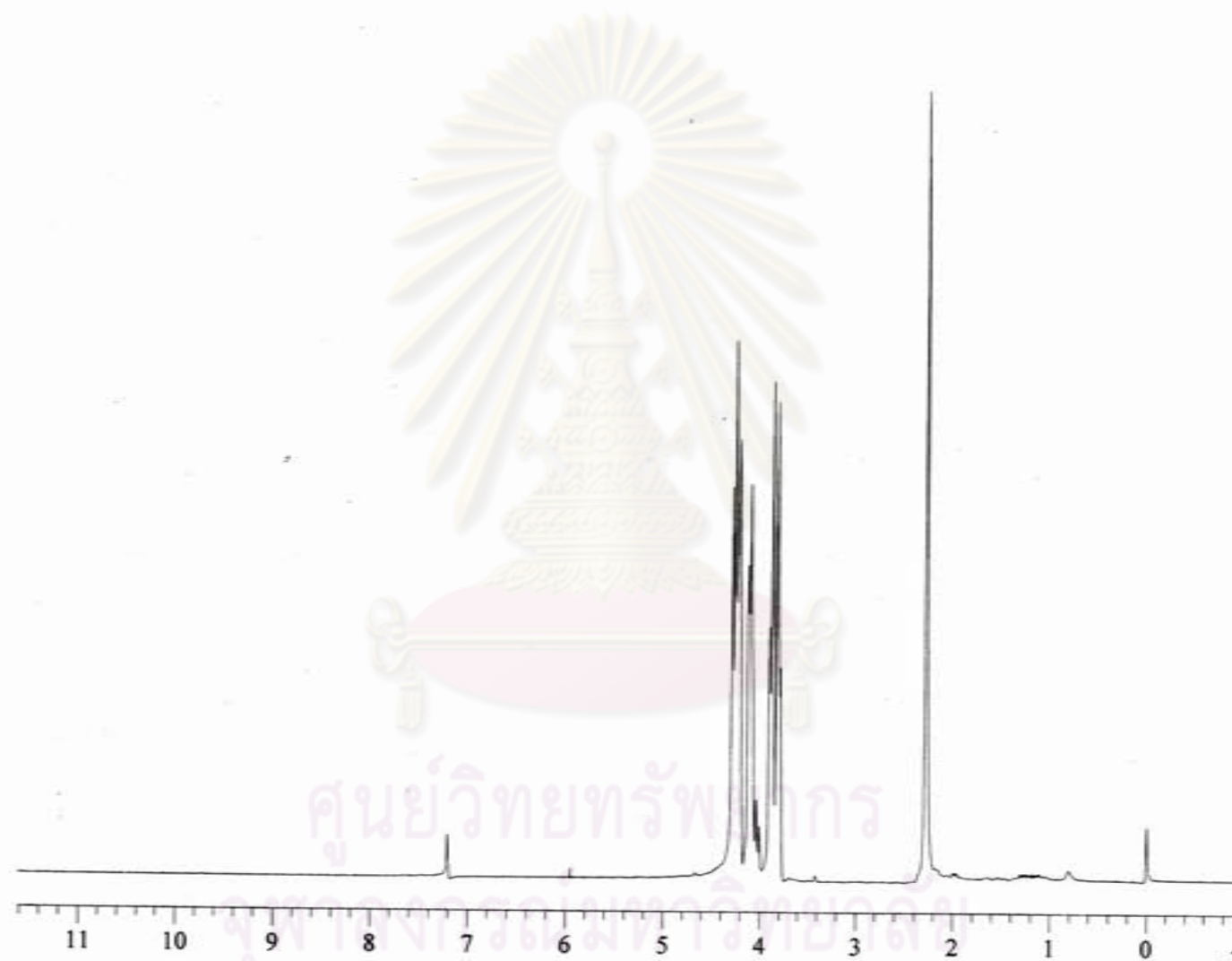


Figure A.16  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene (DBHEDOT)

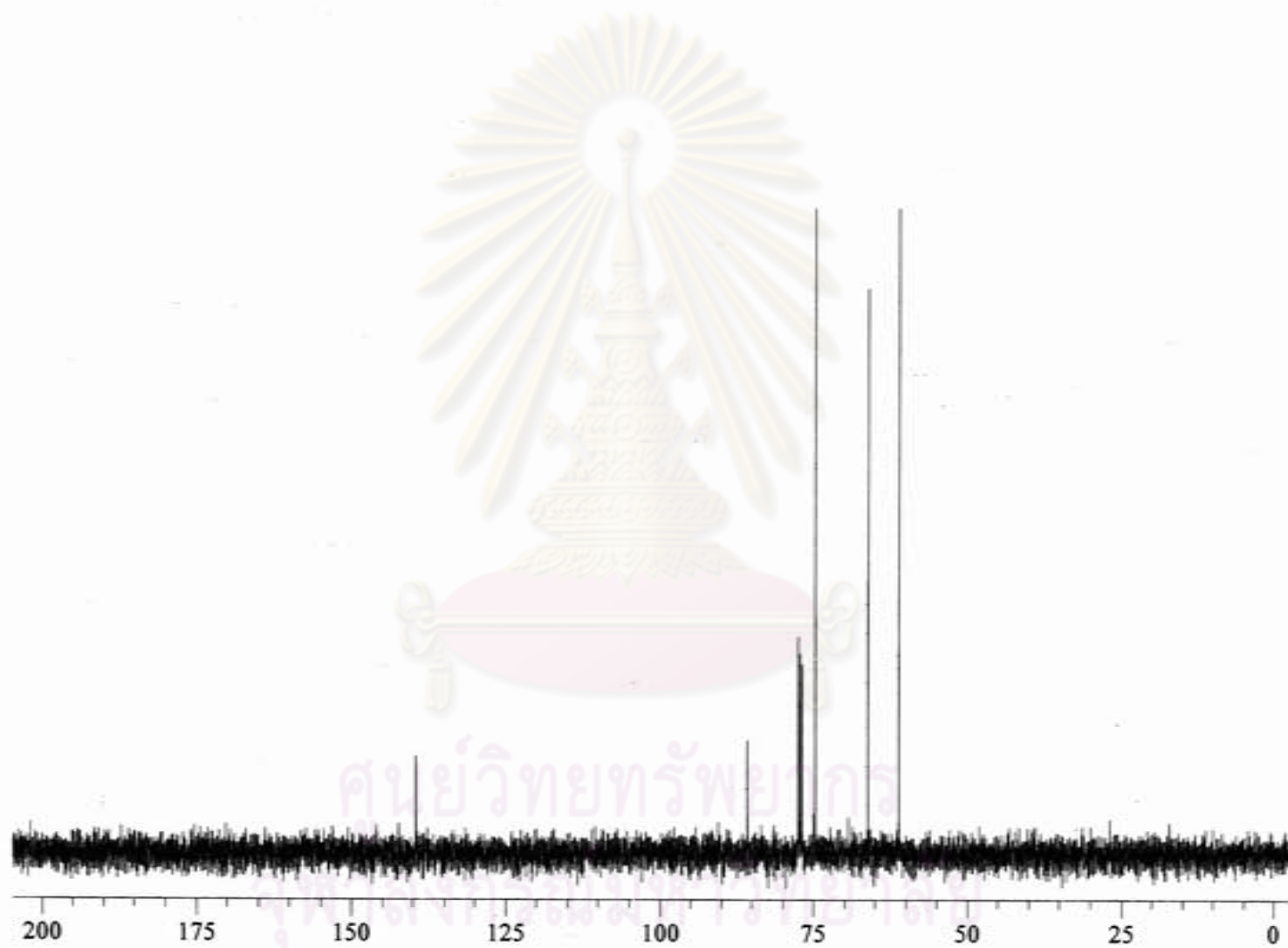


Figure A.17  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene (DBHEDOT)

