การสังเคราะห์ 2,5-ไดโบรโมไทโอฟีนที่มีหมู่แทนที่ที่ตำแหน่งบีตาและเอส,เอส-ไดออกไซด์

นายนิติทัศน์ ถิรศาสตร์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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SYNTHESIS OF β-SUBSTITUTED 2,5-DIBROMOTHIOPHENES AND THEIR *S,S*-DIOXIDES

Mr. Nititad Thirasart

A Thesis Submitted in Partial Fulfillment of the Requirements
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นิติทัศน์ ถิรศาสตร์: การสังเคราะห์ 2,5-ไดโบรโมไทโอฟีนที่มีหมู่แทนที่ที่ตำแหน่งบีตาและเอส,เอส-ไดออกไซด์ (SYNTHESIS OF β-SUBSTITUTED 2,5-DIBROMOTHIOPHENES AND THEIR *S,S*-DIOXIDES)
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งานวิจัยนี้เป็นการหาภาวะที่เหมาะสมในการสังเคราะห์ไทโอฟีนเอส,เอส-ไดออกไซด์ ที่มีหมู่แทนที่ตำแหน่งบีตา ซึ่งได้จากปฏิกิริยาออกซิเดชันด้วยตัวออกซิไดซ์ต่างๆ ตัวแปรที่ศึกษาได้แก่ ชนิดของหมู่แทนที่ตำแหน่งบีตา ชนิดของตัวออกซิไดซ์ เวลาในการทำปฏิกิริยา อุณหภูมิ และตัวทำละลาย แล้วนำผลิตภัณฑ์ที่ได้มาวิเคราะห์โดยใช้เทคนิคทางสเปกโทรสโกปีต่างๆ จากการทดลองพบว่าสามารถสังเคราะห์ 2,5-ไดโบรโมไทโอฟีน 2,5-ไดโบรโม-3-เฮกซิลไทโอฟีน 2,3,5-ไทรโบรโมไทโอฟีน 2,5-ไดโบรโม-3-เมทอกซีไทโอฟีน และ 2,3-ไดโบรโมไทอีโน[3,4-b]-1,4-ไดออกซิน เท่ากับ 64%, 80%, 75%, 56% และ 63% yield ตามลำดับ จากการศึกษาปฏิกิริยาออกซิเดชันของอนุพันธ์ไทโอฟีนชนิดต่างๆ พบว่า ไทโอฟีนที่ออกซิไดซ์ด้วย 30% H_2O_2 ในตัวทำละลาย CH_3CN และ 2,3-ไดโบรโมไทอีโน[3,4-b]-1,4-ไดออกซินที่ ออกซิไดซ์ด้วยโซเดียมเปอร์คาร์บอเนต ในตัวทำละลาย CH_3CN มีแนวโน้มว่าจะได้ผลิตภัณฑ์ที่มีหมู่ไทอีนิลเอส,เอส-ไดออกไซด์ตามที่ต้องการ

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..............................
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา..............................
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NITITAD THIRASART: SYNTHESIS OF β-SUBSTITUTED 2,5-DIBROMOTHIOPHENES AND THEIR *S,S*-DIOXIDES. THESIS ADVISOR: ASSISTANT PROFESSOR WORAWAN BHANTHUMNAVIN, Ph.D. THESIS COADVISOR: ASSISTANT PROFESSOR YONGSAK SRITANA-ANANT, Ph.D. pp ISBN 974-53-1617-2

This research surveyed for suitable conditions to synthesize β-substituted thiophene *S*,*S*-dioxides. Experimental factors under investigation included types of substituents at beta position, types of oxidizing agents, reaction time, temperature, and solvent. The products were analyzed by various spectroscopic methods. 2,5-dibromothiophene, 2,5-dibromo-3-hexylthiophene, 2,3,5-tribromothiophene, 2,5-dibromo-3-methoxythiophene, and 2,3-dibromothieno[3,4-b]-1,4-dioxin have been successfully prepared in 64%, 80%, 75%, 56%, and 63% yield, revealed respectively. The study on the oxidation of several thiophene derivatives found that thiophene oxidized by 30% H_2O_2 in CH_3CN, and 2,3-dibromothieno[3,4-b]-1,4-dioxin by $Na_2CO_3.1/2H_2O_2$ in CH_3CN were likely to give the desired oxidized products.

Program Petrochemistry and Polymer Science Student's signature
Field of study Petrochemistry and Polymer Science Advisor's signature
Academic year 2004 Co-advisor's signature

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LIST OF SCHEMES

LIST OF ABBREVIATIONS

A	: absorbance
$CDCl_3$	: deuterated chloroform
°C	: degree Celsius
g	: gram
MeOH	: methanol
mg	: milligram
min	: minute
h	: hour
mL	: milliliter
mmol	: millimole
NMR	: nuclear magnetic resonance spectroscopy
PT	: polythiophene
DBEDOT	: 2,5-dibromo-3,4-ethylenedioxythiophene
PEDOT	: poly(3,4-ethylenedioxythiophene)
UHP	: urea Hydrogen Peroxide
TFA	: trifluoroacetic acid
TFAA	: trifluoroacetic acid anhydride
NBS	: *N*-bromosuccinimide
TsOH	: toluene-4-sulfonic acid
br	: broad
q	: quartet (NMR)
s	: singlet (NMR)
t	: triplet (NMR)

LIST OF ABBREVIATIONS (Continued)

[o]	: oxidation
H-H	: head to head
H-T	: head to tail
T-T	: tail to tail
Ac	: acetyl
AcOH	: acetic acid
Ph	: phenyl

CHAPTER I

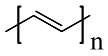
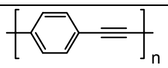
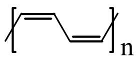
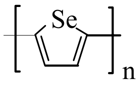
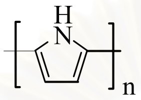
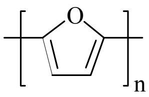
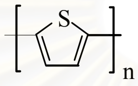
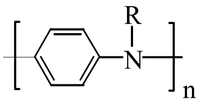
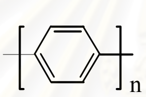
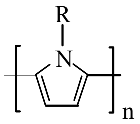
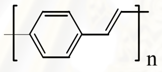
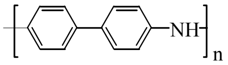
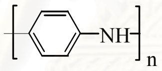
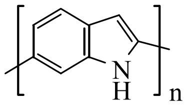
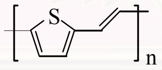
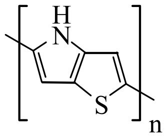
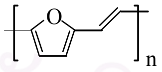
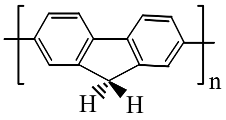
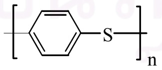
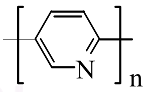
INTRODUCTION

Over the past several decades since the discovery of metallic conductivity in doped polyacetylene,[1] synthetic organic chemists have shown a growing interest in the development of organic conducting molecular and polymeric materials. (**Table 1.1**)[2,3] Their superiority over inorganic materials resides in their architectural flexibility, low cost and ease of processing and fabrication, many strategies have been attempted to improve the conductive properties of various conducting polymers. These included the studies on doping processes, oxidations, structural modifications through additions of substituents,[2] fabrications and so on. The results are promising and new generations of molecular electronics based on organic polymers have already emerged.[4,5] Although with mostly lower magnitude of conductivity than inorganic materials (**Figure 1.1**).

1.1 Applications of organic conducting polymers[3,6-8]

Organic conducting polymer has a unique and practical advantage. Their conductive properties allow the use of electronic tools (computers and interfaces) and other existing and emerging characterization tools to retrieve the information on the behavior of these systems from real *in situ* environments. In addition, their other properties can be manipulated *in situ* using appropriate electronic stimuli. (**Table 1.2**)

Table 1.1 Typical conducting polymers

Name	**Structure**	**Name**	**Structure**
trans-Polyacetylene		Poly(phenylene ethynylene)	
cis-Polyacetylene		Polyselenophene	
Polypyrrole		Polyfuran	
Polythiophene		Poly(*N*-substituted aniline)	
Poly(*p*-phenylene)		Poly(*N*-substituted pyrrole)	
Poly(phenylenevinylene)		Poly(diphenylamine)	
Polyaniline		Poly(indole)	
Poly(thienylenevinylene)		Poly(thieno[3,2-*b*]pyrrole)	
Poly(furylenevinylene)		Poly(fluorene)	
Poly(phenylenesulfide)		Polypyridine	

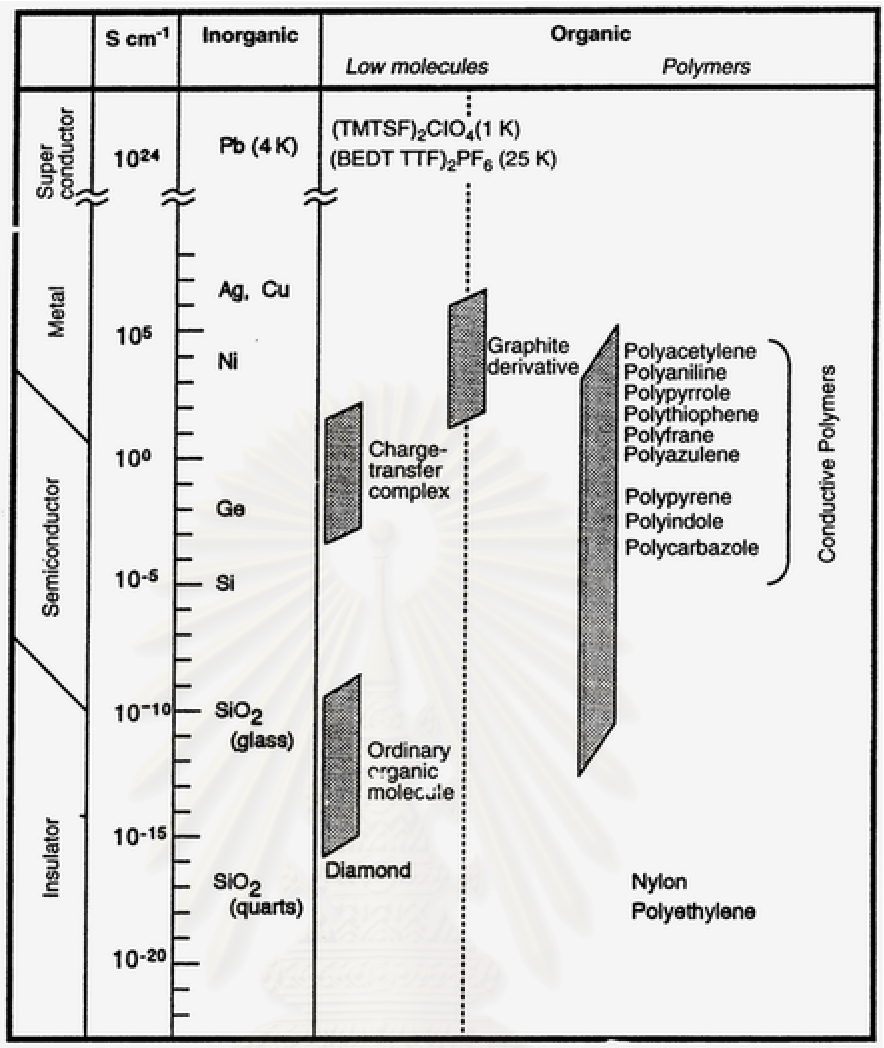


Figure 1.1 Conductivity of various organic compounds in comparison to inorganic materials

Table 1.2 The changes of properties upon electrical stimulation to organic conducting polymers[3]

Property	Typical Change	Potential Application
Conductivity	From 10^{-7} to 10^{3} $S.cm^{-1}$	Electronic components, sensors
Volume	3%	Electromechanical actuators
Color	300-nm shift in absorbance band	Displays, smart windows
Mechanical	Ductile-brittle transition	Artificial muscles
Ion-permeability	From zero to 10^{-8} $mol.cm^{-2}s^{-1}$ in-solution	Membranes

The development of some of these applications to commercial viability has begun for some time. The ability to tailor the electrical properties of these systems is one of their most attractive features and, coupled with improved stability and processability relative to the original conducting polymeric systems, new applications are surely on the horizon. For example:

- Applications utilizing the inherent conductivity of polymer: antistatic coating (metals and polymers), microelectronic devices; plastic chip, and “Stealth” materials for providing a minimal radar profile for military aircrafts and naval vessels
- Electrochemical switching, energy storage and conversion: new rechargeable battery, and redox supercapacitors
- Polymer photovoltaics (light-induced charge separation)
- Display technologies: electrically stimulated light emission: light emitting diode (LED), and flat panel displays
- Electrochromics: advertising displays, smart windows, and memory storage device
- Electromechanical actuators: artificial muscles, window wipers in spacecrafts, rehabilitation gloves, electronic Braille screen and bionic ears for deaf patient
- Separation technologies; novel smart-membrane, and selective molecular recognition (new chromatographic separation media)
- Cellular communication: growth and control of biological cell cultures
- Controlled release devices: ideal hosts for the controlled release of chemical substances
- Corrosion protection: new-generation corrosion protective coatings
- Remotely readable indicators: electronic noses, biosensors, and biomechanic devices

1.2 Conjugated polymer: organic semiconductors

Conjugated polymers are organic semiconductors that with respect to electronic energy levels hardly differ from inorganic semiconductors. Both have their electrons organized in bands rather than in discrete levels and their ground state energy bands either completely filled or completely empty. The band structure of a conjugated polymer originates from the interaction of the π-orbitals of the repeating units throughout the chain. This is exemplified 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 hybridization of the energy levels yielding more and more levels until a point is reached at which there are bands rather than discrete levels. Interaction between the π-electrons of neighboring molecules leads to a three-dimensional band structure.

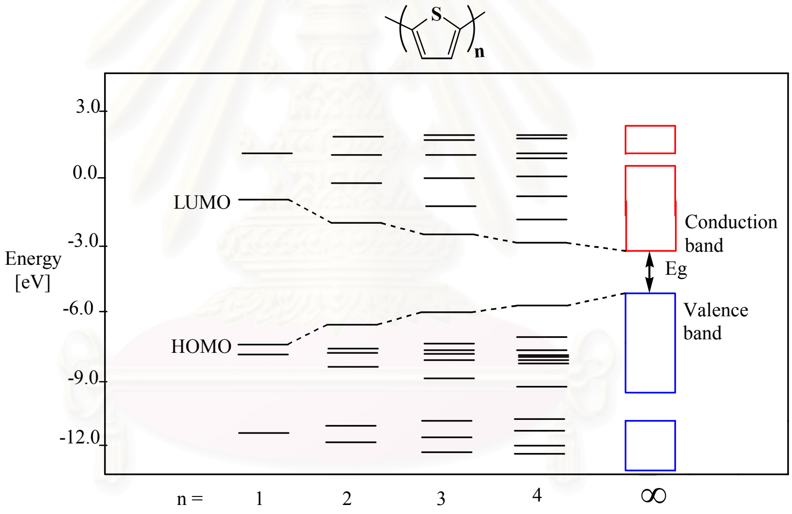


Figure 1.2 Calculated (frontier) energy levels of oligothiophenes with n = 1–4 and of polythiophene. (E_g = band gap energy)

Analogous to semiconductors, the highest occupied band (which originates from the HOMO of a single thiophene unit) is called the valence band, while the lowest unoccupied band (originating from the LUMO of a single thiophene unit) is called the conduction band. The difference in energy between these energy band levels is called the band gap energy or simply, band gap. (E_g)[9] Generally speaking, because conducting polymers possess electrons which are delocalized in π-conjugated system along the whole polymeric chain, its conductivity is much higher than that of other polymers with no conjugated system.[6] These latter non-conjugated polymers are usually known to be insulators.

The difference between π-conjugated polymers and a metal is that in a metal 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 metal or any continuous solid-state structures, N will be a very large number (typically 10^{22} for a 1 cm^3 metal piece). With so many molecular orbitals spaced together in a given range of energies, they form an apparently continuous band of energies (**Figure 1.3**).

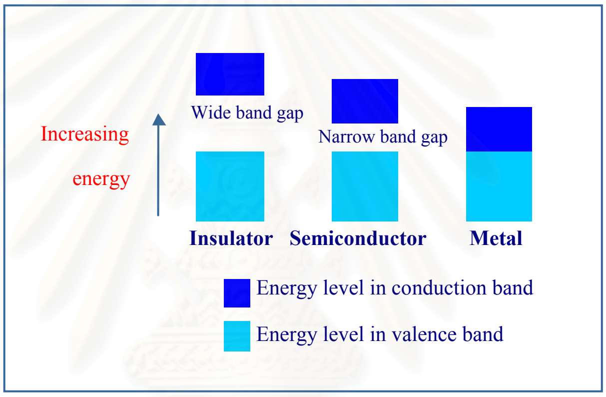


Figure 1.3 Simple band picture explaining the difference between an insulator, a semiconductor and a metal

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 semiconductors and insulators.[10]

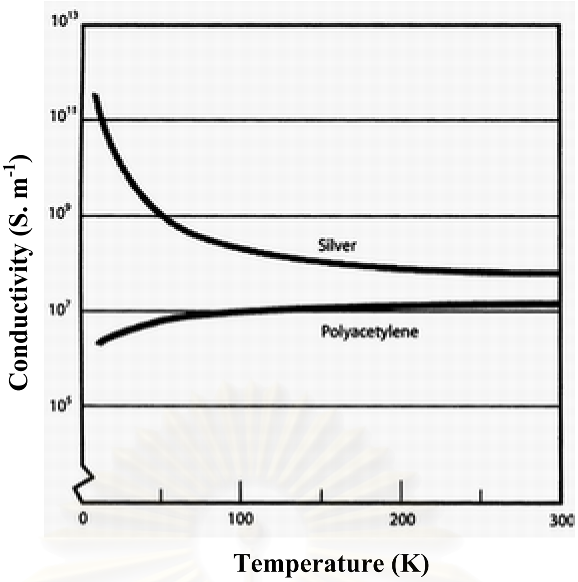


Figure 1.4 The conductivity of conducting polymers decreases with falling temperature in contrast to that of metals.

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

1.3 Polymer doping

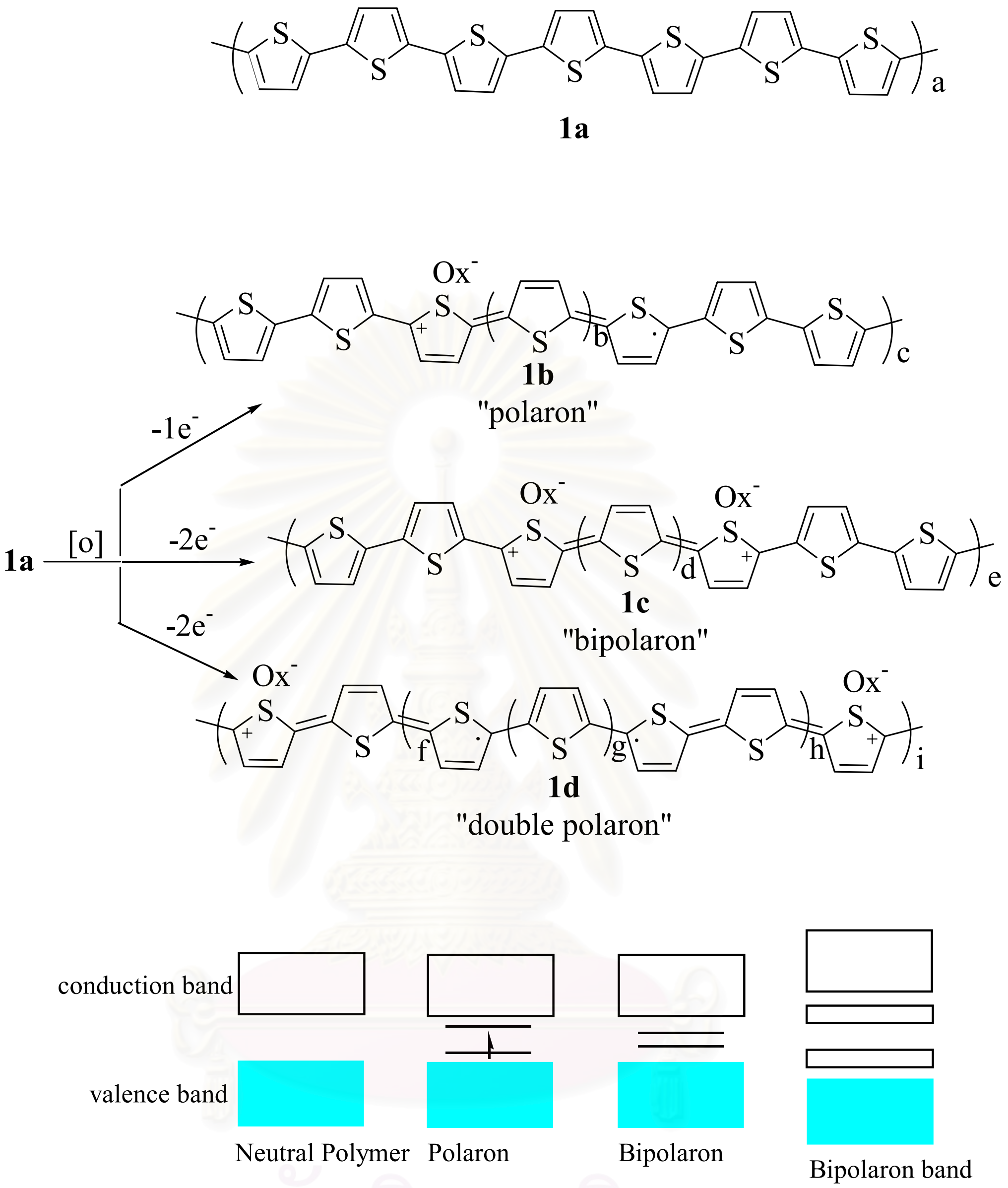
A conjugated polymer, a semiconductor with a finite band gap, can be converted into a conductor by introduction of charges onto the polymer chain. This can be accomplished by doping with different species in order to achieve higher conductivities. The term doping means an addition of some specific chemicals called dopants onto either organic or inorganic semiconductor that changes the oxidation state without extensive altering the structure of semiconductor. Thus, polymer doping is a redox process involving charge transfer with subsequent creation of charged species.[9]

The simple view of doping is that electrons are removed from the valence band (known as oxidation or *p*-doping) or added to the bottom of the conduction band (also called reduction or *n*-doping).[9] Most of the conjugated polymers known today are built up of electron-rich units, making them p-type semiconductors. They can be doped with oxidants like I_2 and $FeCl_3$. The possible changes that occur in a conjugated polymer upon oxidation are exemplified in **Scheme 1.1** for polythiophene.

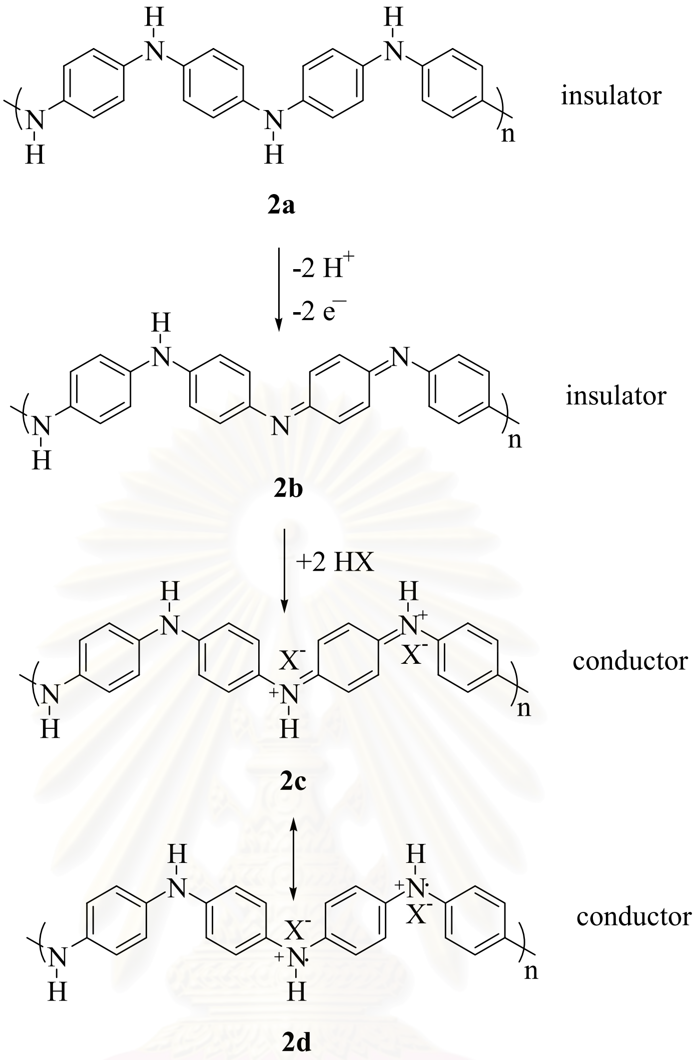
The removal of one electron from the polythiophene chain (**1a**) produces a mobile charge in the form of a radical cation (**1b**), also called a *polaron*. The positive charge tends to induce local atomic displacements, leading to the polaronic behavior. This creates new localized electronic states in the gap, with the lower energy states being occupied by a single unpaired electron. Further oxidation can either convert the polaron into a spinless *bipolaron* (**1c**) that is of lower energy than the creation of two distinct polarons, or introduction of another polaron (**1d**). In either case, introduction of each positive charge also creates a negatively charged counterion (Ox^-). At higher doping levels it becomes possible that two polarons combine to form a bipolaron.[9,11]

For a very heavily doped polymer it is conceivable that the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands and metal-like conductivity.[11]

The second method consists of *acid doping* of conjugated polymers having sites that can be protonated, introducing charges in the main chain. The best known example is polyaniline. (**Scheme 1.2**) The neutral leucoemeraldine form **2a** can be oxidized to the emeraldine base **2b** without introduction of counterions. However, the emeraldine base **2b** only becomes conducting after treatment with a sufficiently strong acid (HX) which protonates the imine nitrogens and, at the same time, introduces a counterion. (X^-) The conducting emeraldine **2c** can also be represented by the mesomeric structure **2d**, in which all phenyl rings are aromatic and radical cations are present on every second nitrogen atom. This degenerate mesomerism is thought to account for a high charge-carrier mobility, and thus high conductivity. However, conformational factors like the crystallinity of polyaniline films also play a crucial role.[9]



Scheme 1.1 Structural and electronic changes in polythiophene upon oxidative doping.



Scheme 1.2 Acid doping in polyaniline

1.4 Effective Conjugation Length (ECL)

An ideal conducting polymer would have its π electrons in the unsaturated bonds conjugated throughout the whole chain. This requirement usually does not hold due to the following: i) Formation of defects in polymer ii) Twisting of planar structure out of conjugation in the polymer.

Examples of the above 2 reasons are shown in **Figure 1.5.** 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 H-H thienyl units in irregular poly(3-alkylthiophene) brought about the twisting of the thienyl ring planes out of coplanarity, caused an increase in the energy needed to allow the flow of electrons through the polymer chain, hence making the polymer chain less conductive.

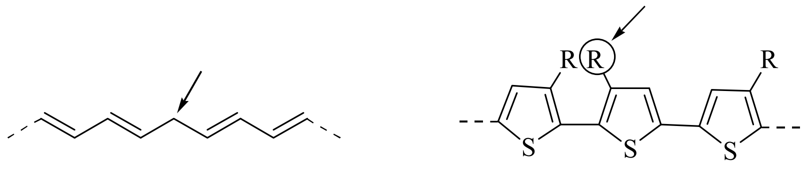

Polyacetylene Poly(3-alkylthiophene)

Figure 1.5 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 1.6**) Twisting of polymer chain would cause the reduction of conjugation in the polymer. The effect of the polymer chain length on optical and conductive properties of soluble oligothiophenes with long alkyl groups has been studied (**Table 1.3**).[12] These compounds (**Figure 1.7**) showed the spectral properties and varied progressively with increasing chain length up to around the 20-mer. The smallest number of monomeric units of a conjugated polymer that shows the highest λ_{max} for that particular polymer corresponds to *effective conjugation length* (ECL). In the case of the experiment on oligothiophenes, the effective conjugation length value was aproximately 20 thienyl units. The conductivity of these iodine-vapor doped oligothiophenes also increased with the chain length, which implied that the extension of the conjugated system to the 27-mer or more may still be advantageous to charge hopping between the adjacent oligomeric chains in the doped state.

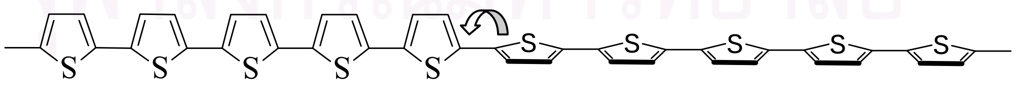


Figure 1.6 Twisting of polythiophene

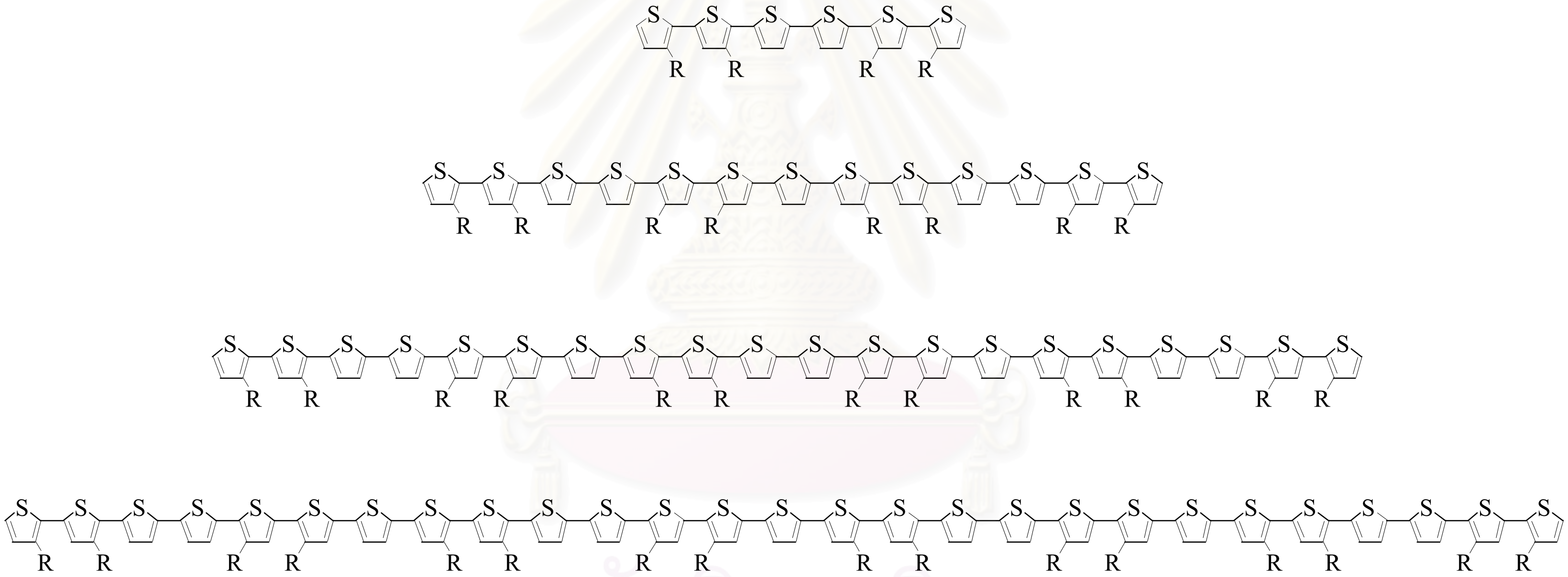


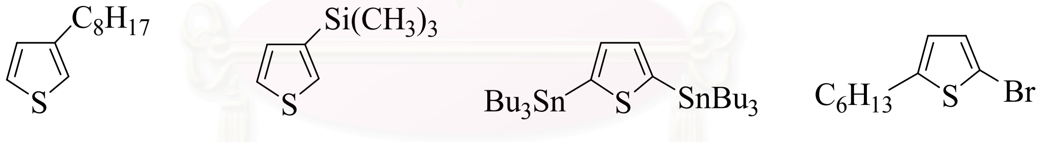
Figure 1.7 Structures of oligothiophene with increasing chain length

Table 1.3 Electronic absorption and conductivities of doped oligothiophenes

Compound	**Number of thienyl units**	λ_{max} **(nm)**	σ **(S.cm^{-1})**
1	6	413	0.041
2	13	453	3.5
3	20	461	7.1
4	27	461	18.5

1.5 Polythiophenes[8,13]

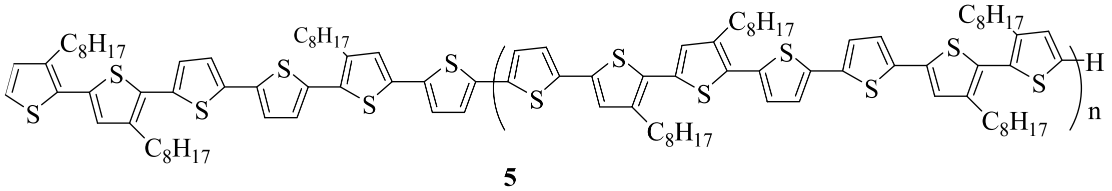
Substituted thiophenes have been of current interest because an addition of long alkyl or silyl groups at β-positions of thiophenes (**1** or **2**) increased solubility of their corresponding polythiophenes and eased functionalization. β-Substituted thiophenes have been polymerized to oligothiophenes or polythiophenes by $FeCl_3$.[14,15] To prevent the unintended oxidative polymerization through the α-α connection, substituents such as Bu_3Sn (**3**), *n*-hexyl or bromo (**4**) were introduced at both α-positions to block the process.[16]



1 **2** **3** **4**

Figure 1.8 α-, and β-substituted thiophenes

Oligothiophenes are among the most investigated model compounds for conductive polymer.[17] Longer oligothiophenes doped with $FeCl_3$ concomitantly increased the effective conjugation length. The development of a series of the longest oligothiophenes with solubilizing octyl groups was successful up to the 48-mer.[18]



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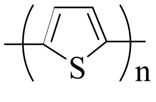
6T: n = 0; **13T**: n = 1; **20T**: n = 2; **27T**: n = 3;
34T: n = 4; **41T**: n = 5; **48T**: n = 6

Figure 1.9 Oligothiophenes

The electronic spectra of oligothiophenes showed a $\pi-\pi^*$ transition in the visible region, which were progressively red-shifted with the chain extension up to the 20-mer: 6T λ_{max} 3.00 eV; 13T 2.74 eV; 20T, 27T, 34T, 41T, and 48T 2.69 eV in THF. Thus, it was concluded that the effective conjugation length of the oligothiophene system could be extended to approximately 20 thiophene units.[18]

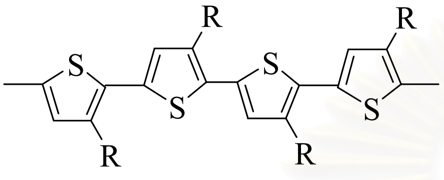
Polythiophene (**PT, 6**)[8,13] is a polymer composed of five membered heterocyclic monomeric units. Polythiophene attracted much attention as a conducting polymer due to ease of synthesis, stability and structural versatility. It has often been considered as a model system for the study of charge transport in conducting polymers with a nondegenerate ground state. Polythiophene has been aimed into main groups resorting to:

- The electrical properties of the doped conducting state, such as antistatic and EMI shielding, PT-based gas sensors, PT-based radiation detector and corrosion protective films
- The electronic properties of the neutral semiconducting state, such as photovoltaic cells and nonlinear optics
- The electrochemical reversibility of the transition between the doped and the undoped state, such as new rechargeable battery, display devices, electrochemical sensors and modified electrodes[12]

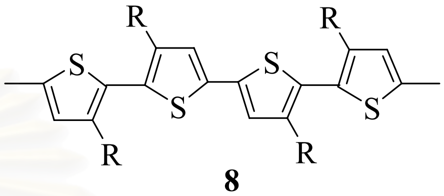


6

Polythiophene[19] with an ideal extended π-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 polymer. With the substituents at the 3-position of thiophene, a number of different regioisomers of polythiophenes namely, head-to-tail (HT, **7**), head-to-head (HH, **8**) and random (**9**) configurations are possible.