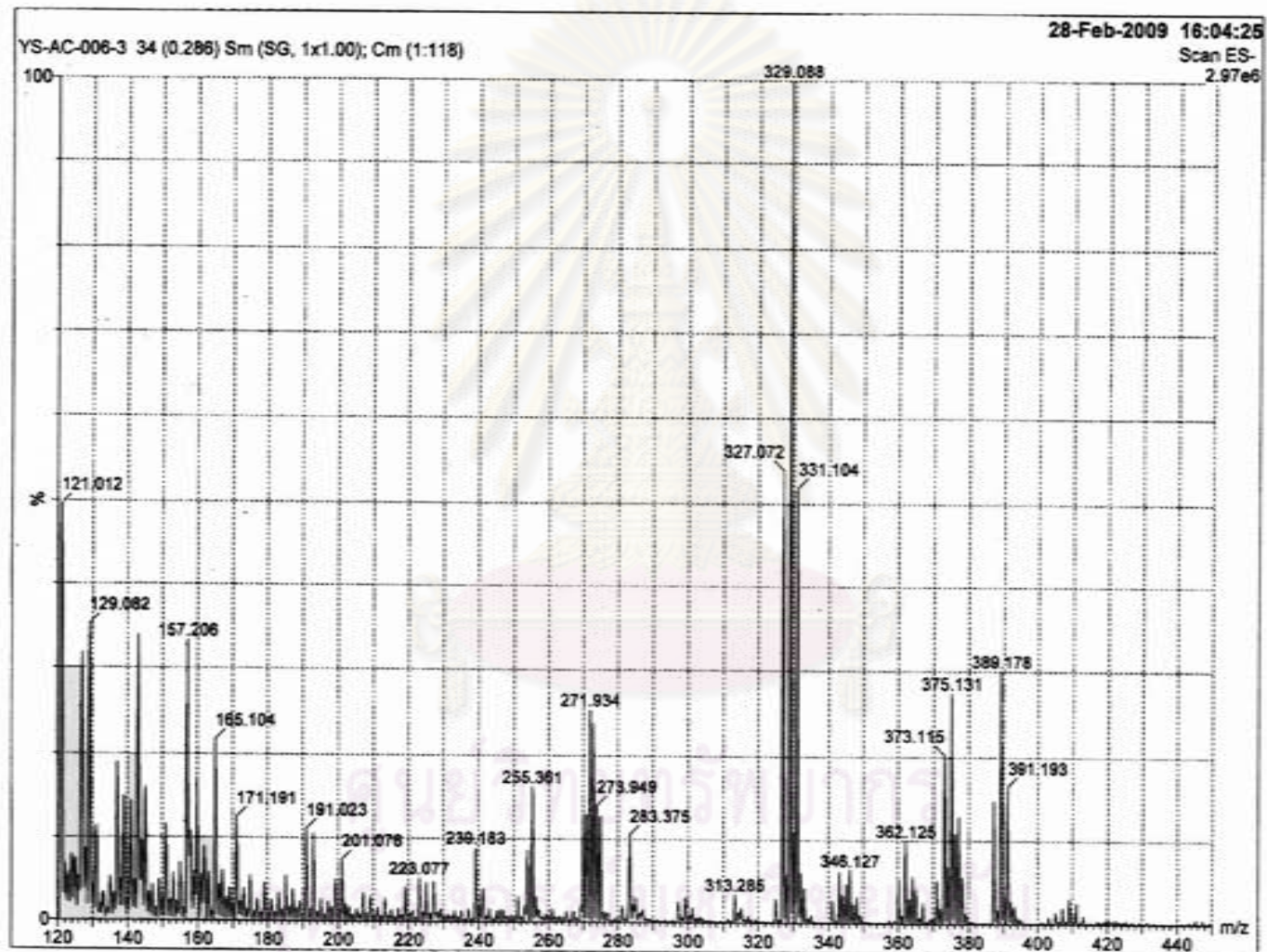


Figure A.18 Mass spectrum of 2'-hydroxymethyl-2,5-dibromo-3,4-ethylenedioxythiophene (DBHEDOT)

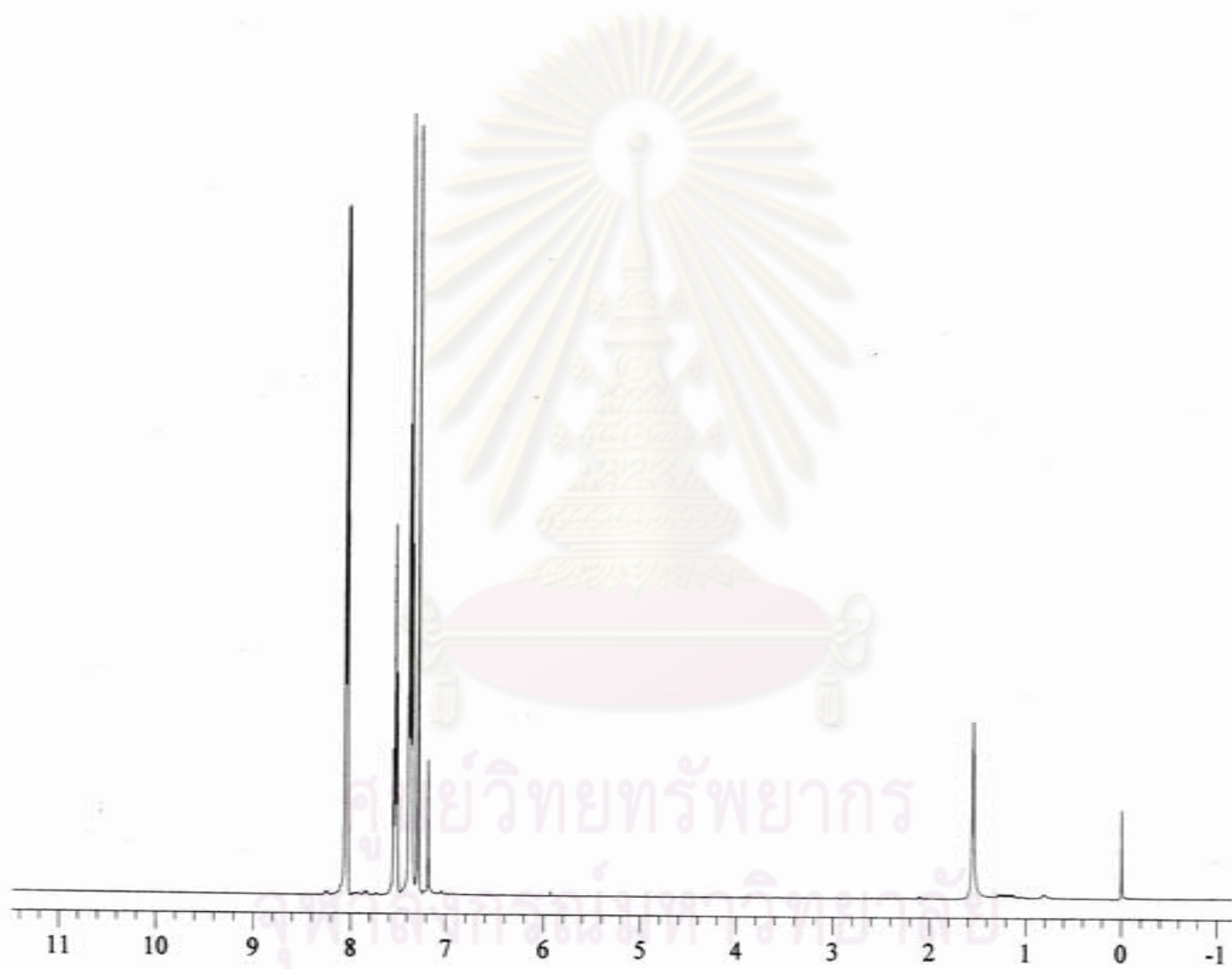


Figure A.19  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of 3,4-dibenzoyloxythiophene

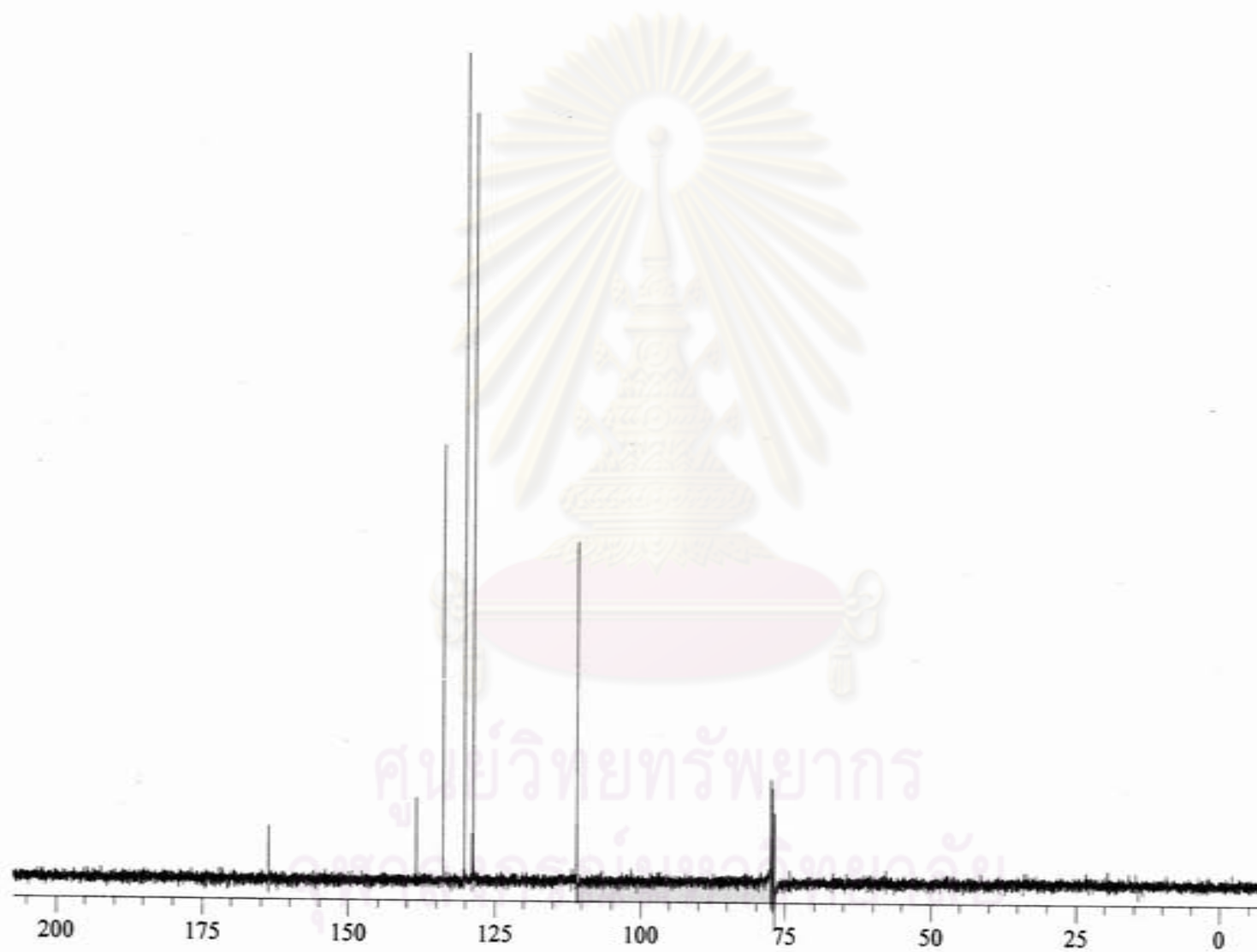


Figure A.20  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of 3,4-dibenzoyloxythiophene

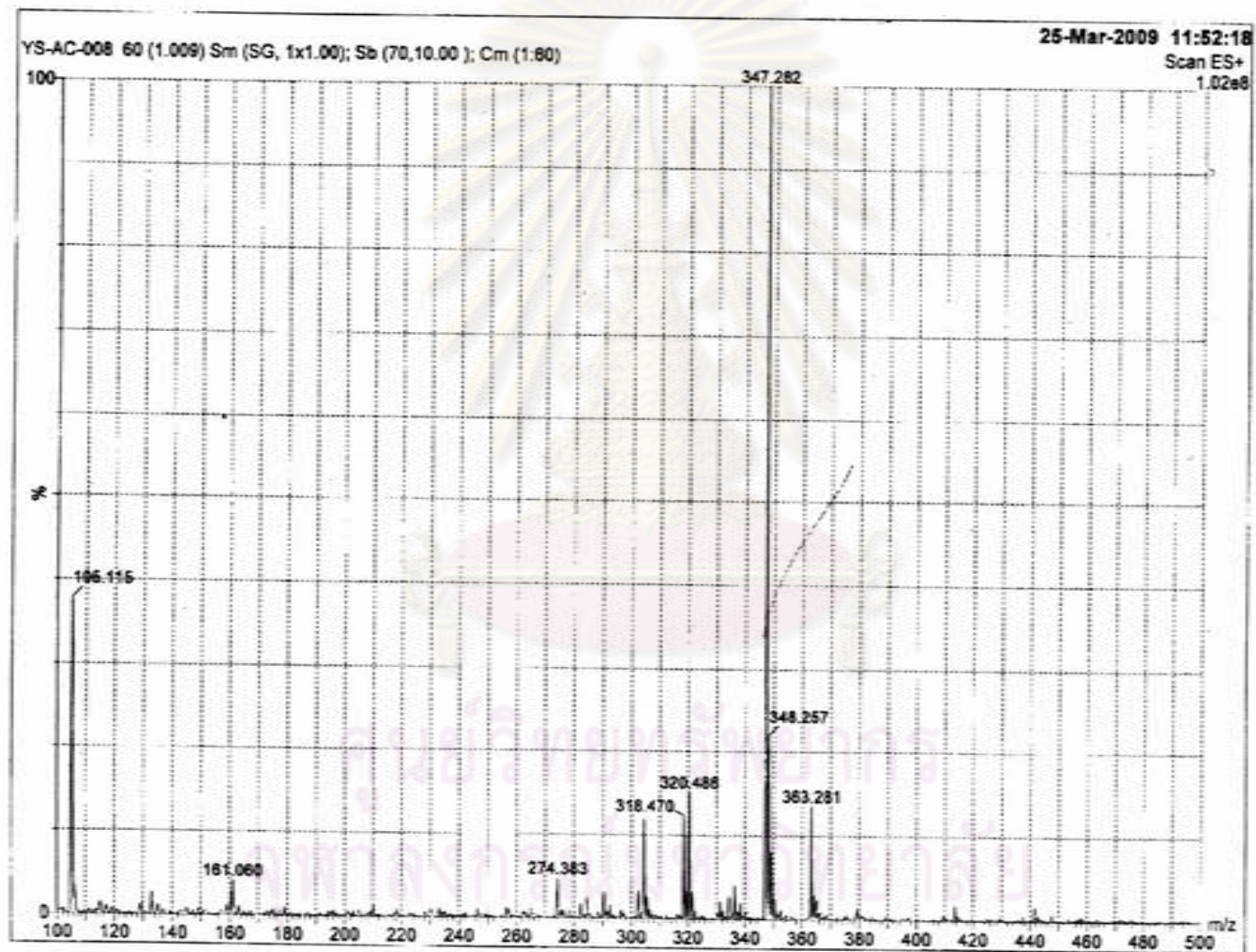
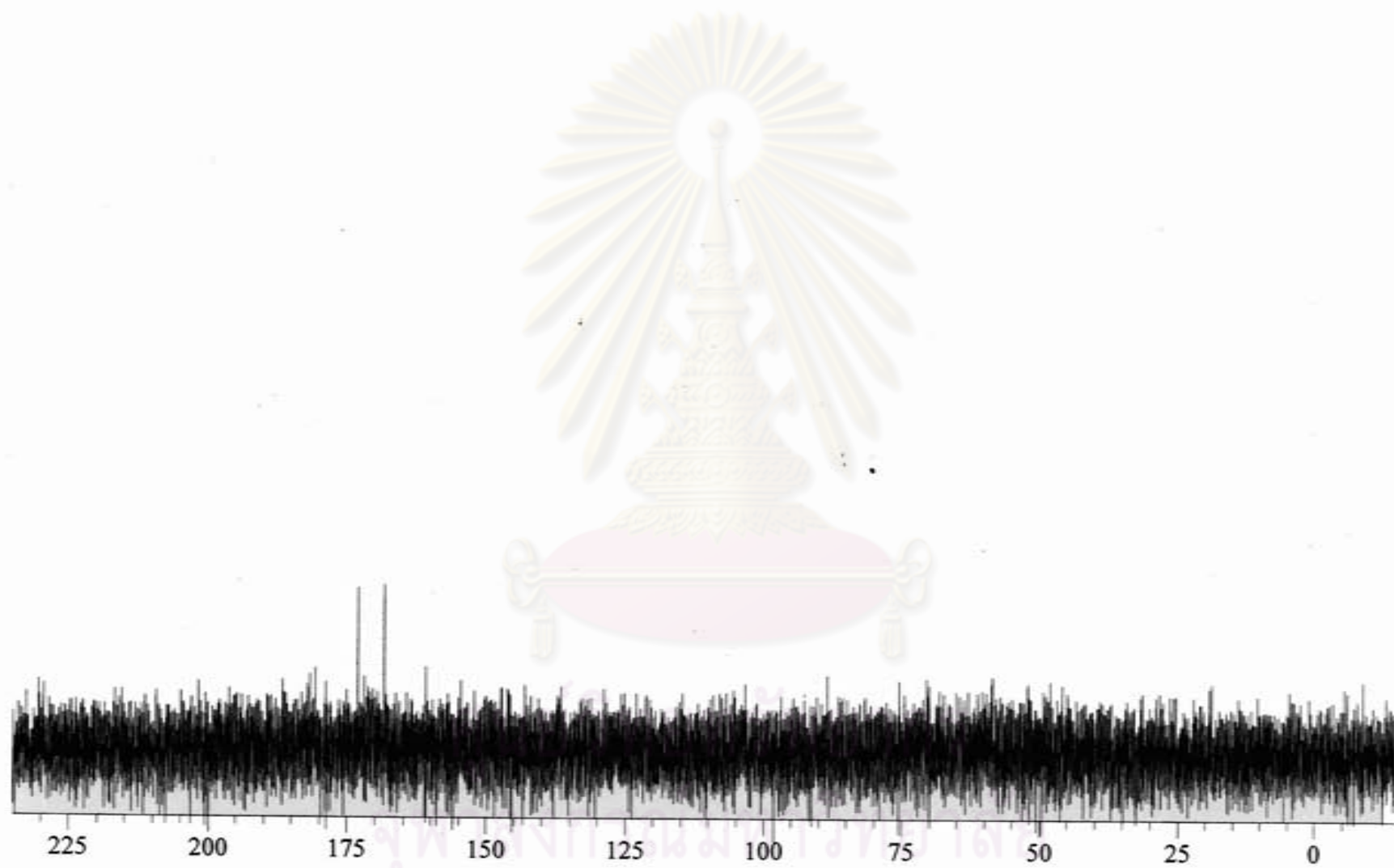


Figure A.21 Mass spectrum of 3,4-dibenzoyloxythiophene



**Figure A.22**  $^{13}\text{C}$ -NMR ( $\text{NaOH}/\text{D}_2\text{O}$ ) spectrum of poly(3,4-dihydroxythiophene) (PDHT)