7



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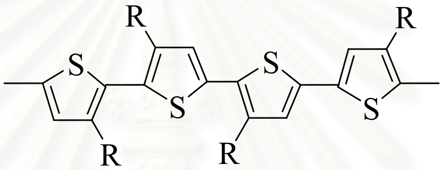

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The head-to-head connection is sterically unfavorable for coplanarity and hence causes a significant loss of conjugation. In the case of random regioisomers, the optimal chain length for certain properties such as conductivity and nonlinear optics has been found[19] to be in the range of seven to nine carbon atoms.

1.6 Polythiophenes with thienyl *S*,*S*-dioxide units

One of the active interest on polythiophene research was the attempted functionalization of polythiophene to decrease band gap. Insertion thienyl *S*,*S*-dioxide in polythiophene can increased λ_{max} and decreased band gap. Addition various substituents on the β-positions, only little attention has been paid to the functionalizations of the thiophene ring itself. Sulfur is a hypervalent atom characterized by several formal oxidation states in which it may be surrounded by more than eight electrons in the valence shell. This allows the functionalization of polythiophene at the thienyl sulfur atom itself, for example, through the formation *S*,*S*-dioxides.

Polythiophene, which is easily oxidized but not easily reduced. Many papers have already been published concerning the way to reduce the band gap of thiophene-based polymers with the hope of making these materials intrinsically conductive. The way of making polythiophene soluble by grafting long alkyl chains was found.[20]

Oligothiophene *S*,*S*-dioxides[21] were obtained by reaction of mono- and dibrominated thiophene *S*,*S*-dioxides with appropriated thienyl stannanes in the presence of $Pd(AsPh_3)_4$. Incorporating one or more thienyl *S*,*S*-dioxide units into the oligomers generally induced longer π-conjugation within the molecules as reflected by shift of maximum wavelength absorption (λ_{max}) to the longer wavelength region (**Table 1.4**). The insertion of the thienyl *S*,*S*-dioxide moieties affected more to the λ_{max} of the longer oligothiophenes, which in turn depended on the position and on the number of sulfonyl groups present in the molecular skeleton. The possibility for the thienyl sulfur atom to disconnect its lone pair from the aromatic system through the formation of the dioxide led to smaller optical gap, as shown by the large red shifts of the maximum wavelength absorption of oligothiophene *S*,*S*-dioxides with respect to that of the parent oligothiophenes. This also led to a dramatic decrease of the LUMO energy and to the consequent increase of the electron affinity. The substituted monomeric thiophenes were oxidized to thiophene *S*,*S*-dioxides by peroxide reagents such as *m*-chloroperoxybenzoic acid (*m*-CPBA) or dimethyldioxirane.[22]

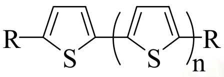
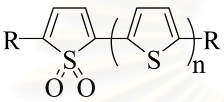
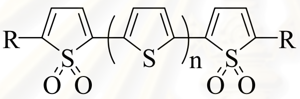
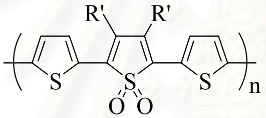
Table 1.4 Maximum Wavelength Absorption (λ_{max}, nm)[a] of *S*,*S*-dioxides and of the parent oligothiophenes.

Oligothiophenes	**α,ω-substituents at the terminals (R)**		
	-H	**-SiMe$_2$(*t*-Bu)**	**-(CH$_2$)$_5$CH$_3$**
T	231	245	254
O	NA[b]	314	300
TT	302	344	340
OT	NA[b]	408	402
OO	NA[b]	406	NA[b]
TTT	352	370	380
TOT	426	440	NA[b]
OTT	NA[b]	460	430
OTO	NA[b]	460	442
TTTT	390	412	400
OTTT	NA[b]	470	448
TOTT	NA[b]	480	NA[b]
OTTO	NA[b]	492	480
TTTTT	416	420	NA[b]
OTTTT	NA[b]	470	NA[b]
TTOTT	NA[b]	512	NA[b]
OTTTO	NA[b]	520	NA[b]
OTOTO	NA[b]	542	NA[b]

[a] In $CHCl_3$, [b] NA = Not available

The thiophene-based oligomers and polymers carrying the nonaromatic thienyl *S*,*S*-dioxide moieties have also been synthesized using the preoxidized thiophene *S*,*S*-dioxide monomer (**Table 1.5**).[20] From UV spectra of the oligothiophenes *S*,*S*-dioxide, Entry 5-13, bathochromic shifts of the maximum wavelength absorption with respect to that of parent oligothiophene were observed.

Table 1.5 Structures, and maximum wavelength absorptions (λ_{max}) of oligothiophenes and polythiophenes with and without thienyl *S*,*S*-dioxide moieties

Entry	**Compound**[a]	**n**	λ_{max}[b] (nm)
1		1	326
2		2	368
3		3	412
4		4	420
5		1	382
6		2	460
7		3	470
8		4	470
9		0	382
10		1	460
11		2	490
12		3	500
13		Polymer	554

[a] R = $SiMe_2Bu$, R' = hexyl, [b] In $CHCl_3$

A recent report on well-defined conducting polymers through endogenous polymerization routes, that is, without addition of initiators or catalysts, has appeared. This polymer was obtained by solid-state polymerization of a structurally pre-organized crystalline monomer. This new method could give rise to a nearly defect-free, highly ordered or even "single crystalline" conjugated polymer. This has been demonstrated by the first solid-state synthesis of conducting PEDOT by facile polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in the solid state (**Figure 1.10**).[23]

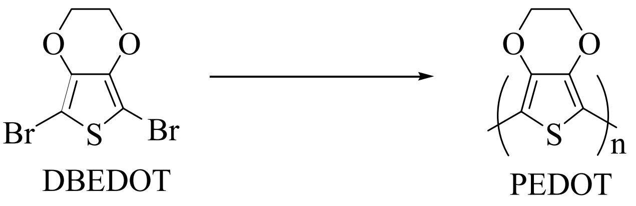


Figure 1.10 Solid-state synthesis of PEDOT

The synthesis of polythiophene containing thienyl *S*,*S*-dioxide units so far appeared to be very complicated and difficult to characterize due to the lack of solubility. Here we carried out attempts to synthesize such monomers carrying various substituents by direct oxidation onto thiophene and dibromothiophene derivatives using various oxidizing agents and conditions. The subsequent preliminary studies on the optical properties of the resulted products are also reported.

1.7 Objectives

1. To synthesize a series of 3-substituted and unsubstituted 2,5-dibromothiophenes.
2. To study and compare the direct oxidation of brominated and debrominated 3-substituted thiophenes and their derivatives.

1.8 Scope of investigation

1. Preparation of the 2,5-dibrominated 3-substituted thiophenes.
2. Preparation of the thiophene with thienyl *S*,*S*-dioxide using various oxidizing agents and conditions.
3. Preparation of the 2,5-dibrominated 3-substituted thiophene with thienyl *S*,*S*-dioxide using various oxidizing agents and conditions.

CHAPTER II

EXPERIMENTAL SECTION

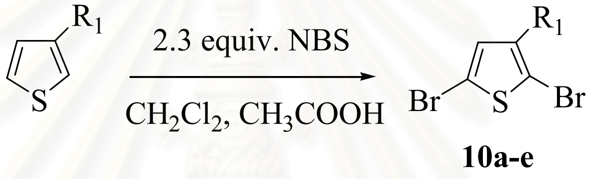
2.1 Chemicals

1. thiophene : Fluka
2. 3-hexylthiophene : Fluka
3. 3-bromothiophene : Fluka
4. 3-methoxythiophene : Fluka
5. thiophene-3-carboxylic acid : Fluka
6. thieno[3,4-b]-1,4-dioxin : Aldrich
7. *m*-chloroperoxybenzoic acid : Aldrich
8. 30% hydrogen peroxide : Merck
9. trifluoroacetic acid : Fluka
10. trifluoroacetic anhydride : Acros Organics
11. peroxymonosulfate triple salts (oxone) : Riedel-deHaën
12. tetrabutylammonium salt (oxone) : Fluka
13. urea hydrogen peroxide : Merck
14. sodium percarbonate : Riedel-deHaën
15. toluene-4-sulfonic acid (TsOH) : Merck
16. *N*-bromosuccinimide : Acros Organics
17. sodium hydroxide : Merck
18. sodium bisulphite : Merck
19. methanol : Labscan
20. dichloromethane : BDH
21. chloroform : BDH
22. deuterated chloroform : Merck
23. potassium bromide : Merck

2.2 Instrument and apparatus

1. Infrared Spectrophotometer : Perkin Elmer or Nicolet (Impact 410)
2. Nuclear Magnetic Resonance Spectrometer : Bruker, ACF 400 MHz
3. UV-Visible Spectrophotometer : HP 8453
4. Rotary Evaporator

2.3 General procedure for the synthesis of 2,5-dibromothiophene derivatives (10-11).



10a-e

R_1 = H, $^{n}C_6H_{13}$, Br, OCH_3, COOH

Appropriate thiophene derivatives were added to a 20 mL solution of a 50:50 (v/v) mixture of dichloromethane:glacial acetic acid. NBS was added to the reaction mixture in small portions. After addition, the reaction mixture was heated at 50 °C for 10 min, and then allowed to cool to room temperature. The reaction mixture was diluted with 20 mL of water. The dichloromethane layer was washed once with 10 mL of 0.5 M KOH and once with water, and dried over magnesium sulfate. Solvent was removed by rotary evaporator. The corresponding dibromothiophene derivatives were obtained (**10a-e**).

2,5-dibromothiophene (**10a**: R_1 = H)**.** The compound was prepared from a reaction of 1.35 g (16 mmol) of thiophene, and 6.05 g (34 mmol) of NBS. The product was obtained as a brown liquid in 2.48 g (64%). It was soluble in dichloromethane, chloroform, and acetonitrile. ^{1}H-NMR ($CDCl_3$): δ (ppm) 6.9 (2H, s, Ar-$\underline{H}$); ^{13}C-NMR ($CDCl_3$): δ (ppm) 111, 136; IR: (cm^{-1}) 1569, 1724 (C=C stretching), 3098 (Aromatic C-H stretching).

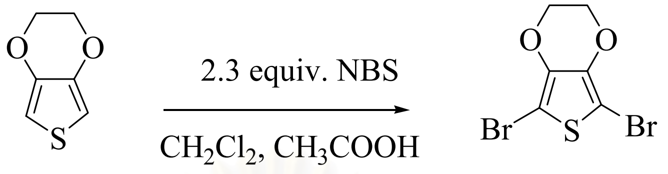
2,5-dibromo-3-hexylthiophene (**10b**: R_1 = $^{n}C_6H_{13}$). The compound was prepared from a reaction of 1.35 g (8 mol) of 3-hexylthiophene, and 3.02 g (17 mmol) of NBS. The product was obtained as a yellow liquid in 2.09 g (80%). It was soluble in dichloromethane, chloroform, and acetonitrile. ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.9 (3H, br, Ar-$(CH_2)_5$-C$\underline{H}_3$), 1.3 (6H, br, Ar-CH_2-CH_2-($C_3\underline{H}_6$)-CH_3), 1.6 (2H, br, Ar-CH_2-C$\underline{H}_2$-), 2.5 (2H, br t, Ar-C$\underline{H}_2$-), 6.9 (H, s, Ar-$\underline{H}$); ^{13}C-NMR ($CDCl_3$): δ (ppm) 108, 110, 131, 143; IR: (cm^{-1}) 1541, 1715 (C=C stretching), 2856 (Aliphatic C-H stretching), 2955 (Aromatic C-H stretching); and MS, M^+ = 326.

2,3,5-tribromothiophene (**10c**: R_1 = Br). The compound was prepared from a reaction of 1.32 g (8 mol) of 3-bromothiophene, and 3.02 g (17 mmol) of NBS. The product was obtained as a deep orange liquid in 1.95 g (75%). It was soluble in dichloromethane, chloroform, and acetonitrile. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.1 (H, s, Ar-$\underline{H}$); ^{13}C-NMR ($CDCl_3$): δ (ppm) 110.6, 112.1, 113.6, 132.3; IR: (cm^{-1}) 1640, 1717 (C=C stretching), 3096 (Aromatic C-H stretching); and MS, M^+ = 322.

2,5-dibromo-3-methoxythiophene (**10d**: R_1 = OCH_3). The compound was prepared from a reaction of 1.28 g (11 mol) of 3-methoxythiophene, and 42.34 g (23 mmol) of NBS. The procedure was slightly modified by running the reaction at room temperature for 10 min. The product was obtained as a deep green solid in 1.71 g (56%). The product was soluble in dichloromethane, chloroform, and partially acetonitrile. ^{1}H-NMR ($CDCl_3$): δ (ppm) 1.6 (3H, br, Ar-C$\underline{H}_3$), 3.9, 4.2 (3H, br s, Ar-OC$\underline{H}_3$), 6.8 (H, s, Ar-$\underline{H}$); ^{13}C-NMR ($CDCl_3$): δ (ppm) 45, 60, 90, 120; IR: (cm^{-1}) 1610, 1691 (C=C stretching), 2930 (Aliphatic C-H stretching), 3086 (Aromatic C-H stretching).

2,5-dibromothiophene-3-carboxylic acid (**10e**: R_1 = COOH). The compound was prepared from a reaction of thiophene-3-carboxylic acid (8 mmol) was added to a 20 mL solution of a 50:50 (v/v) mixture of dichloromethane:glacial acetic acid. NBS (17 mmol) was added to the reaction mixture in small portions. After addition, the reaction mixture was heated at 50 °C for 10 min, and then allowed to cool to room temperature. The reaction mixture was diluted with 20 mL of water, and the layer were separated. The dichloromethane layer was washed once with water. The organic phase was evaporated by rotary evaporator. A portion of the crude product was recrystallized. Light gray solid was obtained in 0.42 g. It was soluble in dichloromethane, chloroform, and acetonitrile.

2,3-dibromothieno[3,4-b]-1,4-dioxin (**11**).



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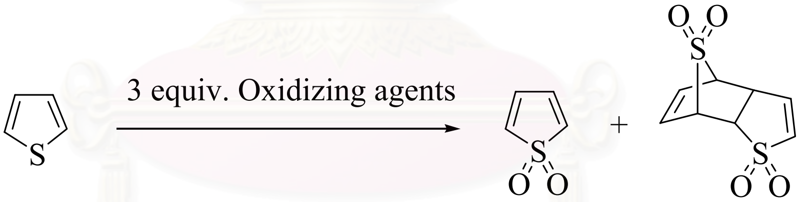
The compound was prepared from a reaction of 1.36 g (9 mol) of thieno[3,4-b]-1,4-dioxin, and 3.63 g (20 mmol) of NBS were used. Followed the slightly modified protocol for the synthesis of **10d**. The procedure was slightly modified by running the reaction at room temperature for 10 min. The product was obtained as blue crystal in 1.80 g (63%). It was soluble partially in dichloromethane, chloroform, and acetonitrile. ^{1}H-NMR ($CDCl_3$): δ (ppm) 4.2 (4H, br, $-C\underline{H}_2-C\underline{H}_2-$); IR: ($cm^{-1}$) 1597 (C=C stretching), 2991 (Aliphatic C-H stretching).