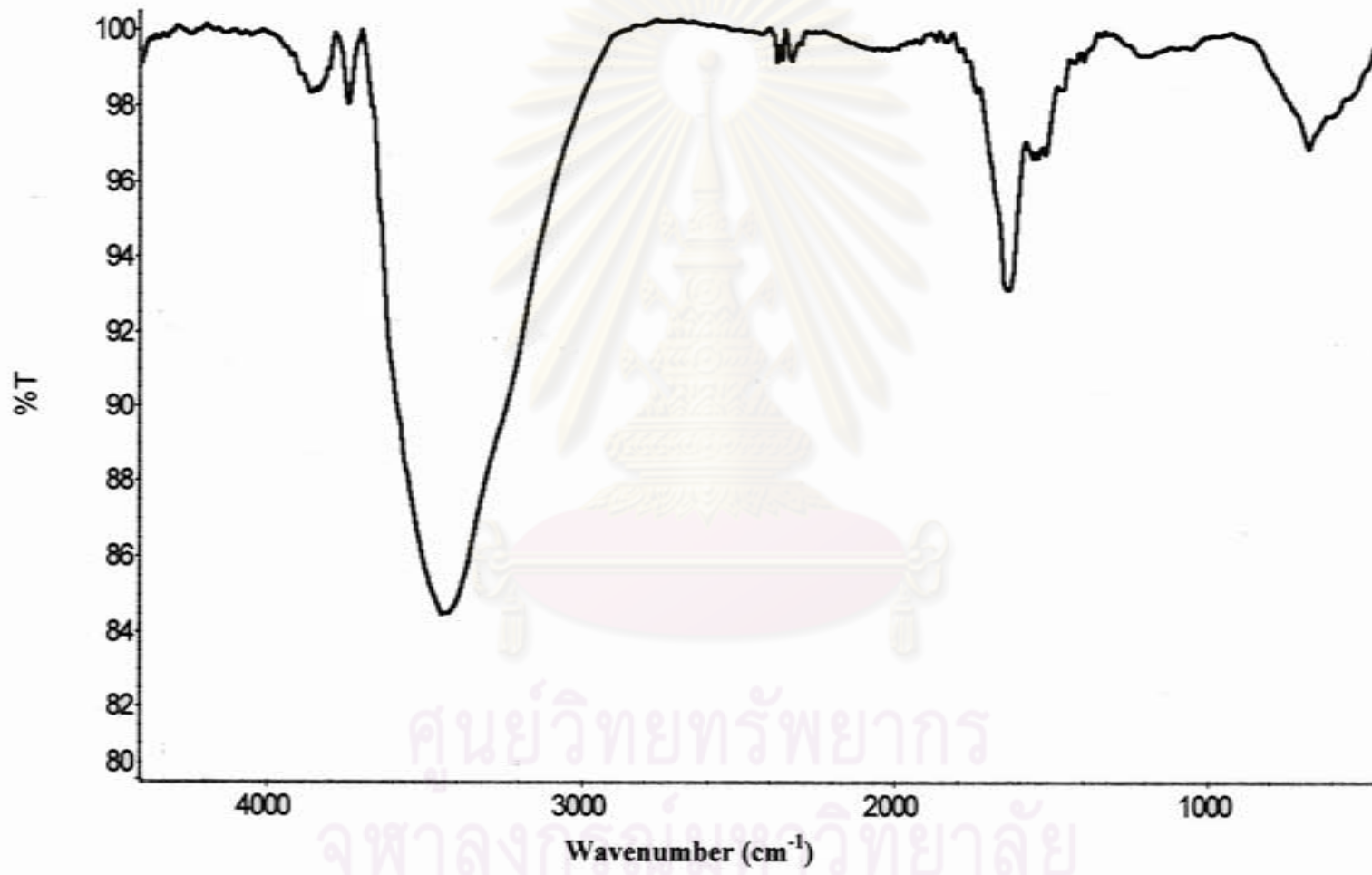


Figure A.23 IR spectrum of the soluble part of poly(3,4-dihydroxythiophene) in acetone (PDHT)

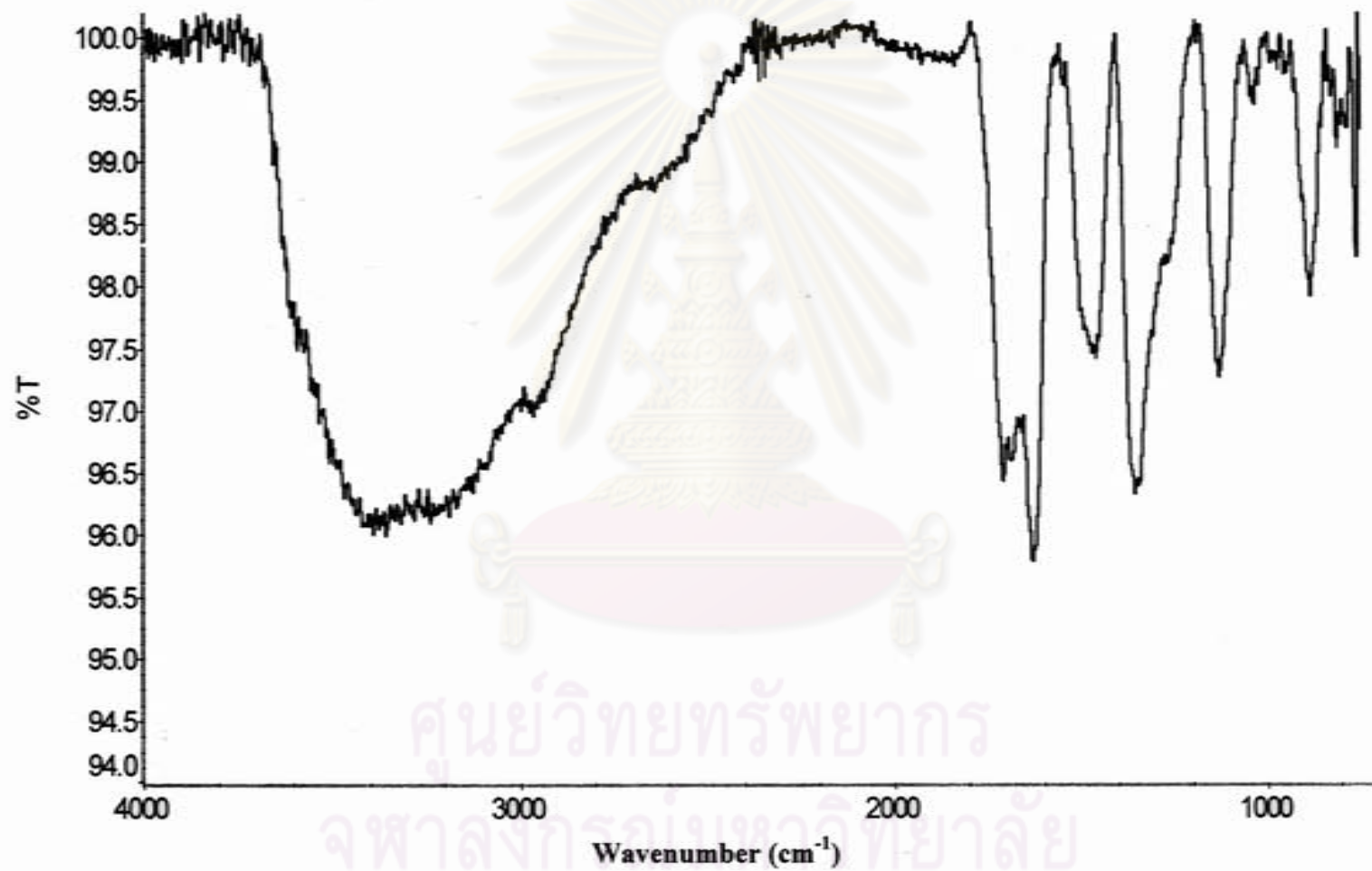


Figure A.24 IR spectrum of poly(3,4-dihydroxythiophene) (PDHT) (solid)

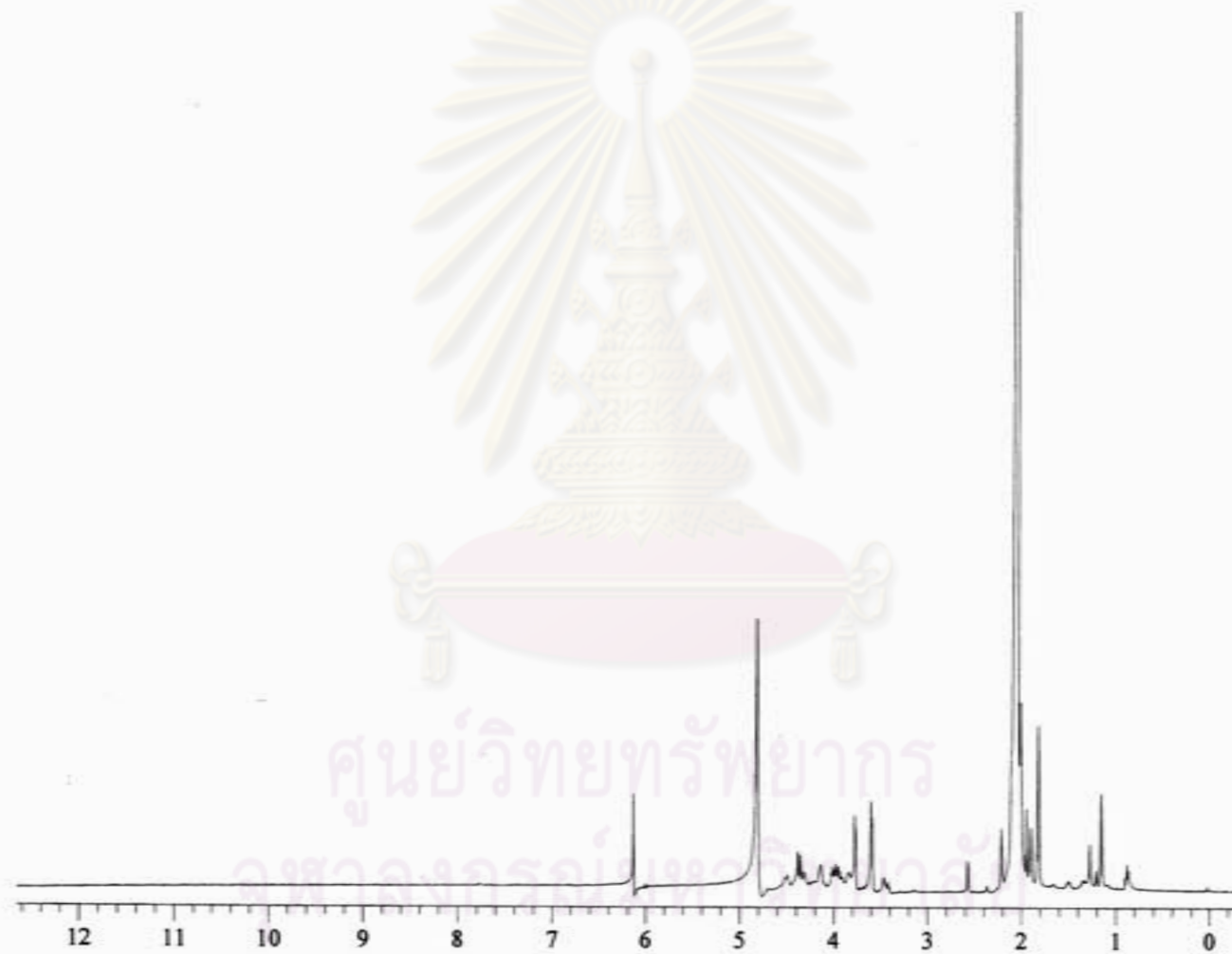


Figure A.25  $^1\text{H-NMR}$  (Acetone- $d_6$ ) spectrum of poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene (PHEDOT)

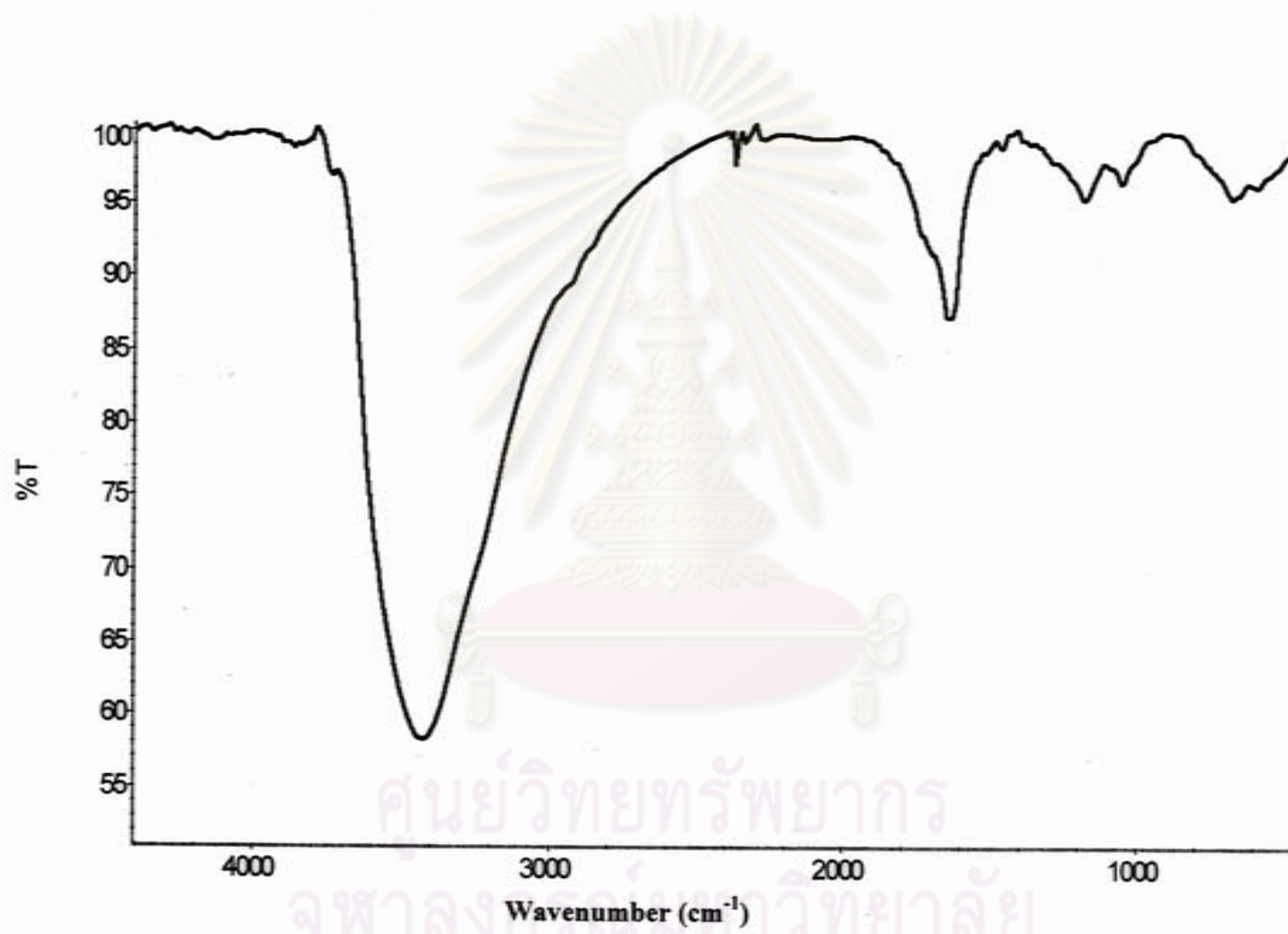


Figure A.26 IR spectrum of the soluble part of poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene) in acetone (PHEDOT)

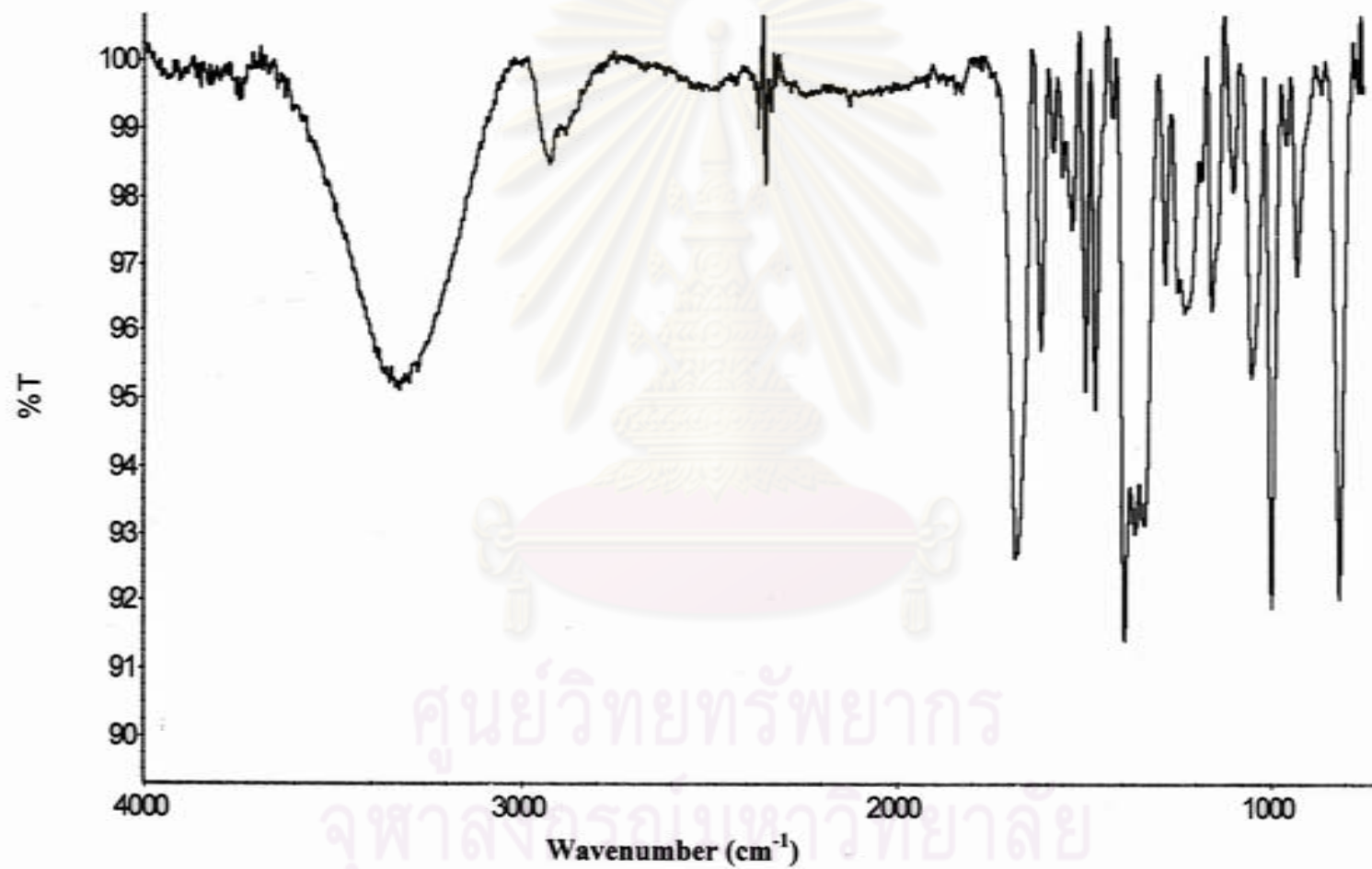


Figure A.27 IR spectrum of poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene) (PHEDOT) (solid)