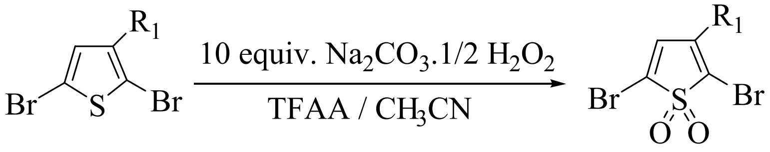
2.4 General procedure for the oxidation of unsubstituted thiophene derivatives.



Thiophene (10 mmol) was added to 25 mL of an organic solvents in a round bottom flask. An oxidizing agent (30 mmol) was added to the reaction mixture in small portions. After addition, the reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was diluted with 25 mL of water, $NaHSO_3$ was then added to the reaction mixture in small portions. The reaction mixture was dried over magnesium sulfate. Solvent was removed by rotary evaporator to give the product.

List of oxidizing agents used include: *m*-CPBA/CH_2Cl_2, 30% H_2O_2 (aq.)/CH_2Cl_2/TFA, 30% H_2O_2 (aq.)/CH_3CN/TFA, oxone potassium monopersulfate triple salts, oxone tetrabutylammonium salt, and UHP/CH_3CN/TFA.

2.5 General procedure for the synthesis 2,5-dibromothiophene *S,S*-dioxide derivatives (12-13).



10a-d **12a-d**

$R_1 = H, {}^{n}C_6H_{13}, Br, OCH_3$

Appropriate 2,5-dibromothiophene derivatives (50 mmol) were added to a 20 mL of acetonitrile. $Na_2CO_3.1/2H_2O_2$ (500 mmol) was added to the reaction mixture in small portions and then TFAA (0.6 mL, 5 mmol) was added to the reaction mixture. After addition, the reaction mixture was cooled to 0 ^{o}C for 30 min, and then the reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was diluted with 20 mL of water, and the dichloromethane layer was washed once with 10 mL of 0.5 M KOH and once with water, and dried over magnesium sulfate. Solvent was removed by rotary evaporator to give the product (**12-13**).

2,5-dibromothiophene *S,S*-dioxide (**12a**: $R_1 = H$)

The product was obtained as a colorless liquid in 0.85 g (62%). It was soluble in dichloromethane, chloroform, and acetonitrile. ^1H-NMR ($CDCl_3$): δ (ppm) 6.9 (2H, s, Ar-$\underline{H}$).

2,5-dibromo-3-hexylthiophene *S,S*-dioxide (**12b**: $R_1 = {}^{n}C_6H_{13}$)

The product was obtained as a colorless liquid in 0.82 g (46%). It was soluble in dichloromethane, chloroform, and acetonitrile. ^1H-NMR ($CDCl_3$): δ (ppm) 0.9 (3H, br, Ar-$(CH_2)_5$-$C\underline{H}_3$), 1.3 (6H, br, Ar-CH_2-CH_2-$(C_3\underline{H}_6)$-CH_3), 1.6 (2H, br, Ar-CH_2-$C\underline{H}_2$-), 2.5 (2H, br t, Ar-$C\underline{H}_2$-), 6.9 (H, s, Ar-$\underline{H}$)**.**

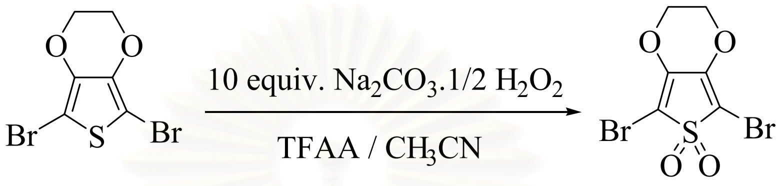
2,3,5-tribromothiophene *S,S*-dioxide (**12c**: $R_1 = Br$)

The product was obtained as a colorless liquid in 0.65 g (37%). It was soluble in dichloromethane, chloroform, and acetonitrile. ^1H-NMR ($CDCl_3$): δ (ppm) 7.1 (H, s, Ar-$\underline{H}$).

2,5-dibromo-3-methoxythiophene *S,S*-dioxide (**12d**: $R_1 = OCH_3$)

The product was obtained as a light green solid in 0.87 g (57%). The product was soluble in dichloromethane, chloroform, and acetonitrile. ^{1}H-NMR ($CDCl_3$): δ (ppm) 1.6 (3H, br, Ar-C$\underline{H}_3$), 3.9, 4.2 (3H, br s, Ar-OC$\underline{H}_3$), 6.8 (H, s, Ar-$\underline{H}$)**.**

2,3-dibromothieno [3,4-b]-1,4-dioxin (**11**) ***S,S*-dioxide** (**13**).



11 **13**

The product was obtained as a light blue solid in 0.62 g (37%). It was soluble in dichloromethane, chloroform, and acetonitrile. ^{1}H-NMR ($CDCl_3$): δ (ppm) 4.1, 4.2, 4.3 (4H, br, -C$\underline{H}_2$-C$\underline{H}_2$-).

CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of 2,5-dibromothiophene derivatives

The synthesis of 2,5-dibromothiophene derivatives using NBS was found to give varied percent yields depending on the β-substituted thiophenes used as shown in **Table 3.1**. The products were analyzed by ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy. All data are complied in the Appendix. The data were compared to the literature data.[24]

Table 3.1 Synthesis of 2,5-dibromothiophene derivatives.

Entry	**Thiophene derivatives**	**Condition**	**Yield (%)**
1	thiophene	Reflux^{a}, 10 min	64
2	3-hexylthiophene	Reflux^{a}, 10 min	80
3	3-bromothiophene	Reflux^{a}, 10 min	75^{b}
4	3-methoxythiophene	RT, 10 min	56
5	thiophene-3-carboxylic acid	Reflux^{a}, 10 min	NA^{c}
6	thieno[3,4-b]-1,4-dioxin	RT, 10 min	63

^{a} The reflux temperature is approximately 50 °C

^{b} Mix with some 2,5-dibromothiophene

^{c} NA = Not available

2,5-dibromothiophene (**10a**) was obtained as a brown liquid in 2.48 g (64%). It was soluble in dichloromethane, chloroform, and acetonitrile. From ^{1}H-NMR spectrum ($CDCl_3$), it showed characteristic signals of the hydrogens of the aromatic protons of thiophene ring at δ (ppm) 6.9 (2H, s, Ar-$\underline{H}$). ^{13}C-NMR spectrum ($CDCl_3$), it showed characteristic signals of the carbons of thiophene ring at δ (ppm) 111, 136. IR spectrum, it showed peaks at 1569, 1724 (C=C stretching), 3098 (Aromatic C-H stretching) (cm^{-1}).

2,5-dibromo-3-hexylthiophene (**10b**) was obtained as a yellow liquid in 2.09 g (80%). It was soluble in dichloromethane, chloroform, and acetonitrile. From ^{1}H-NMR spectrum ($CDCl_3$), it showed characteristic signals of the hydrogens at δ (ppm) 0.9 (3H, br, Ar-$(CH_2)_5$-$C\underline{H}_3$), 1.3 (6H, br, Ar-CH_2-CH_2-$(C_3\underline{H}_6)$-CH_3), 1.6 (2H, br, Ar-CH_2-$C\underline{H}_2$-), 2.5 (2H, br t, Ar-$C\underline{H}_2$-), 6.9 (H, s, Ar-$\underline{H}$). ^{13}C-NMR spectrum ($CDCl_3$), it showed characteristic signals of the carbons at δ (ppm) 108, 110, 131, 143. IR spectrum, it showed peaks at 1541, 1715 (C=C stretching), 2856 (Aliphatic C-H stretching), 2955 (Aromatic C-H stretching) (cm^{-1}). MS, M^+ = 326.

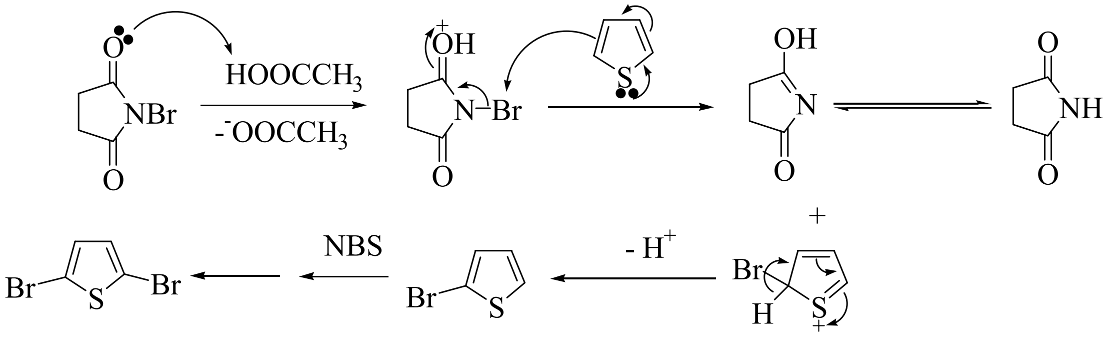
2,3,5-tribromothiophene (**10c**) was obtained as a deep orange liquid in 1.95 g (75%). It was soluble in dichloromethane, chloroform, and acetonitrile. From ^{1}H-NMR spectrum ($CDCl_3$), it showed characteristic signals of the hydrogens of the aromatic protons of thiophene ring at δ (ppm) 7.1 (H, s, Ar-$\underline{H}$). ^{13}C-NMR spectrum ($CDCl_3$), it showed characteristic signals of the carbons of thiophene ring at δ (ppm) 110.6, 112.1, 113.6, 132.3. IR spectroscopy spectrum, it showed peaks at 1640, 1717 (C=C stretching), 3096 (Aromatic C-H stretching) (cm^{-1}). MS, M^+ = 322.

2,5-dibromo-3-methoxythiophene (**10d**) was obtained as a deep green solid in 1.71 g (56%). It was soluble in dichloromethane, chloroform, and partially acetonitrile. From ^{1}H-NMR spectrum ($CDCl_3$), it showed characteristic signals of the hydrogens at δ (ppm) 1.6 (3H, br, Ar-$C\underline{H}_3$), 3.9, 4.2 (3H, br s, Ar-$OC\underline{H}_3$), 6.8 (H, s, Ar-$\underline{H}$). ^{13}C-NMR spectrum ($CDCl_3$), It showed characteristic signals of the carbons at δ (ppm) 45, 60, 90, 120. IR spectrum, it showed peaks at 1610, 1691 (C=C stretching), 2930 (Aliphatic C-H stretching), 3086 (Aromatic C-H stretching) (cm^{-1}).

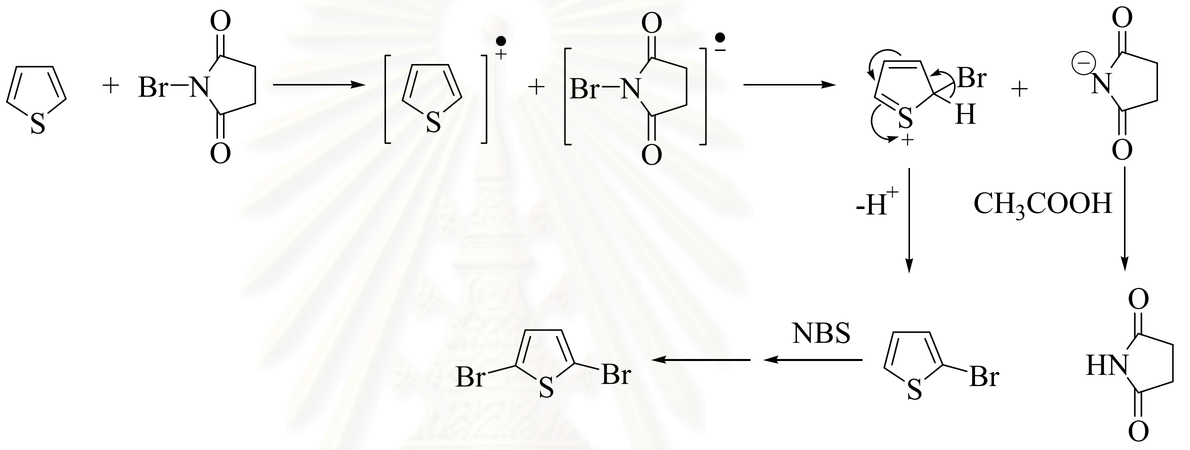
However, 2,5-dibromothiophene-3-carboxylic acid (**10e**) was not obtained. An unknown light gray solid was separated out from the reaction mixture after quenching. It was soluble in dichloromethane, chloroform, and acetonitrile. There was no sign of signals corresponding to carboxyl groups. It was assumed that the desired product was much more difficult to prepare because of the strong electron withdrawing carboxyl group at the β-position. The thiophene ring was deactivated toward electrophiles and perhaps stronger condition or longer reaction time was needed to achieve such bromination.

2,3-dibromothieno[3,4-b]-1,4-dioxin (**11**) was obtained as a blue crystal in 1.80 g (63%). It was partially soluble in dichloromethane, chloroform, and acetonitrile. From ^{1}H-NMR spectrum ($CDCl_3$), and IR spectrum. The desired 2,3-dibromothieno[3,4-b]-1,4-dioxin was first obtained and slowly turned into deep blue, insoluble solid. From previous report on this compound,[23] the solid state polymerization was suggested to spontaneously occur, giving the insoluble polyethylenedioxythiophene (PEDOT, **Figure 1.10**) which is what seemed to be the case here.

The mechanisms of the bromination on thiophene ring are proposed into 2 possible pathways (**Scheme 3.1**).[25] First, the more likely mechanism in such a polar solvent is the acid catalyzed electrophilic aromatic substitution (**Scheme 3.1a**). Another possible pathway is the radical-based single electron transfer followed by aromatic substitution (**Scheme 3.1b**).



(**a**) Acid catalyzed polar mechanism



(**b**) Radicals mechanism

Scheme 3.1 Mechanisms of thiophene bromination

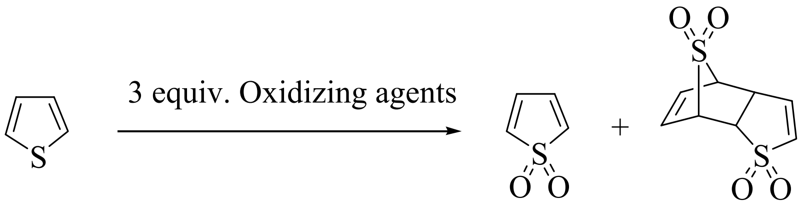
2,5-dibromothiophene-3-carboxylic acid (**10e**) has not been successfully synthesized. It maybe accounted for as followed: because thiophene-3-carboxylic acid has the strong electron withdrawing carboxyl group at the 3-position of the thiophene ring which deactivates the thiophene ring toward electrophilic brominating agent based on the polar mechanism. Similarly, the radicals mechanism could not operate either due to the inability of the thiophene ring to donate the electron.

3.2 Synthesis of thiophene *S*,*S*-dioxide

3.2.1 Oxidation of thiophene derivatives with various oxidizing agents

The synthesis of thiophene *S*,*S*-dioxide derivatives by various oxidizing agents at room temperature for 24 h are shown in **Table 3.2**.

Table 3.2 Synthesis of thiophene *S*,*S*-dioxide derivatives by using various oxidizing agents.



Entry	Substrate	Oxidizing agents[a]	Solvent /Acid additive
1	thiophene	*m*-CPBA	CH_2Cl_2
2	thiophene	30% H_2O_2 (aq.)	CH_2Cl_2/TFA
3	thiophene	30% H_2O_2 (aq.)	CH_3CN/TFA
4	thiophene	oxone (potassium monopersulfate triple salt)	acetone/TFA
5	thiophene	oxone (tetrabutyl-ammonium salt)	acetone/TFA
6	thiophene	UHP	CH_3CN/TFA
7	3-hexylthiophene	UHP	CH_3CN/TFA
8	2,5-dibromothiophene	UHP	CH_3CN/TFA

[a] Mole ratios of substrate : oxidizing agent = 1 : 3

From **Table 3.1**, entry **3** was the only condition that showed the potential to give the thiophene *S*,*S*-dioxide. Because there are many signals around 6-7 ppm in ^{1}H-NMR spectra that could correspond to the diene structure resulted from the oxidation of sulfur atom in thiophene ring. The product has not yet been purified. However. entries **1**, **2**, **4**, **5**, and **6** did not give the desired product. The reasons could be the insufficient power of the oxidizing agents used or in most cases, especially thiophene, the oxidation was too strong and the desired product was decomposed before quenching the reaction.

It was envisaged that Urea hydrogen peroxide (UHP) is a potentially appropriate oxidizing agent because of its readily solubility in organic solvent and strong oxidizing power. However, the results showed that there was another product that gave broad signals around 6-9 ppm in ^{1}H-NMR spectra. This effectively masked all the signals that could be used to indicate the presence of the diene moiety of the thiophene *S*,*S*-dioxide. The undesired product was assumed to be urea, the inseparable by-product from the oxidizing agent itself.

3.2.2 Oxidation of 2,5-dibromothiophene derivatives with $Na_2CO_3.1/2H_2O_2$

To overcome the problem of the presence of by-product from UHP, sodium percarbonate ($Na_2CO_3.1/2H_2O_2$) was used as an alternative oxidizing agent potentially suitable for this case. The compound can be readily removed from of the reaction mixture by acid washing when the reaction is complete, solving the problem of leftover by-product that cannot be separated as in the case of UHP.