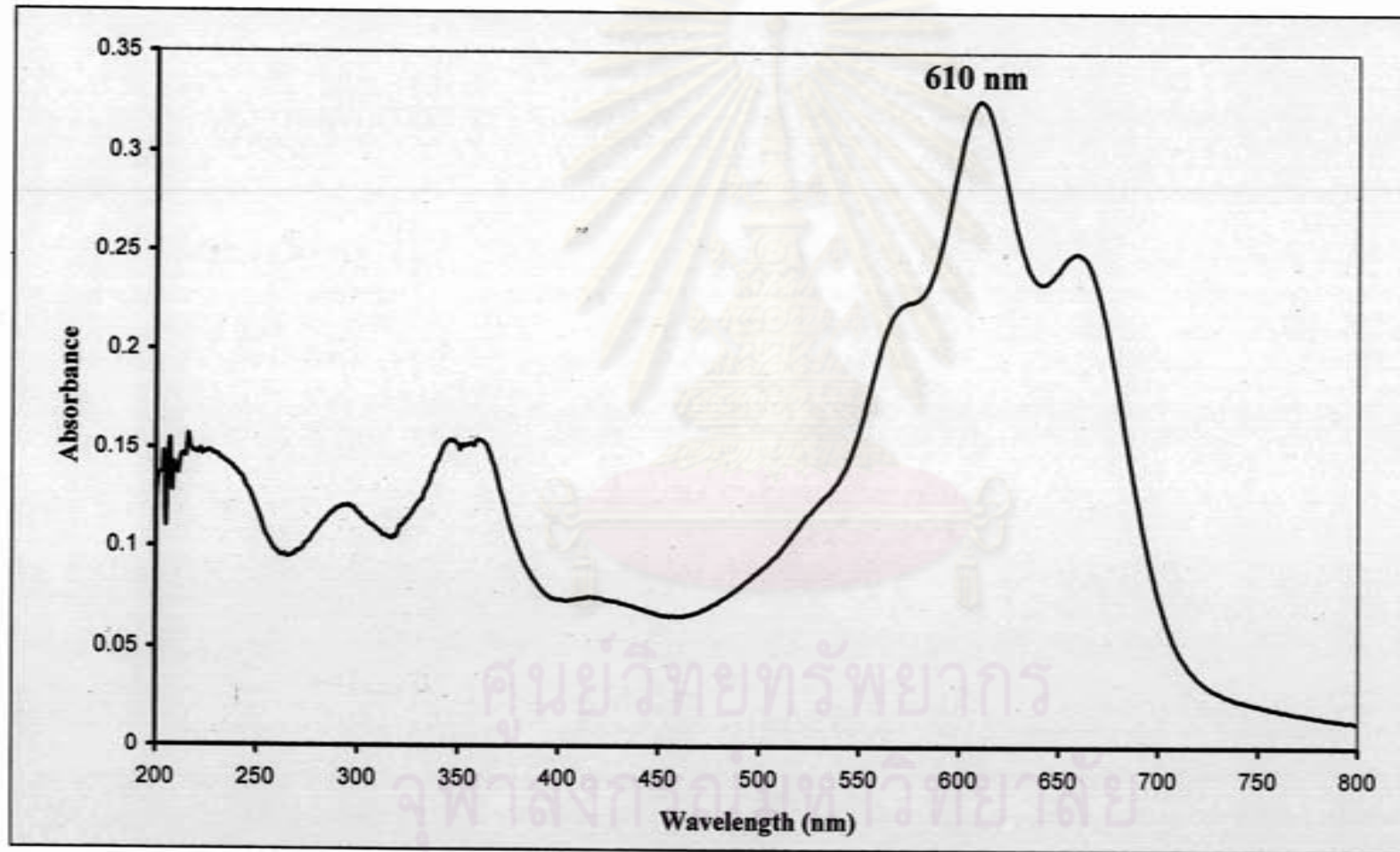


Figure A.28 UV-visible spectrum of poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene) (PHEDOT) in MeOH

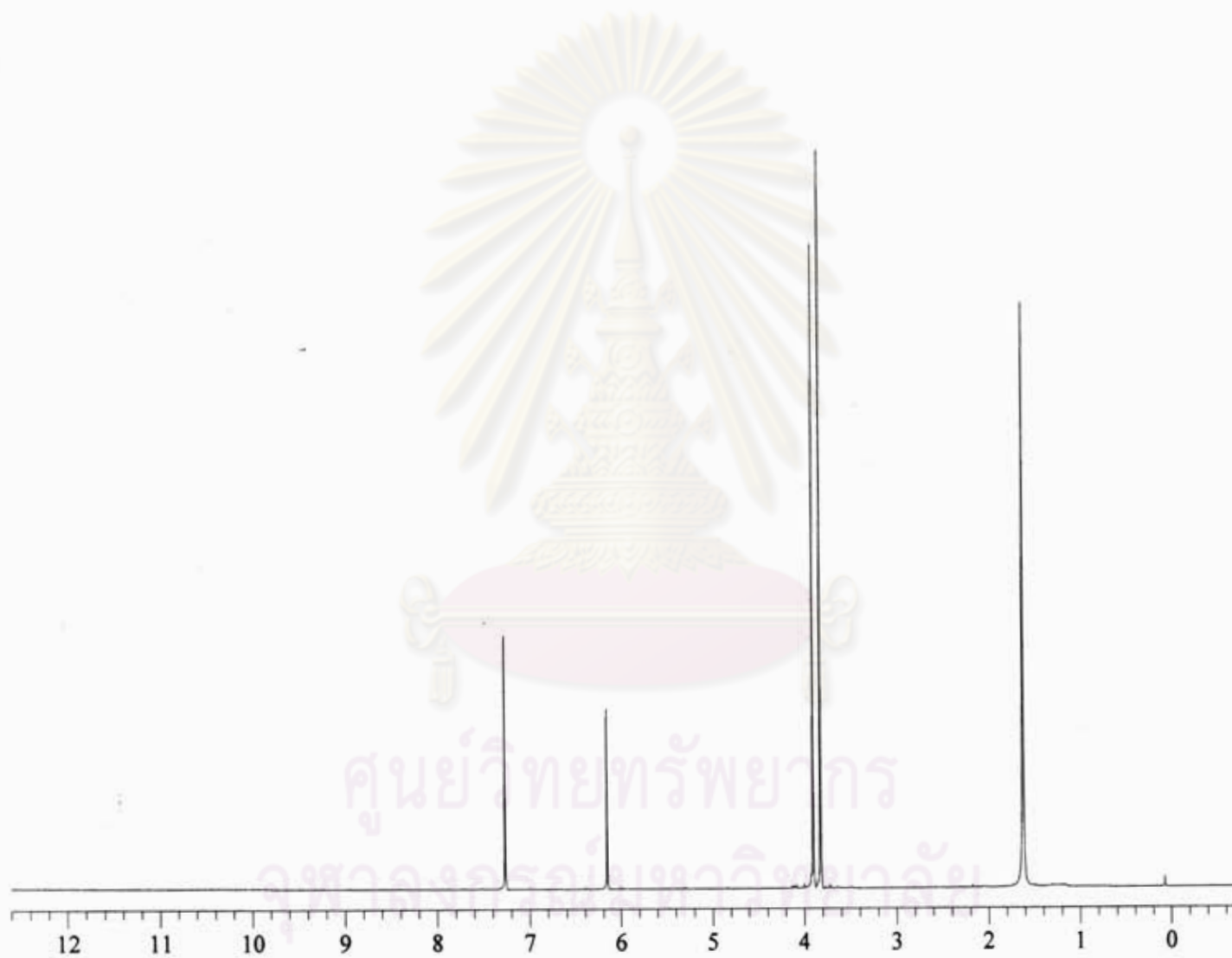
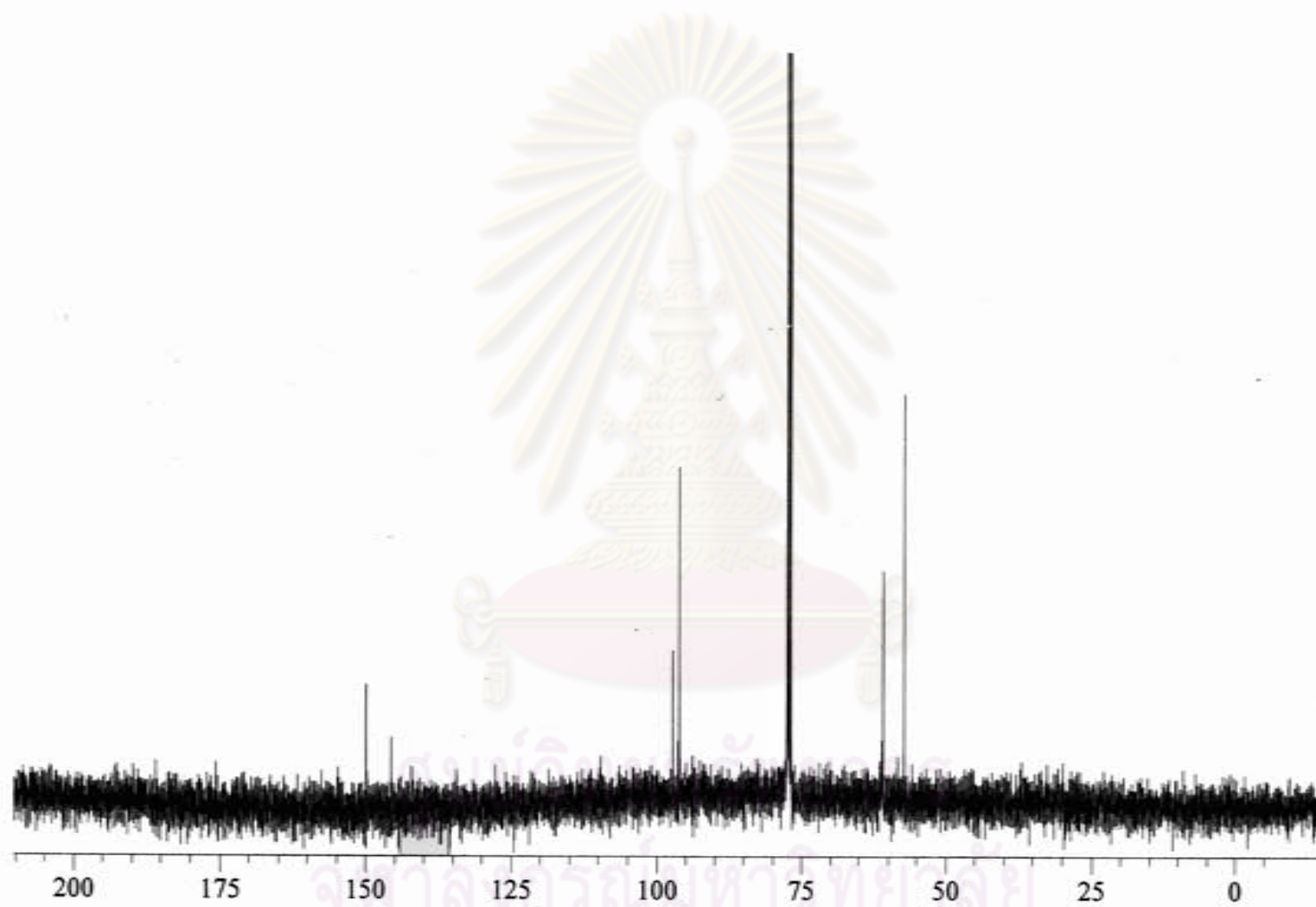


Figure A.29  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of 2-bromo-3,4-dimethoxythiophene (BDMT) 1



**Figure A.30**  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of 2-bromo-3,4-dimethoxythiophene (BDMT) 1



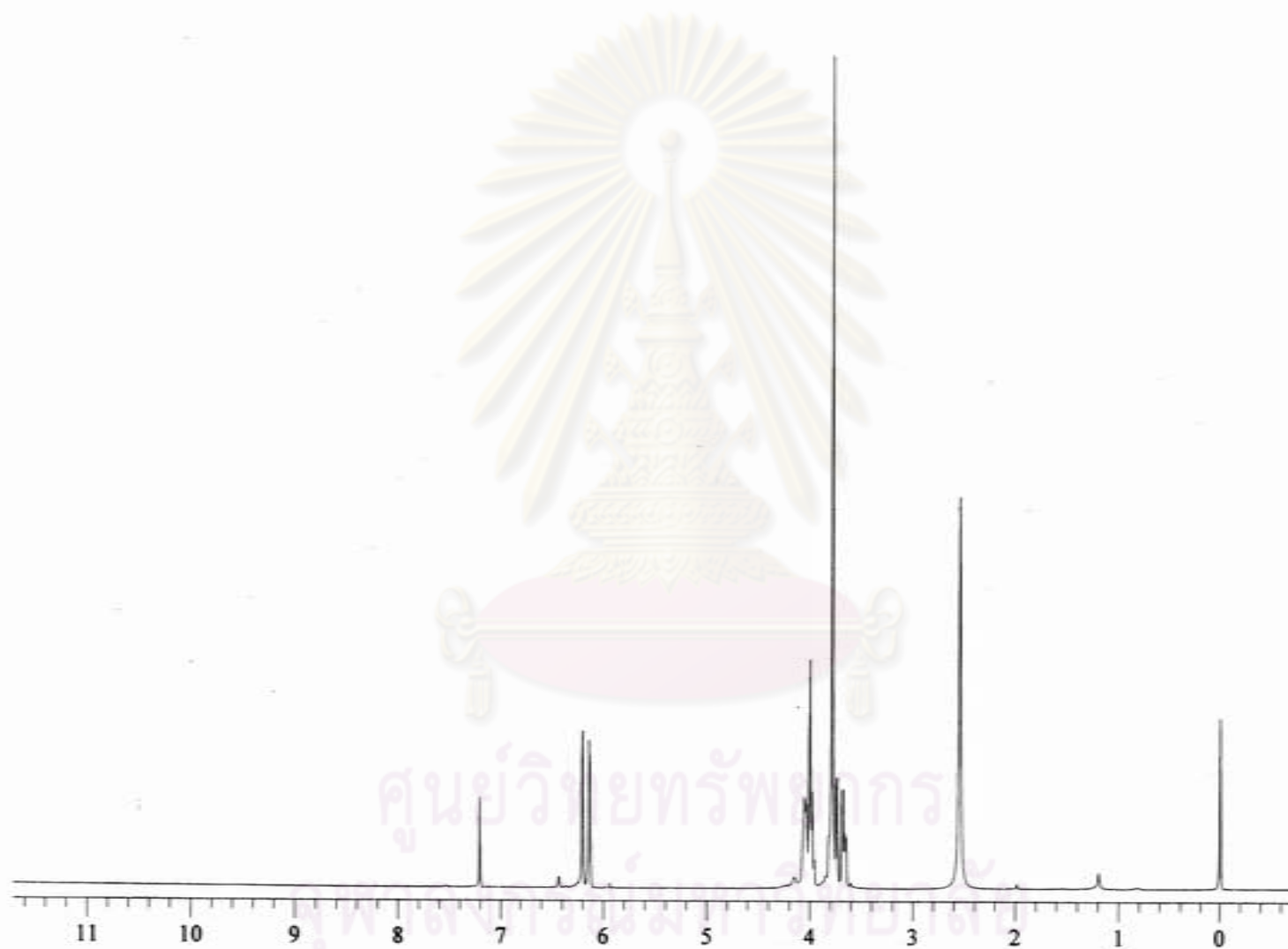


Figure A.31  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum of intermediate 3

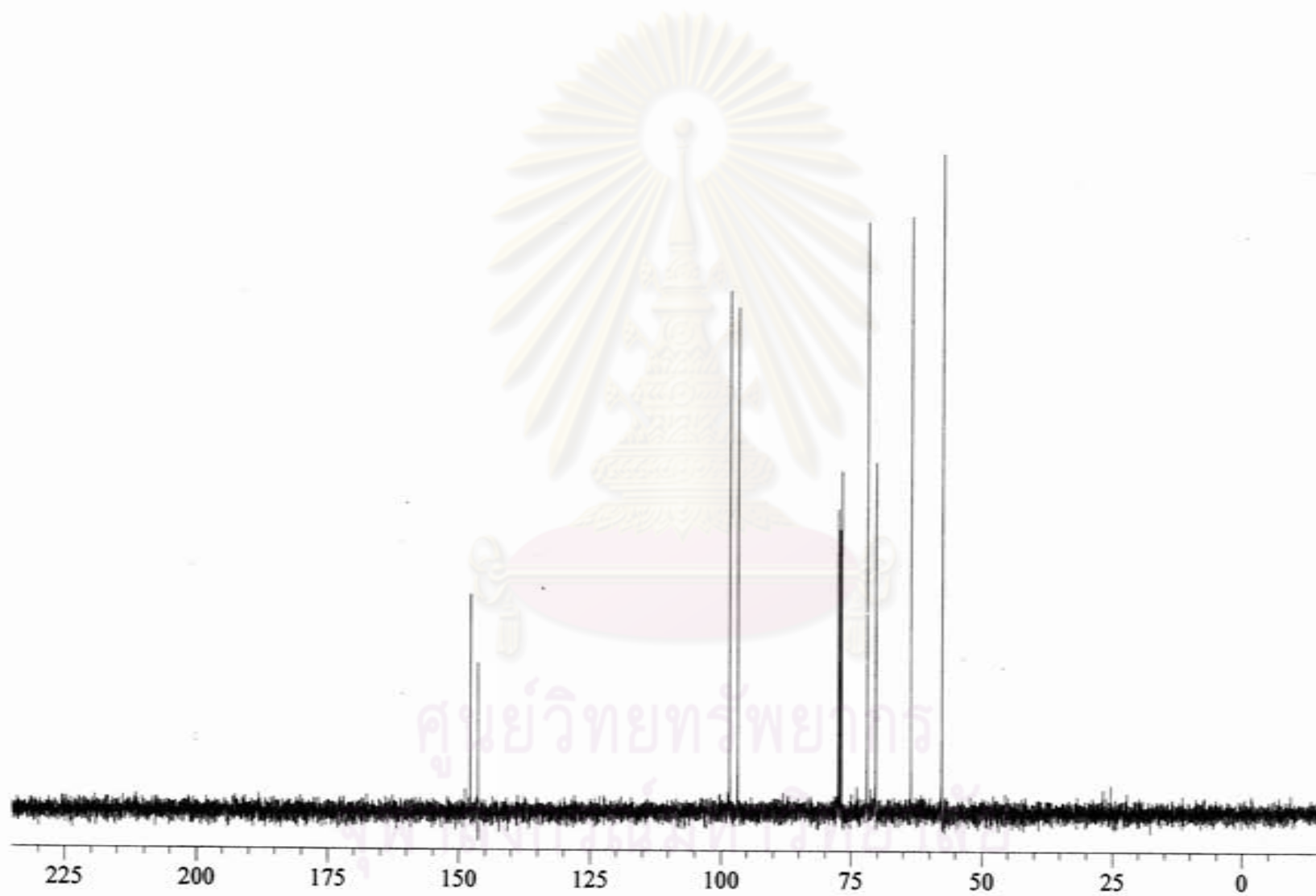


Figure A.32  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) spectrum of intermediate 3