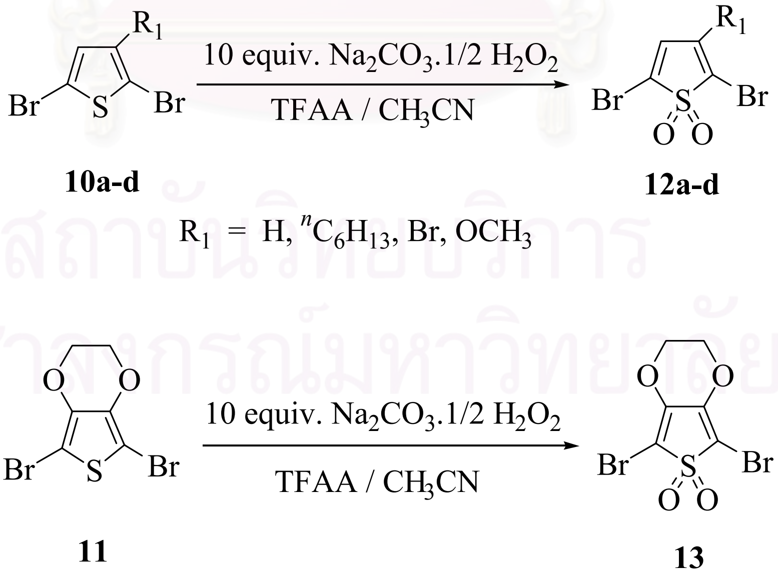


Figure 3.1 Attempted synthesis of 2,5-dibromothiophene *S*,*S*-dioxide derivatives by oxidizing with $Na_2CO_3.1/2H_2O_2$.

The results showed that all 3-substituted dibromothiophene derivatives (**Figure 3.1**) could not be oxidized to their corresponding dioxide products. Only the starting materials were recovered. The soluble part of 2,3-dibromothieno[3,4-b]-1,4-dioxin (**11**), however, showed some additional signals around 4-5 ppm in ^{1}H-NMR spectrum, suggesting that there were other products containing dioxoethylene bridges similar to the substrate. This is suggestive of the presence the oxidized products. Nevertheless, as indicated earlier in section 3.1, **11** was supposed to readily polymerize to give the PEDOT. The oxidized mixture obtained here also suffered the insolubility problem and could not be clearly characterized.

Although, dioxide products could not be synthesized by using various oxidizing agents such as 30% $H_2O_2/CH_3CN/TFA$ and $Na_2CO_3.1/2H_2O_2$, another oxidizing agent is worth evaluated as an alternative. Recent rapidly developing dioxirane chemistry has demonstrated its remarkable reactivity and selectivity in transferring oxygen to an electron-rich center of substrates.[27] Therefore, future work employing dioxirane would be of great interest.

CHAPTER IV

CONCLUSION

Five derivatives of dibromo β-substituted thiophenes have been successfully synthesized using NBS in acetic acid. However, 2,5-dibromothiophene-3-carboxylic acid has not been successfully synthesized by this method because thiophene-3-carboxylic acid has the strong electron withdrawing group at β-position of thiophene ring which deactivated the thiophene ring. The resulting 2,3-dibromothieno[3,4-b]-1,4-dioxin was assumed to undergo solid state polymerization to PEDOT afterwards.

Thiophene has been oxidized by 30% H_2O_2 in CH_3CN/TFA, that showed the potential to give the thiophene *S,S*-dioxide. Although the product was unable to be purified. thiophene, 3-hexylthiophene, and 2,5-dibromothiophene could not be oxidized by the oxidizing agents used. The reasons could be the insufficient power of the oxidizing agents or the oxidizing agents were too strong and the desired products were lost before quenching the reaction. The oxidized 2,3-dibromothieno[3,4-b]-1,4-dioxin showed some additional ^{1}H-NMR indication. There were other products containing dioxoethylene bridges. That might correspond to the desired oxidized products. However, 2,3-dibromothieno[3,4-b]-1,4-dioxin substrate was assumed to partly undergo solid state polymerization to the insoluble PEDOT that could not be clearly characterized.

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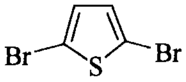
APPENDIX



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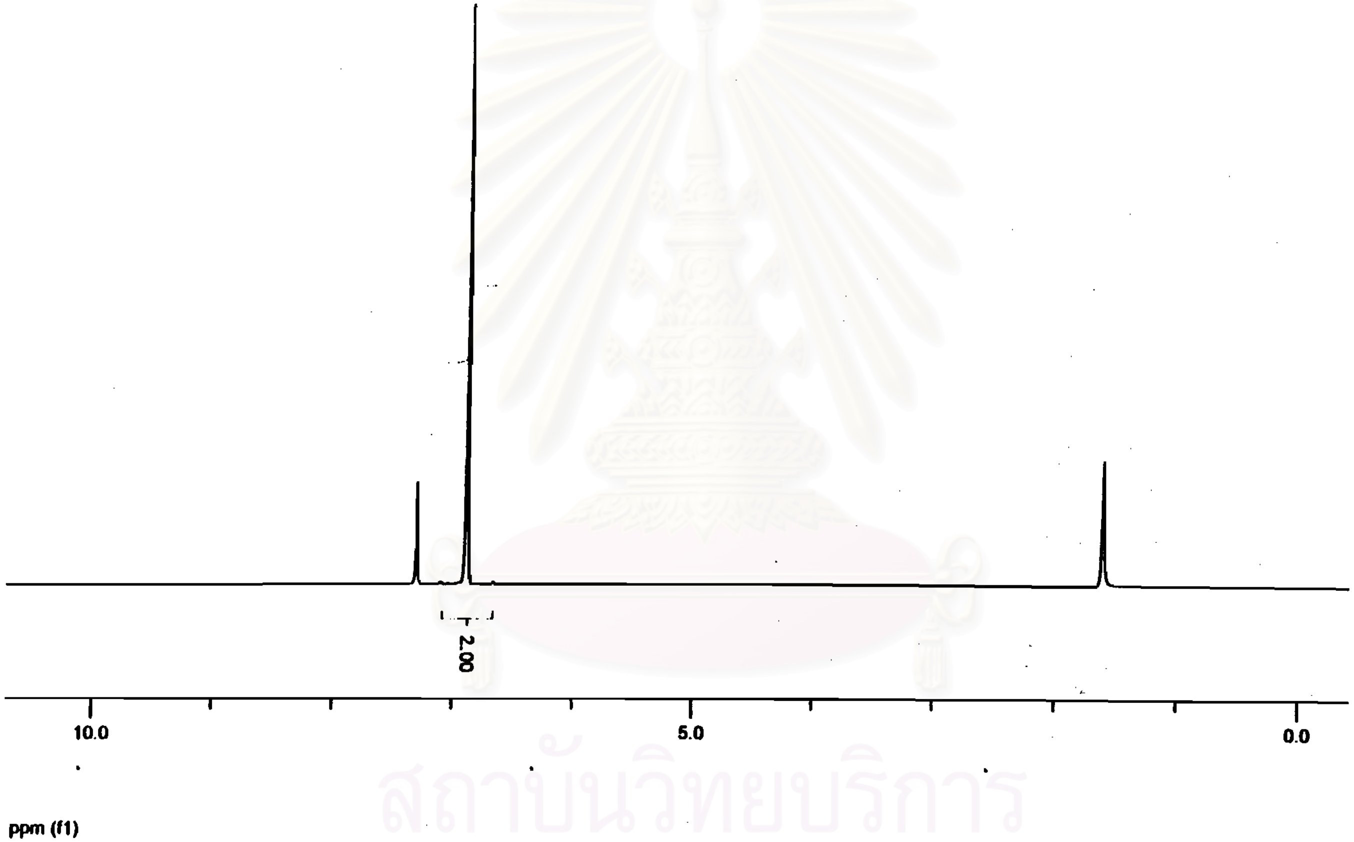
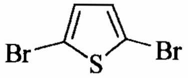


Figure A-1 ^{1}H-NMR ($CDCl_3$) spectrum of 2,5-dibromothiophene



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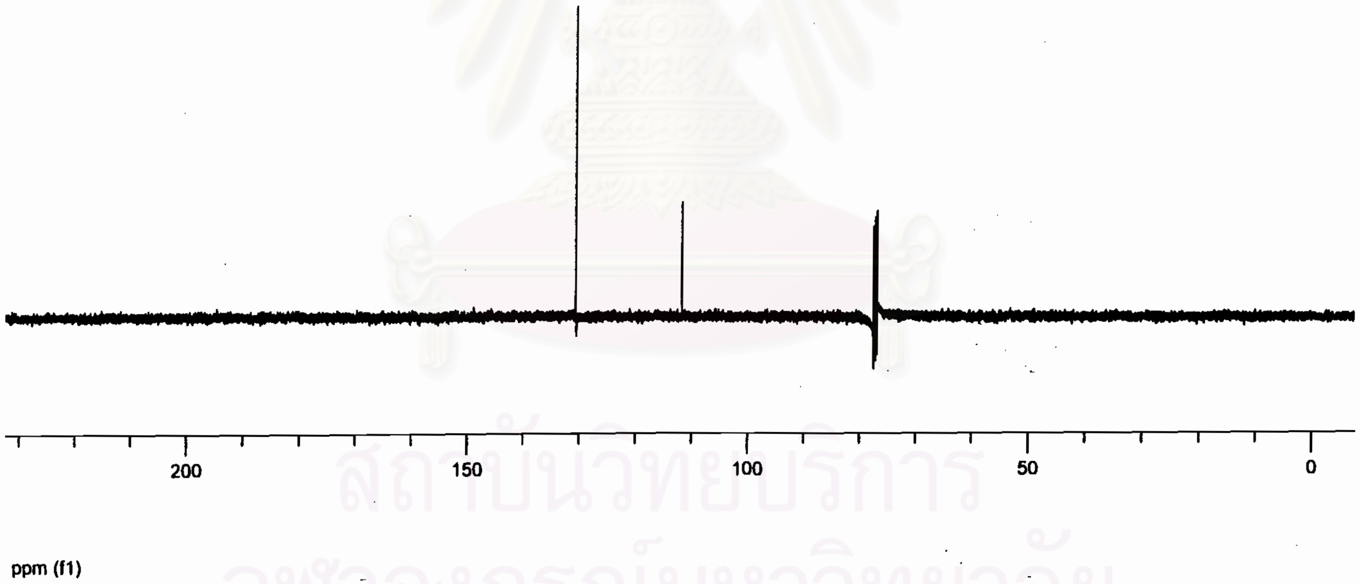
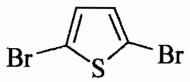


Figure A-2 ^{13}C-NMR (CDCl$_3$) spectrum of 2,5-dibromothiophene



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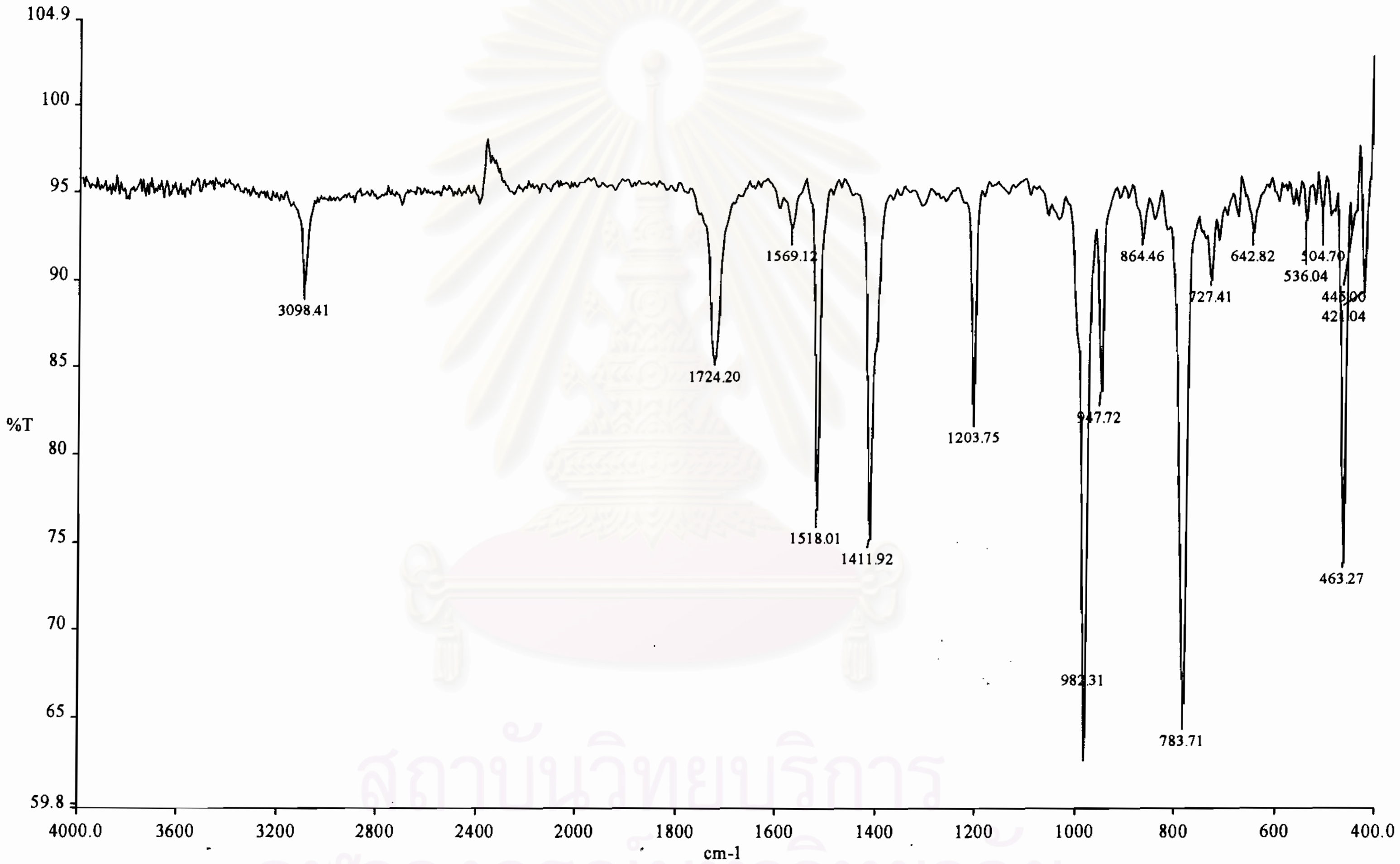
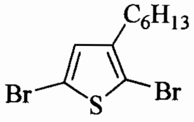


Figure A-3 FT-IR (film) spectrum of 2,5-dibromothiophene



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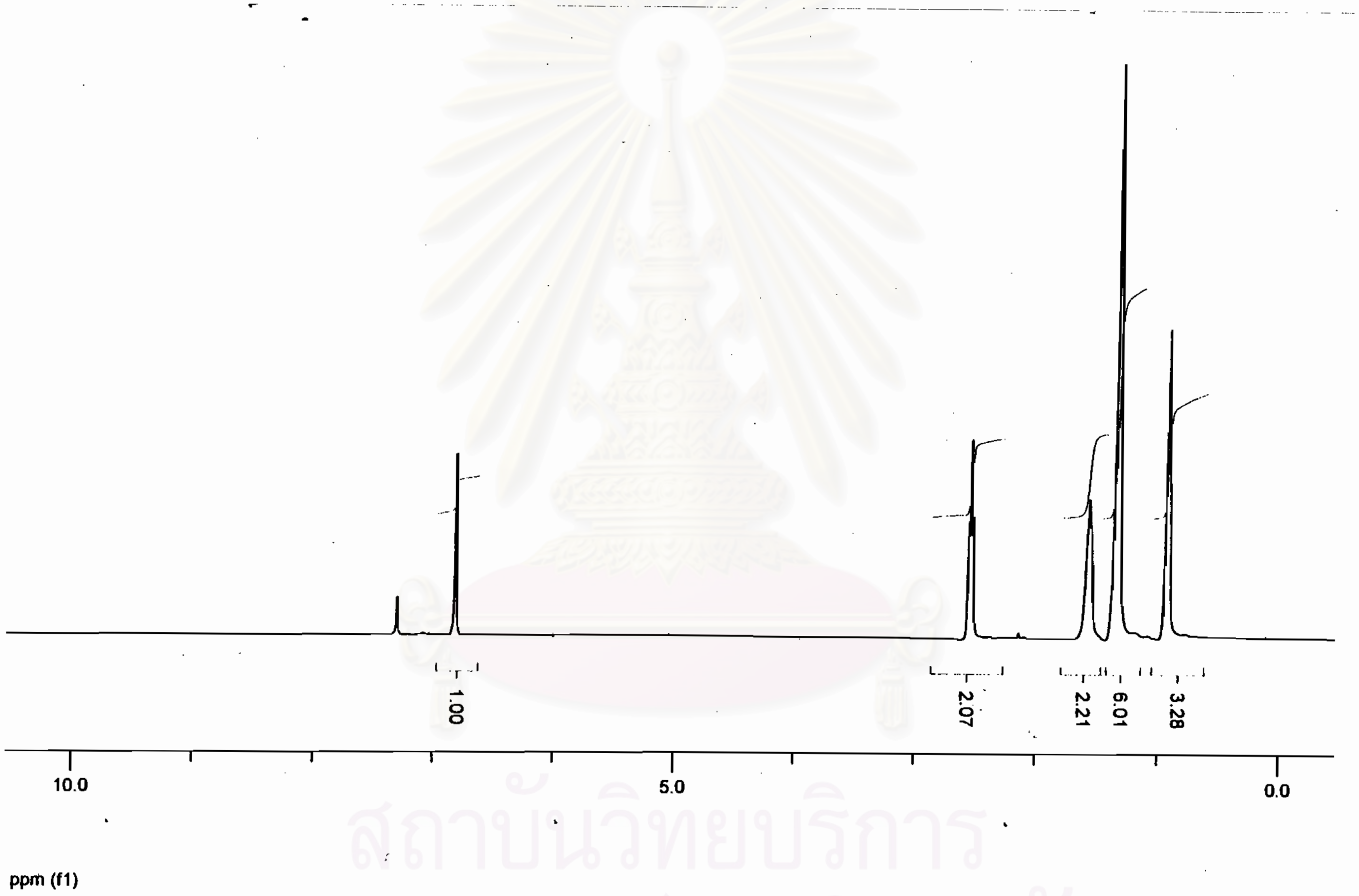
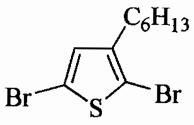


Figure A-4 ^{1}H-NMR ($CDCl_3$) spectrum of 2,5-dibromo-3-hexylthiophene



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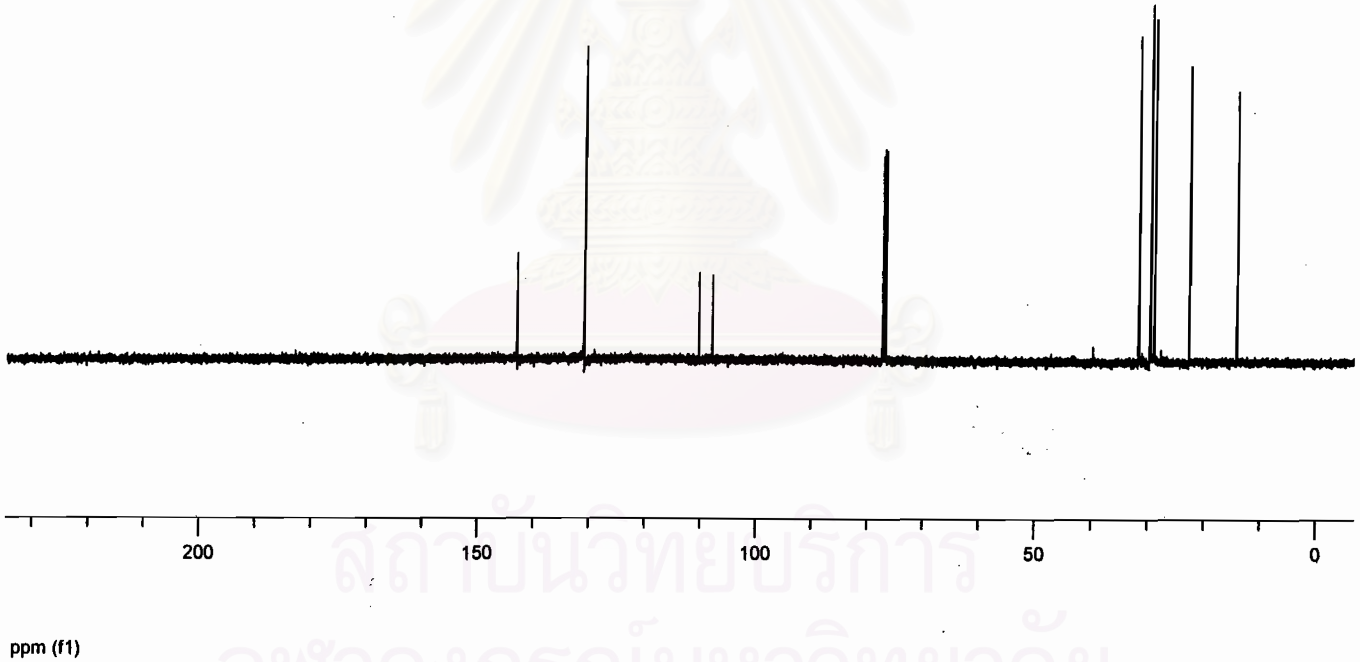
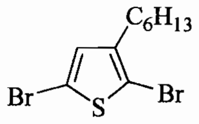


Figure A-5 ^{13}C-NMR ($CDCl_3$) spectrum of 2,5-dibromo-3-hexylthiophene



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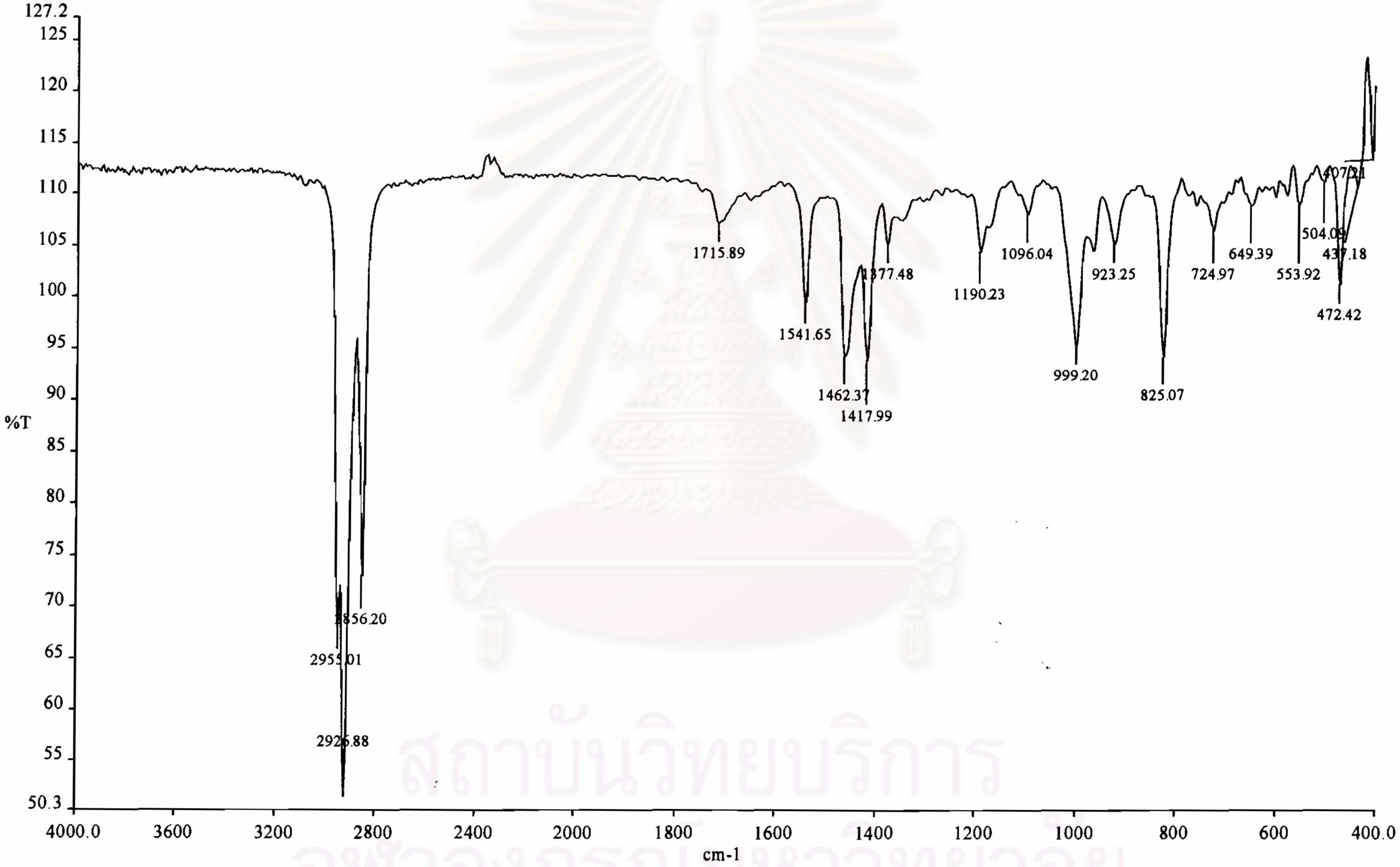
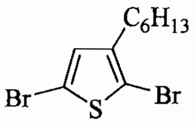


Figure A-6 FT-IR (film) spectrum of 2,5-dibromo-3-hexylthiophene



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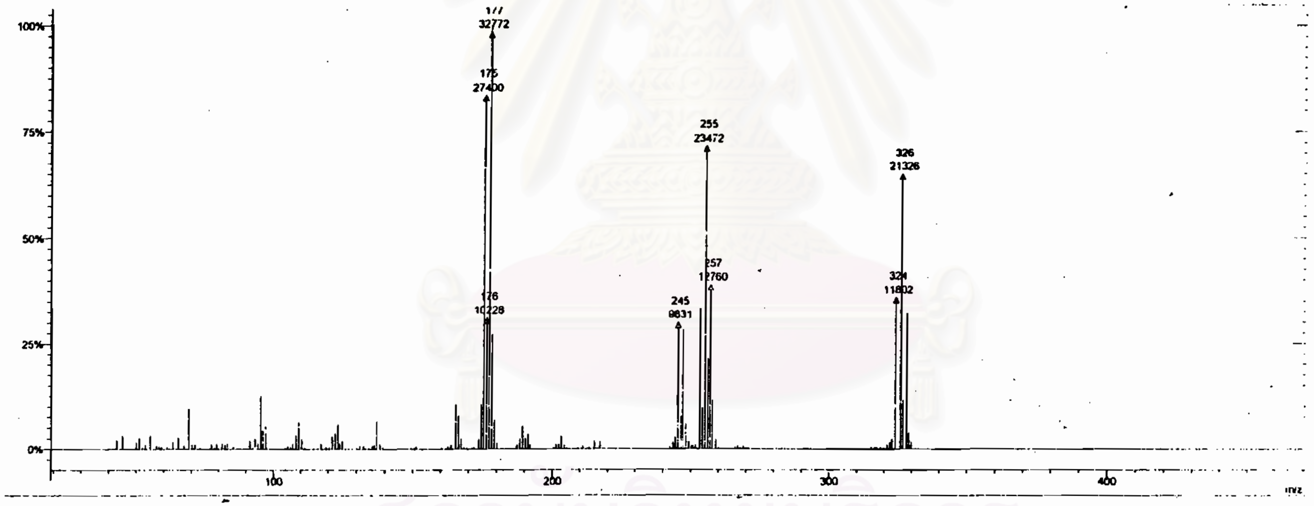
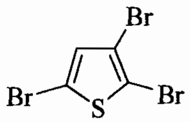


Figure A-7 MS spectrum of 2,5-dibromo-3-hexylthiophene



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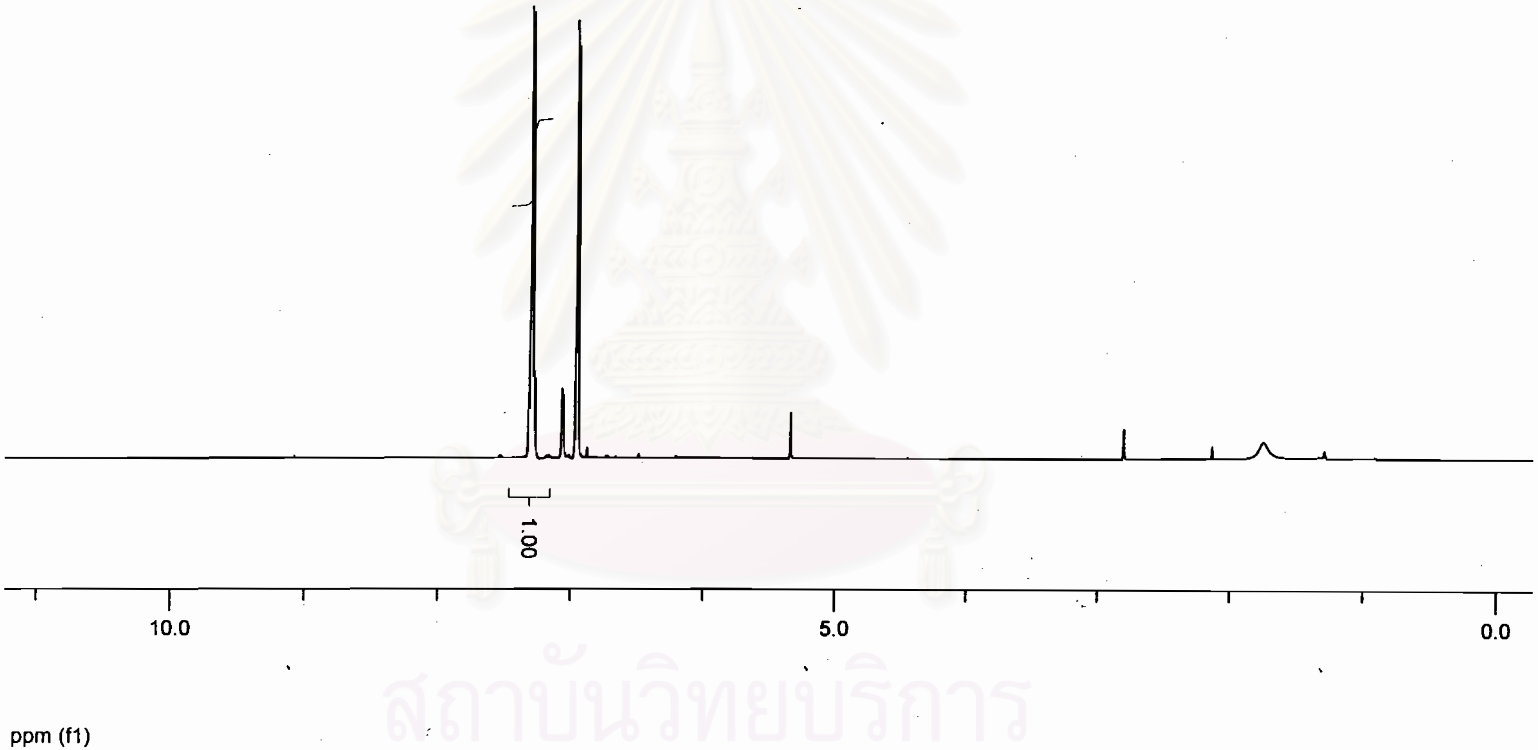
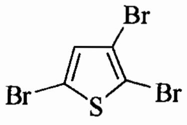


Figure A-8 ^{1}H-NMR ($CDCl_3$) spectrum of 2,3,5-tribromothiophene



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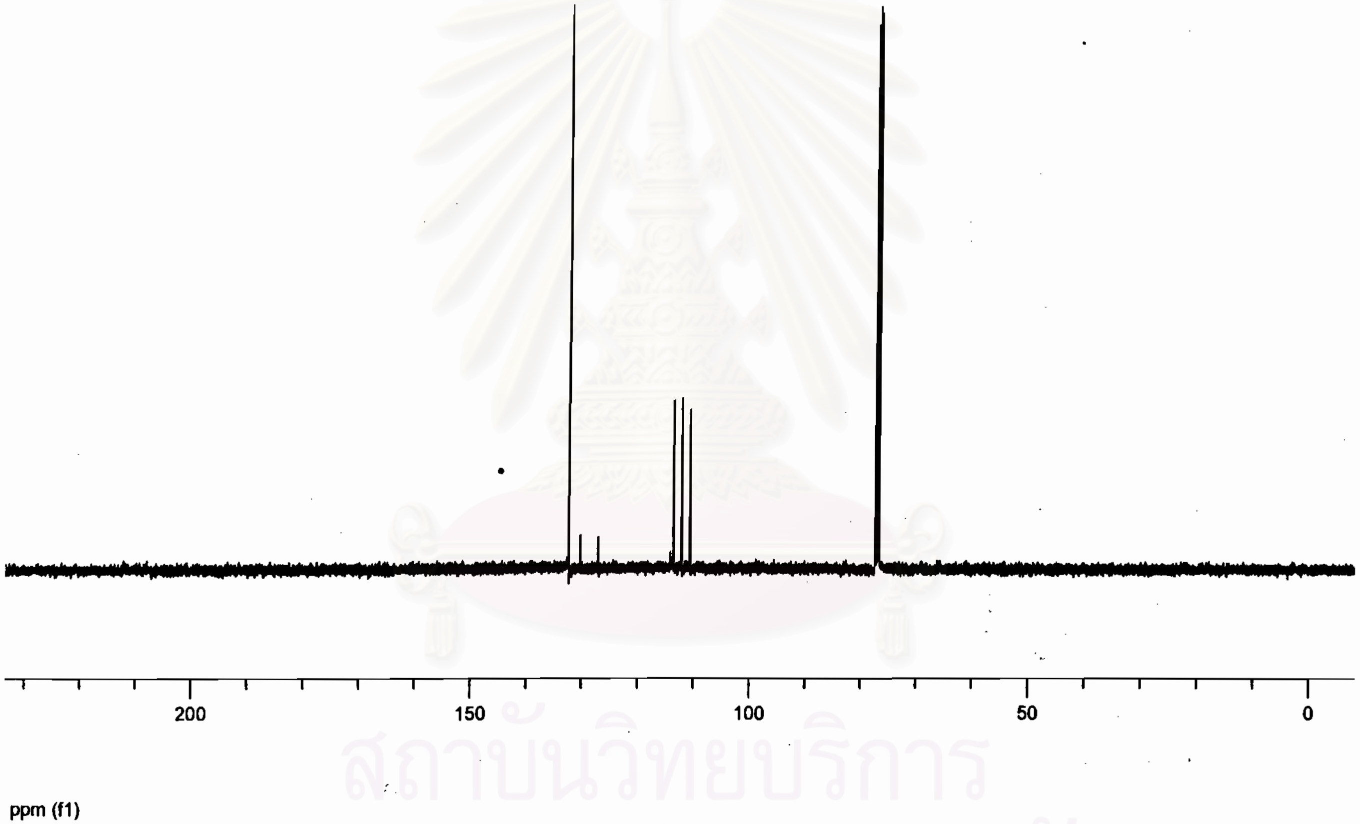
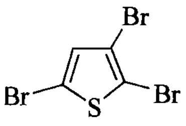


Figure A-9 ^{13}C-NMR ($CDCl_3$) spectrum of 2,3,5-tribromothiophene



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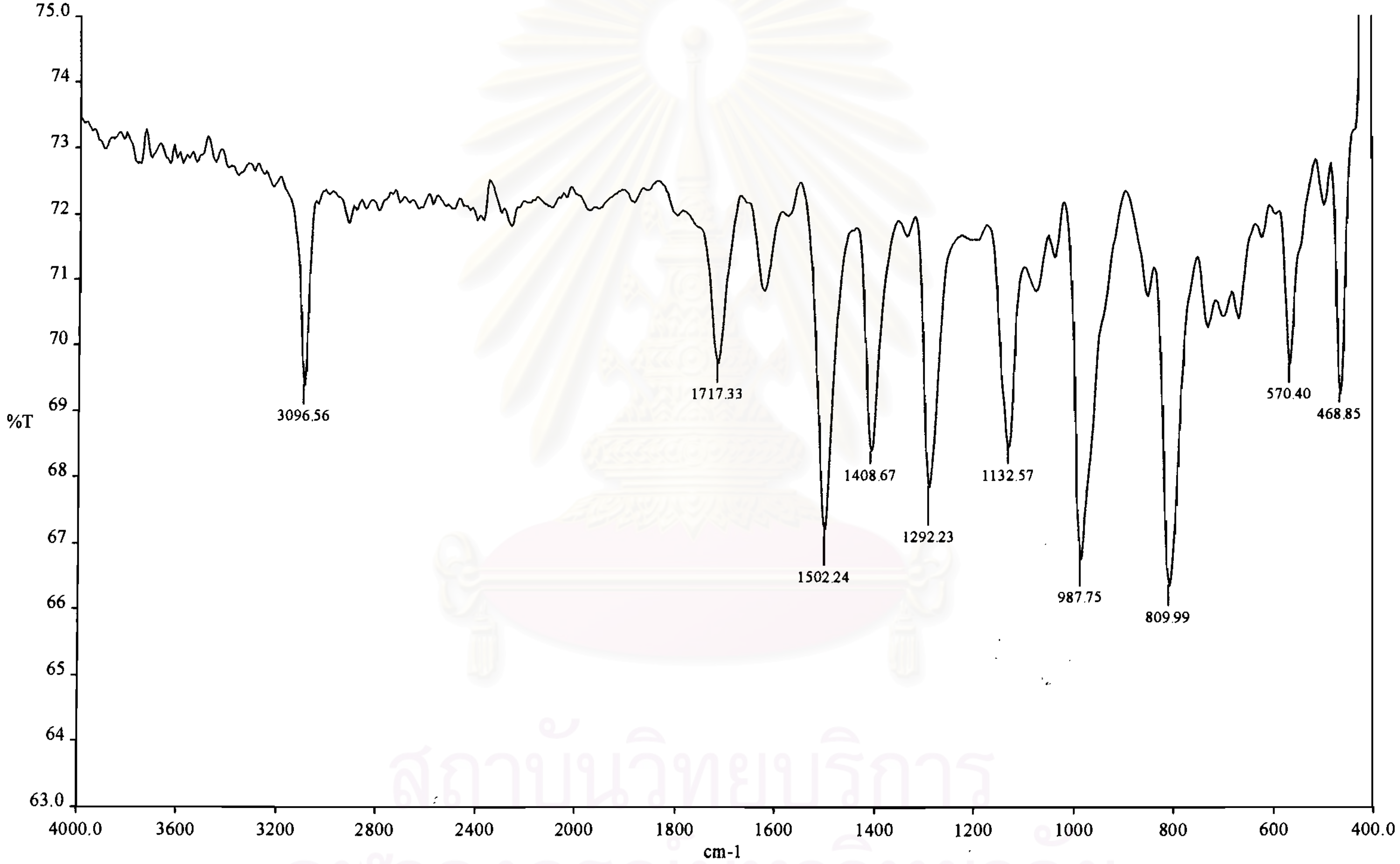
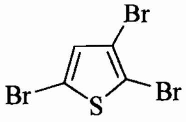


Figure A-10 FT-IR (film) spectrum of 2,3,5-tribromothiophene



10c

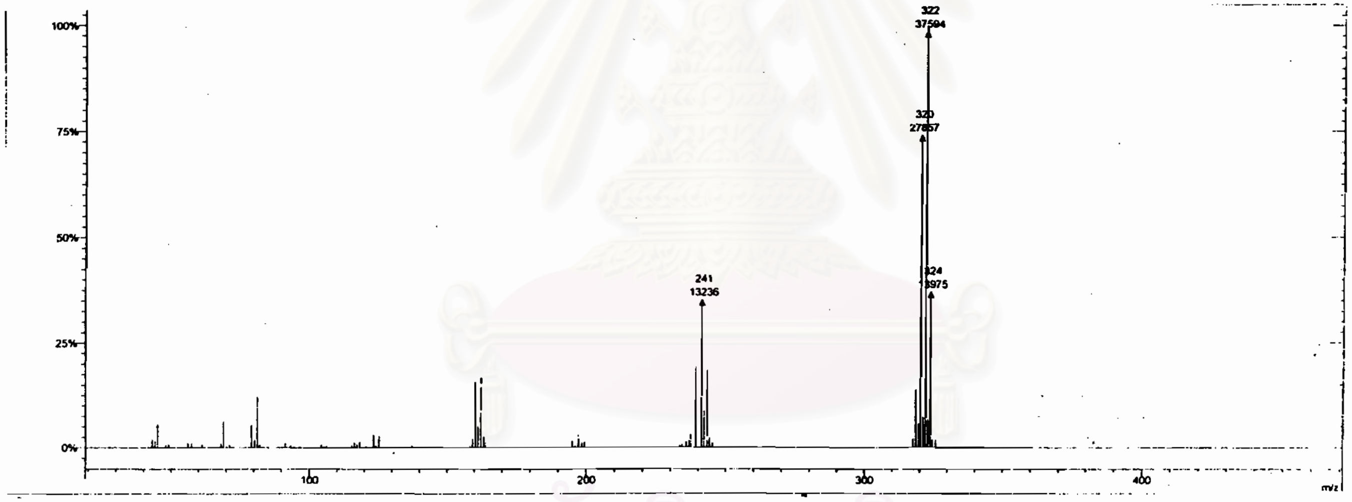
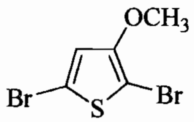


Figure A-11 MS spectrum of 2,3,5-tribromothiophene



10d

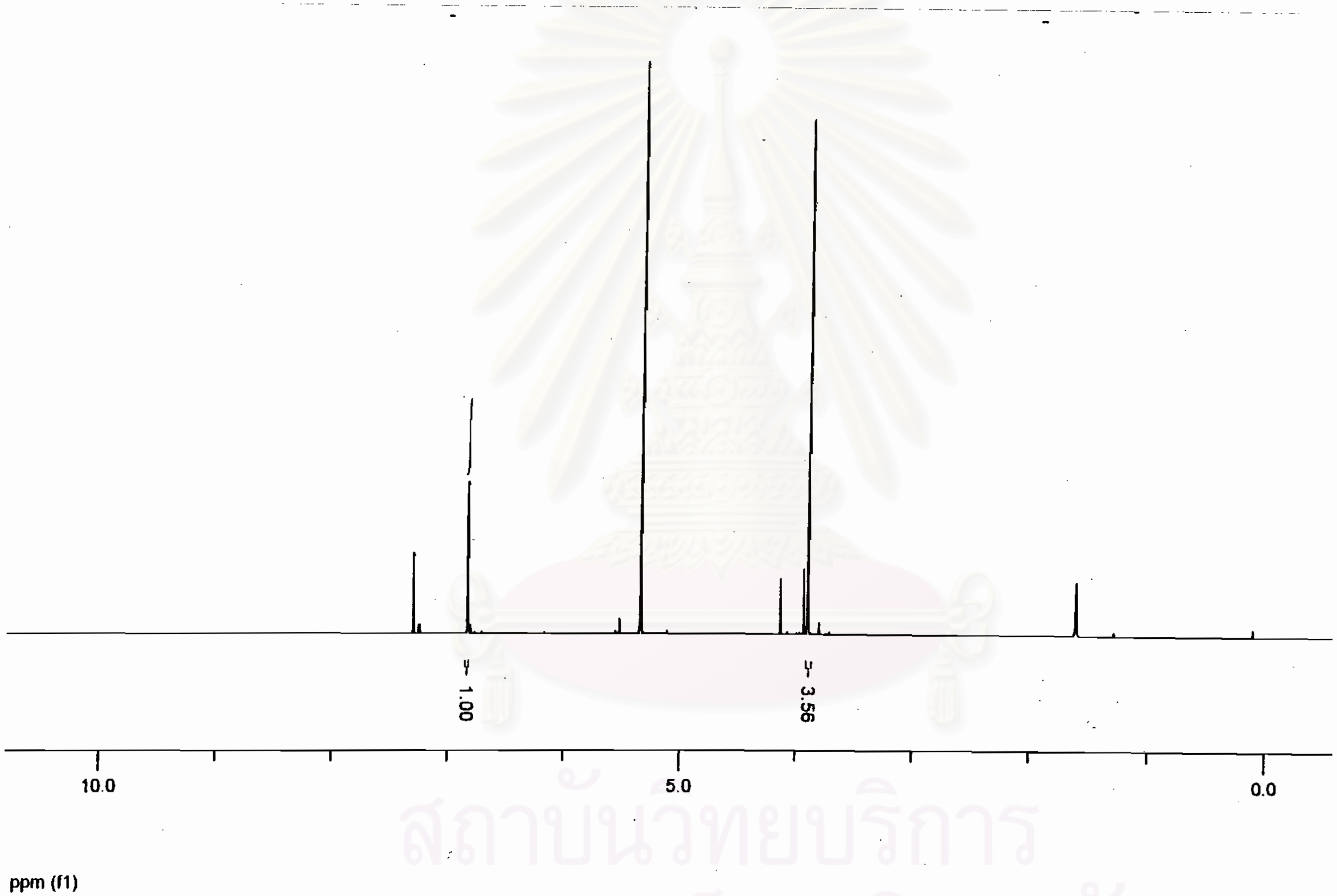
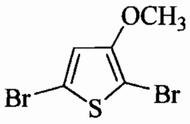


Figure A-12 ^{1}H-NMR ($CDCl_3$) spectrum of 2,5-dibromo-3-methoxythiophene



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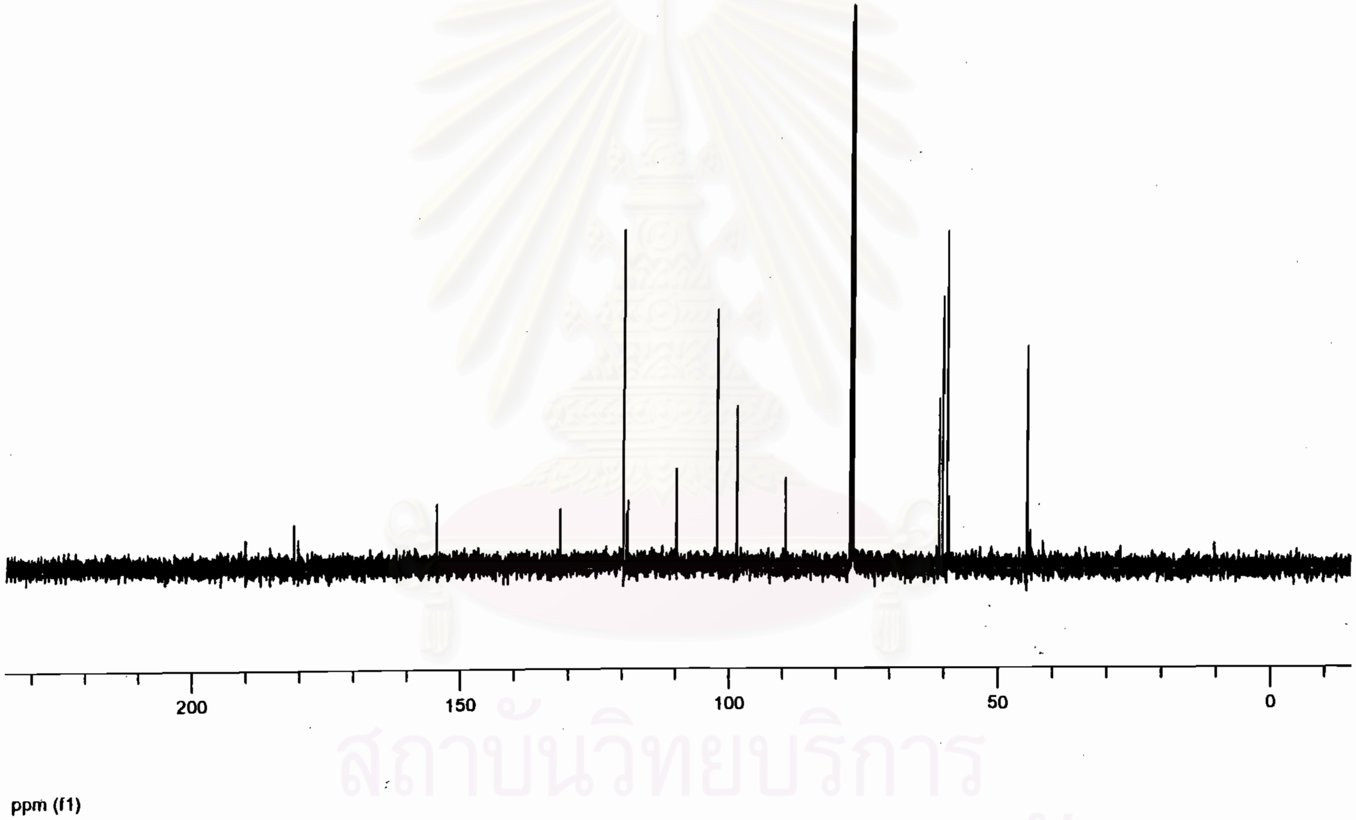
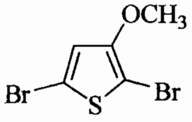


Figure A-13 ^{13}C-NMR (CDCl$_3$) spectrum of 2,5-dibromo-3-methoxythiophene



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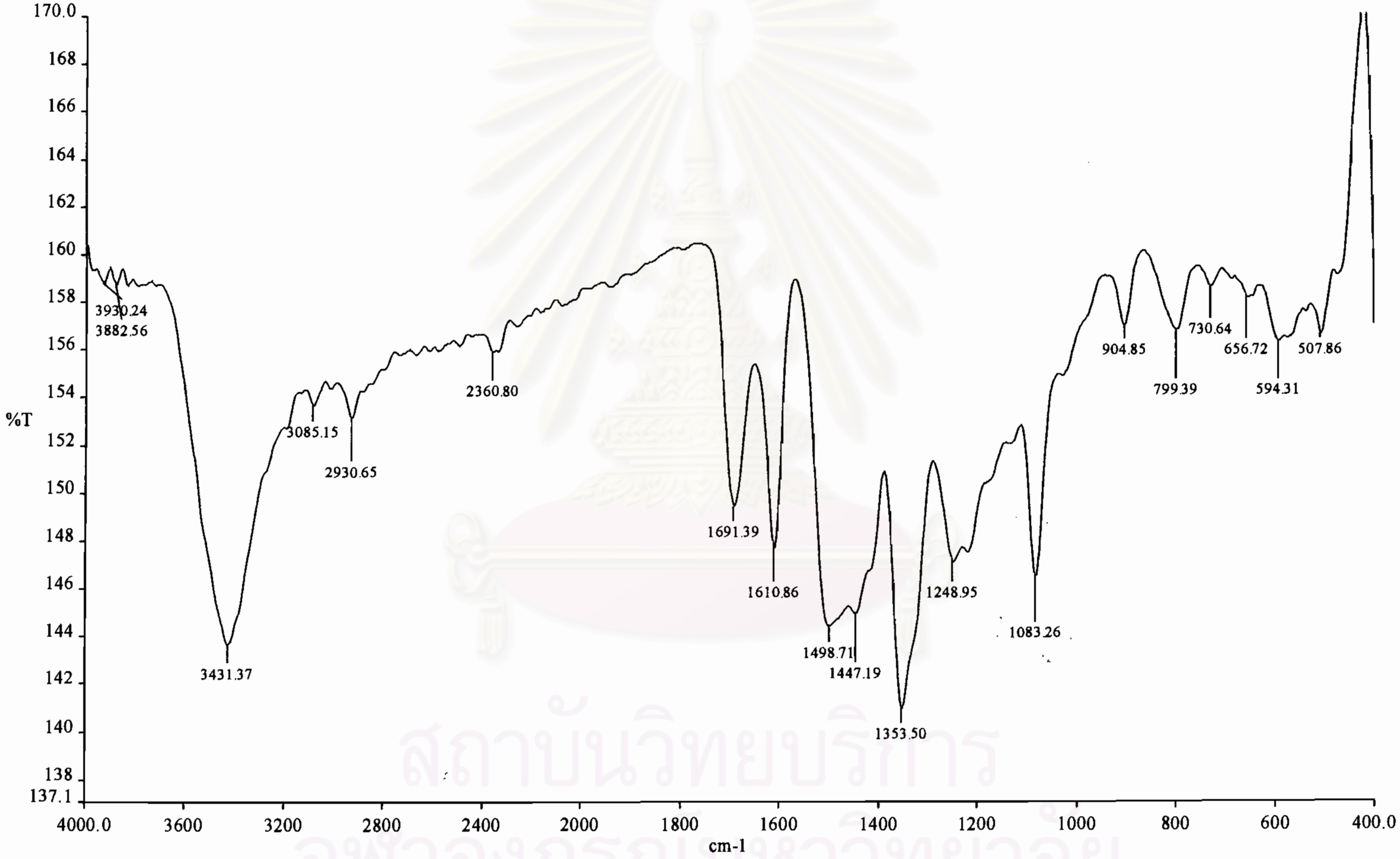
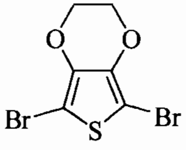


Figure A-14 FT-IR (film) spectrum of 2,5-dibromo-3-methoxythiophene



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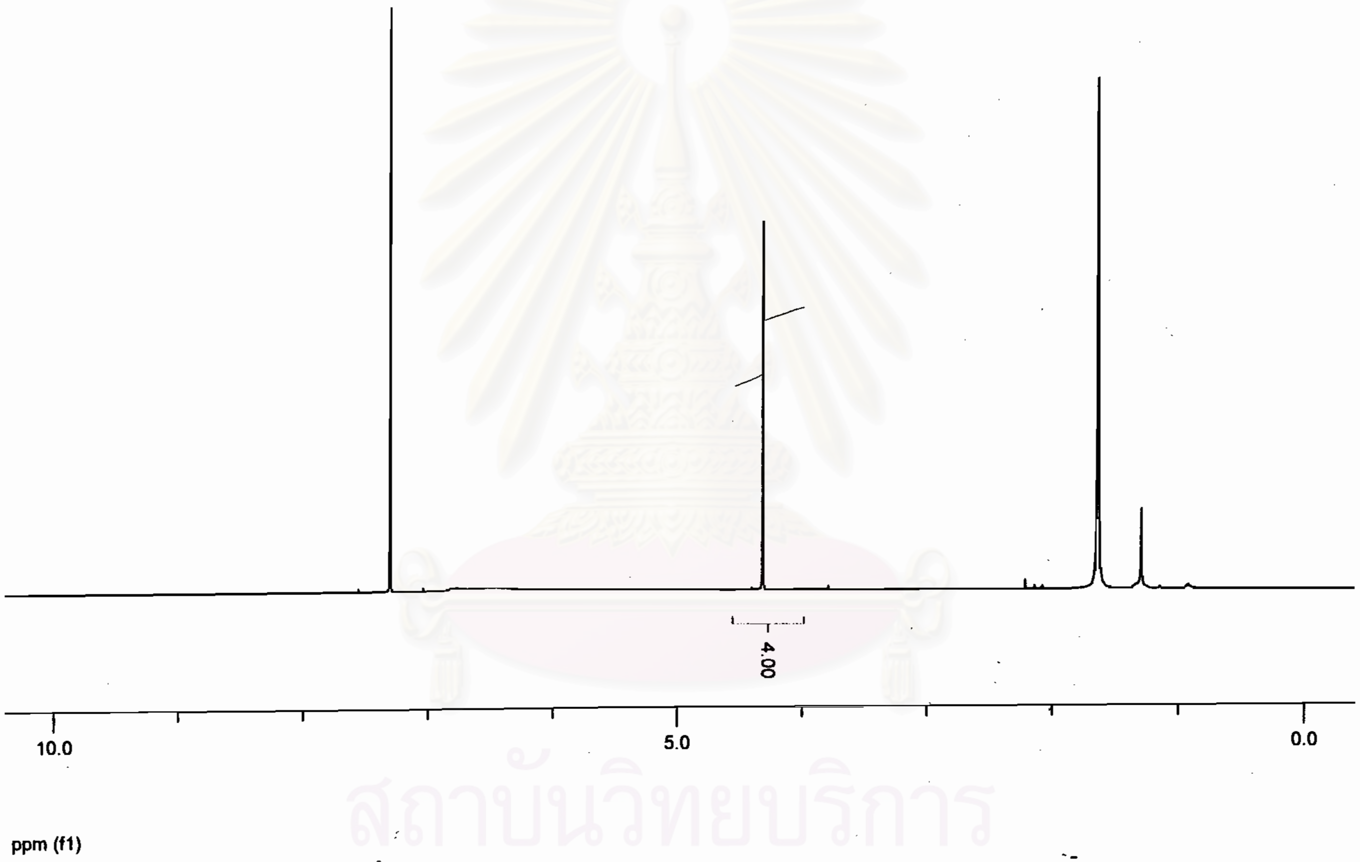
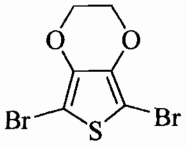


Figure A-15 ^{1}H-NMR ($CDCl_3$) spectrum of 2,3-dibromothieno[3,4-b]-1,4-dioxin



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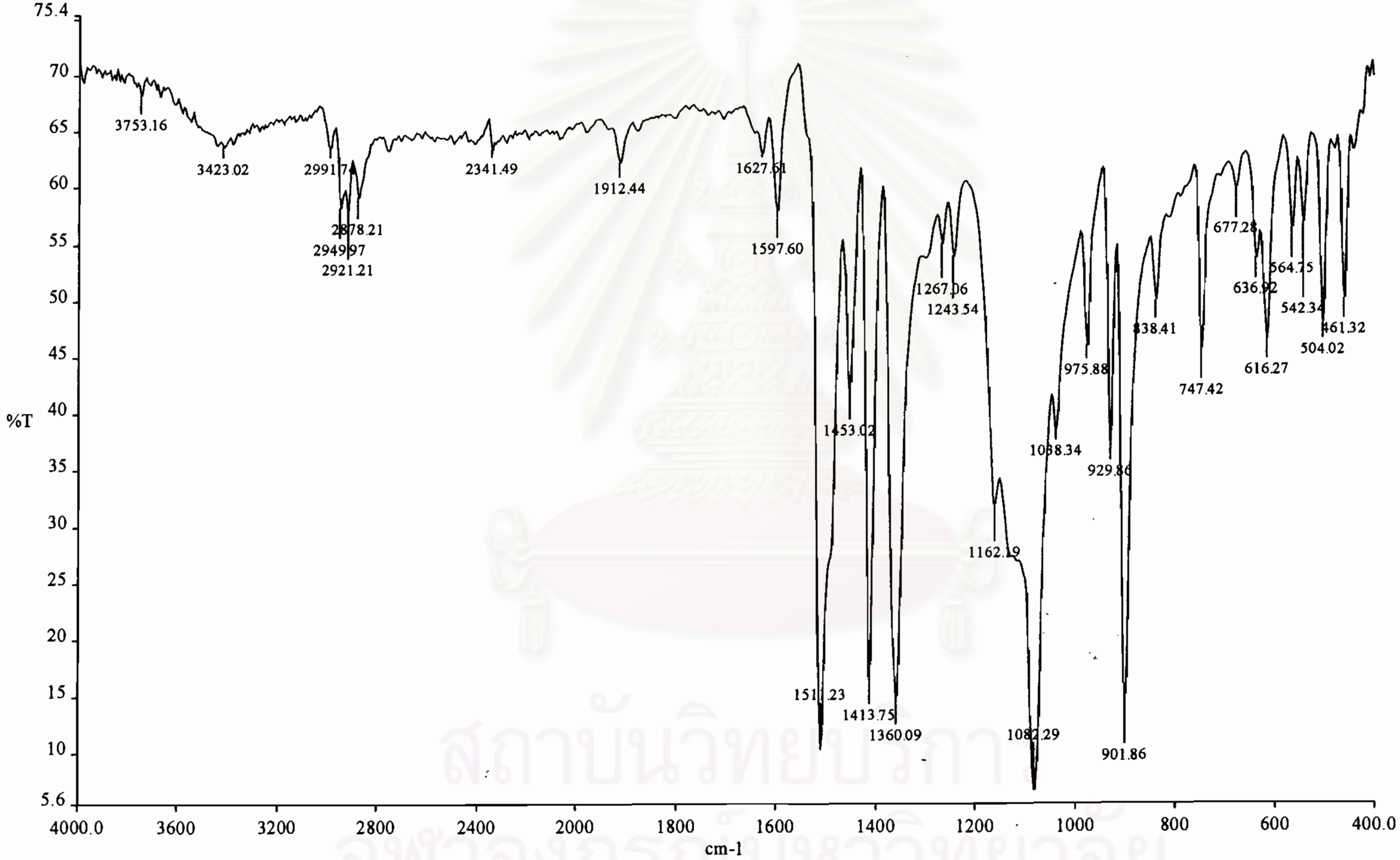

Figure A-16 FT-IR (KBr) spectrum of 2,3-dibromothieno[3,4-b]-1,4-dioxin

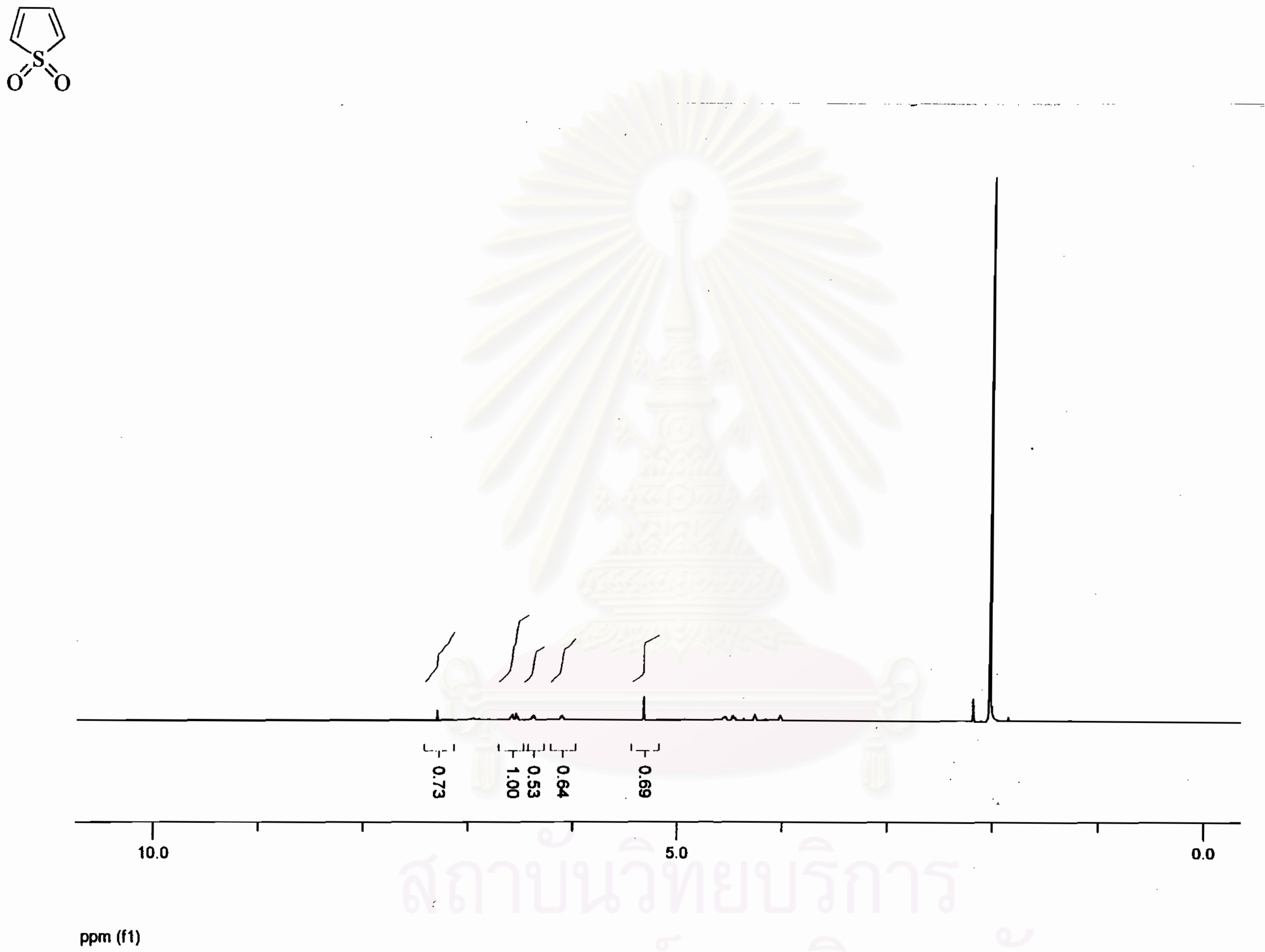

Figure A-17 ^{1}H-NMR ($CDCl_3$) spectrum of thiophene *S,S*-dioxide

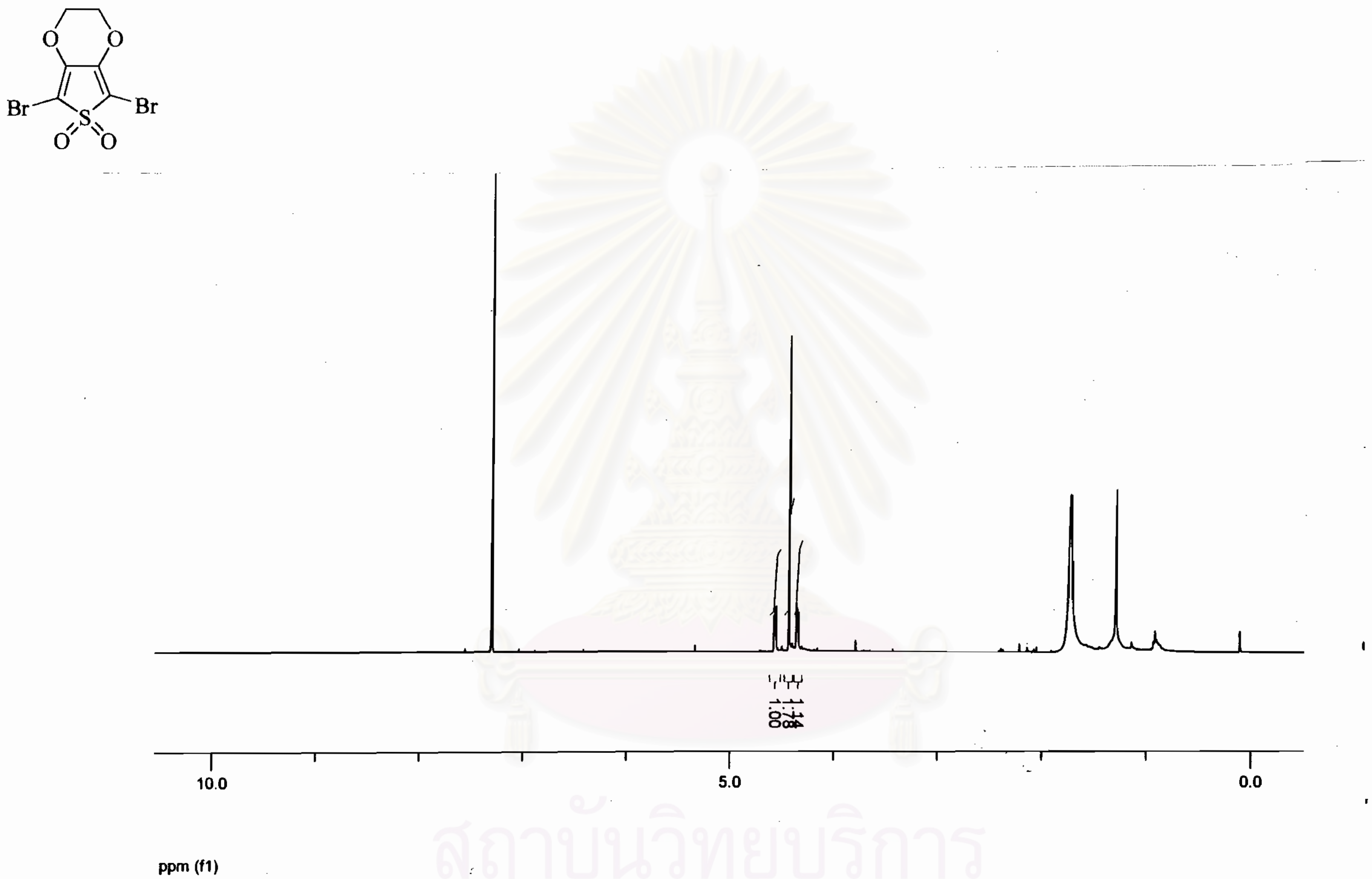

Figure A-18 ^{1}H-NMR ($CDCl_3$) spectrum of 2,3-dibromothieno[3,4-b]-1,4-dioxin *S,S*-dioxide

VITAE

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