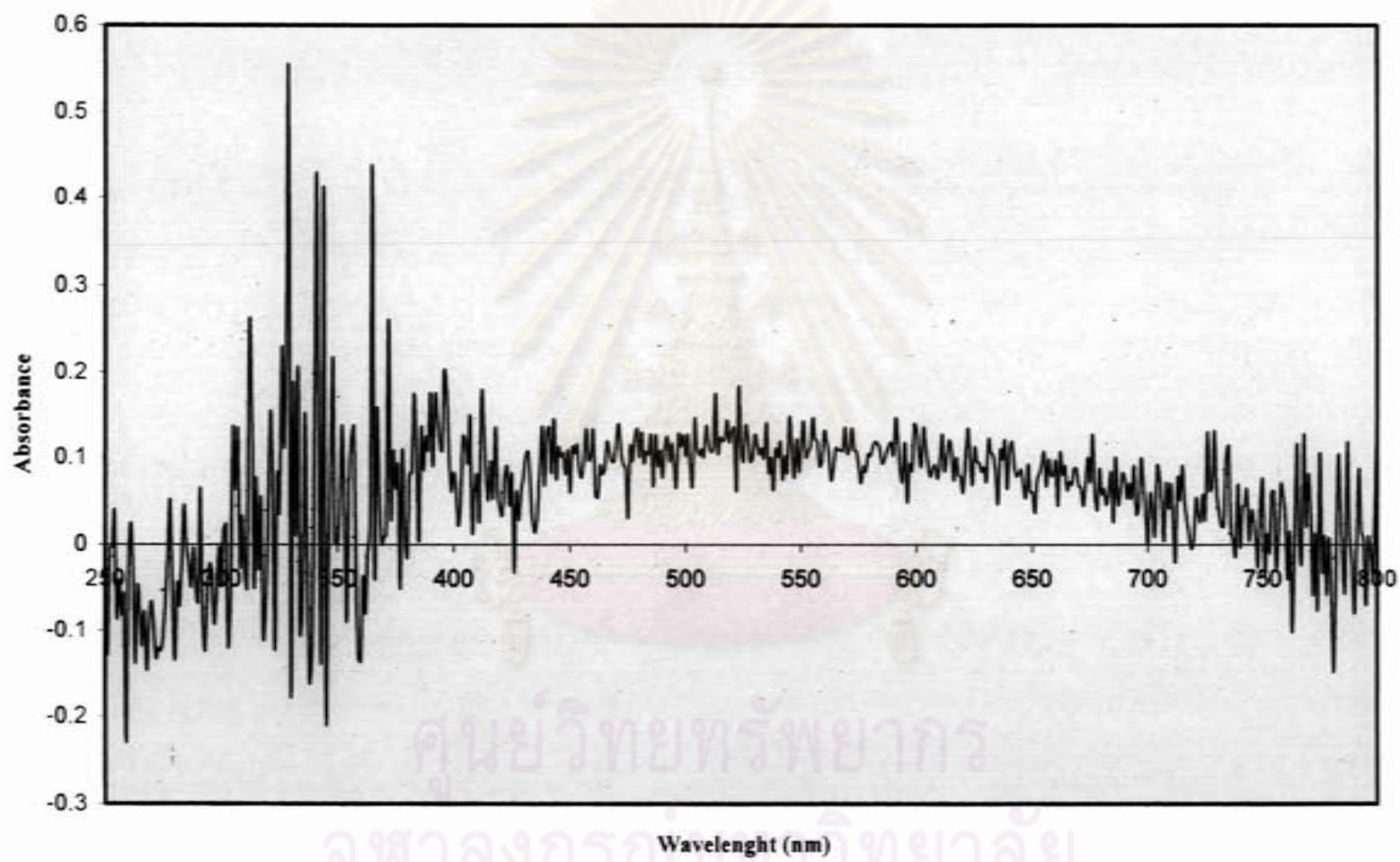


Figure A.33 UV-visible spectrum of poly(3,4-dihydroxythiophene) (PDHT) (solid)

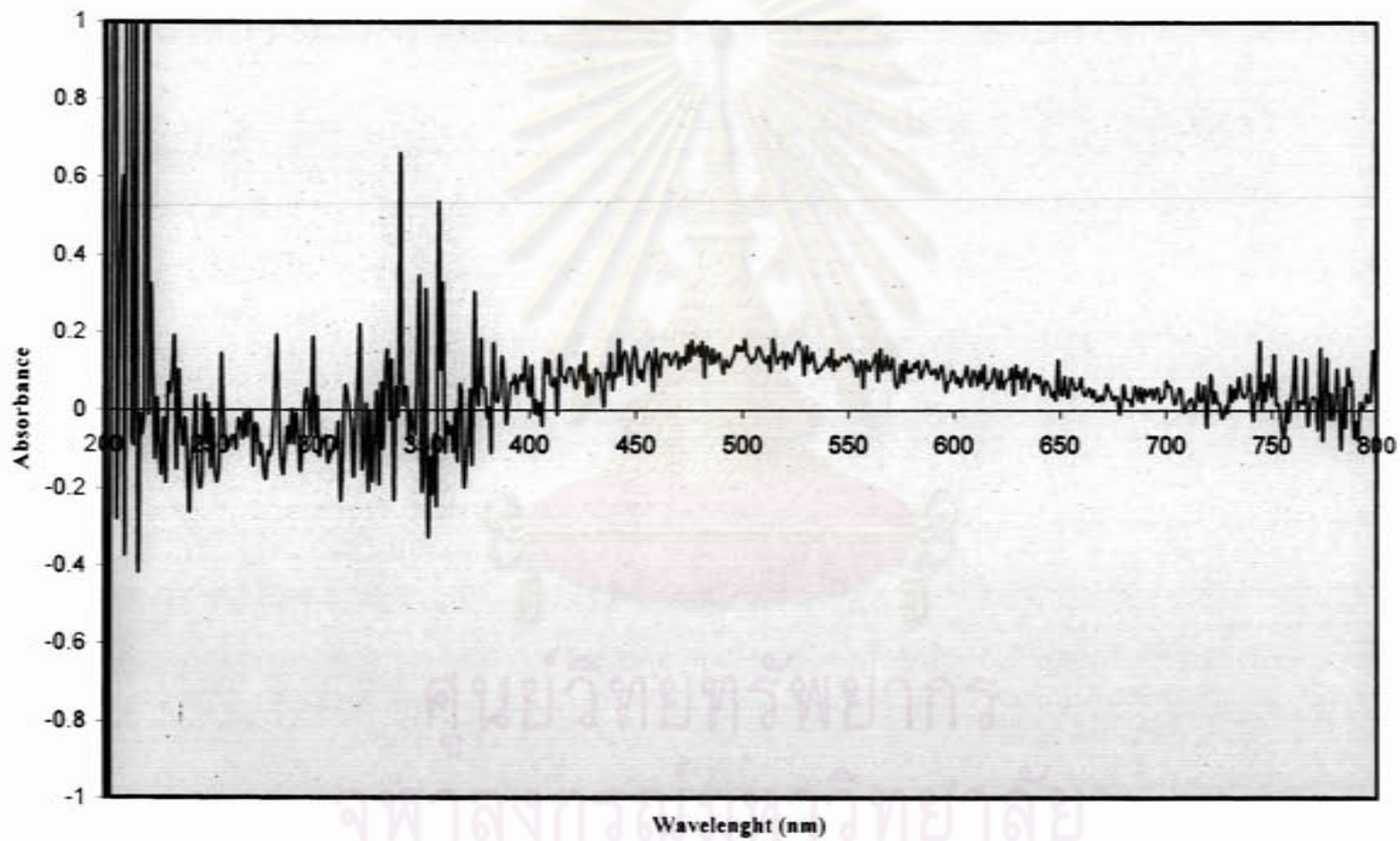


Figure A.34 UV-visible spectrum of poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene) (PHEDOT) (solid)

## VITA

Miss Apiradee Chanphen was born on January 25, 1983 in Samutprakarn, Thailand. She received a bachelor degree of science from Department of Chemistry, Faculty of Science, Mahidol University, Thailand in 2005. She was admitted to a Master's Degree Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and completed the program in 2008. Her address is 100/464 Moo 10 Srinakarin Road, Tambol Bangmuang, Amphor Muang, Samutprakarn 10270.



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย