

การสังเคราะห์พอลิ(3,4-ไดอัลคอกซีไทโอฟีน) ที่สามารถแปรรูปได้



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SYNTHESIS OF PROCESSIBLE POLY(3,4-DIALKOXY THIOPHENE)




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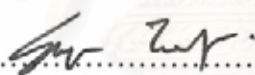
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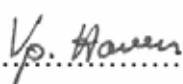
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งานวิจัยนี้เป็นการศึกษาการปรับเปลี่ยนหมู่แทนที่โดยปฏิกิริยาแลกเปลี่ยนหมู่อีเทอร์ จากเอทิลีนไดออกซีบริดจ์ บน 3,4-เอทิลีนไดออกซีไทโอเฟน 2,5-ไดโบรโม-3,4-เอทิลีนไดออกซีไทโอเฟน และ พอลิ(3,4-เอทิลีนไดออกซีไทโอเฟน) ไปเป็นอนุพันธ์ของไดอัลคอกซีอื่นๆ ตามด้วยปฏิกิริยาโบรมิเนชัน และพอลิเมอไรเซชันทั้งแบบเฟสของแข็งและแบบเชื่อมต่อกทางเคมี จากการศึกษาการปรับเปลี่ยนหมู่แทนที่พบว่าสามารถสังเคราะห์ 3,4-ไดเมทอกซีไทโอเฟน 3,4-ไดบิวทอกซีไทโอเฟน 2,5-ไดโบรโม-3,4-ไดเมทอกซีไทโอเฟน และ 2,5-ไดโบรโม-3,4-ไดบิวทอกซีไทโอเฟน ได้เท่ากับ 8.5, 42.5, 18.7 และ 10.2% ตามลำดับ โดยพบว่ากรดพาราโทลูอินซัลโฟนิกเป็นตัวเร่งปฏิกิริยาที่เหมาะสมที่สุดในปฏิกิริยาแลกเปลี่ยนหมู่อีเทอร์ ปฏิกิริยาโบรมิเนชันด้วยเอ็นบีเอส จะให้ผลิตภัณฑ์ 2,5-ไดโบรโม-3,4-เอทิลีนไดออกซีไทโอเฟน 2,5-ไดโบรโม-3,4-ไดเมทอกซีไทโอเฟน 2,5-ไดโบรโม-3,4-ไดบิวทอกซีไทโอเฟน 2,5-ไดโบรโม-3-เมทอกซีไทโอเฟน และ 2,5-ไดโบรโมไทโอเฟน-3-คาร์บอกซิลิก เอซิด เท่ากับ 65.7, 76.1, 32.6, 26.3 และ 30.1% ตามลำดับ ปฏิกิริยาพอลิเมอไรเซชันแบบเชื่อมต่อกทางเคมีจะให้ผลิตภัณฑ์ พอลิ(3,4-เอทิลีนไดออกซีไทโอเฟน) พอลิ(3,4-ไดเมทอกซีไทโอเฟน) พอลิ(3,4-ไดบิวทอกซีไทโอเฟน) และพอลิ(3-เมทอกซีไทโอเฟน) เท่ากับ 92.3, 61.8, 62.2 และ 77.0% ตามลำดับ ขณะที่ปฏิกิริยาพอลิเมอไรเซชันแบบเฟสของแข็งจะเกิดขึ้นเฉพาะกับ 2,5-ไดโบรโม-3,4-เอทิลีนไดออกซีไทโอเฟนเท่านั้น พอลิ(3,4-เอทิลีนไดออกซีไทโอเฟน) ที่สังเคราะห์ผ่านกระบวนการพอลิเมอไรเซชันแบบเฟสของแข็งและผ่านการโคปด้วยไอโอดีนจะมีค่าการนำไฟฟ้าสูงที่สุด

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.....ลายมือชื่อนิสิต..... ทิงชัย ศิริกุล
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KEYWORD: 3,4-DIALKOXYTHIOPHENE / ETHER EXCHANGE / THIOPHENE / SOLID STATE POLYMERIZATION

THONGCHAI SIRAKUL: SYSTHESIS OF PROCESSIBLE POLY(3,4-DIALKOXY THIOPHENE). THESIS ADVISOR: ASST. PROF. YONGSAK SRITANA-ANANT, Ph.D., THESIS COADVISOR: ASST. PROF. WORAWAN BHANTHUMNAVIN, Ph.D., 85 pp.

This research studied the substituents modification by ether exchange from ethylene dioxy bridges on EDOT, DBrEDOT and PEDOT to other dialkoxy derivatives followed by the bromination and polymerization either through solid state polymerization (SSP) or oxidative coupling processes. The products from the modifications: 3,4-dimethoxythiophene (DMT), 3,4-dibutoxythiophene (DBT), 2,5-dibromo-3,4-dimethoxythiophene (DBrDMT) and 2,5-dibromo-3,4-dibutoxy thiophene (DBrDBT) were obtained in 8.5, 42.5, 18.7 and 10.2% yield respectively. The best acid catalyst in the ether exchange was *p*-toluenesulfonic acid (PTSA). The brominations with NBS gave 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT), 2,5-dibromo-3,4-dimethoxythiophene (DBrDMT), 2,5-dibromo-3,4-dibutoxythiophene (DBrDBT), 2,5-dibromo-3-methoxythiophene (DBrMT) and 2,5-dibromothiophene-3-carboxylic acid in 65.7, 76.1, 32.6, 26.3 and 30.1% yield respectively. Oxidative coupling polymerizations yielded PEDOT, PDMT, PDBT and PMT in 92.3, 61.8, 62.2 and 77.0% yield, respectively. Solid state polymerization was achieved only with 2,5-dibromo-3,4-ethylenedioxythiophene giving PEDOT. The highest conductivity of iodine doped polymer belongs to PEDOT synthesized through SSP process.

Field of study Petrochemistry and Polymer Science Student's signature Thongchai Sirakul
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สถาบันวิทยบริการ
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CONTENTS

	Page
ABSTRACT IN THAI	iv
ABSTRACT IN ENGLISH	v
ACKNOWLEDGEMENTS	vi
LIST OF TABLES	xi
LIST OF SCHEMES	xi
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xv
CHAPTER I : INTRODUCTION	1
1.1 Applications of organic conducting polymers	2
1.2 Conjugated polymers: organic semiconductors.....	3
1.3 Structural basis of functionalization.....	6
1.4 Polythiophene.....	7
1.5 Synthesis of polythiophene.....	8
1.5.1 Electrochemical polymerization	9
1.5.2 Oxidative coupling polymerization with iron (III) chloride	9
1.5.3 Grignard coupling and other chemical polymerizations....	11
1.6 Poly(3,4-dialkoxythiophene)	12
1.7 Synthesis of 3,4-dialkoxythiophene monomers.....	13
1.7.1 From disodium 2,3-di(ethoxycarbonyl)- 3,4-thiophenediolate	13
1.7.2 From 3,4-dibromothiophene.....	13
1.8 Solid state synthesis of a conducting polythiophene (PEDOT)	14
1.9 Effective conjugation length (ECL).....	17
1.10 Effect of doping.....	18
1.10.1 Chemical doping by charge transfer	19
1.10.2 Electrochemical doping	19
1.11 Statement of the problem.....	22

	Page
1.12 Objectives	22
1.13 Scope of the investigation	23
 CHAPTER II : EXPERIMENTAL SECTION.....	 24
2.1 Chemicals	24
2.2 Instruments and apparatus	25
2.3 Ether exchange of 3,4-ethylenedioxythiophene (EDOT)	26
2.3.1 3,4-dibutoxythiophene (DBT; R = n-Bu) using n-butanol .	26
2.3.1.1 p-toluenesulfonic acid (PTSA) as the catalyst ...	26
2.3.1.2 Methanesulfonic acid (MSA) as the catalyst	27
2.3.1.3 Concentrated sulfuric acid (H ₂ SO ₄) as the catalyst	27
2.3.1.4 Concentrated hydrochloric acid (HCl) as the catalyst	27
2.3.2 3,4-dibutoxythiophene (DBT; R = n-Bu) using n-butyl chloride	27
2.3.3 Effect 3,4-dimethoxythiophene (DMT; R = CH ₃) using methanol	28
2.3.3.1 p-toluenesulfonic acid (PTSA) as the catalyst...	28
2.3.3.2 p-toluenesulfonic acid (PTSA) as the catalyst with an addition of 2,2-dimethoxypropane ...	28
2.4 Ether exchange of 3,4-dimethoxythiophene (DMT)	29
2.4.1 3,4-dibutoxythiophene (DBT) using n-butanol	29
2.5 Bromination of thiophene derivatives	29
2.5.1 2,5-dibromo-3,4-diethylenedioxythiophene	30
2.5.2 2,5-dibromo-3,4-dimethoxythiophene	30
2.5.3 2,5-dibromo-3,4-dibutoxythiophene	31
2.5.4 2,5-dibromo-3-methoxythiophene	31
2.5.5 2,5-dibromothiophene-3-carboxylic acid	32
2.6 Ether exchange of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT)	32

	Page
2.6.1 2,5-dibromo-3,4-dimethoxythiophene	32
2.6.2 2,5-dibromo-3,4-dibutoxythiophene	33
2.6.3 2,5-dibromo-3,4-bis(2-bromoethoxy)thiophene	33
2.6.3.1 With methanol as solvent	33
2.6.3.2 Without solvent	34
2.6.4 3,4-bis(benzyloxy)-2,5-dibromothiophene	34
2.6.4.1 With toluene	35
2.6.4.2 Without toluene	35
2.7 Polymerization by oxidative coupling	36
2.7.1 Poly(3,4-ethylenedioxythiophene)	36
2.7.2 Poly(3,4-dimethoxythiophene)	36
2.7.3 Poly(3,4-dibutoxythiophene)	37
2.7.4 Poly(3-methoxythiophene)	37
2.8 Ether exchange of Poly(3,4-ethylenedioxythiophene)	38
2.9 Solid state polymerization (SSP)	38
2.9.1 Poly(3,4-ethylenedioxythiophene)	39
2.9.2 Poly(3,4-dimethoxythiophene)	39
2.10 Conductivity measurement using Four-point probe conductometer	39
 CHAPTER III : RESULTS AND DISCUSSION	 40
3.1 Synthesis of 3,4-dialkoxythiophene derivatives	40
3.2 Synthesis of poly(3,4-dialkoxythiophene) derivatives	46
3.3 Bromination of thiophene derivatives	47
3.4 Polymerization by oxidative coupling	50
3.5 Polymerization by solid state polymerization (SSP)	52
3.6 Conductivity measurement	52
 CHAPTER IV : CONCLUSIONS	 55
 REFERENCES.....	 56

	Page
APPENDICES.....	61
APPENDIX A.....	62
APPENDIX B.....	81
VITA.....	85



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

Tables	Page
1.1 Conductivity Data of PEDOT polymers	16
2.1 Ether exchange of PEDOT using various acid catalyst	38
3.1 Synthesis of 3,4-dialkoxythiophene derivatives	41
3.2 Ether exchange of poly(3,4-ethylenedioxythiophene).....	47
3.3 Synthesis of 2,5-dibromothiophene derivatives	48
3.4 Polymerization of thiophene derivatives by oxidative coupling	50
3.5 Conductivity of the polythiophene derivatives in neutral and I ₂ doped state	53
B-1 Examples of the calculations of conductivity	83

LIST OF SCHEMES

Schemes	Page
3.1 Mechanism of thiophene derivatives upon ether exchange by <i>p</i> -toluene sulfonic acid (PTSA) and alcohol	45
3.2 Mechanism of thiophene derivatives upon ether exchange by anhydrous aluminium chloride (AlCl ₃) and alkyl chloride.....	46
3.3 Bromination mechanism through electrophilic aromatic substitution	49
3.4 Bromination mechanism through radical-based single electron transfer followed by aromatic substitution	49

LIST OF FIGURES

Figures	Page
1.1 Molecular structures of some conjugated polymers.....	1
1.2 Calculated (frontier) energy levels of oligothiophenes with n = 1–4 and of polythiophene (E_g = band gap energy).....	3
1.3 Simple band picture explaining the difference between an insulator, a semiconductor, and a metal.....	4
1.4 The conductivity of conducting polymers decreases with falling temperature in contrast to that of metals.....	5
1.5 Regioisomers of the poly(3-alkylthiophene)s.....	8
1.6 The electrochemical method for the synthesis of P3ATs (R = H, Me, Ph).	9
1.7 The oxidative coupling reaction of 3-alkylthiophene by $FeCl_3$	10
1.8 The McCullough method for the regiospecific synthesis of P3AT	11
1.9 Synthesis route of 3,4-dialkoxythiophene from disodium 2,3-di(ethoxy carbonyl)-3,4-thiophenediolate.....	13
1.10 Synthesis route of 3,4-dialkoxythiophene from 3,4-dibromothiophene ...	14
1.11 Synthesis of dihalo-EDOT monomers	15
1.12 Solid state polymerization of EDOT	16
1.13 A defect in polyacetylene and steric induced structural twisting in poly(3-alkylthiophene).....	17
1.14 Twisting of polythiophene	17
1.15 Schematic representation of polythiophene in the undoped, singly, and doubly oxidized (left), and singly and doubly reduced (right) states	20
1.16 Polaron and bipolaron of polythiophene	20
1.17 UV-vis-nir spectroelectrochemical curves recorded for regioregular poly(3-octylthiophene) in 0.1 M Bu_4NBF_4 solution in acetonitrile.....	21
3.1 Synthesis Route of 3,4-dialkoxythiophene derivatives	40
3.2 The expected product from the reactions in Table 3.1.....	42
A-1 The 1H -NMR (400 MHz, $CDCl_3$) of 3,4-dibutoxythiophene	63
A-2 The ^{13}C -NMR (400 MHz, $CDCl_3$) of 3,4-dibutoxythiophene.....	63

	Page
A-3 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 3,4-dimethoxythiophene.....	64
A-4 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 3,4-dimethoxythiophene	64
A-5 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,2-dimethyl-1,3-dioxolane	65
A-6 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-ethylenedioxy thiophene	66
A-7 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-ethylenedioxy thiophene	66
A-8 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-dimethoxy thiophene	67
A-9 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4- dimethoxy thiophene	67
A-10 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-dibutoxy thiophene	68
A-11 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4- dibutoxy thiophene	68
A-12 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3-methoxy thiophene	69
A-13 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3-methoxy thiophene	69
A-14 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromothiophene-3- carboxylic acid	70
A-15 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) 2-bromo-3,4-dibutoxythiophene	71
A-16 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2-bromo-3,4-dibutoxythiophene.	71
A-17 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2-bromo-3-methoxy-4-ethylene dioxythiophene	72
A-18 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2-bromo-3-methoxy-4-ethylene dioxythiophene	72
A-19 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of the crown product (6)	73
A-20 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of the crown product (6)	73
A-21 MS spectrum of the crown product (6)	74
A-22 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 1-benzyl-4-methylbenzene	75
A-23 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 1-benzyl-2-methylbenzene	75

	Page
A-24 The ^1H -NMR (400 MHz, CDCl_3) of dibenzylether	76
A-25 The ^{13}C -NMR (400 MHz, CDCl_3) of dibenzylether	76
A-26 The ^1H -NMR (400 MHz, CDCl_3) of Poly(3,4-dimethoxythiophene)	77
A-27 The ^1H -NMR (400 MHz, CDCl_3) of Poly(3,4-dibutoxythiophene)	77
A-28 The ^1H -NMR (400 MHz, CDCl_3) of Poly(3-methoxythiophene)	78
A-29 UV-visible spectra of poly(3,4-ethylenedioxythiophene); PEDOT	79
A-30 UV-visible spectra of poly(3,4-dimethoxythiophene); PDMT	79
A-31 UV-visible spectra of poly(3,4-dibutoxythiophene); PDBT	80
A-32 UV-visible spectra of poly(3-methoxythiophene); PMT	80
B-1 Conductivity measurement by Four-point Probe method	82



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF ABBREVIATIONS

CH ₃ COOH	: acetic acid
AlCl ₃	: anhydrous aluminium chloride
NBS	: <i>N</i> -bromosuccinimide
Bu	: butyl
cm	: centimeter
°C	: degree celsius
CDCl ₃	: deuterated chloroform
CH ₂ Cl ₂	: dichloromethane
DMP	: 2,2-dimethoxypropane
DMT	: 3,4-dimethoxythiophene
DBrDBT	: 2,5-dibromo-3,4-dibutoxythiophene
DBrDMT	: 2,5-dibromo-3,4-dimethoxythiophene
DBrEDOT	: 2,5-dibromo-3,4-ethylenedioxythiophene
DBT	: 3,4-dibutoxythiophene
EDOT	: 3,4-ethylenedioxythiophene
eV	: electron volt
FeCl ₃	: anhydrous ferric chloride
g	: gram
GPC	: gel permeation chromatography
h	: hour
HH	: head to head
HOMO	: highest occupied molecular orbital
HT	: head to tail
IR	: infrared spectrophotometer
LED	: light emitting diode
LUMO	: lowest unoccupied molecular orbital
<i>M</i> _n	: number average molecular weight
MS	: mass spectrum
MeOH	: methanol
Me	: methyl
μL	: microliter

μmol	: micromole
mg	: milligram
min	: minute
mL	: milliliter
mmol	: millimole
MSA	: methanesulfonic acid
nir	: near infrared
nm	: nanometer
NMR	: nuclear magnetic resonance spectroscopy
Ph	: phenyl
P3AT	: poly(3-alkylthiophene)
PDBT	: poly(3,4-dibutoxythiophene)
PDMT	: poly(3,4-dimethoxythiophene)
PEDOT	: poly(3,4-ethylenedioxythiophene)
PMT	: poly(3-methoxythiophene)
ppm	: part per million
PT	: polythiophene
S	: Siemens
SSP	: solid state polymerization
TT	: tail to tail
t_r	: retention time
PTSA	: <i>p</i> -toluenesulfonic acid
UV	: ultra-violet
vis	: visible
wt	: weight
m	: multiplet (NMR)
p	: pentet (NMR)
q	: quartet (NMR)
s	: singlet (NMR)
t	: triplet (NMR)

CHAPTER I

INTRODUCTION

The last few decades of the field of material science have been marked by the growing importance taken by two classes of materials, organic polymers and inorganic semiconductors. Thus, the lightness of weight, processibility, and resistance against corrosion of organic polymers has led in many applications to the replacement of metal or to the creation of original materials. In such a context, it is not very surprising the properties of organic polymers and of semiconductors rapidly become a subject of considerable interest for both academic and industrial researchers in domains as different as organic chemistry, solid-state physics, and electrochemistry. Conjugated polymers are at present intensively studied in view of their multiple potential technological applications such as smart windows, batteries and polymer modified electrodes [1,2]. In 1977, polyacetylene doped with iodine was found by Shirakawa, MacDiarmid, Heeger and coworkers to have metallic conductivity [3]. This discovery was awarded with the Nobel prize in chemistry in 2000. Polyacetylene is not a technologically important material, since it is quite unstable to oxygen and difficult to process. The most practically important types of conducting polymers are poly(*para*-phenylenevinylene, polypyrrole, polythiophene, polyaniline, polyfluorene and their derivatives. Their chemical structures are shown in **Figure 1.1**.

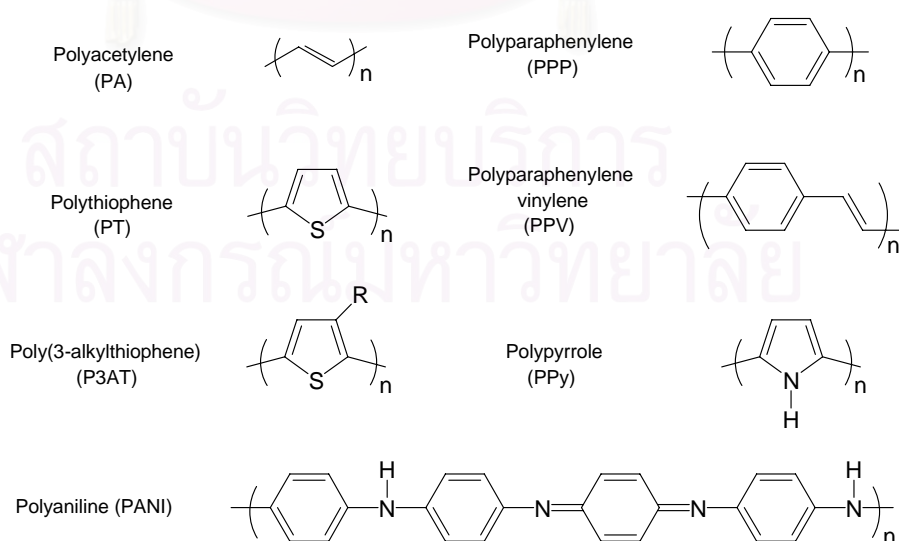


Figure 1.1 Structures of some conjugated polymers

1.1 Applications of organic conducting polymers

Organic conducting polymer has a unique and practical advantage. Their conductive properties allow the use of electronic tools (computer and interfaces) and other existing and emerging characterization tools to retrieve the information on the behavior of these systems from real *in situ* environments [4].

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 (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-induced charge separation)**
- **Display technologies**
Light emitting diode (LED), flat panel displays
- **Electrochromics**
Advertising display, smart windows, memory storage devices
- **Electromechanical actuators**
Artificial muscles, windows wipers in spacecrafts, rehabilitation gloves, electronic Braille screen, bionic ears for deaf patient
- **Separation technologies**
Novel smart-membrane, selective molecular recognition
- **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 biomechanical devices

1.2 Conjugated polymers: organic semiconductors

Conjugated polymers [5,6] 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 are either completely filled or completely empty. The band structure of a conjugated polymer originates from the interaction of the π -orbitals of the repeating units throughout the chain. 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 rehybridization of the energy levels yielding more and more sublevels until a point 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.

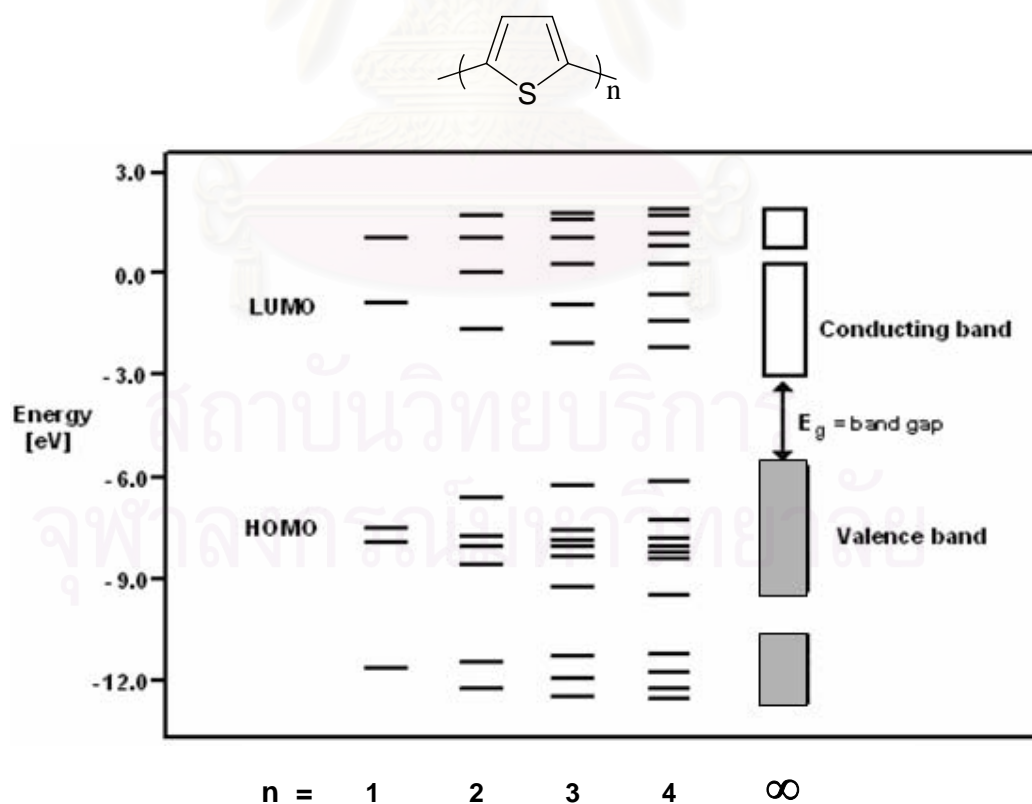


Figure 1.2 Calculated (frontier) energy levels of oligothiophenes with $n = 1-4$ and of polythiophene (E_g = band gap energy)

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

The difference between π -conjugated polymers and metals is that in metals, the orbitals of the atoms overlap with the equivalent orbitals of their neighboring atoms in all directions to form molecular orbitals similar to those of isolated molecules. With N numbers of interacting atomic orbitals, there would be N molecular orbitals. In the metals or any continuous solid-state structures, N will be a very large number (typically 10^{22} for 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**).

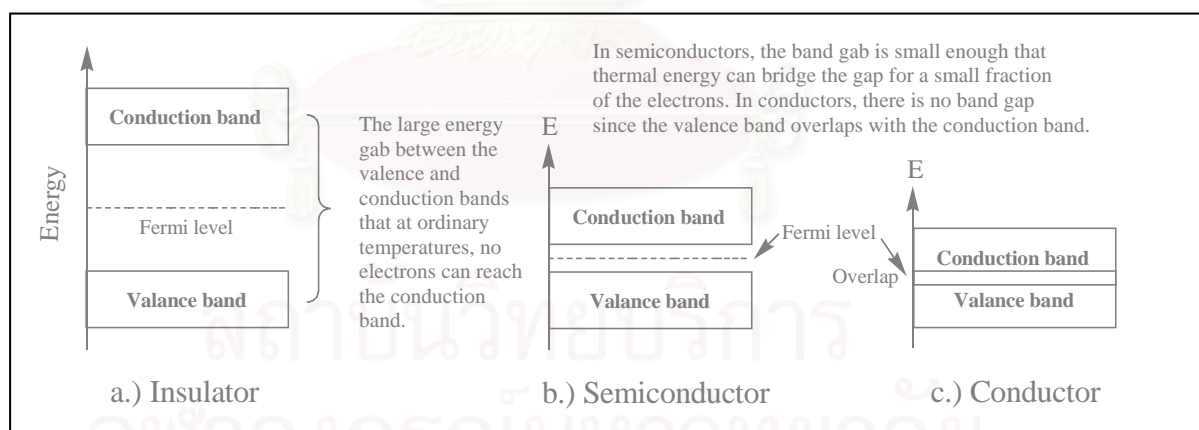


Figure 1.3 Simple band picture explaining the difference between an insulator, a semiconductor, and a metal.

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

An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperature. The position of the Fermi level which relates to the conduction band is a crucial factor in determining electrical properties.

The conductivity of the metal is due either to partly-filled valence or conduction band, or to the band gap being near zero, so that with any weak electric field the electrons easily redistribute. Electrons are excited to the higher energy bands and leave unfilled bands or “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.

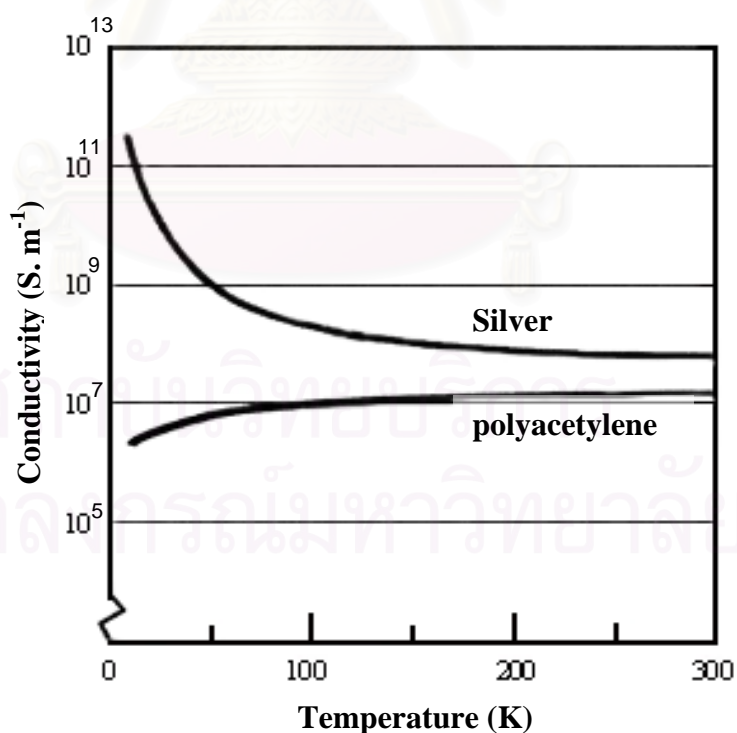


Figure 1.4 The conductivity of conducting polymers decreases with falling temperature in contrast to that of metals.

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

1.3 Structural basis of functionalization

Among the various possible strategies for modification of conducting polymers, the polymerization of monomer modified by the 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 a modified conducting polymers in which a specific function will be coupled to the conjugated π system requires that the modification of the monomer structure remains 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 a functional conducting polymer from a substituted monomer in respect of the above prerequisites implies a detailed comprehension of the structural effects of substitution (inductive, mesomeric and steric) at the various stages of organization of the materials, *i.e.* [1]

- 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

1.4 Polythiophene [7]

Polythiophene is a polymer composed of five membered heterocyclic monomeric units. It is environmentally stable and highly resistant to heat. Polythiophene attracted much attention as a conducting polymer due to ease of synthesis, stability, and structural versatility. It has often been considered a model system for the study of charge transport in conducting polymers with a nondegenerate ground state. Polythiophene has been aimed or used in many applications such as:

- The electrical properties of the doped conducting state, such as antistatic and EMI shielding, gas sensors, radiation detector, and corrosion protective films.
- The electronic properties of the natural semiconducting state, such as photovoltaic cells and nonlinear optics.
- The electrochemical reversibility of the transition between the doped and the undoped states, such as new rechargeable battery, display devices, electrochemical sensor and modified electrodes [1].

Polythiophene 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.

Unsubstituted conjugated polymers are generally insoluble, thereby presenting a significant disadvantage for their characterization and possible technological applications. The standard procedure of attaching long, flexible pendant chains to the conjugated backbone can often have deleterious effects on the electrical conductivity of polymers in their oxidized (conducting) states. A significant discovery demonstrated that polythiophene belongs to one of few cases in which substitution of hydrogen at the 3-position by an alkyl chain or an electron donating group with flexible chain does not affect the conductivity of the polymer, while impart solubility and consequently enhance processibility [8].

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 1.5**). Although HT coupling are generally favored, about 15-20% of HH coupling are often observed. This is not surprising since the less repulsive HT coupling are expected.

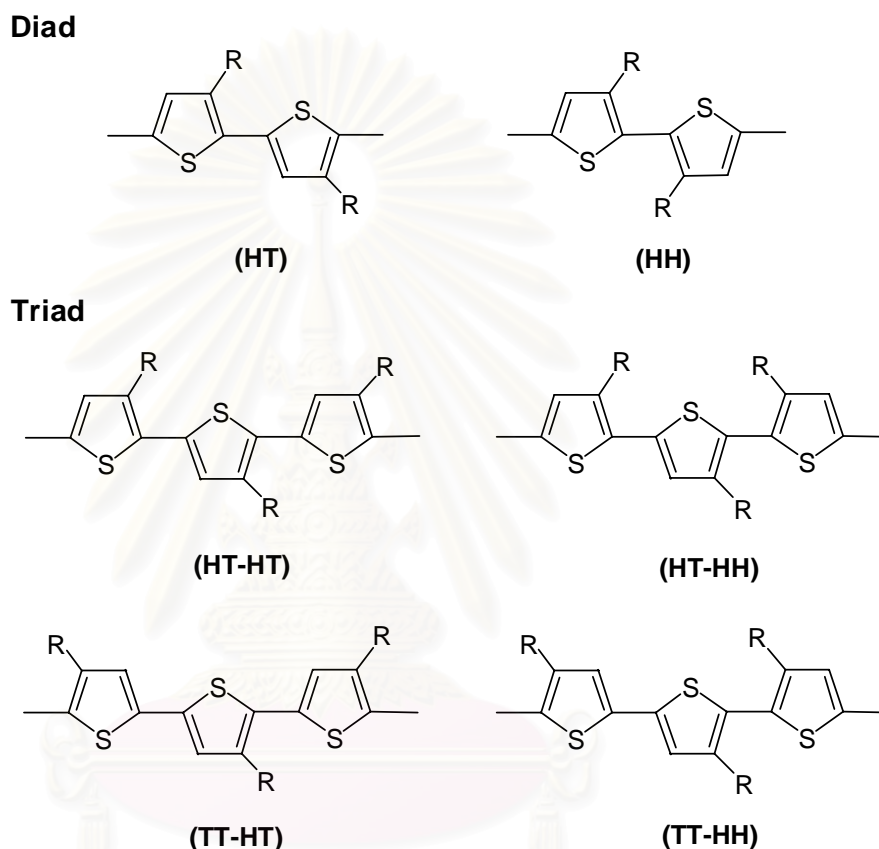


Figure 1.5 Regioisomers of poly(3-alkylthiophene)s

1.5 Synthesis of polythiophene

Polythiophene was prepared for the first time by electrochemical polymerization [9]. Since a film is produced on the anode during polymerization, this method is suitable for the preparation of polymers such as polythiophene and poly(3-methylthiophene), which is not processible after polymers are formed. However, in electrochemical polymerization, the yield of polymers is low and the polymers often do not have a well-defined structure. On the other hand, since facile oxidative polymerization with iron (III) chloride produces polythiophene in high yield, this

method is suitable for processable polythiophenes such as poly(3-alkylthiophene) because the electrochemical polymerization can give the polymer at only on the electrode surface. The molecular weight of polymer obtained by this method is sufficiently high for a film to be cast. The method has contributed a lot to the advancement in the science of polythiophenes. Grignard coupling is also an important route to produce polythiophenes. Polymers created by this method often show lower conductivity than those obtained by other methods. This technique is still important for the preparation of polymers with a well-defined structure, since no migration of substituents takes place during the coupling reaction.

1.5.1 Electrochemical polymerization [10]

A polymeric film can be obtained by electrochemical polymerization. This is a very useful method for preparing polymers such as polythiophene, poly(3-methylthiophene), and poly(3-phenylthiophene) (**Figure 1.6**), 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.

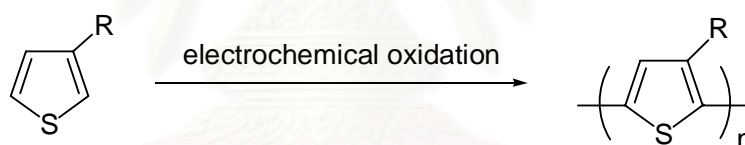


Figure 1.6 The electrochemical method for the synthesis of P3ATs (R = H, Me, Ph).

Polythiophene is not stable at the potentials used for the electrochemical polymerization of thiophene. Thus, polythiophene deposited on the anode at the earlier stages of the polymerization is overoxidized and has deteriorated, while electrochemical polymerization produces new polymer.

1.5.2 Oxidative coupling polymerization with iron (III) chloride

This method is easily accessible to almost all scientists who wish to obtain almost any polythiophene derivatives and will provide sufficient amounts of the polymer for laboratory use. The poly(3-alkylthiophene)s obtained from this method are soluble in common organic solvents and their film can be formed by simply casting its solution on a substrate. In addition, many 3-alkylthiophenes are commercially available.

Sugimoto and coworkers [11] explored transition metal halides as oxidizing agent for polymerization of 3-hexylthiophene and found that iron (III) chlorides were effective (**Figure 1.7**). The yield was 70%. The films obtained by casting a solution of the resulting poly(3-hexylthiophene) showed similar characteristics to those of the electrochemically prepared one.

Poly(3-alkylthiophene) was undoped from trace of FeCl_3 by exhaustive extraction with methanol, but this polymer still remained in partially doped states. Completely undoped polymer was obtained by reduction with an aqueous solution of hydrazine.

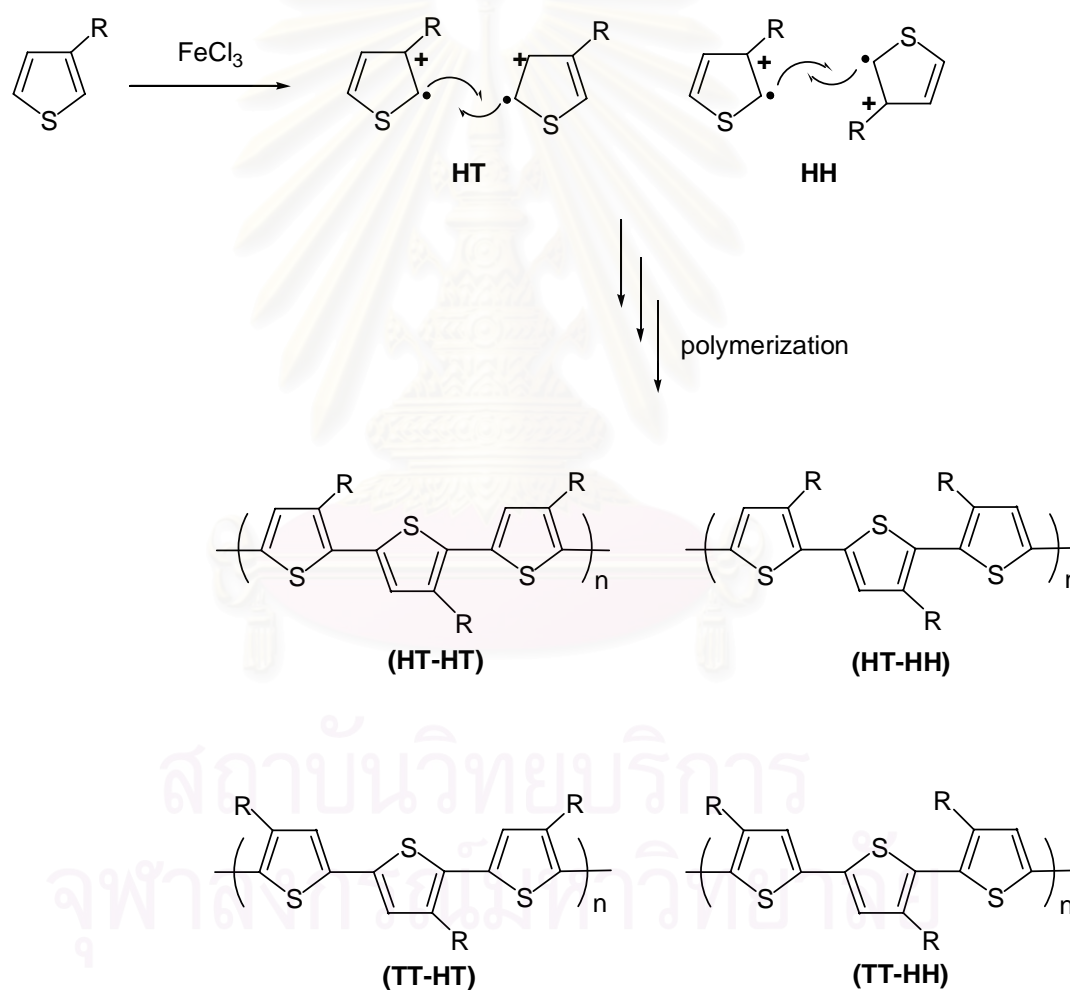


Figure 1.7 The oxidative coupling reaction of 3-alkylthiophene by FeCl_3 .

Amou [12] studied the polymerization mechanism and polymerization conditions and found that a lower temperature and a lower concentration were effective for increasing the %HT. Niemi [13] studied the mechanism of the

polymerization of 3-alkylthiophene with iron (III) chloride. Only solid iron (III) chloride was active as an oxidative polymerization agent for 3-alkylthiophene. 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 necessary initially to obtain high conversion in polymerization. A feasible polymerization mechanism for 3-alkylthiophene was developed on the basis of the crystal structure of iron (III) chloride and quantum chemical computations of thiophene derivatives. Polymerization was proposed to proceed through a radical mechanism.

1.5.3 Grignard coupling and other chemical polymerizations

Polymerization using a metal-catalyzed cross-coupling technique has been investigated extensively [14,15]. The reaction is believed to proceed firstly by an oxidative addition of an organic halide with a metal catalyst. Transmetalation between the catalyst complex and a reactive Grignard or other organometallic reagents (or disproportionation) then generate a diorganometallic complex. The last step involves reductive elimination of the coupled product with regeneration of the metal catalyst.

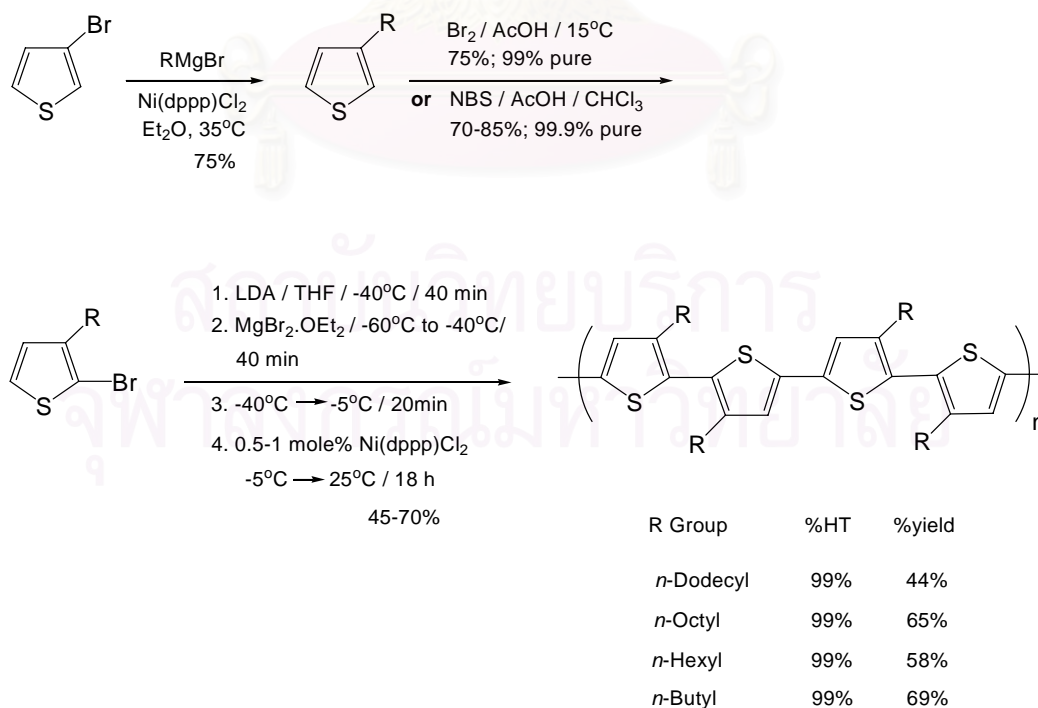


Figure 1.8 The McCullough method for the regiospecific synthesis of P3ATs

The first synthesis of regioregular HT-P3AT was reported by McCullough and coworkers [16] in early 1992 (**Figure 1.8**). This new synthetic method [17-21] regiospecifically generates 2-bromo-5-(bromomagnesio)-3-alkylthiophene, which is polymerized with catalytic amounts of Ni(dppp)Cl₂ using Kumada cross-coupling methods [22] 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 recently prepared sample of HT-poly(dodecylthiophene) had $M_n = 130,000$ (PDI = 2.1).

1.6 Poly(3,4-dialkoxythiophene)

Substitution of the polythiophene ring at β position with flexible alkyl, or alkyl containing one or more ether groups leads to the conducting polymers of unusual properties such as processability and stereoselectivity [23]. Introduction of electron-donating alkoxy substituent into the thiophene ring results also in diminution of polymerization potential and significant increase of the polymer electroactivity in aqueous solution, in comparison with that of poly(3-alkylthiophene) analogues. If the oxygen is directly attached to the ring, the conducting p-doping state of the polymer is substantially stabilized by stabilization of the positive charge in the polymer backbone [24].

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; ECL) by elimination of 2,4' or α,β couplings [25].

Poly(3,4-ethylenedioxythiophene); PEDOT is an excellent example of highly conducting polymer (conductivity up to 500 S.cm^{-1} in doped state), very stable and optical transparent in the oxidized state. These properties make the polymer attractive as an electrode material in rechargeable polymer batteries, capacitors, electrochromic devices and suitable as antistatic coatings [23]. However, PEDOT is insoluble in organic solvents, hence cannot be fabricated into desired forms. Nevertheless, one

may expect that the increase of the alkyl chain length in the alkoxy group could lead to a soluble polymer in organic solvents.

1.7 Synthesis of 3,4-dialkoxythiophene monomers

1.7.1 From disodium 2,3-di(ethoxycarbonyl)-3,4-thiophenediolate

The starting compound was disodium 2,3-di(ethoxycarbonyl)-3,4-thiophenediolate obtained from a condensation of diethyl 3-thioglutarate with diethyl oxalate under basic conditions (NaOH/EtOH), according to Hinsberg [23]. A direct alkylation of disodium salt, hydrolysis and decarboxylation, respectively, led to high synthetic yield of about 30%. (**Figure 1.9**).

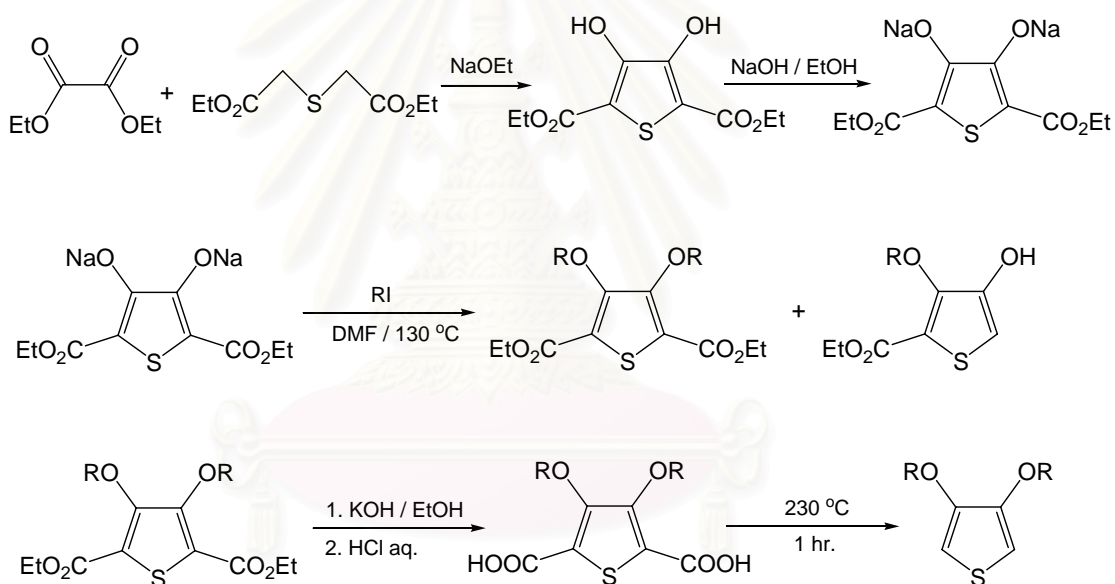


Figure 1.9 Synthesis of 3,4-dialkoxythiophene from disodium 2,3-di(ethoxy carbonyl)-3,4-thiophenediolate

1.7.2 From 3,4-dibromothiophene

3,4-dialkoxythiophene has been prepared from 3,4-dibromothiophene and sodium alkoxide in the presence of copper oxide and potassium iodide, using conditions reported by Bryce and coworkers (**Figure 1.10**) [26,27].

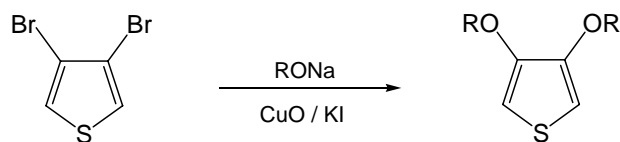


Figure 1.10 Synthesis of 3,4-dialkoxythiophene from 3,4-dibromothiophene

1.8 Solid state synthesis of PEDOT

PEDOT is one of the most industrially important conjugated polymers because of its excellent electronic properties (electrical conductivity, electrochromic properties, etc.) and high stability. Due to the regioregularity of the only possible monomeric structure, it has a very high conductivity (up to 550 S.cm^{-1} 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, such as an antistatic coating on plastics and an electrode in solid electrolyte capacitors [25].

Polymerization by traditional oxidative coupling using FeCl_3 in organic solvents gives an insoluble blue black polymer powder. The limitations of traditional polymerization methods can be a serious problem for PEDOT applications as well as for in-depth investigation of molecular order in this conducting polymer [28]. 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 the product, while requiring inexpensive equipment, and uncomplicated and environmentally sound procedures. However, at solid-state polymerization low temperatures, rate of the reaction are slow compared to polymerization in the melt phase because of the reduced mobility of the reacting species, and the slow diffusion of the by-products [29].

A facile solid-state polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) to give PEDOT through an unprecedented catalyst-free cross-coupling reaction has been studied by Meng and coworkers [30,31]. Dihalogen-substituted derivatives of 3,4-ethylenedioxythiophene (EDOT) have been prepared by direct halogenation of EDOT according to known procedure (**Figure 1.11**) [31]. The EDOT derivatives are colorless crystalline materials which can be almost quantitatively sublimed by gentle heating in a vacuum (or oven at normal pressure in a nitrogen flow, for small quantities).

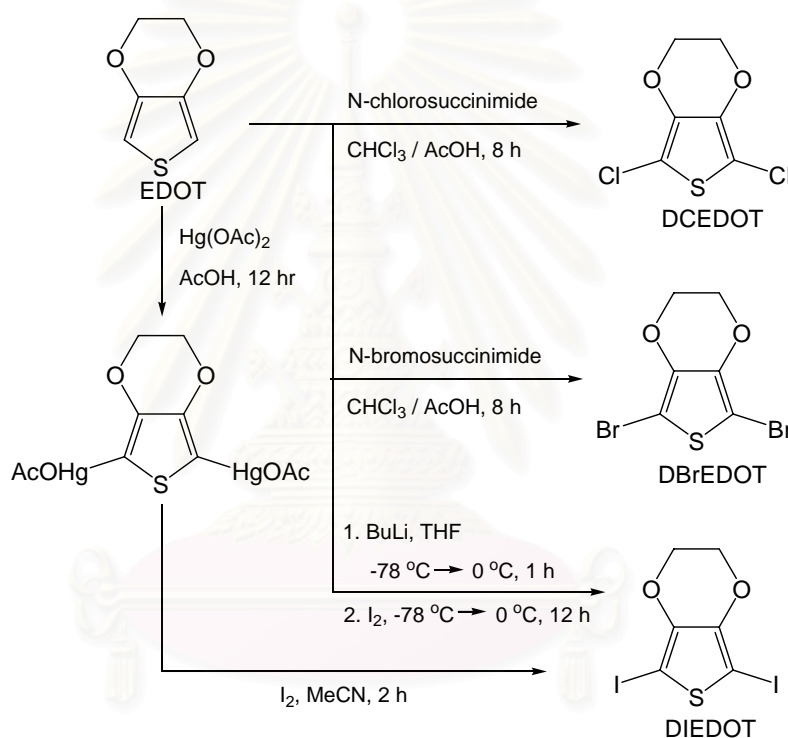


Figure 1.11 Synthesis of dihalo-EDOT monomers [31]

The polymerization of DBrEDOT was discovered by chance as a result of prolonged storage (2 years) of the monomer at room temperature (**Figure 1.12**). The colorless crystalline DBrEDOT transformed into a black material without apparent change of morphology. Surprisingly, the conductivity of this decomposition product appeared to be very high (up to $80 \text{ S}\cdot\text{cm}^{-1}$) for organic solid. When the reaction occurred in a close vial, release of a significant amount of elemental bromine was detected. However, quick heating above the melting point resulted in a non-decomposing and very slowly polymerizing melt of DBrEDOT.

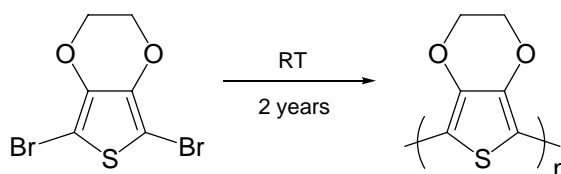


Figure 1.12 Solid state polymerization of EDOT

Table 1.1 Conductivity data of PEDOT polymers

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

^a Prepared from solid state polymerization

^b Prepared from oxidative coupling polymerization by FeCl₃

^c cannot be obtained

^d very small value

The room temperature conductivity of different solid state polymerization-PEDOT samples was measured by the four-point probe method (**Table 1.1**). The highest conductivity belongs to the polymer prepared at lowest temperature and longest reaction time, which may reflect an achievement of a higher degree of order. Indeed, heating above the monomer's melting point (120 °C) resulted in dramatically reduced conductivity (0.1 S.cm⁻¹), which rises up to 5.8 S cm⁻¹ after doping with iodine, approaching the value of the FeCl₃-synthesized PEDOT (7.6 S.cm⁻¹). Not very significant but certain increase in conductivity of solid state polymerization-PEDOT (about 2 times) was usually found upon exposing the sample to iodine vapor.

From the experiment, they concluded that heating 2,5-dibromo-3,4-ethylenedioxythiophene in the solid state resulted in an unprecedented self-coupling reaction and gave highly conducting and relatively well-ordered bromine-doped poly(3,4-ethylenedioxythiophene). Furthermore, heating DBrEDOT above its melting point led to polymer with a lower conductivity.

1.9 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 two reasons above are shown in **Figure 1.13**. 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.

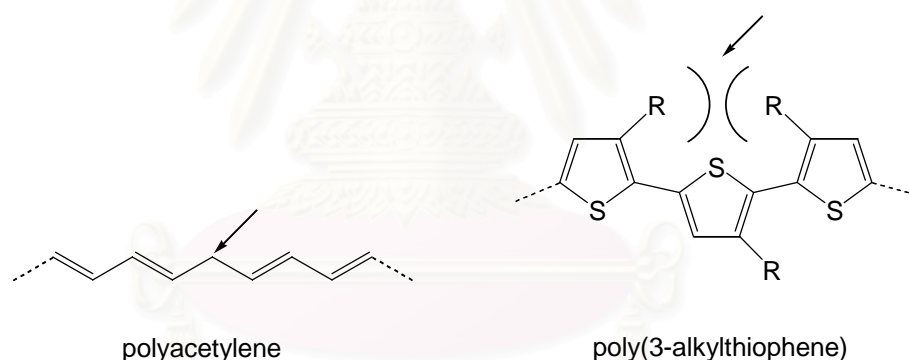


Figure 1.13 A defect in polyacetylene and steric induced structural twisting in poly(3-alkylthiophene)

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 1.14**). Twisting of polymer chain would also cause the reduction of conjugation in the polymer.

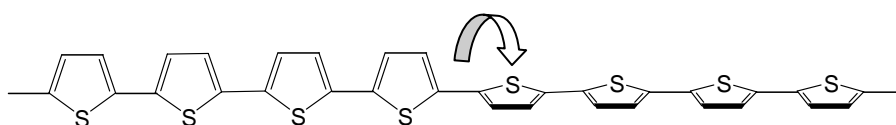


Figure 1.14 Twisting of polythiophene

1.10 Effect of doping [32]

The doping is an addition of an agent into the polymer and is expected to improve the conductivity of the polymer. Reversible “doping” of conducting polymers, with associated control of the electrical conductivity over the full range from insulator to metal, can be accomplished either by chemical doping or by electrochemical doping. Concurrent 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. Metallic polymers are, therefore, salts. The electrical conductivity results from the existence of charge carriers (through doping) and from the ability of those charge carriers to move along the π -bonded “highway”. Consequently, doped conjugated polymers are good conductors for two reasons:

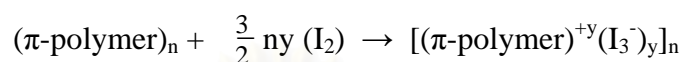
1. Doping introduces carriers into the electronic structure. Since every repeating unit is a potential redox site, conjugated polymers can be doped *n*-type (reduced) or *p*-type (oxidized) to a relatively high density of charge carriers.
2. The attraction of an electron in one unit to the nuclei in 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.

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

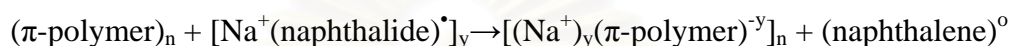
1.10.1 Chemical doping by charge transfer

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

1. *p*-type



2. *n*-type

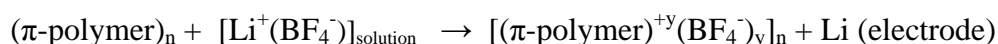


When the doping level is sufficiently high, the electronic structure evolves toward that of a metal.

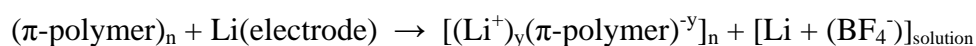
1.10.2 Electrochemical doping

Although chemical (charge transfer) doping is an efficient and straightforward process, it is typically 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 invented 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*-type



2. *n*-type



In conducting polymers with a non-degenerate ground state, the charge introduced upon doping can be stored in a form of polarons and bipolarons. Polythiophene, polaron, and bipolaron can be visualized as follows (**Figure 1.15**).

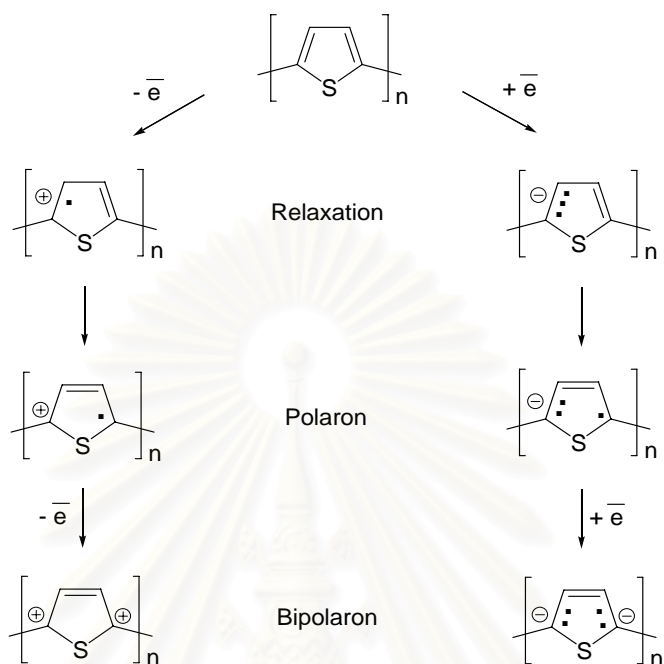


Figure 1.15 Schematic representation of polythiophene in the undoped, singly, and doubly oxidized (left), and singly and doubly reduced (right) states.

The polythiophene and derivatives were often doped by the oxidative doping because they are electron rich and favor to lose electron as indicated in **Figure 1.16**.

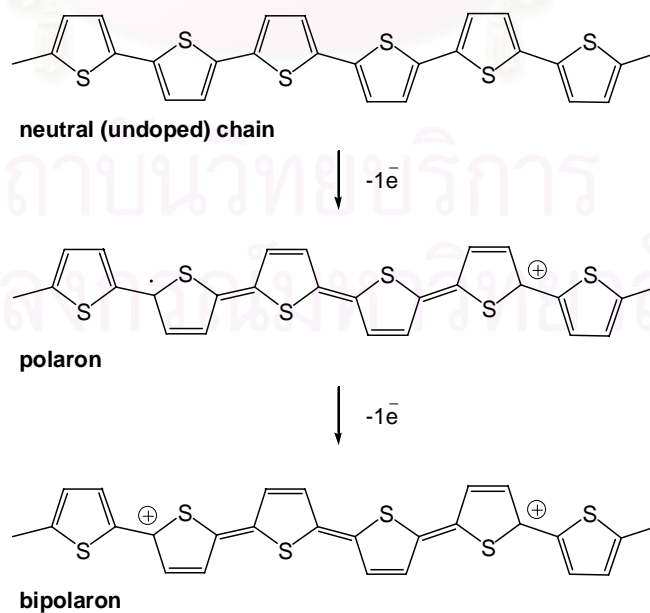


Figure 1.16 Polaron and bipolaron of polythiophene.

In **Figure 1.17** UV-vis-nir spectroelectrochemical curves recorded for different electrode potentials are shown for regioregular poly(3-octylthiophene) prepared using the method of McCullough and coworkers [21]. Cyclic voltammograms of poly(3-octylthiophene) unambiguously indicate that oxidative doping of this polymer is a two-step phenomenon since two overlapping redox couples are clearly seen. This two-step oxidation is also manifested in UV-vis-nir spectroelectrochemical studies. The spectra recorded for increasing doping levels show gradual bleaching of the $\pi\text{-}\pi^*$ transition with simultaneous growth of two peaks at 780 nm and 1780 nm, usually ascribed to the formation of bipolaron sub-gap states [33].

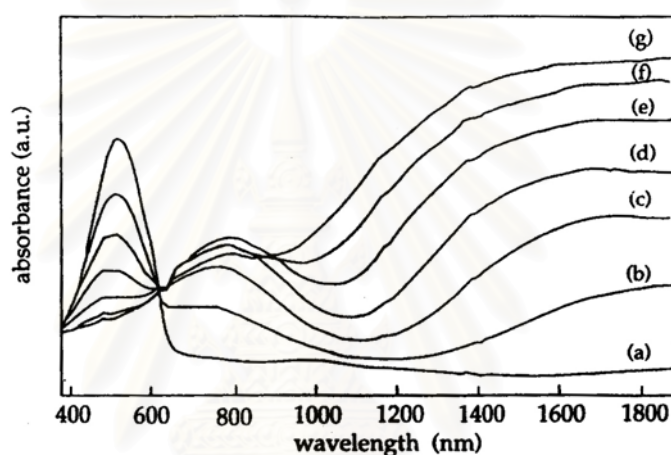


Figure 1.17 UV-vis-nir spectroelectrochemical curves recorded for regioregular poly(3-octylthiophene) in 0.1 M Bu_4NBF_4 solution in acetonitrile: (a) $E = 0$ mV; (b) $E = 500$ mV; (c) $E = 800$ mV; (d) $E = 900$ mV; (e) $E = 1000$ mV; (f) $E = 1200$ mV; (g) $E = 1400$ mV. (E measured vs Ag/AgCl reference electrode).

Poly(3-alkylthiophenes) are found to undergo continuous structural transformations upon doping with iodine vapor [34]. The X-ray diffraction resulted from oriented iodine-doped poly(3-*n*-octylthiophene) (P3OT) and poly(3-*n*-dodecylthiophene) (P3DT) films, highlighting the general features of this doping process and the presence of striking structural behavior unavailable to unsubstituted systems. It was found that there is extreme sensitivity of the side-group orientations to the presence of the dopant ions. This conformational change, when combined with rotation of the polymeric backbone about its chain axis, results in dramatic variations

in the interlayer spacing within semicrystalline regions of the film. Initial doping is marked by a rapid increase in the interlayer repeat.

1.11 Statement of the problem

Polythiophene represents a class of conducting polymers, which was environmentally stable, easy to synthesize, and structurally versatile. However, unsubstituted polythiophenes are insoluble and have low conducting in undoped state (neutral form), thereby presenting a significant disadvantage for possible technological applications. Incorporation of alkoxy substituents onto thiophene ring has been shown to induce a smaller bandgap and lower the oxidation potential. Thus derivatization of thienyl ring by substitutions with alkoxy containing one or more ether groups at β positions would lead to higher solubility together with good electrical and optical properties. An alternate approach to obtaining derivatized polymers with high conductivity is well-ordered polymer synthesis or polymerization of a structurally pre-organized crystalline monomer (solid-state polymerization; SSP). This research will aim at functionalization of thiophene and polythiophene derivatives carrying alkoxy functional groups. Furthermore, we will study conductivity of polymers, which were synthesized from oxidative coupling polymerization with ferric chloride (FeCl_3) and solid-state polymerization (SSP).

1.12 Objectives

The goal of the project emphasizes the modification of substituents on polythiophene derivatives to poly(3,4-dialkoxythiophene)s and study the processes of polymerizations of thiophene derivatives monomer either through the traditional oxidative coupling method or solid-state polymerization (SSP), in order to achieve better compromise between processible and conductive properties of the polymers.

1.13 Scope of the investigation

The sequential investigation was carried out as follows.

1. Literature survey on related research.
2. Synthesis of 3,4-dialkoxythiophene by ether exchange reactions of 3,4-ethylenedioxythiophene (EDOT).
3. Preparation of 2,5-dibromo-3,4-dialkoxythiophene derivatives by direct bromination of
 - a. 3,4-ethylenedioxythiophene (EDOT).
 - b. 3,4-alkoxythiophene monomer from 2.
 - c. 3-methoxythiophene.
 - d. Thiophene-3-carboxylic acid.
4. Preparation of 2,5-dibromo-3,4-dialkoxythiophene derivative by ether exchange reactions of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) from 3a.
5. To synthesize poly(3,4-dialkoxythiophene) derivatives from 3,4-dialkoxythiophene monomers from 2 by
 - a. Oxidative coupling polymerization.
 - b. Solid state polymerization (SSP).
6. To synthesize poly(3,4-dialkoxythiophene) derivatives by ether exchange reactions of poly(3,4-ethylenedioxythiophene); PEDOT from 5a.
7. Study the conductivity of poly(3,4-dialkoxythiophene) derivatives from solid-state polymerization (SSP) process from 5a, compared with oxidative coupling polymerization with ferric chloride (FeCl_3) from 5b.
8. Data analysis

CHAPTER II

EXPERIMENTAL SECTION

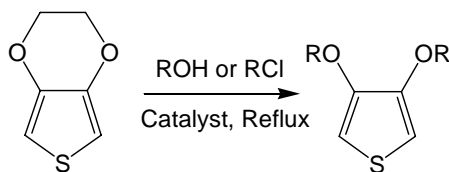
2.1 Chemicals

1. acetone	:	Merck
2. chloroform	:	Distilled from commercial grade
3. dichloromethane	:	Distilled from commercial grade
4. hexane	:	Distilled from commercial grade
5. toluene	:	Lab-scan
6. hydrochloric acid (37%)	:	Lab-scan
7. concentrated sulfuric acid	:	Lab-scan
8. cyclohexane	:	Lab-scan
9. deuterated chloroform	:	Wilmad
10. ferric chloride anhydrous	:	Riedel-deHaën
11. aluminium chloride anhydrous	:	Riedel-deHaën
12. <i>N</i> -bromosuccinimide (NBS)	:	Acros
13. <i>p</i> -toluenesulfonic acid monohydrate	:	Fluka
14. methanesulfonic acid	:	Fluka
15. 2,3-dihydrothieno[3,4- <i>b</i>]-1,4-dioxin	:	Aldrich
16. 3-methoxythiophene	:	Fluka
17. thiophene-3-carboxylic acid	:	Fluka
18. methanol	:	Lab-scan
19. <i>n</i> -butanol	:	Lab-scan
20. <i>n</i> -butyl chloride	:	Acros
21. benzyl alcohol	:	Merck
22. 2-bromoethanol	:	Acros
23. 2,2-dimethoxypropane	:	Merck

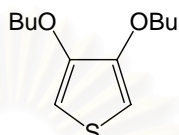
2.2 Instruments and apparatus

1. Nuclear Magnetic Resonance Spectrometer : Varian Mercury plus 400 operated at 399.84 MHz for ^1H and 100.54 MHz for ^{13}C nuclei
2. UV-visible Spectrophotometers : HP 8453 and UV-2550 SHIMADZU
3. Isotemp vacuum oven : Fisher Scientific 285 A
4. Gel Permeation Chromatograph : Water 600E
5. Gas Chromatograph : Varian CP-3800, CP-sil 8 column (30m x 0.25mm), injection volume = 1 μL , split ratio = 200, column flow = 2 mL/min and column oven = 250 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$
6. Infrared Spectrophotometer : Nicolet, Impact 410
7. Four-point probe conductometer : KEITHLEY Semiconductor Characterization System 4200
8. Mass Spectroscopy : Micromass Quattro micro API

2.3 Ether exchange of 3,4-ethylenedioxythiophene (EDOT)



2.3.1) 3,4-Dibutoxythiophene (DBT; R = n-Bu) using *n*-butanol



General procedure, 3,4-ethylenedioxythiophene (EDOT) 2 mmol was added 7.3 mL (80 mmol) *n*-butanol in a round bottom flask. An acid catalyst (see below) was added to the reaction mixture in small portions. The solution was refluxed for 24 h. The reaction mixture was then poured into a saturated NaHCO_3 solution. After the organic layer was washed with water several times. The reaction mixture was dried over anhydrous MgSO_4 . Solvent was removed by rotary evaporator. The crude mixture was obtained as dark solution and further purified by column chromatography eluted with 8:2 of hexane to dichloromethane. The product was obtained as a light yellow liquid. It was soluble in dichloromethane, chloroform and hexane. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 0.97 (6H, t, Ar-O-(CH_2) $_3$ -CH $_3$), 1.48 (4H, m, Ar-O-(CH_2) $_2$ -CH $_2$ - CH_3), 1.80 (4H, p, Ar-O- CH_2 -CH $_2$ - CH_2 - CH_3), 3.98 (4H, t, Ar-O-CH $_2$ -(CH_2) $_2$ - CH_3), 6.16 (2H, s, Ar-H) (**Figure A-1**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 13.9, 19.2, 31.1, 70.2, 96.8, 147.5 (**Figure A-2**, Appendix A). Gas chromatographic analysis gave retention time (t_r) 18.955 min.

2.3.1.1) *p*-Toluenesulfonic acid (PTSA) as the catalyst

3,4-Dibutoxythiophene was prepared from a reaction of 0.2790 g (2 mmol) of 3,4-ethylenedioxythiophene (EDOT) and 0.7685 g (4 mmol) of *p*-toluenesulfonic acid (PTSA). The product was obtained in 0.1906 g (42.5%).

2.3.1.2) Methanesulfonic acid (MSA) as the catalyst

3,4-Dibutoxythiophene was prepared from a reaction of 0.2844 g (2 mmol) of 3,4-ethylenedioxythiophene (EDOT) and 0.26 mL (4 mmol) methane sulfonic acid (MSA). The product was obtained in 0.0975 g (21.4%).

2.3.1.3) Concentrated sulfuric acid (H₂SO₄) as the catalyst

3,4-Dibutoxythiophene was prepared from a reaction of 0.2841 g (2 mmol) of 3,4-ethylenedioxythiophene (EDOT) and 0.56 mL (10 mmol) concentrated sulfuric acid (H₂SO₄). The product was obtained in 0.0371 g (8.1%)

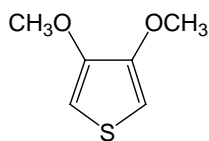
2.3.1.4) Concentrated hydrochloric acid (HCl) as the catalyst

3,4-Dibutoxythiophene was prepared from a reaction of 0.2857 g (2 mmol) of 3,4-ethylenedioxythiophene (EDOT) and 1.67 mL (20 mmol) conc. HCl. No product was obtained in this case.

2.3.2) 3,4-Dibutoxythiophene (DBT; R = n-Bu) using n-butyl chloride

To the solution of 0.2814 g (2 mmol) of 3,4-ethylenedioxythiophene (EDOT) in 15 mL *n*-butyl chloride was added 0.5339 g (4 mmol) of anhydrous aluminium chloride (AlCl₃). The reaction mixture was refluxed for 20 h and then quenched with 10 mL water. The organic layer was washed once with water and dried over anhydrous MgSO₄. Solvent was removed by rotary evaporator. The crude mixture was purified by column chromatography eluted with 8:2 of hexane to dichloromethane. The product was obtained as a pale-yellow liquid in 0.1325 g (29.3%). Its ¹H-NMR and ¹³C-NMR spectra are identical to those obtained from Section 2.3.1.

2.3.3) 3,4-Dimethoxythiophene (DMT; R = CH₃) using methanol



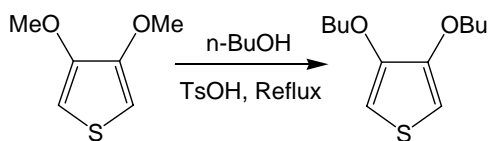
2.3.3.1) *p*-Toluenesulfonic acid (PTSA) as the catalyst

To the solution of 0.2842 g (2 mmol) of 3,4-ethylenedioxythiophene (EDOT) in 3.3 mL (80 mmol) of methanol was added 0.7629 g (4 mmol) of *p*-toluenesulfonic acid (PTSA). The solution was refluxed for 2 h and then poured into saturated NaHCO₃ solution. The organic layer was extracted by dichloromethane, washed with water and dried over anhydrous MgSO₄. The organic phase was evaporated by rotary evaporator. The crude mixture was purified by column chromatography eluted with 8:2 of hexane to ethyl acetate. The product was obtained as a pale-yellow liquid in 0.0244 g (8.5%). It was soluble in dichloromethane and chloroform. ¹H-NMR (CDCl₃): δ (ppm) 3.84 (6H, s, Ar-OCH₃), 6.18 (2H, s, Ar-H) (**Figure A-3**, Appendix A); ¹³C-NMR (CDCl₃): δ (ppm) 57.8, 96.5, 148.0 (**Figure A-4**, Appendix A). Gas chromatographic analysis gave retention time (t_r) 12.895 min.

2.3.3.2) *p*-Toluenesulfonic acid (PTSA) as the catalyst with an addition of 2,2-dimethoxypropane

The reaction was repeated following the procedure in Section 2.3.3.1 but was added 2,2-dimethoxypropane 1.24 mL (10 mmol) after the 2 h reflux. The reaction was then further refluxed for an additional 30 min before being quenched by saturated NaHCO₃ solution, extracted and purified by the similar procedure as described in Section 2.3.3.1. A Light gray solid was obtained instead of the desired product in 0.1311 g (see discussion section). It was soluble in dichloromethane, chloroform. ¹H-NMR (CDCl₃): δ (ppm) 1.76 (6H, s, -O-C-CH₃), 4.13 (4H, s, -O-CH₂-CH₂-O-) (**Figure A-5**, Appendix A).

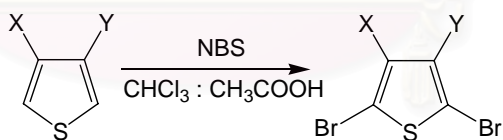
2.4 Ether exchange of 3,4-dimethoxythiophene (DMT)



2.4.1) 3,4-Dibutoxythiophene (DBT) using *n*-butanol

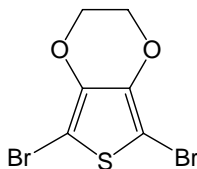
The compound was prepared from a reaction of 0.2850 g (2 mmol) of 3,4-dimethoxythiophene (DMT) from Section 2.3.3.1, and 0.7619 g (4 mmol) of *p*-toluenesulfonic acid (PTSA) was added to a 7.3 mL (80 mmol) of *n*-butanol. The solution was refluxed 24 h and then poured into saturated NaHCO₃ solution. The organic layer was extracted by dichloromethane, washed with water several times and dried over anhydrous MgSO₄. Solvent was removed by rotary evaporator. The crude mixture was purified by column chromatography eluted with 8:2 of hexane to dichloromethane. The product was obtained as a pale-yellow liquid in 0.3866 g (85.7%). Its ¹H-NMR and ¹³C-NMR spectra are identical to those obtained from Section 2.3.1

2.5 Bromination of thiophene derivatives



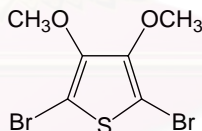
General procedure : A thiophene precursor was added to a 24 mL solution of a 2:1 (v/v) mixture of chloroform:glacial acetic acid. 2.5 equivalents of *N*-bromosuccinimide (NBS) was added to the reaction mixture in small portions. After the addition, the reaction mixture was stirred at ambient temperature for 4-6 h. In case of thiophene-3-carboxylic acid, the reaction mixture was heated at 50 °C for 4 h and then allowed to cool to room temperature. The reaction mixture was quenched by adding water. The chloroform layer was washed with saturated NaHCO₃ solution three times and once with water and dried over anhydrous MgSO₄. Solvent was removed by rotary evaporator. The crude mixture was purified by column chromatography. The corresponding dibromothiophene derivatives were obtained.

2.5.1) 2,5-Dibromo-3,4-diethylenedioxythiophene (DBrEDOT);



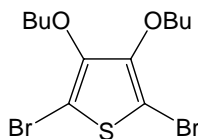
The compound was prepared from a reaction of 2.5536 g (18 mmol) of 3,4-ethylenedioxythiophene (EDOT) and 8.0172 g (45 mmol) of NBS. The crude mixture was purified by column chromatography eluted with 6:4 of hexane to dichloromethane. The product was recrystallized by methanol and obtained as a white needle crystal in 3.5410 g (65.7%). It was soluble in dichloromethane, chloroform and acetonitrile. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 4.26 (4H, s, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) (**Figure A-6**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 64.9, 85.5, 139.7 (**Figure A-7**, Appendix A). Gas chromatographic analysis gave retention time (t_r) 20.312 min.

2.5.2) 2,5-Dibromo-3,4-dimethoxythiophene (DBrDMT; X = Y = OCH_3)



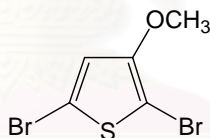
The compound was prepared from a reaction of 0.1451 g (1 mmol) of 3,4-dimethoxythiophene (DMT) from Section 2.3.3.1 and 0.4461 g (2.5 mmol) of NBS. The crude mixture was purified by column chromatography eluted with 8:2 of hexane to dichloromethane. The product was obtained as a white solid in 0.2314 g (76.1%). It was soluble in dichloromethane, chloroform and acetonitrile. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 3.90 (6H, s, $\text{Ar}-\text{OCH}_3$) (**Figure A-8**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 61.2, 95.0, 148.2 (**Figure A-9**, Appendix A). Gas chromatographic analysis gave retention time (t_r) 17.236 min.

2.5.3) 2,5-Dibromo-3,4-dibutoxythiophene (DBrDBT; X = Y = OBu)



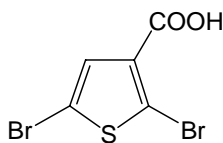
The compound was prepared from a reaction of 0.2289 g (1 mmol) of 3,4-dibutoxythiophene (DBT) from Section 2.3.1.1 and 0.4446 g (2.5 mmol) of NBS. The crude mixture was purified by column chromatography eluted with hexane. The product was obtained as a pale-yellow liquid in 0.1261 g (32.6%). It was soluble in dichloromethane, chloroform and acetonitrile. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 0.96 (6H, t, Ar-O-(CH_2) $_3$ -CH $_3$), 1.49 (4H, h, Ar-O-(CH_2) $_2$ -CH $_2$ -CH $_3$), 1.71 (4H, p, Ar-O-CH $_2$ -CH $_2$ -CH $_2$ -CH $_3$), 4.05 (4H, t, Ar-O-CH $_2$ -(CH_2) $_2$ -CH $_3$) (**Figure A-10**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 13.8, 19.0, 31.9, 73.6, 95.3, 147.6 (**Figure A-11**, Appendix A). Gas chromatographic analysis gave retention time (t_r) 22.333 min.

2.5.4) 2,5-Dibromo-3-methoxythiophene (DBrMT; X = H and Y = OCH $_3$)



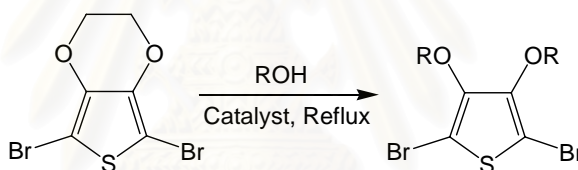
The compound was prepared from a reaction of 0.1170 g (1 mmol) of 3-methoxythiophene (MT) and 0.4452 g (2.5 mmol) of NBS. The crude mixture was purified by column chromatography eluted with hexane. The product was obtained as a colorless to pale-yellow liquid in 0.0720 g (26.3%). It was soluble in dichloromethane, chloroform and acetonitrile. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 3.85 (3H, s, Ar-OCH $_3$), 6.78 (1H, s, Ar-H) (**Figure A-12**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 59.3, 89.5, 109.8, 119.8, 154.4 (**Figure A-13**, Appendix A). Gas chromatographic analysis gave retention time (t_r) 15.832 min.

2.5.5 2,5-Dibromothiophene-3-carboxylic acid (X = H and Y = COOH)



The compound was prepared from a reaction of 0.1278 g (1 mmol) of thiophene-3-carboxylic acid and 0.4439 g (2.5 mmol) of NBS. The product was obtained as a white needle crystal in 0.0863 g (30.1%). It was soluble in acetone and partially soluble in dichloromethane and chloroform. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.00 (1H, broad, Ar-COOH), 7.40 (1H, s, Ar-H) (**Figure A-14**, Appendix A).

2.6 Ether exchange of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT)



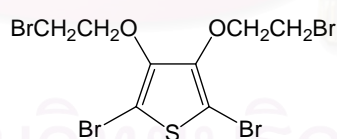
2.6.1 2,5-Dibromo-3,4-dimethoxythiophene (DBrDMT; R = CH₃)

To the solution of 0.2995 g (1 mmol) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) from Section 2.5.1 in 9.7 mL (240 mmol) of methanol was added 0.3831 g (2 mmol) of *p*-toluenesulfonic acid (PTSA). The reaction mixture was refluxed for 21 h. The reaction mixture was quenched with saturated NaHCO_3 solution and added about 20 mL of dichloromethane. The separated water layer was extracted with more dichloromethane three times. The combined dichloromethane extract was washed with water and dried with anhydrous MgSO_4 . The filtered solution was concentrated by rotary evaporator and purified by column chromatography eluted with 8:2 of hexane to dichloromethane. The desired product was obtained in 0.0565 g (18.7%). Its characterization appeared to be identical to the product obtained from Section 2.5.2.

2.6.2) 2,5-Dibromo-3,4-dibutoxythiophene (DBrDBT; R = n-Bu)

The reaction followed the similar procedure as in Section 2.6.1 except using 3.7 mL (40 mmol) of *n*-butanol and the solution was refluxed for 9 h. The crude mixture was purified by column chromatography eluted with hexane. The desired product was obtained in the first fraction ($R_f = 0.65$ in 9:1 of hexane to dichloromethane TLC system) in 0.0394 g (10.2%). Its characterization appeared to be identical to the product obtained from Section 2.5.3. The second colorless liquid fraction was soluble in dichloromethane and chloroform ($R_f = 0.45$ in 9:1 of hexane to dichloromethane TLC system) in 0.1213 g. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 0.96 (6H, m), 1.48 (4H, m), 1.70 (2H, p), 1.76 (2H, p), 3.92 (2H, t), 4.01 (2H, t) and 6.11 (1H, s) (**Figure A-15**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 13.77, 13.81, 19.05, 19.24, 31.07, 32.00, 69.58, 72.92, 96.16, 97.93, 145.10, and 149.40 (**Figure A-16**, Appendix A). Gas chromatographic analysis gave retention time (t_r) 21.029 min. The third fraction ($R_f = 0.30$ in 9:1 of hexane to dichloromethane TLC system) was obtained as a pale-yellow liquid in 0.0517 g. Its $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra are identical to those obtained from Section 2.3.1

2.6.3) 2,5-Dibromo-3,4-bis(2-bromoethoxy)thiophene (R = $\text{CH}_2\text{CH}_2\text{Br}$)



2.6.3.1) With methanol as solvent

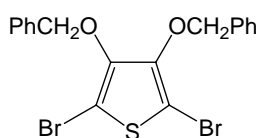
To the solution of 0.2996 g (1 mmol) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) from Section 2.5.1 in 0.81 mL (20 mmol) of methanol and 0.28 mL (4 mmol) bromoethanol was added 0.7637 g (4 mmol) of *p*-toluenesulfonic acid (PTSA). The reaction was refluxed for 2 h, quenched with saturated NaHCO_3 solution, and obtained the crude product using the similar procedure as in Section 2.6.1. The crude product was purified by column chromatography eluted with 2:8 of hexane to dichloromethane. The

first fraction was obtained as liquid ($R_f = 0.82$ in dichloromethane TLC system) in 0.0210 g. It was soluble in dichloromethane, chloroform and acetonitrile. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 3.44 (3H, s, Ar-OCH₃), 4.21 (2H, t, Ar-O-CH₂-CH₂-OH), 4.35 (2H, t, Ar-O-CH₂-CH₂-OH), 5.95 (1H, s, Ar-H) (**Figure A-17**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 55.3, 64.1, 66.3, 80.8, 132.9, 152.1 (**Figure A-18**, Appendix A). The second colorless liquid fraction was obtained in 0.1124 g and soluble in dichloromethane and chloroform ($R_f = 0.35$ in dichloromethane TLC system). $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 3.54 (4H, t), 4.23 (4H, s), 4.52 (4H, t) (**Figure A-19**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 27.9, 64.4, 65.0, 133.8, 161.8 (**Figure A-20**, Appendix A).

2.6.3.2) Without solvent

To the solution of 0.3007 g (1 mmol) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) from Section 2.5.1 in 1.42 mL (20 mmol) of bromoethanol was added 0.3887 g (2 mmol) of *p*-toluenesulfonic acid (PTSA). The reaction mixture was stirred at 80 °C for 1 h and poured into saturated NaHCO₃ solution. The mixture was extracted and purified by the similar procedure as described in 2.6.1 except using 2:8 of hexane to dichloromethane as eluent. The colorless liquid was obtained in 0.2578 g and soluble in dichloromethane and chloroform. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 3.54 (4H, t), 4.23 (4H, s), 4.52 (4H, t) (**Figure A-19**, Appendix A); $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm) 27.9, 64.4, 65.0, 133.8, 161.8 (**Figure A-20**, Appendix A). Gas chromatographic analysis gave retention time (t_r) 25.404 min.

2.6.4) 3,4-Bis(benzyloxy)-2,5-dibromothiophene (R = CH₂Ph)



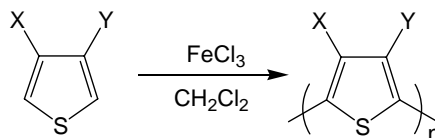
2.6.4.1) With toluene

The compound was prepared from a reaction of 0.2917 g (1 mmol) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) from Section 2.5.1, and 0.3851 g (2 mmol) *p*-toluenesulfonic acid (PTSA) was added to mixture between 0.21 mL (2 mmol) benzyl alcohol and a 3 mL toluene. The reaction mixture was refluxed for 7 h, quenched with saturated NaHCO₃ solution, and obtained the crude product using the similar procedure as in Section 2.6.1. The crude product was purified by column chromatography eluted with hexane. The first fraction was obtained as liquid ($R_f = 0.48$ in hexane TLC system) It was soluble in dichloromethane and chloroform. ¹H-NMR (CDCl₃): δ (ppm) 2.24 (3H, s), 3.99 (2H, s), 7.09 (4H, s), 7.15(m) (**Figure A-22**, Appendix A). The second colorless liquid fraction was soluble in dichloromethane and chloroform ($R_f = 0.40$ in hexane TLC system). ¹H-NMR (CDCl₃): δ (ppm) 2.31 (3H, s), 3.94 (2H, s), 7.09 (4H, s), 7.34 (m) (**Figure A-23**, Appendix A).

2.6.4.2) Without toluene

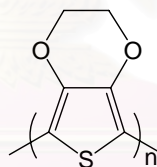
The compound was prepared from a reaction of 0.2967 g (1 mmol) of 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) from Section 2.5.1, and 0.3894 g (2 mmol) *p*-toluenesulfonic acid (PTSA) was added to a 1.03 mL (10 mmol) benzyl alcohol. The reaction mixture was stirred at 110 °C for 5 h and poured into saturated NaHCO₃ solution. The mixture was extracted and purified by similar procedure as described in 2.6.1 except using hexane as eluent. The obtained colorless liquid was soluble in dichloromethane and chloroform. ¹H-NMR (CDCl₃): δ (ppm) 4.51 (4H, s), 7.35 (m) (**Figure A-24**, Appendix A); ¹³C-NMR (CDCl₃): δ (ppm) 33.6, 128.4, 128.8, 129.0, 137.8 (**Figure A-25**, Appendix A).

2.7 Polymerization by oxidative coupling



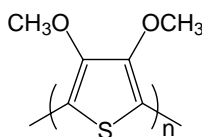
General procedure : Exact amount of thiophene monomer was dissolved in dichloromethane 4 mL. The solution was slowly added into a stirred suspension of 3 equivalents of anhydrous ferric chloride in dichloromethane 4 mL. When the addition was completed, the mixture was stirred for an additional 24 h at room temperature. The polymer was then precipitated by an addition of 20 mL methanol. The precipitate was filtered and rinsed with methanol until the washed solution was colorless. The remaining ferric chloride in the precipitate was exhaustively removed by soxhlet extraction with methanol for 24 h. The resulting polymer was then dried to give the corresponding polythiophene derivatives.

2.7.1 Poly(3,4-ethylenedioxythiophene); (PEDOT; X—Y = OCH₂CH₂O)



The compound was prepared from a reaction of 0.8537 g (6 mmol) of 3,4-ethylenedioxythiophene (EDOT) and 3.0495 g (18 mmol) of anhydrous ferric chloride (FeCl₃). The product was obtained as a dark blue solid in 0.7882 g (92.3%). It was insoluble in all organic solvents.

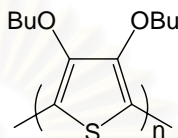
2.7.2 Poly(3,4-dimethoxythiophene); (PDMT; X = Y = OCH₃)



The compound was prepared from a reaction of 0.2890 g (2 mmol) of 3,4-dimethoxythiophene (DMT) from Section 2.3.3.1 and 0.9834 g (6 mmol)

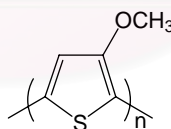
of anhydrous ferric chloride (FeCl_3). The product was obtained as a dark blue solid in 0.1789g (61.8%). It was partially soluble in dichloromethane and chloroform. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 3.95 (broad) (**Figure A-26**, Appendix A).

2.7.3 Poly(3,4-dibutoxythiophene); (PDBT; X = Y = OBu)



The compound was prepared from a reaction of 0.4291 g (1.88 mmol) of 3,4-dibutoxythiophene (DBT) from Section 2.3.1.1 and 0.9172 g (5.65 mmol) of anhydrous ferric chloride (FeCl_3). The product was obtained as a red brown solid in 0.2667 g (62.2%). It was soluble in dichloromethane and chloroform. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 0.98 (broad), 1.50 (broad), 1.87 (broad), 4.12 (broad) (**Figure A-27**, Appendix A).

2.7.4 Poly(3-methoxythiophene); (PMT; X = H and Y = OCH₃)



The compound was prepared from a reaction of 0.2283 g (2 mmol) of 3-methoxythiophene (MT) and 0.9801 g (6 mmol) of anhydrous ferric chloride (FeCl_3). The product was obtained as a dark blue solid in 0.1757 g (77.0%). It was partially soluble in dichloromethane and chloroform. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 3.98 (broad), 6.13 (broad), 6.88 (broad) (**Figure A-28**, Appendix A).

2.8 Ether exchange of poly(3,4-ethylenedioxythiophene); (PEDOT)

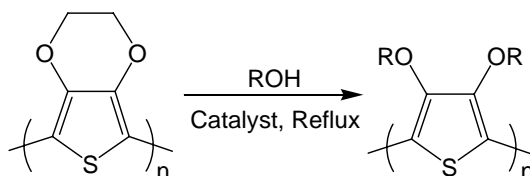
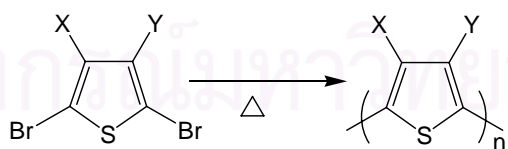


Table 2.1 Ether exchange of PEDOT using various acid catalyst

Entry	Substrate 1	Substrate 2	Acid catalyst
1	PEDOT	<i>n</i> -butanol	PTSA
2	PEDOT	<i>n</i> -butanol	conc. H ₂ SO ₄
3	PEDOT	<i>n</i> -butanol	conc. HCl
4	PEDOT	methanol	conc. HCl

Poly(3,4-ethylenedioxythiophene); (PEDOT) from Section 2.7.1 was added appropriate alcohols and acid catalysts in a round bottom flask (shown in **Table 2.1**). The solution was refluxed until poly(3,4-ethylenedioxythiophene) was more soluble. The reaction mixture was quenched by saturated NaHCO₃ solution. The remaining insoluble polymer was filtered and rinsed with water several times. The filtrate was extracted by dichloromethane and dried over anhydrous MgSO₄. Solvent was removed by rotary evaporator. Unfortunately, none of the desired polymer was obtained in all entries (see discussion section).

2.9 Solid state polymerization (SSP)



2.9.1 Poly(3,4-ethylenedioxythiophene); (PEDOT; X—Y = OCH₂CH₂O)

The compound was prepared from an incubation of 0.4308 g of crystallized 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) from Section 2.5.1 at 80 °C for 4 h. The color of the crystals changed from white to

dark blue with brown vapor appeared. The product was insoluble in all organic solvents. The reaction was repeated as in above except using an incubation at room temperature for 3 days. The result was similar to using the incubation at 80 °C for 4 h.

2.9.2) Poly(3,4-dimethoxythiophene); (PDMT; X = Y = OCH₃)

The reaction was repeated using 0.2314 g of 2,5-dibromo-3,4-dimethoxythiophene (DBrDMT) from Section 2.5.2 as the starting monomer. Unfortunately, no polymer was observed with the applied reaction (an incubation at 80 °C for 24 h and direct heating at 100 °C for 5 days).

2.10 Conductivity measurement using Four-point probe conductometer

A polymer from Section 2.71 to 2.74 and 2.9.1 was pressed for pellet except Section 2.7.3 was cast by pouring a polymer solution into a glass slide then heated to 40 ° to evaporate CH₂Cl₂. Polymer pellets and film, were measured conductivity by Four-point probe conductometer. The measurement was repeated using I₂ doped polymers. Those polymer pellets and film placed in an iodine chamber. After 24 h, the conductivity of each pellets and film were measured immediately after being taken out of the container by a Four-point probe conductometer (**Appendix B**).

CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of 3,4-dialkoxythiophene derivatives

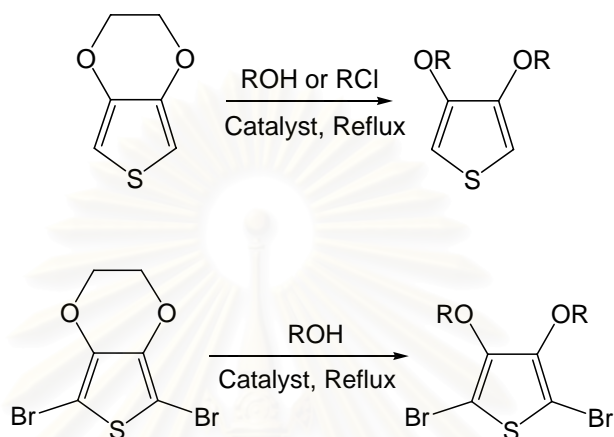


Figure 3.1 Synthesis route of 3,4-dialkoxythiophene derivatives

The synthesis of 3,4-dialkoxythiophene derivatives by ether exchange reaction of EDOT or DBrEDOT using various acid catalysts at reflux temperature are shown in **Table 3.1**.

From **Table 3.1**, entries 1-5, it was found that *p*-toluenesulfonic acid (PTSA) was the best acid catalyst for ether exchange reaction. Concentrated H₂SO₄ (entry 3) gave the desired DBT (**Figure 3.2**) product (see **Figure 3.1**) in very low yield (8.1%). Side reactions usually associated with the use of conc. H₂SO₄ were assumed to be responsible for such unsatisfactory result. Concentrated HCl (entry 4) did not give any desired DBT product. The weaker and volatile nature of the acid could be accounted for this unsuccessful reaction.

From **Table 3.1**, entry 6 gave the desired product (DMT) in very low yield (8.5%). This suggested that the equilibrium of the reaction may drive towards the reactant (EDOT) rather than the desired product (DMT). This suggestion was confirmed by large amount of the EDOT reactant which had been recovered (0.1743 g, 61.3%).

Table 3.1 Synthesis of 3,4-dialkoxythiophene derivatives

Entry	Substrate	Reagent	Acid catalyst	Condition	Expected product ^a	% yield
1	EDOT	<i>n</i> -butanol	PTSA	reflux	DBT	42.5
2	EDOT	<i>n</i> -butanol	MSA	reflux	DBT	21.4
3	EDOT	<i>n</i> -butanol	conc. H ₂ SO ₄	reflux	DBT	8.1
4	EDOT	<i>n</i> -butanol	conc. HCl	reflux	DBT	- ^b
5	EDOT	<i>n</i> -butyl chloride	AlCl ₃	reflux	DBT	29.3
6	EDOT	methanol	PTSA	reflux	DMT	8.5
7	EDOT	methanol	PTSA	reflux / DMP ^c	DMT	- ^d
8	DBrEDOT	methanol	PTSA	reflux	DBrDMT	18.7
9	DBrEDOT	<i>n</i> -butanol	PTSA	reflux	DBrDBT	10.2
10	DBrEDOT	bromoethanol	PTSA	reflux / methanol ^e	1	- ^d
11	DBrEDOT	bromoethanol	PTSA	80 °C	1	- ^d
12	DBrEDOT	benzyl alcohol	PTSA	reflux / toluene ^e	2	- ^b
13	DBrEDOT	benzyl alcohol	PTSA	110 °C	2	- ^b
14	DMT	<i>n</i> -butanol	PTSA	reflux	DBT	85.7

^a See **Figure 3.2**

^b No product was observed

^c 5 eqv of DMP was added

^d gave other products (See discussion)

^e used as solvent

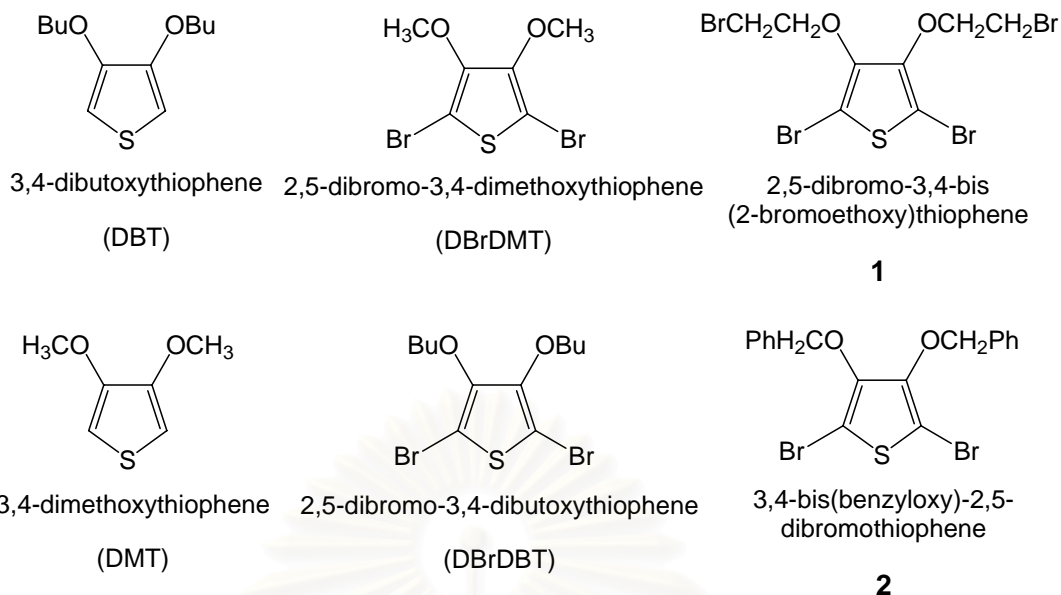
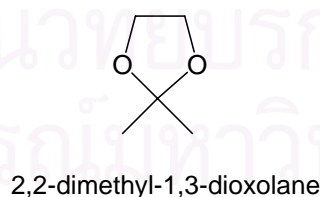


Figure 3.2 The expected product from the reactions in **Table 3.1**

However, there may still be a possibility that the reaction might have yielded more of the desired product by using a trapping agent to drive the equilibrium. In this study, 2,2-dimethoxypropane (DMP) was used for such purpose (**Table 3.1**, entry 7). It was expected that DMP is a potential ethylene glycol trapping agent. The result showed that the trapped product, 2,2-dimethyl-1,3-dioxolane (**3**), was obtained and confirmed by a $^1\text{H-NMR}$ spectrum (**Figure A-5**, Appendix A). However, this reaction did not give any desired product (DMT) as expected, Its absence may be due to the side reactions of DMP substituted at the α -positions of thiophene monomer. Thus, an α,α' -disubstituted thiophene derivative such as DBrEDOT was used as the substrate in place of EDOT for the similar ether exchange reactions.

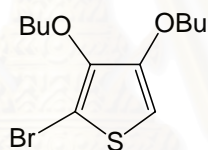


3

From **Table 3.1**, entry 8 showed that the isolated yield of the desired product (DBrDMT) synthesized from α,α' -disubstituted thiophene derivative, though still low, significantly increased (18.7%) in comparison to that from entry 6 (8.5%), which was obtained from ether exchange of thiophene derivative with no substituent at α -

positions. The product has been characterized by $^1\text{H-NMR}$ (**Figure A-8**, Appendix A) and $^{13}\text{C-NMR}$ (**Figure A-9**, Appendix A).

The result suggested that the incorporation of bromo substituents at α -positions on the thiophene unit could help avoid the possible side reactions at these positions. The same condition in entry 1 (**Table 3.1**) was repeated in entry 9 using DBrEDOT as well. However, entry 9 gave the desired product (DBrDBT) (10.2%) in much lower yield than entry 1 (42.5%). It was first assumed that debromination of 2,5-dibromothiophene derivative may competitively occur at high reflux temperature. In fact, these debrominated by-products were obtained. From $^1\text{H-NMR}$, the first by-product was characterized as monobrominated product 2-bromo-3,4-dibutoxythiophene (**4**), with the characteristic signals of a α -hydrogen at 6.11 ppm (**Figure A-15**, Appendix A). The second by-product was the fully debrominated product (3,4-dibutoxythiophene) with its $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra matching those obtained from entries 1-3 and 5.

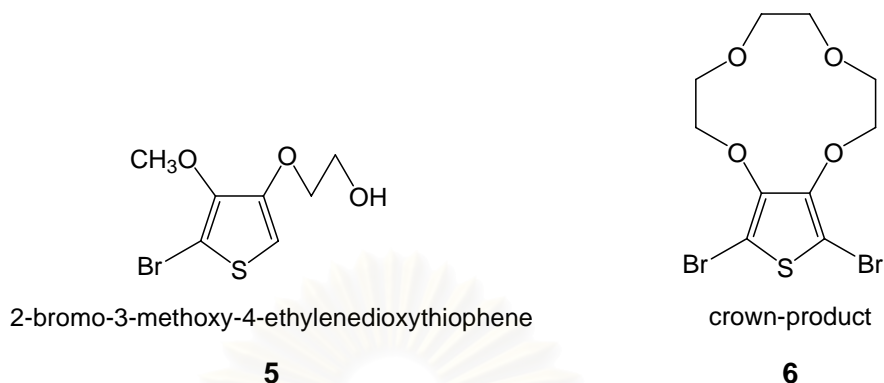


2-bromo-3,4-dibutoxythiophene

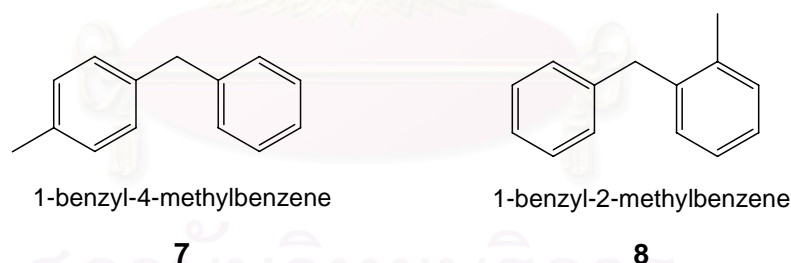
4

In entry 10, bromoethanol was used as the reagent and methanol as the solvent. The reaction did not yield the expected product 2,5-dibromo-3,4-bis(2-bromoethoxy)thiophene (**1**) (**Figure 3.2**). Two other products were identified. The first product was 2-bromo-3-methoxy-4-ethylenedioxythiophene (**5**) (8.3%) according to its $^1\text{H-NMR}$ spectrum (**Figure A-17**, Appendix A) and $^{13}\text{C-NMR}$ spectrum (**Figure A-18**, Appendix A). The compound could arise from the competitive reaction with the solvent methanol together with partial debromination. The second product was characterized to be the cyclic crown-product (**6**). $^1\text{H-NMR}$ spectrum (**Figure A-19**, Appendix A). $^{13}\text{C-NMR}$ spectrum (**Figure A-20**, Appendix A) and mass spectrum (**Figure A-21**, Appendix A) confirmed the structure. Further substitutions replacing the bromine atoms of the desired product 2,3-dibromo-3,4-bis(2-bromoethoxy)thiophene were presumed to take place to form **6** (29.0%). In entry 11, the reaction

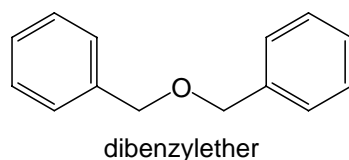
followed the similar procedure as in entry 10 except using bromoethanol as solvent as well. The result showed that **6** was the only product obtained (66.3%).



From **Table 3.1**, entry 12 and 13 used benzyl alcohol as the reagent with and without toluene as the solvent respectively. Entry 12 did not give the desired product 3,4-bis(benzyloxy)-2,5-dibromothiophene (**2**) (**Figure 3.2**) but instead gave two other by-products. The first by-product was identified to be 1-benzyl-4-methylbenzene (**7**) from $^1\text{H-NMR}$ spectrum (**Figure A-22**, Appendix A). The second by-product was 1-benzyl-2-methylbenzene (**8**) from $^1\text{H-NMR}$ spectrum (**Figure A-23**, Appendix A). Both by-products could occur from electrophilic aromatic substitution of toluene by benzyl cation generated from benzyl alcohol and acid at high temperature.



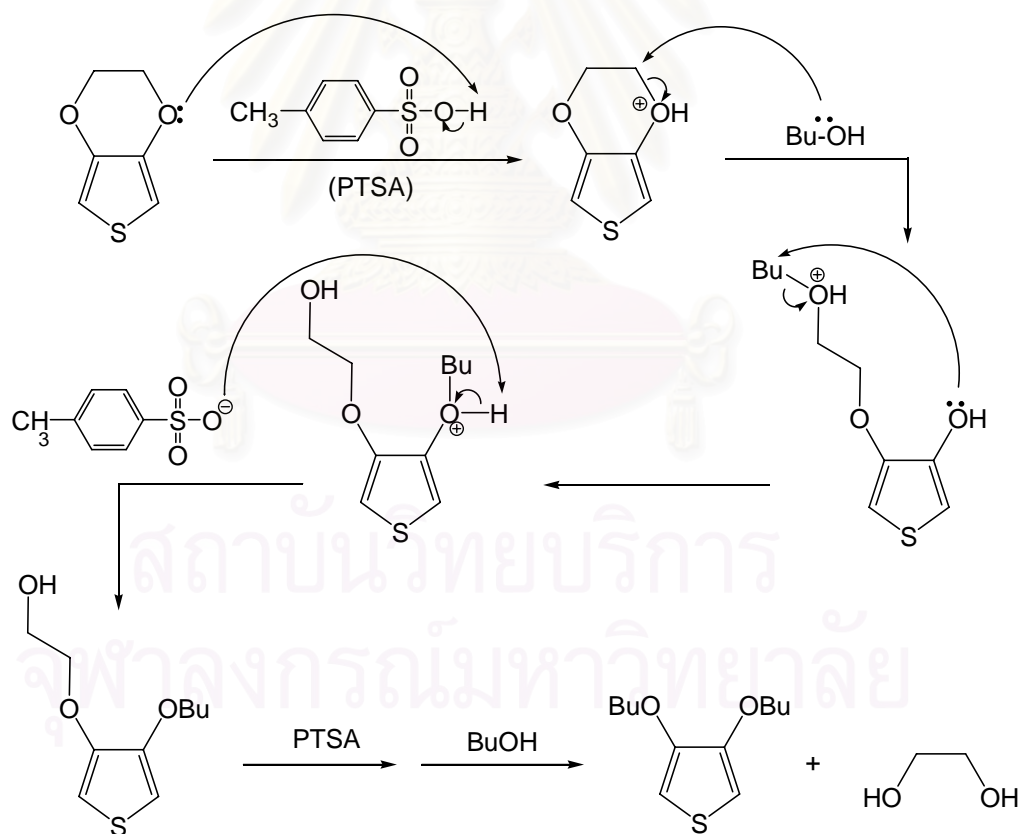
Entry 13 used benzyl alcohol also as the solvent instead of toluene. The desired product (3,4-bis(benzyloxy)-2,5-dibromothiophene (**2**) (**Figure 3.2**) was not yet obtained but the reaction gave another unexpected product. Its $^1\text{H-NMR}$ spectrum (**Figure A-24**, Appendix A) and $^{13}\text{C-NMR}$ spectrum (**Figure A-25**, Appendix A) identified the product to be dibenzylether (**9**), the usual product generally obtained from acid-catalyzed condensation of benzyl alcohol. From these results, it could be concluded that benzyl alcohol is definitely not a suitable reagent because it could react with other aromatic compounds or itself before reacting with our substrate in ether exchange reaction.

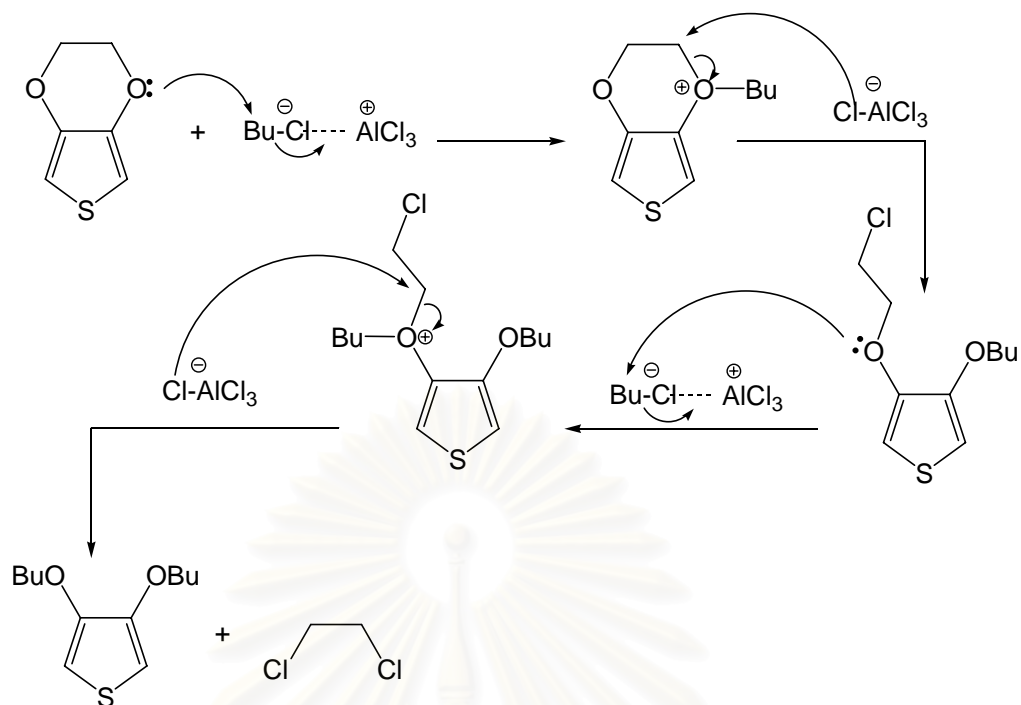


9

The unsuccessful exchange in entry 6 indicated that DMT could be used as the more effective substrate than EDOT. Consequently, the same condition in entry 1 was repeated with DMT in place of EDOT (entry 14). The result showed that the desired product (DBT) was obtained in good yield (85.7%), supporting the indication above.

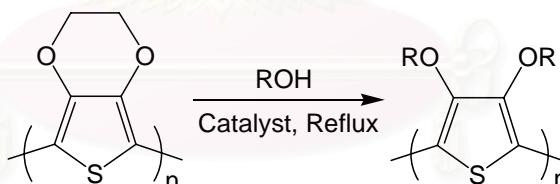
The mechanism of the ether exchange reaction of thiophene derivatives by either (a) *p*-toluenesulfonic acid (PTSA) and alcohol or (b) anhydrous aluminium chloride (AlCl_3) and butyl chloride were proposed as shown in **Scheme 3.1** and **3.2** respectively.





Scheme 3.2 Mechanism of thiophene derivatives upon ether exchange by anhydrous aluminium chloride (AlCl_3) and butyl chloride.

3.2 Synthesis of poly(3,4-dialkoxythiophene) derivatives



The synthesis of poly(3,4-dialkoxythiophene) derivative by ether exchange of PEDOT using various acid catalysts and alcohols as the reagent and solvent are shown in **Table 3.2**.

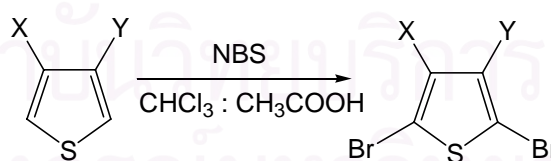
In entry 1, the reaction was quenched and purified after 3 days. It did not give the expected polymer (PDBT). Instead, the butyl *p*-toluenesulfonate ester was obtained as the major product, presumably from the usual esterification of the organic acid and the alcohol reagent. This result indicated that organic acids (such as PTSA and MSA) could not be used in the long refluxing reaction, in which the esterification would become competitive.

Table 3.2 Ether exchange of poly(3,4-ethylenedioxythiophene).

Entry	Reagent	Acid catalyst	Condition
1	<i>n</i> -butanol	PTSA	Reflux, 3 days
2	<i>n</i> -butanol	conc. H ₂ SO ₄	Reflux, 12 days
3	<i>n</i> -butanol	conc. HCl	Reflux, 14 days
4	methanol	conc. HCl	Reflux, 14 days

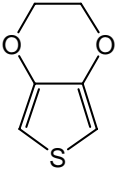
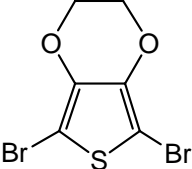
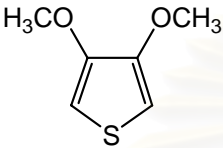
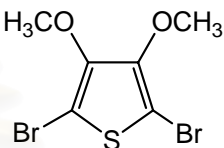
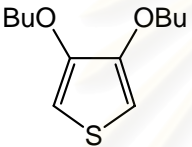
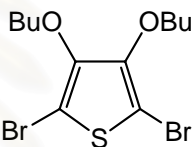
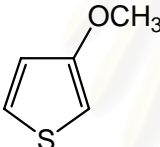
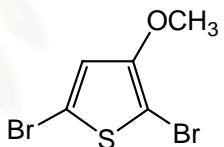
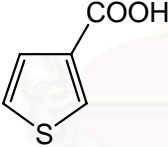
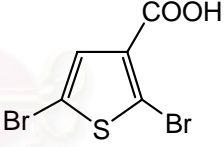
In entries 2-4, inorganic acids (conc. H₂SO₄ and HCl) were used as the catalyst in place of organic acid (PTSA). When each reaction was quenched, the remaining insoluble polymer was filtered and characterized by IR. Unfortunately, their IR spectra were identical to that of the substrate (PEDOT). The filtrate that was characterized by ¹H-NMR, did not give any signals expected from the potential soluble polymer. The result showed that the ether exchange reaction of PEDOT was not successful. The heterogeneous nature of the substrate and inefficiency of the catalyst may be the reasons for the unusually long reaction time without yet any success.

3.3 Bromination of thiophene derivatives

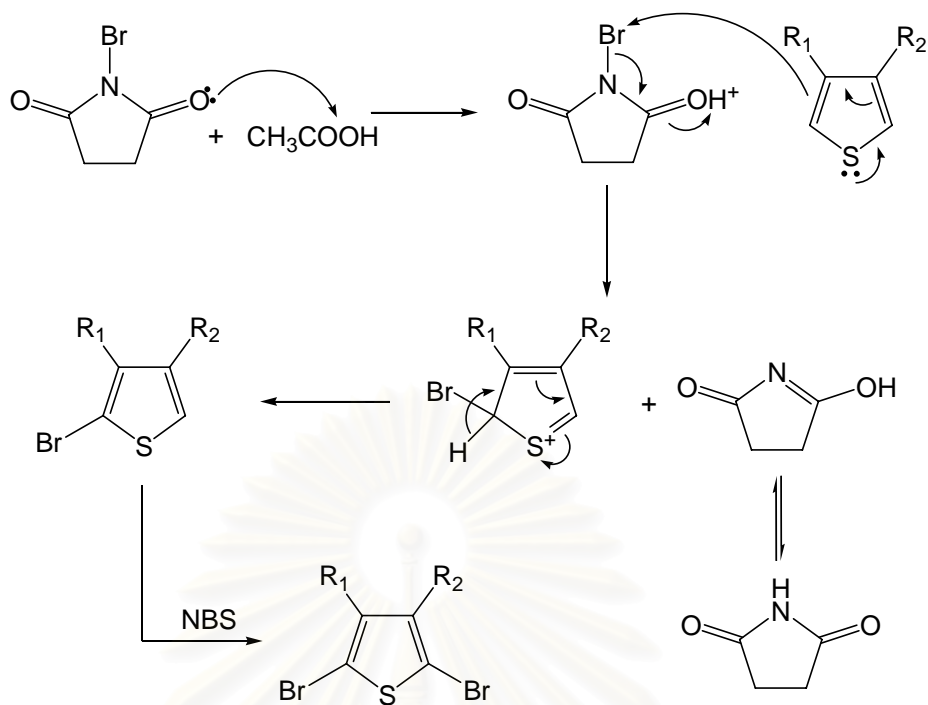


Bromination of thiophene derivatives using *N*-bromosuccinimide (NBS) was adapted from the method by Kellogg and coworkers [35], which reported by yielded relatively pure 2,5-dibromothiophene in about 60 % yield from simple thiophene. The synthesis of other 2,5-dibromothiophene derivatives in this work using *N*-bromosuccinimide (NBS) was found to give varied percent yields depending on the β -substituents on the thiophene ring used as shown in **Table 3.3**.

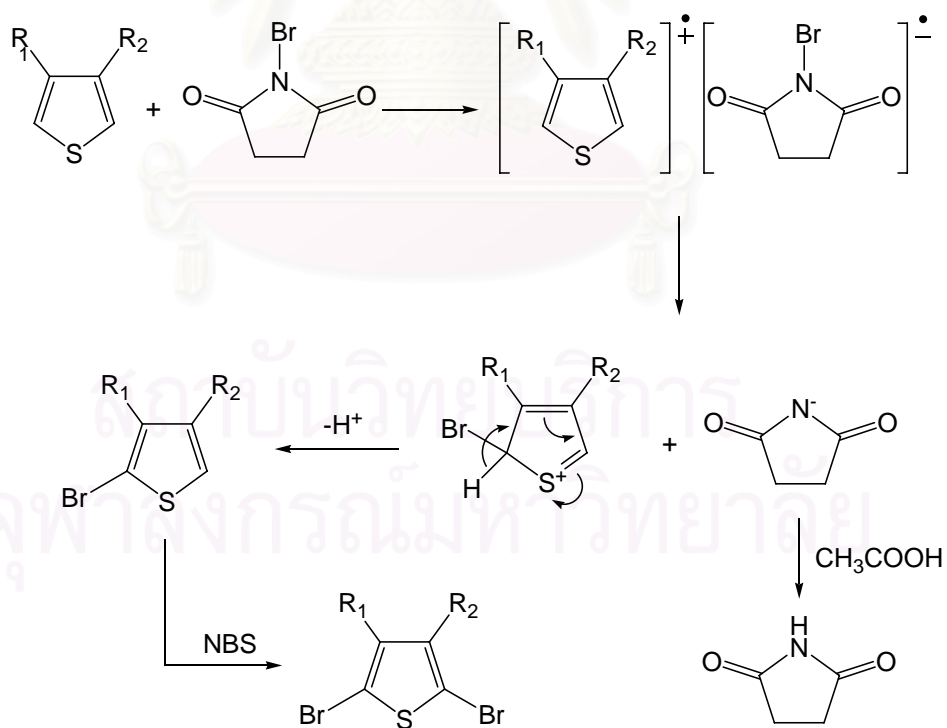
Table 3.3 Synthesis of 2,5-dibromothiophene derivatives

Entry	Thiophene derivative	Condition	Product	% yield
1		RT, 5 h 30 min		65.7
2		RT, 4 h		76.1
3		RT, 6 h		32.6
4		RT, 5 h 30 min		26.3
5		50 °C, 4 h		30.1

The mechanisms of the bromination on thiophene ring are proposed into 2 possible pathways (**Scheme 3.3 and 3.4**) [35,36]. First and more likely mechanism in such polar solvent is the acid-catalyzed electrophilic aromatic substitution (**Scheme 3.3**). Another possible pathway is the radical-based single electron transfer followed by aromatic substitution (**Scheme 3.4**).

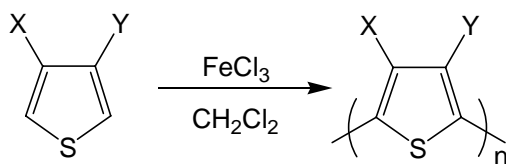


Scheme 3.3 Bromination mechanism through electrophilic aromatic substitution.



Scheme 3.4 Bromination mechanism through radical-based single electron transfer followed by aromatic substitution.

3.4 Polymerization by oxidative coupling



The synthesis of polythiophene derivatives by oxidative coupling polymerization using anhydrous ferric chloride was adapted from that reported by Tepveera [5]. It gave polythiophene derivatives in relatively good percent yields as shown in **Table 3.4**.

Table 3.4 Polymerization of thiophene derivatives by oxidative coupling

Entry	Polymer	%yield	λ_{\max} (nm)		M_n
			solid state	solution	
1		92.3	548	- ^a	- ^a
2		61.8	639	423 ^b	2795 ^b
3		62.2	456	462	4296
4		77.0	- ^c	573 ^b	464 ^b

^a polymer is insoluble in organic solvent

^b measured from the partially soluble fraction

^c no apparent value

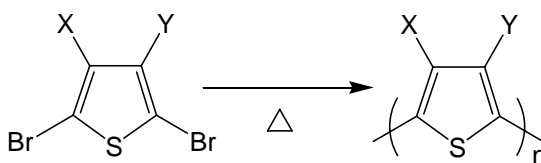
Oxidative coupling polymerization of EDOT gave an insoluble dark blue solid in 92.3%. It was analyzed by IR spectroscopy that gave the spectrum which was consistent with the literature [31]. The optical properties of PEDOT was also analyzed by UV-Vis spectroscopy. Its solid state powder showed the maximum of absorption at 548 nm, also well corresponds to the reported value [31].

From **Table 3.4** entry 2, PDTM was obtained as a dark blue solid in 61.8%. The $^1\text{H-NMR}$ spectrum of the partially soluble fraction showed the characteristic signal of the hydrogens of the methoxy groups at 3.95 ppm (**Figure A-26**, Appendix A). The solid powder showed the maximum of absorption at 639 nm while only at 423 nm was observed for the part that soluble in dichloromethane solution (**Figure A-30**, Appendix A). The molecular weight of the soluble part of poly(3,4-dimethoxythiophene); PDTM was approximately 2795, containing 19 monomer units on average.

In entry 3, PDTB was obtained as a red-brown solid 62.2%. Maximum of absorption of PDTB in the solid state occurs at slightly shorter wavelength (456 nm) than in solution (462 nm) (**Figure A-31**, Appendix A) which might be the result from more steric interactions among the long-chain substituents and the polymer backbone, disfavoring the coplanar conformation and consequently, reducing the effective conjugation length (ECL). Its molecular weight was approximately 4296 measured by GPC, which showed that this soluble product roughly contained 19 monomer units.

In entry 4, PMT was obtained as a dark blue solid in 77.0%. The polymer was scarcely soluble in dichloromethane. This small soluble fraction showed the relatively long wavelength of maximum of absorption at 573 nm (**Figure A-32**, Appendix A) despite the low molecular weight was approximately 464 measured by GPC, corresponding to only about 4 monomer units. The absence of one β -substituent may dramatically reduce the steric repulsion between adjacent units and allow more coplanarity in the polymer chain.

3.5 Polymerization by solid state polymerization (SSP)



The synthesis of polythiophene derivatives by solid state polymerization (SSP) adapted from the method used by Meng and coworkers [31]. The solid state polymerization was suggested to spontaneously occur and give doped polymer by simple heating of dibromo derivatives of EDOT monomer. The stacking, congested structure of DBrEDOT in the crystal with close halogen-halogen contacts forced the debromination with in situ solid state polymerization of these compounds.

In this work, PEDOT was obtained as an insoluble dark blue crystal by incubation of colorless crystalline DBrEDOT at 80 °C for 4 h or at ambient temperature for 3 days. During the reaction, a significant amount of red-brown bromine vapor appeared over the crystal pad.

When DBrDMT was used as the monomer in place of DBrEDOT, no physical change was observed with the similar reaction conditions used to obtain PEDOT. In this case, DBrDMT may not pack close enough to induce solid state polymerization in the same way. This observation suggested that such a special mode of polymerization may be considered as a specific case for the polymerization of DBrEDOT to PEDOT.

3.6 Conductivity measurement

The solid surface conductivity of the synthesized conductive polymers, both in neutral or doped states (with I₂ vapor), were measured by the four-point probe technique [37-39] (**Appendix B**). The polymers were pressed into pellets before the conductivity measurements except PDBT, which was cast as a film on glass slides. Doped polymer was prepared by placing in an iodine chamber for 24 h, and its conductive property was measured immediately after being taken out of the container.

Table 3.5 Conductivity of the polythiophene derivatives in neutral and I₂ doped state

Entry	Polymer ^a	States	Resistance (R), Ω	Conductivity (σ), S.cm ⁻¹
1	PEDOT	neutral	2.56	4.31
2	PEDOT	doped	6.48 x 10 ⁻¹	17.03
3	SSP-PEDOT ^b	neutral	1.51	7.32
4	SSP-PEDOT ^b	doped	2.30 x 10 ⁻¹	47.89
5	PDBT	neutral	3.75 x 10 ⁸	2.94 x 10 ⁻⁸
6	PDBT	doped	3.33 x 10 ⁶	3.31 x 10 ⁻⁶
7	PDMT	neutral	1.55 x 10 ⁸	7.12 x 10 ⁻⁸
8	PDMT	doped	9.81 x 10 ³	1.12 x 10 ⁻³
9	PMT	neutral	6.66 x 10 ⁷	1.66 x 10 ⁻⁷
10	PMT	doped	1.71 x 10 ⁴	6.45 x 10 ⁻⁴

^a synthesized by chemical polymerization

^b synthesized by solid state polymerization

From **Table 3.5**, the conductivity of PEDOT from SSP (entry 3) was greater than PEDOT, from oxidative coupling polymerization (entry 1) in both neutral and doped states. This corresponds well to the original report on the methodology that the polymer synthesized from solid state polymerization tends to have better conductivity than other methods of polymerization [30,31]. Higher molecular weight due to limited side reactions and polymer degradation and higher degree of order within crystal were suggested to be the reasons for the better conductive property.

In other entries, the lowest conductivity belong to PDBT (entry 6), reflecting the highest steric interactions of the bulky substituents among the derivatives tested, which lead to less coplanar conformation, thereby reducing the electrical conductivity. The irregular chemical structure arose from some α,β -couplings in PMT probably introduced the defects in the polymer chain and hence decreased its conductivity, similarly to the case of polymers from other monosubstituted thiophene monomers such as 3-alkylthiophene [40].



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CHAPTER IV

CONCLUSION

3,4-Dialkoxythiophene derivatives have been successfully prepared by ether exchange of 3,4-ethylenedioxythiophene (EDOT) or 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) using appropriate alcohol and acid catalysts. The best acid catalysts to obtain the highest % yield was *p*-toluenesulfonic acid (PTSA). The poor leaving ethylene glycol moiety was the first possible reason for the low yield in the ether exchange probably because the equilibrium favoured the reactant. The second important reason could be due to other side reactions at the empty α -positions on the thiophene ring.

The ether exchange of poly(3,4-ethylenedioxythiophene) was not successful. The heterogeneous nature of the reaction may need an even longer time to achieve the synthesis.

Five derivatives of 2,5-dibromothiophene have been successfully synthesized using NBS in acetic acid and chloroform solution. The ether exchange of some derivatives at high reflux temperature was found to cause the partial debromination of these derivatives.

Poly(3,4-alkoxythiophene) and poly(3-methoxythiophene) have been successfully prepared by oxidative coupling polymerization of 3,4-dialkoxythiophene or 3-methoxythiophene monomers with anhydrous ferric chloride. The solid state polymerization (SSP) was successfully carried out with 2,5-dibromo-3,4-ethylenedioxythiophene (DBrEDOT) leading to poly(3,4-ethylenedioxythiophene), while all attempts with 2,5-dibromo-3,4-dimethoxythiophene were failed. This solid state polymerization (SSP) methodology might be a rather specific case for PEDOT.

From the Four-point probe conductivity measurements, the polymer synthesized from solid state polymerization exhibited better conductivity than those from oxidative coupling polymerization, possibly due to limited side reactions and polymer degradation, and better order of the polymer structure. While the steric interactions among bulky substituents could lead to reduction of the conductivity.

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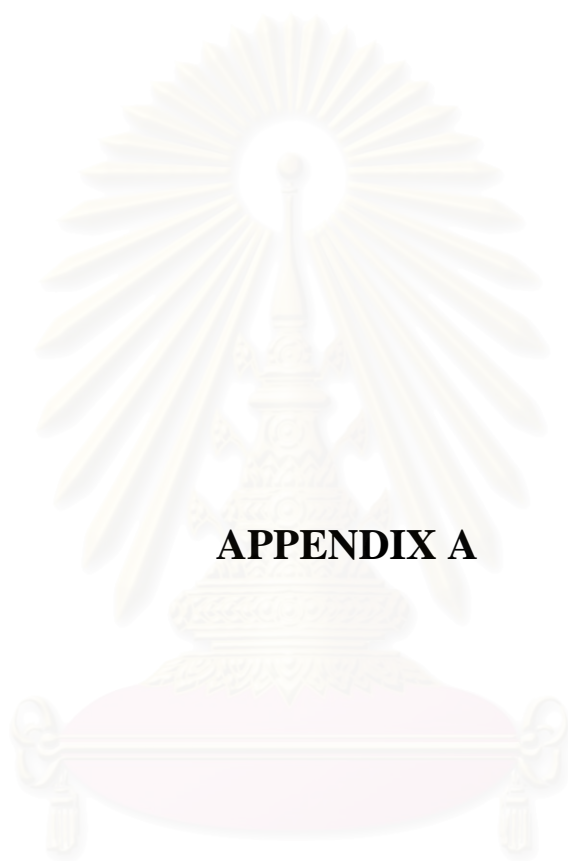
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APPENDICES

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APPENDIX A

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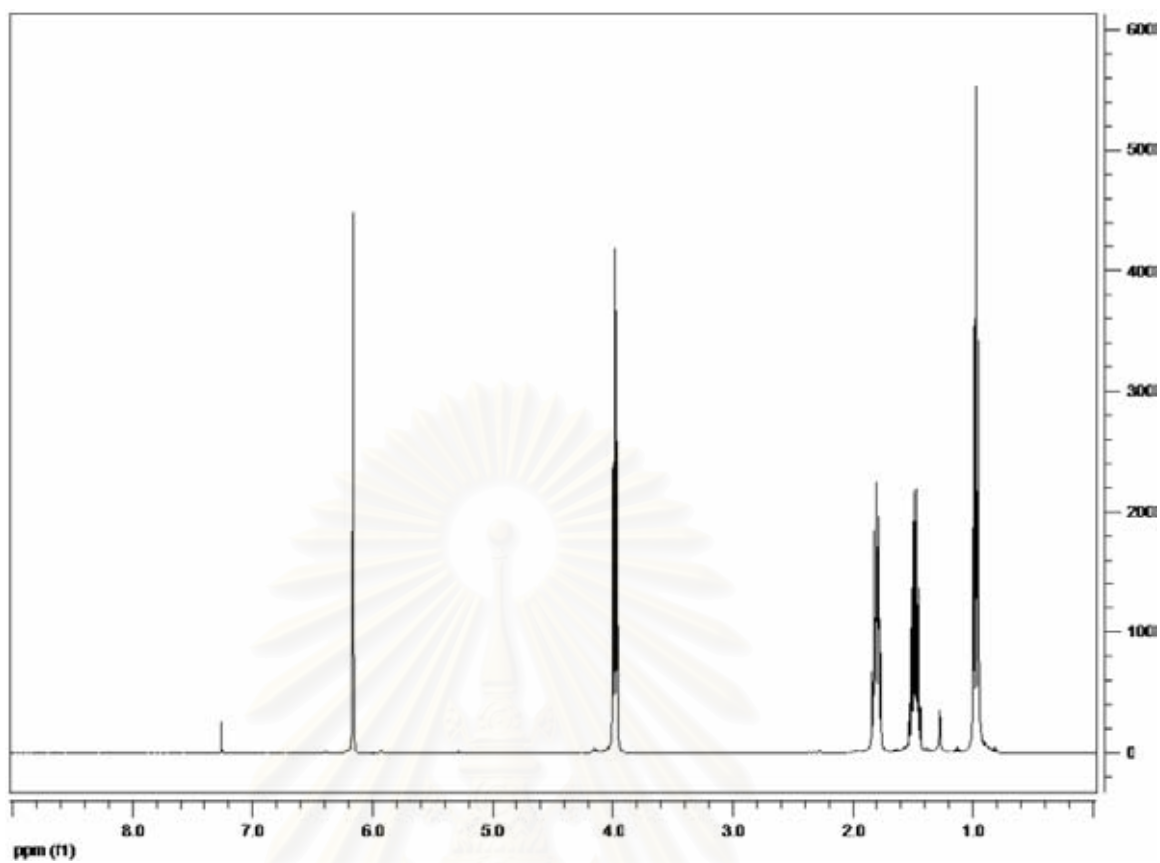


Figure A-1 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 3,4-dibutoxythiophene

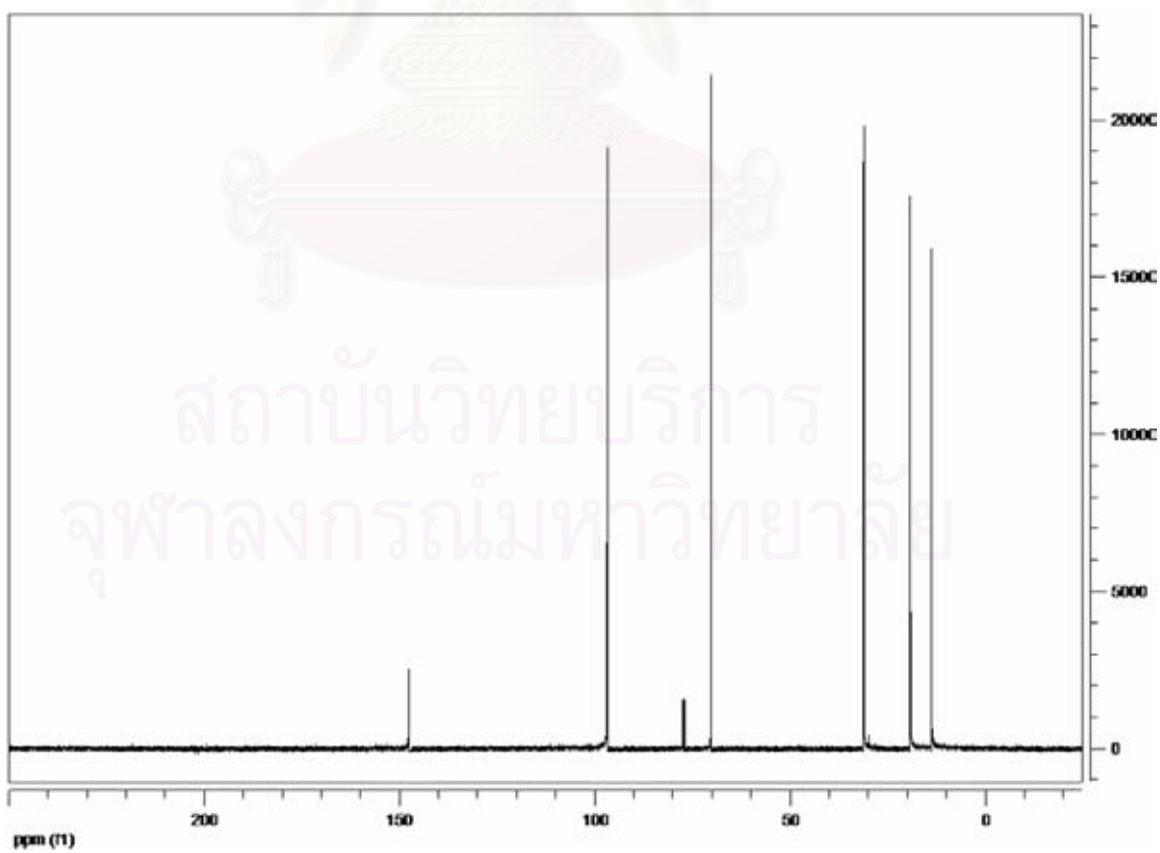


Figure A-2 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 3,4-dibutoxythiophene

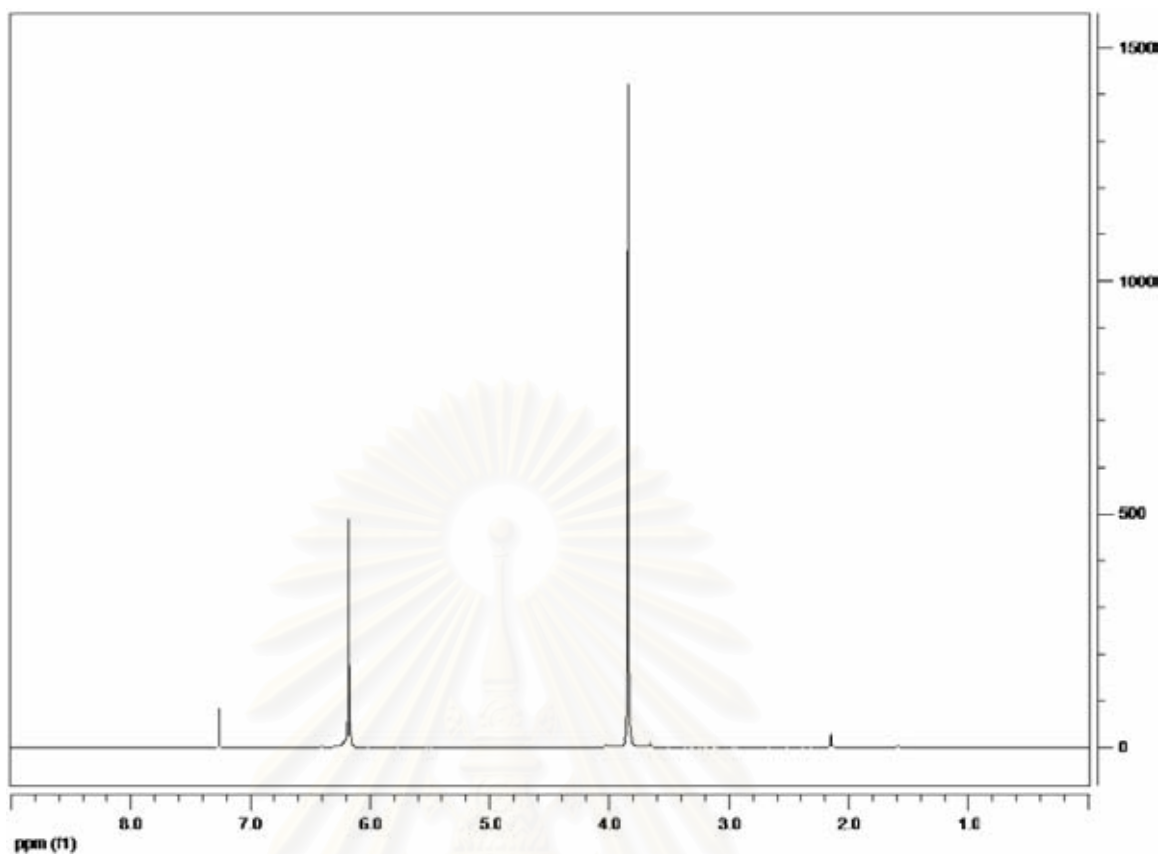


Figure A-3 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 3,4-dimethoxythiophene

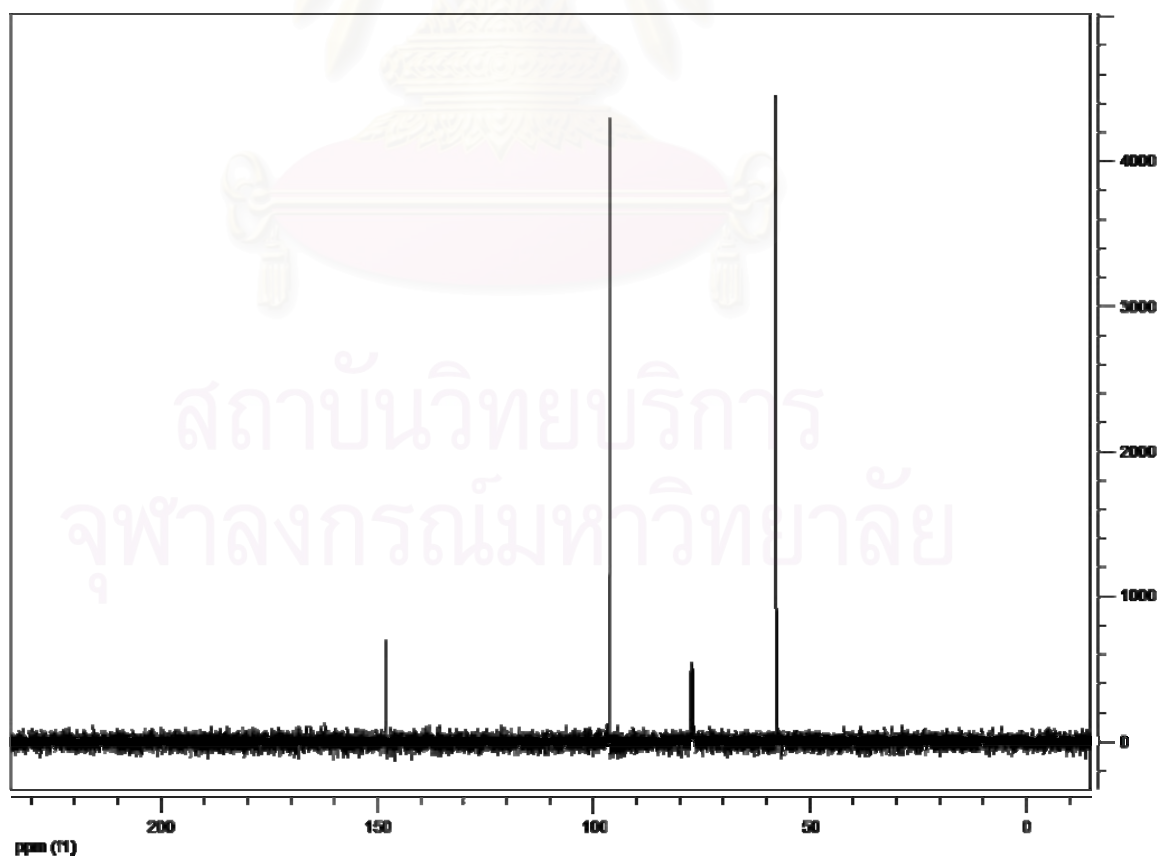


Figure A-4 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 3,4-dimethoxythiophene

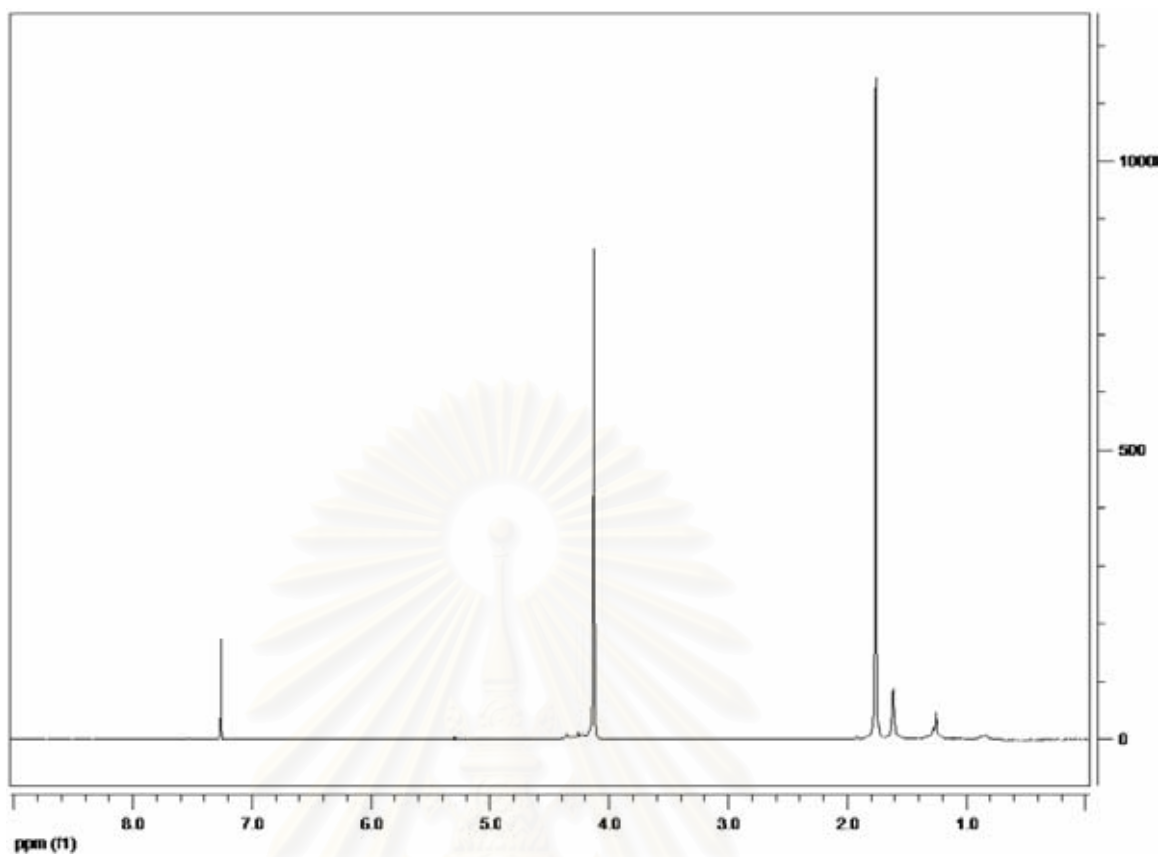


Figure A-5 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,2-dimethyl-1,3-dioxolane

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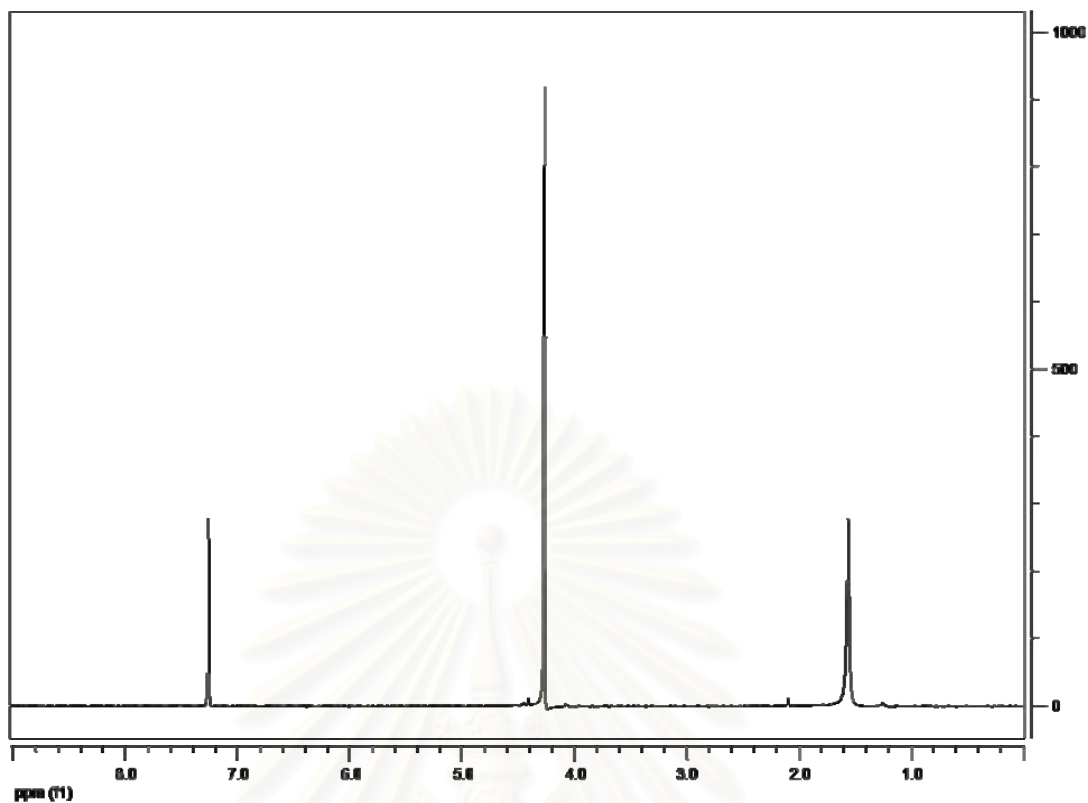


Figure A-6 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-ethylenedioxythiophene

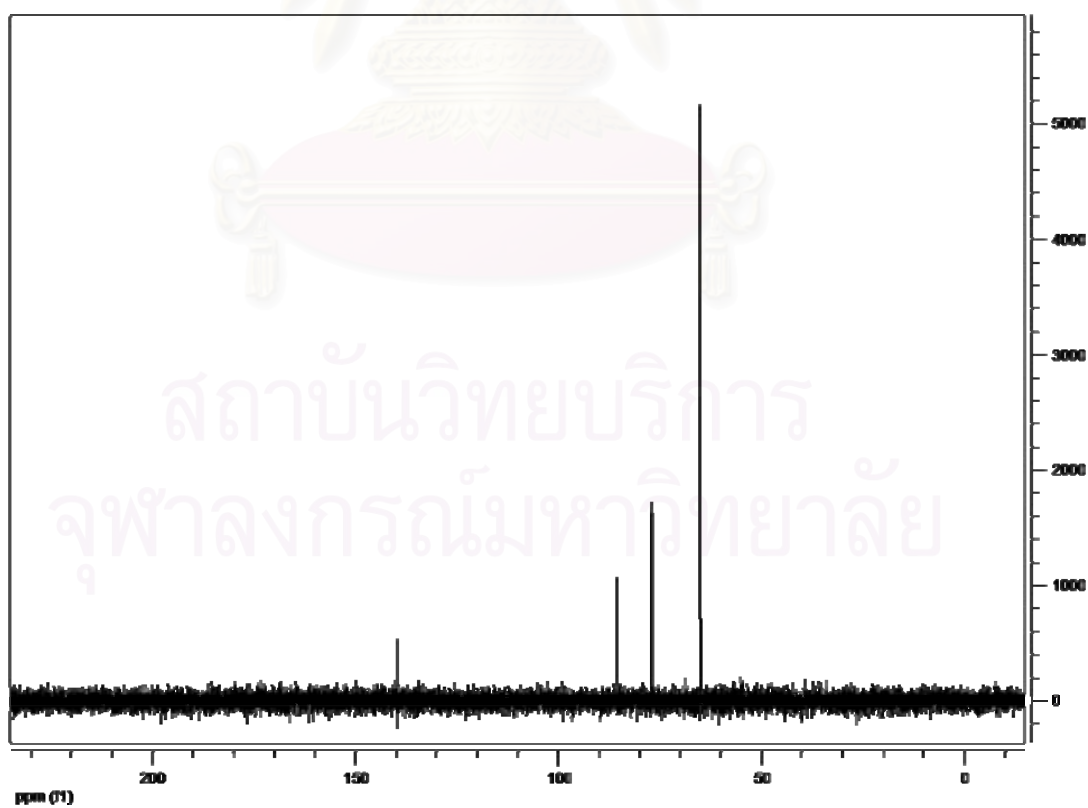


Figure A-7 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-ethylenedioxythiophene

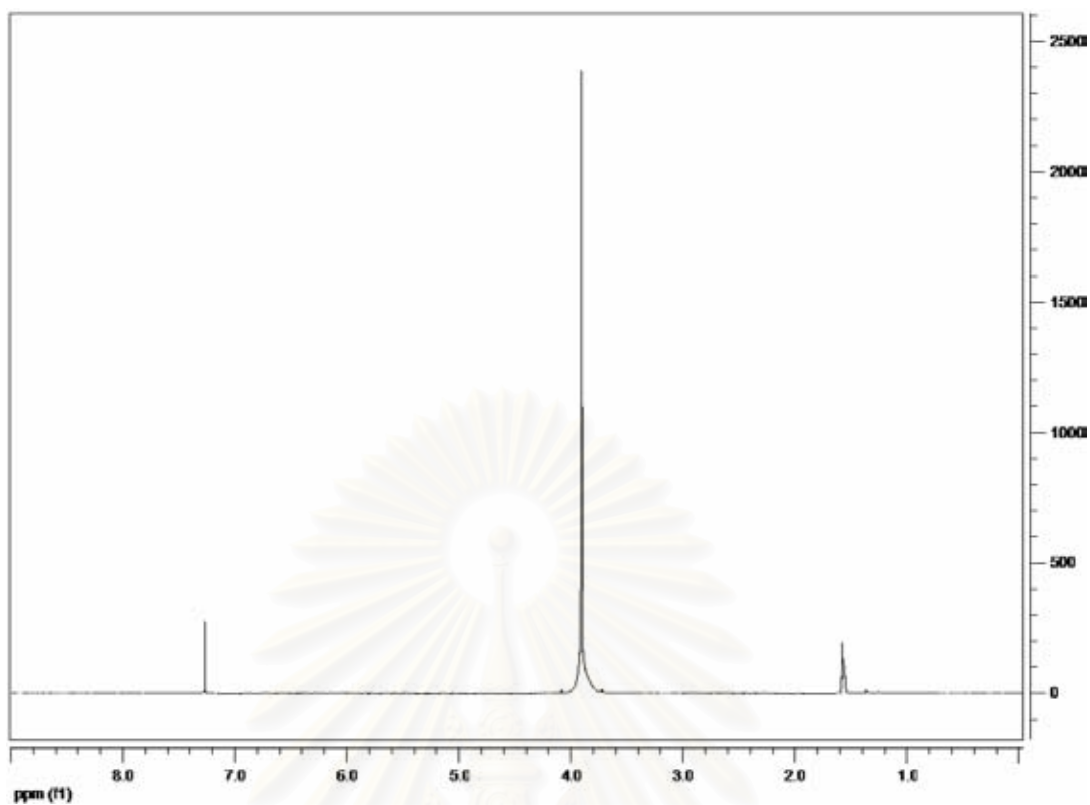


Figure A-8 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-dimethoxythiophene

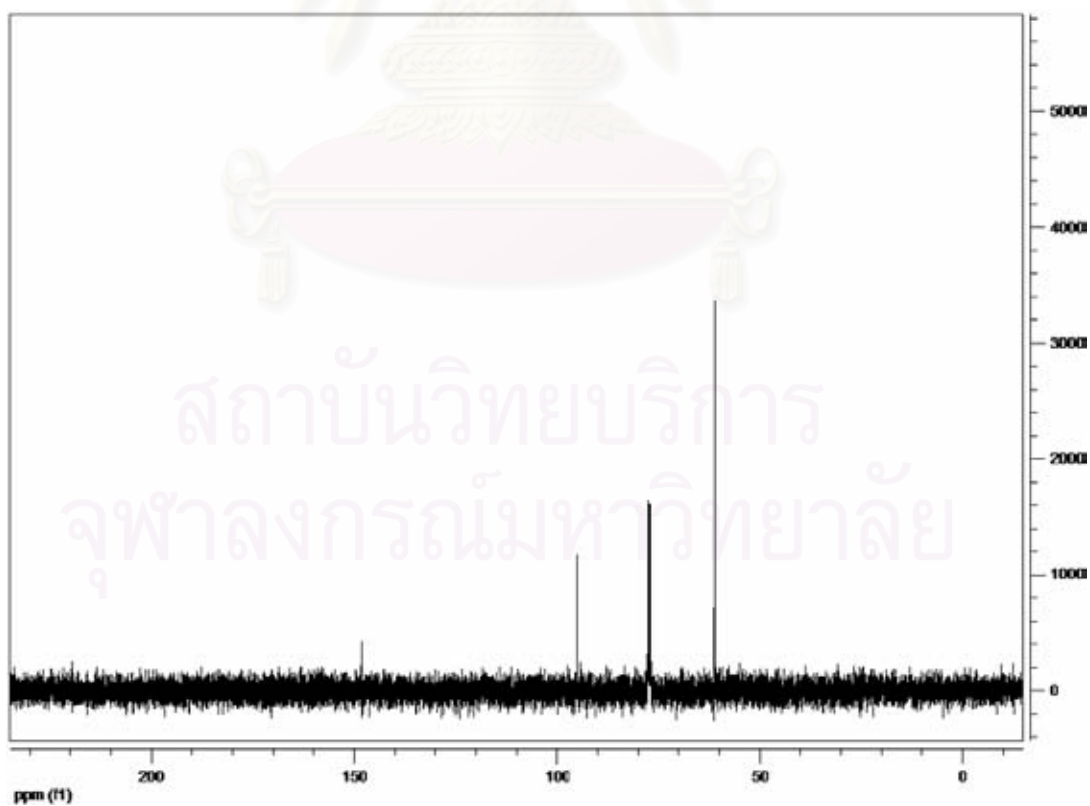


Figure A-9 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-dimethoxythiophene

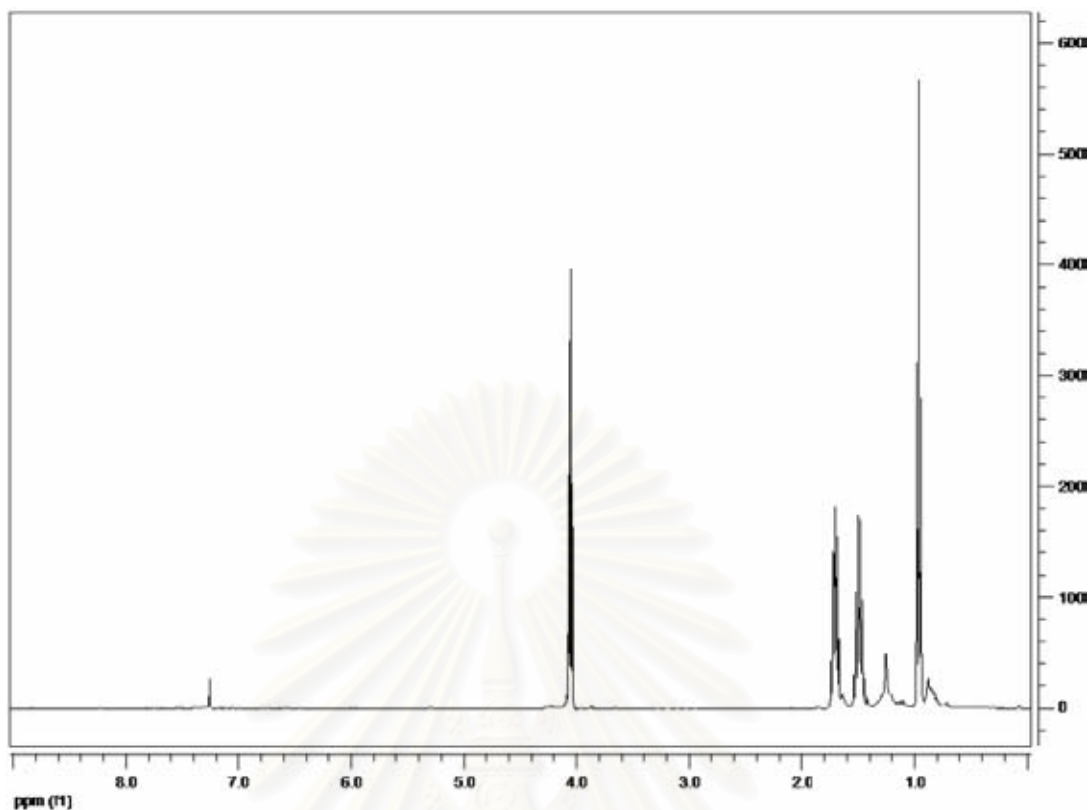


Figure A-10 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-dibutoxythiophene

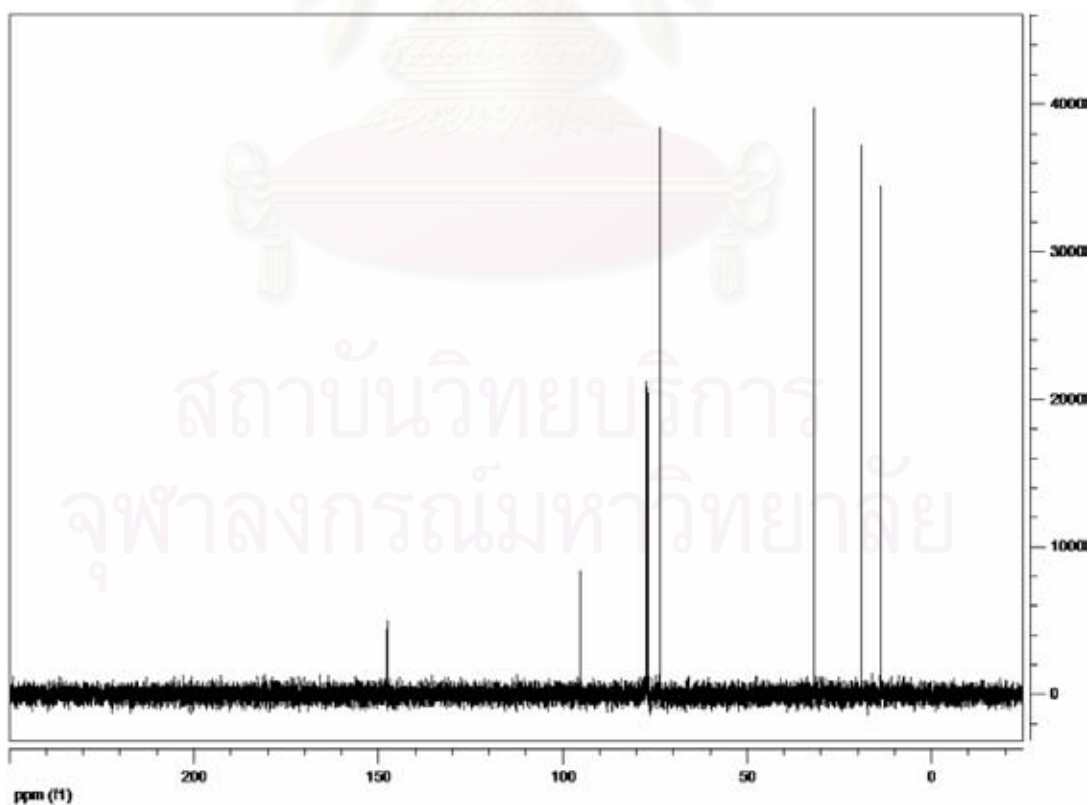


Figure A-11 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3,4-dibutoxythiophene

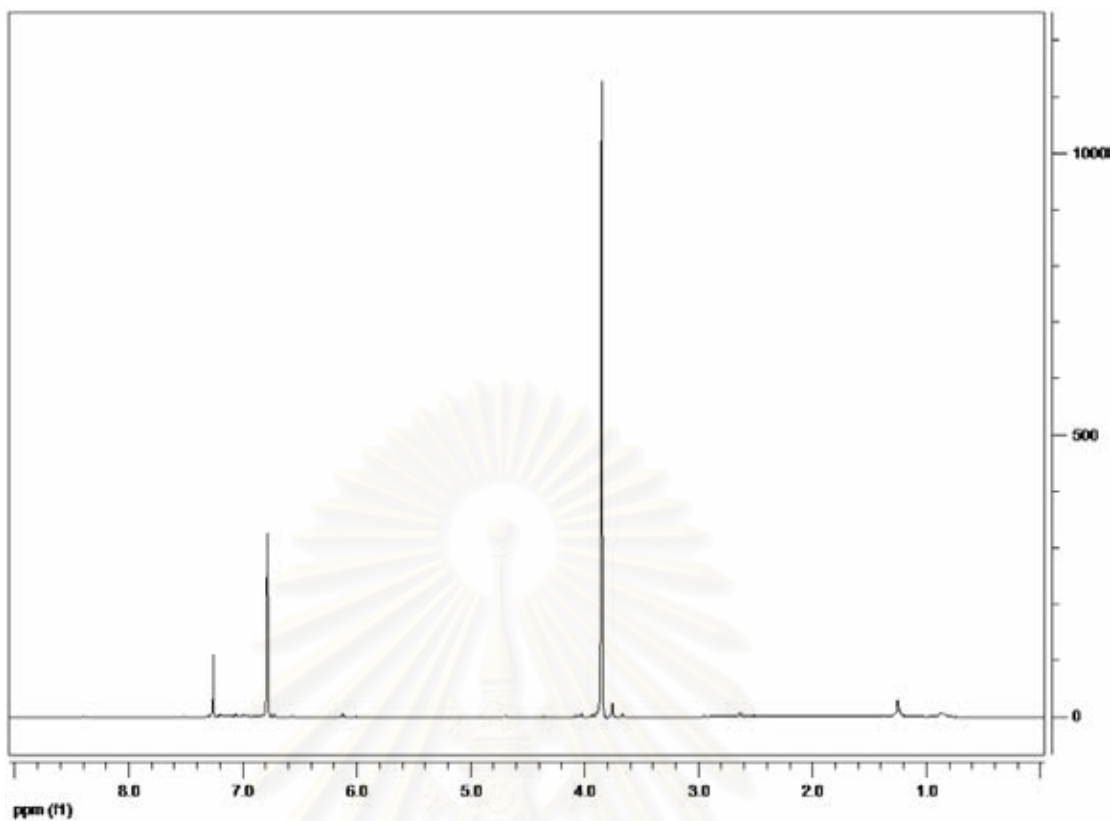


Figure A-12 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3-methoxythiophene

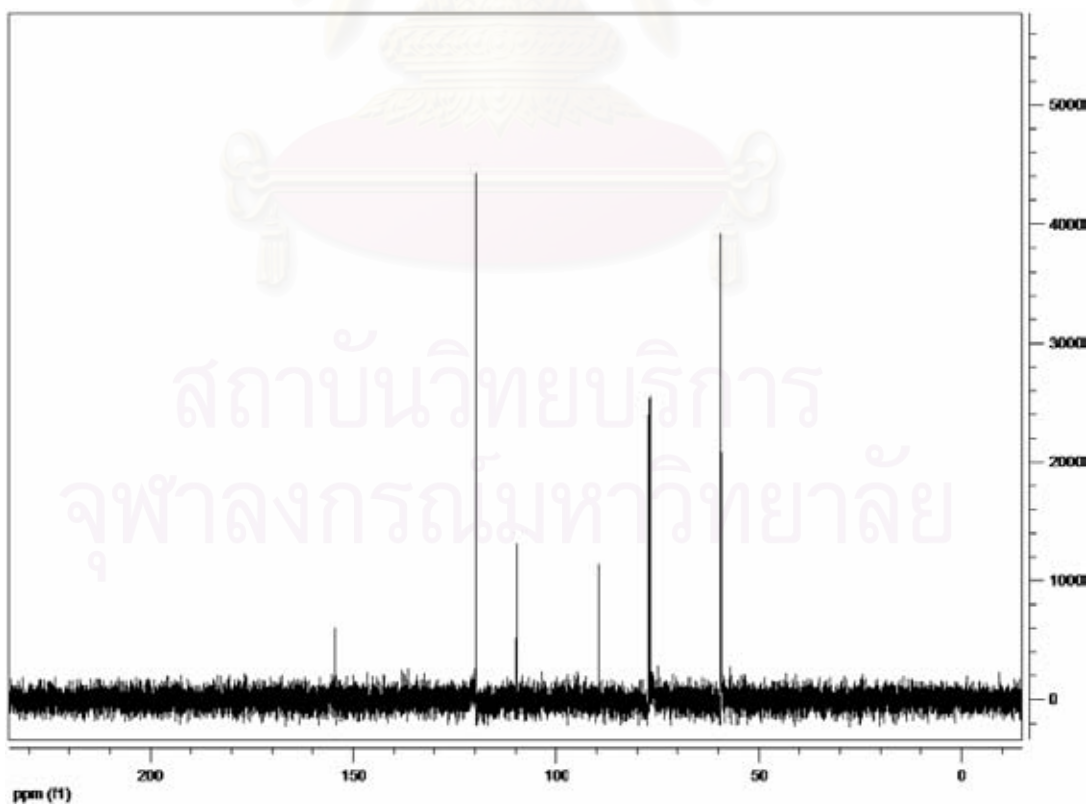


Figure A-13 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromo-3-methoxythiophene

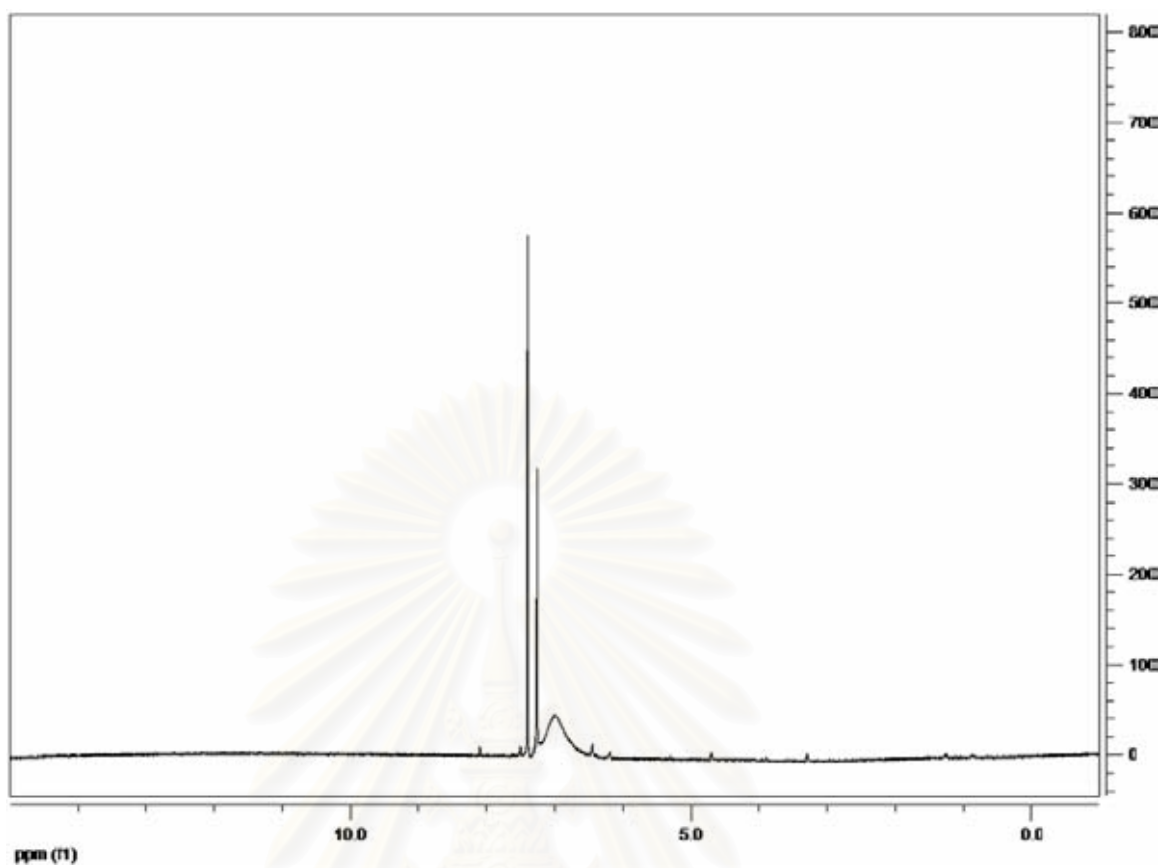


Figure A-14 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2,5-dibromothiophene-3-carboxylic acid

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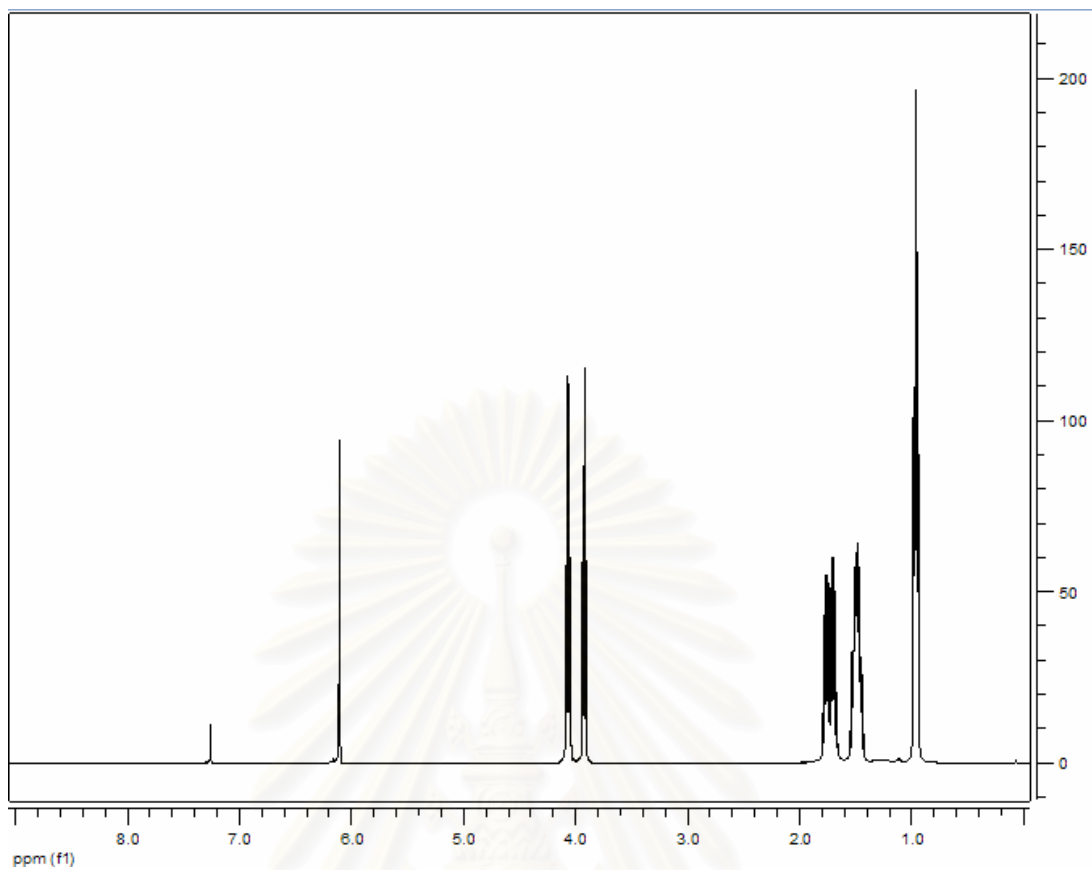


Figure A-15 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) 2-bromo-3,4-dibutoxythiophene

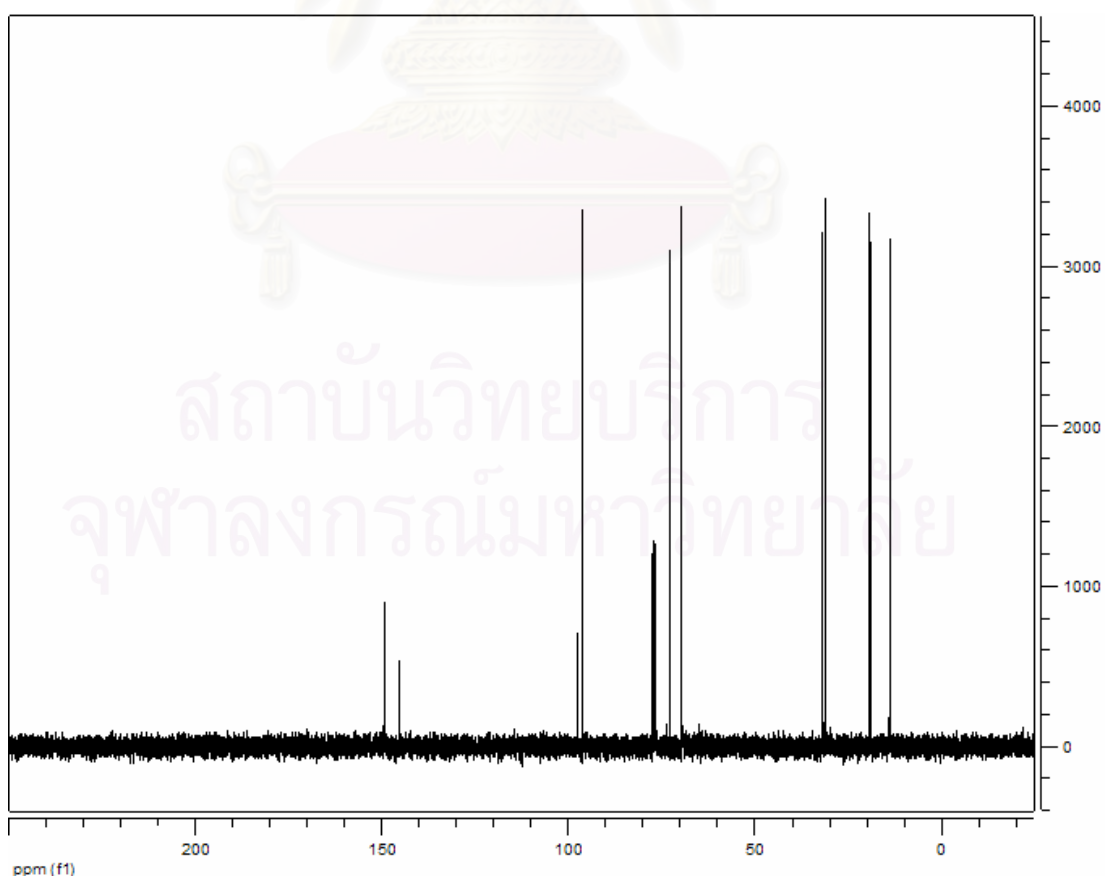


Figure A-16 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2-bromo-3,4-dibutoxythiophene

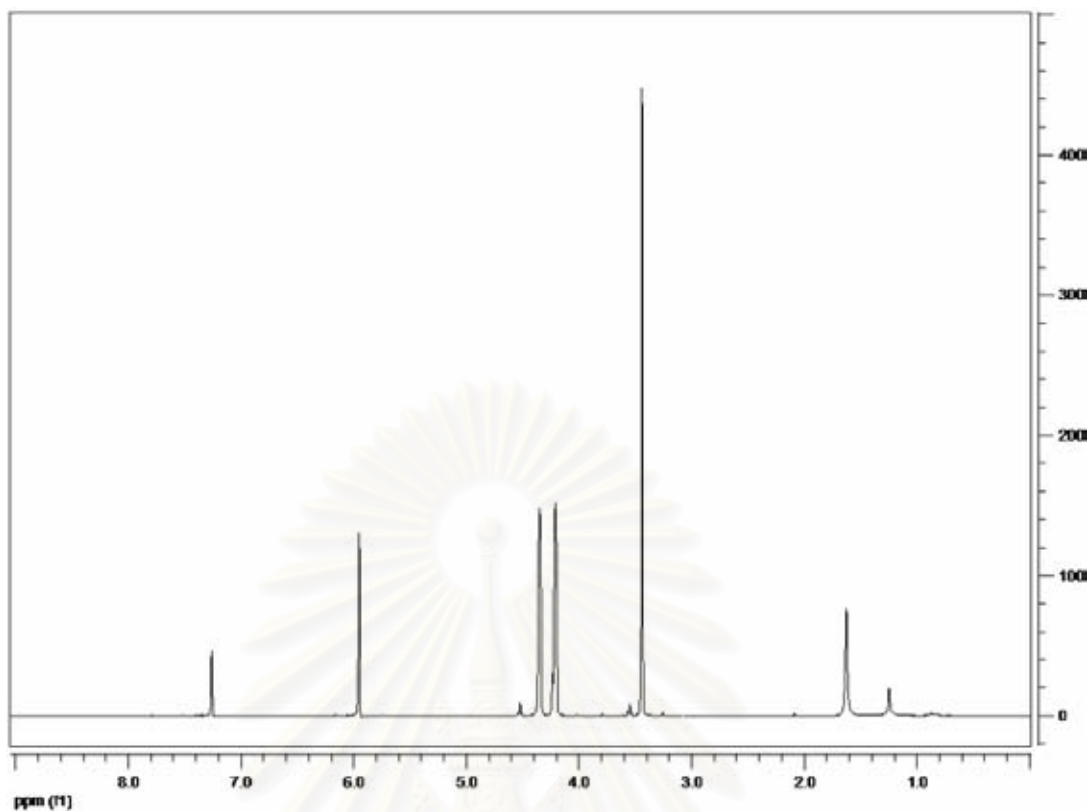


Figure A-17 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 2-bromo-3-methoxy-4-ethylenedioxythiophene

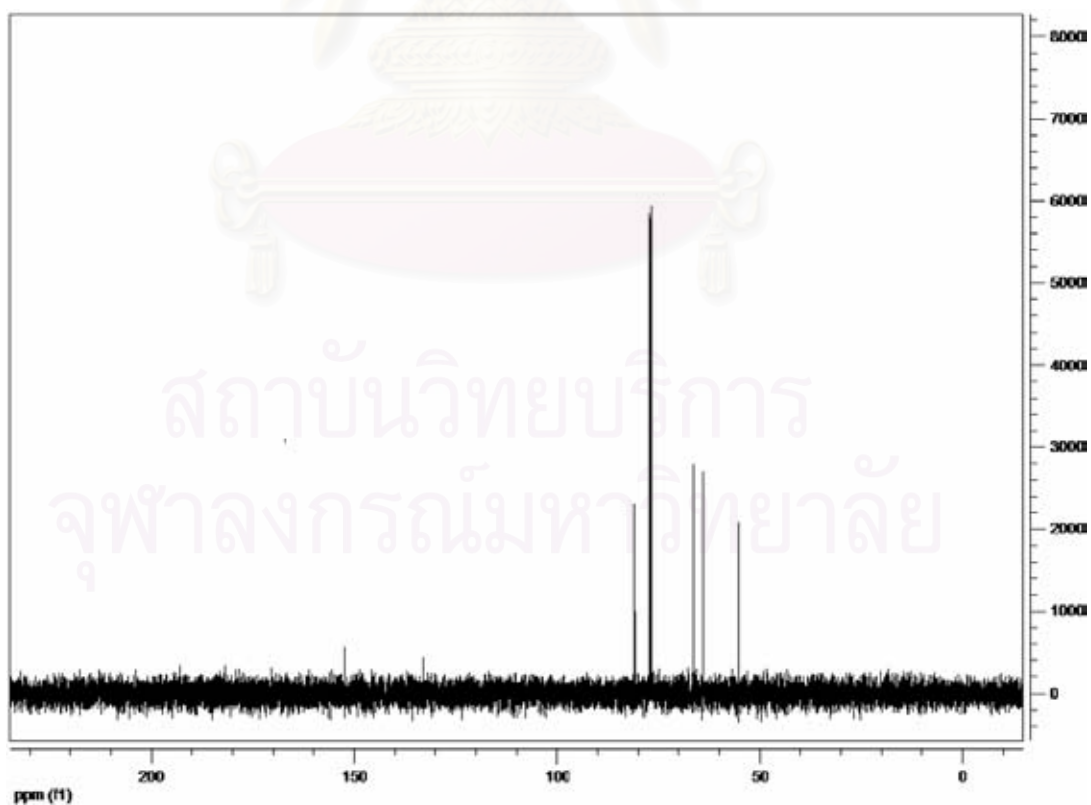


Figure A-18 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 2-bromo-3-methoxy-4-ethylenedioxythiophene

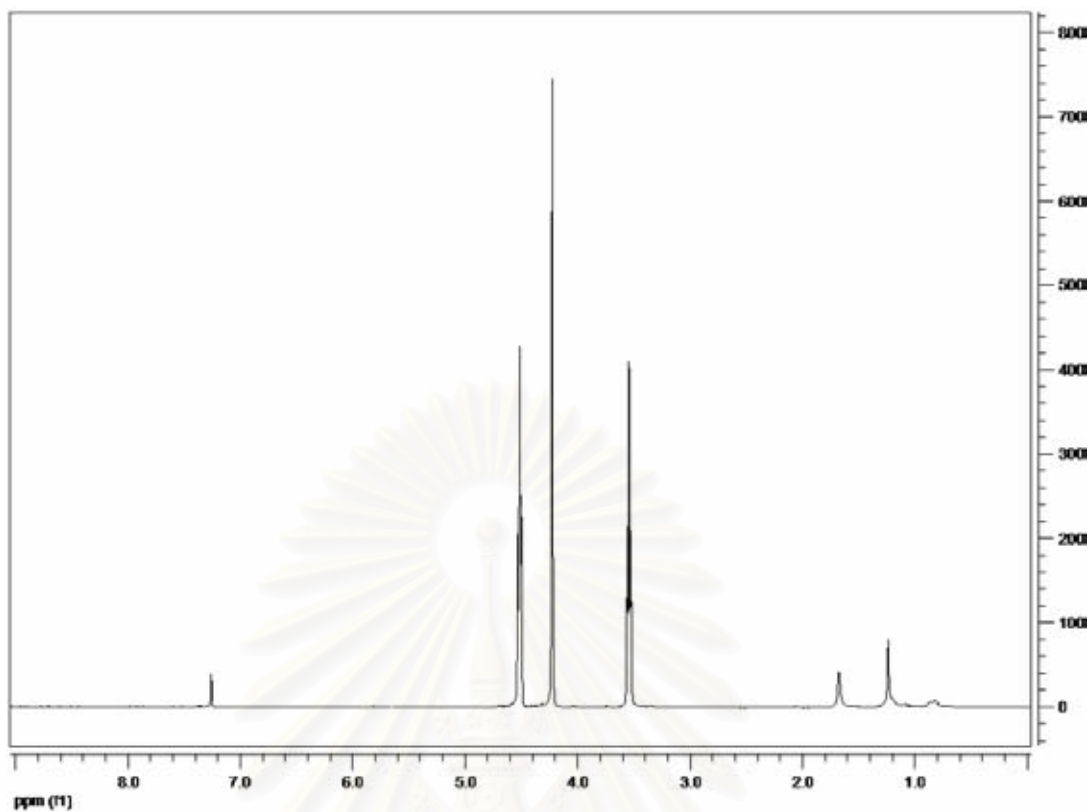


Figure A-19 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of the crown product (6)

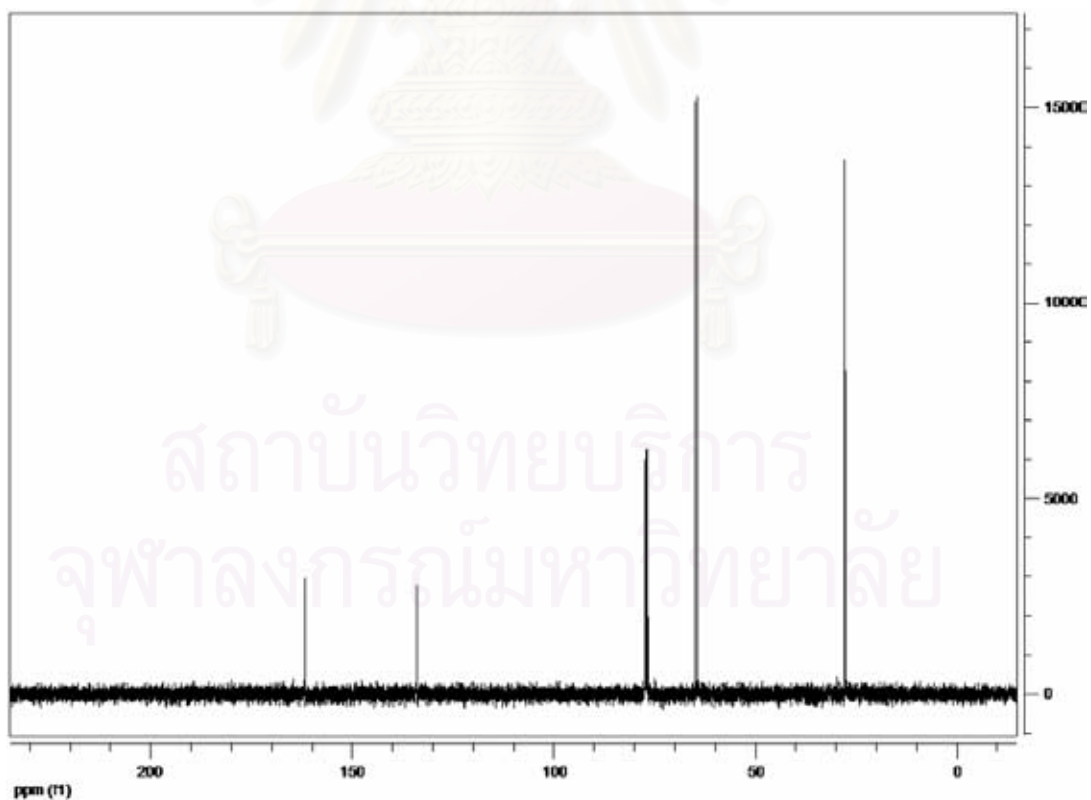


Figure A-20 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of the crown product (6)

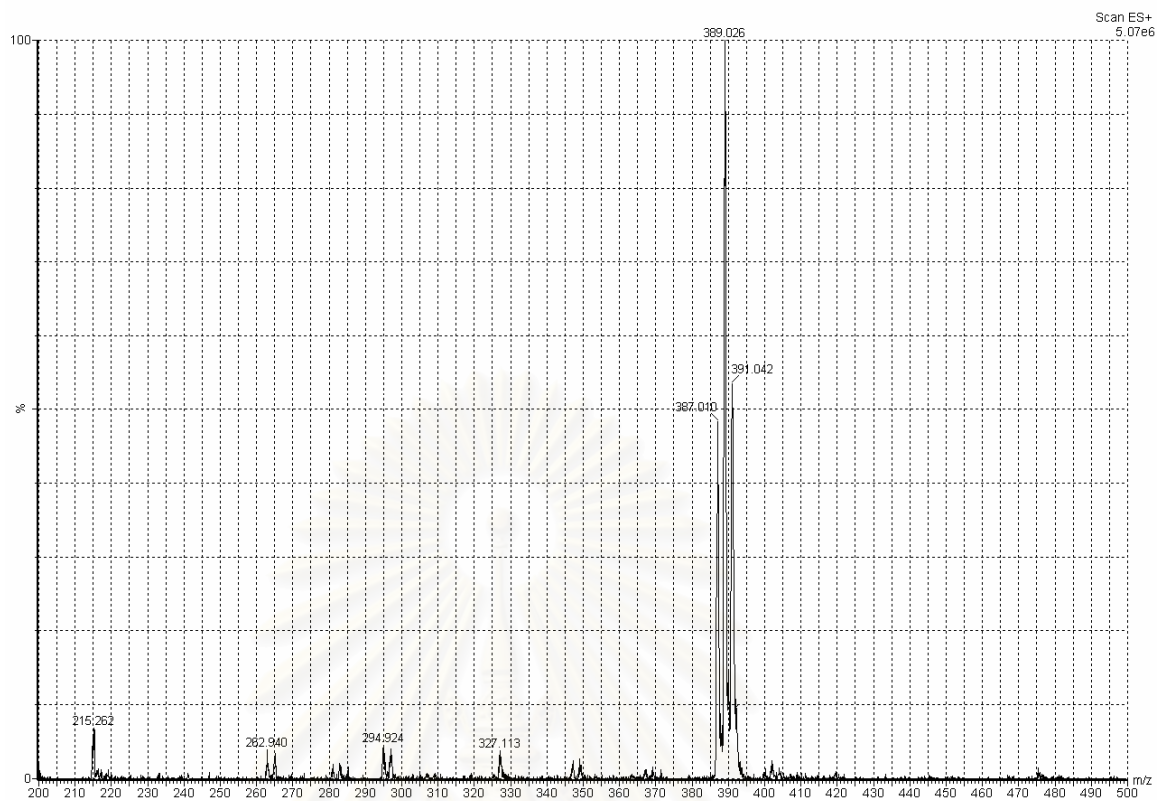


Figure A-21 MS spectrum of the crown product (6)

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จุฬาลงกรณ์มหาวิทยาลัย

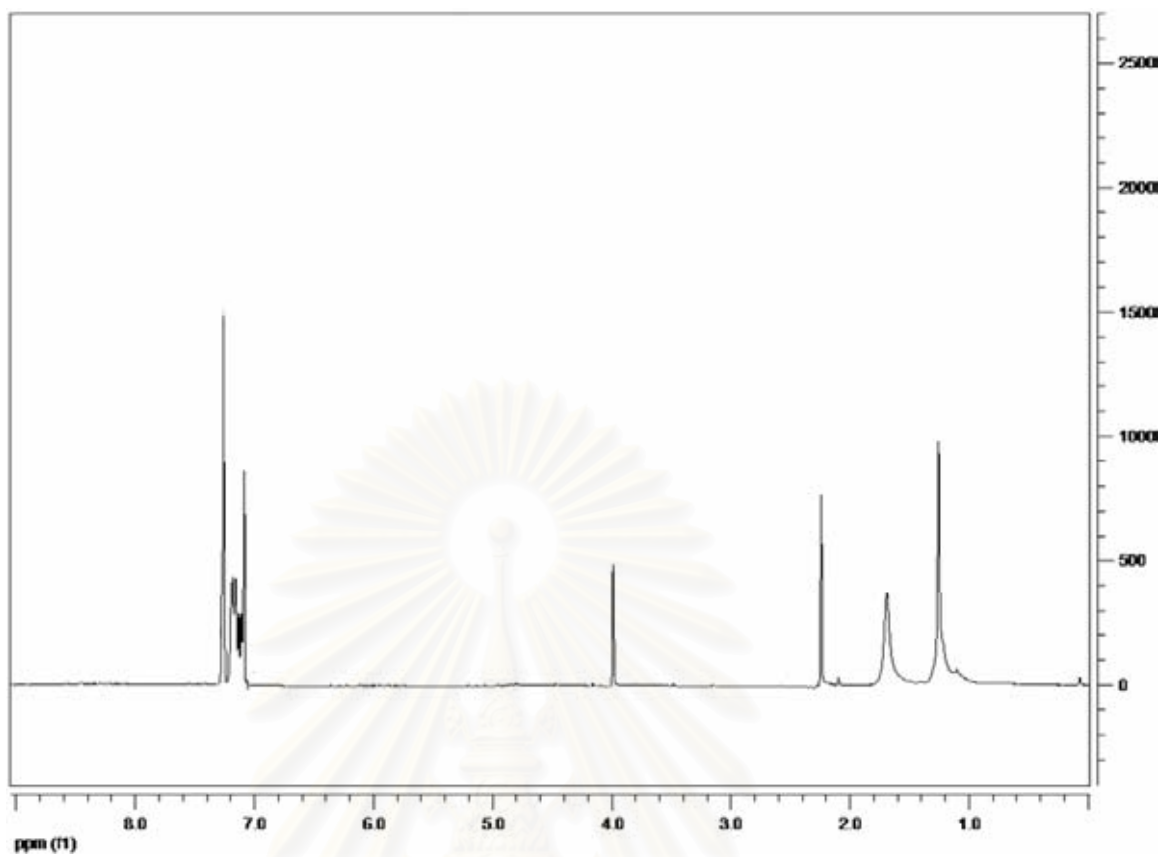


Figure A-22 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of 1-benzyl-4-methylbenzene

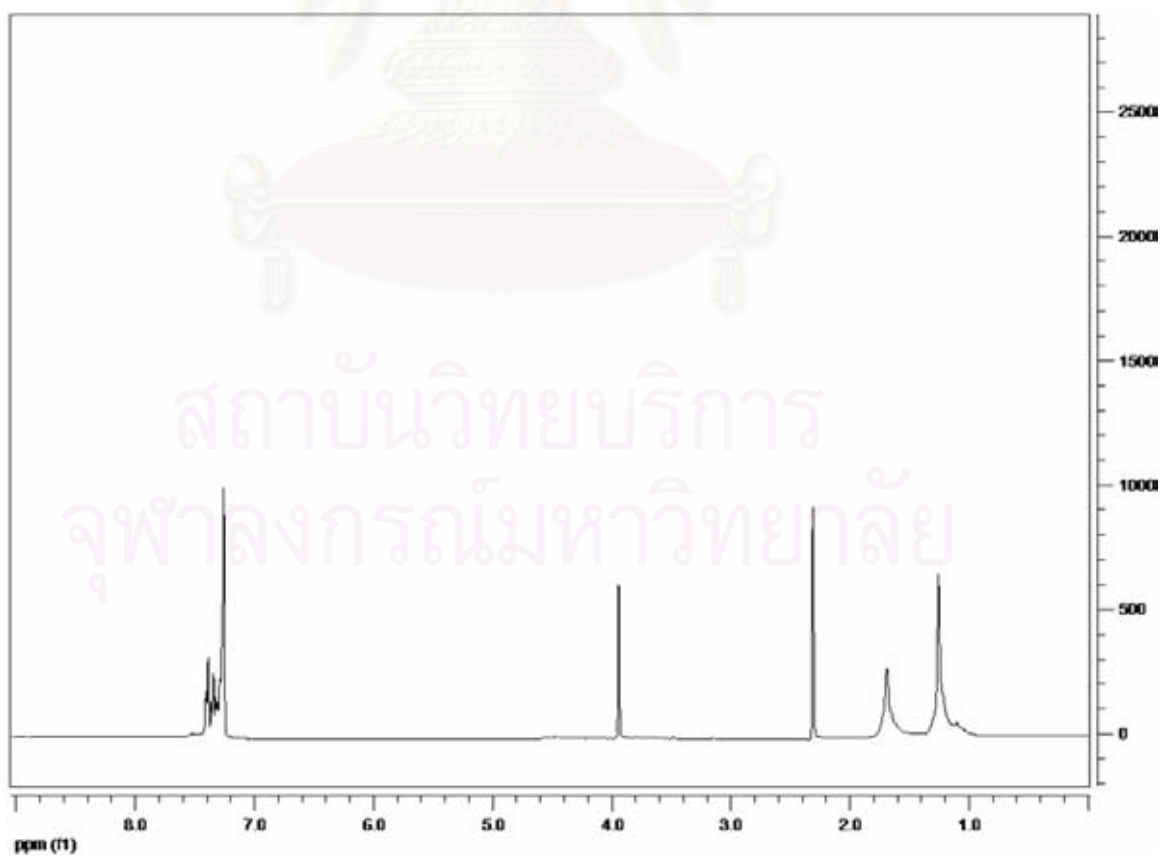


Figure A-23 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of 1-benzyl-2-methylbenzene

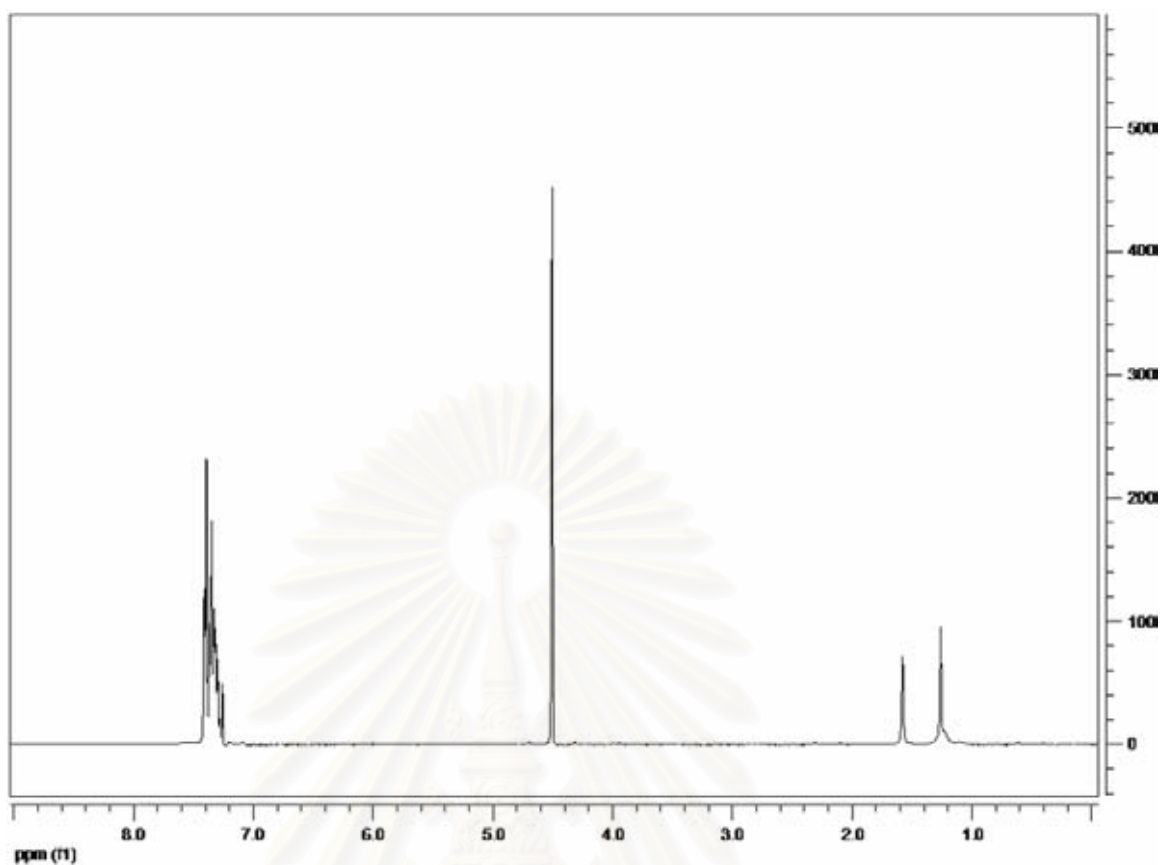


Figure A-24 The $^1\text{H-NMR}$ (400 MHz, CDCl_3) of dibenzylether

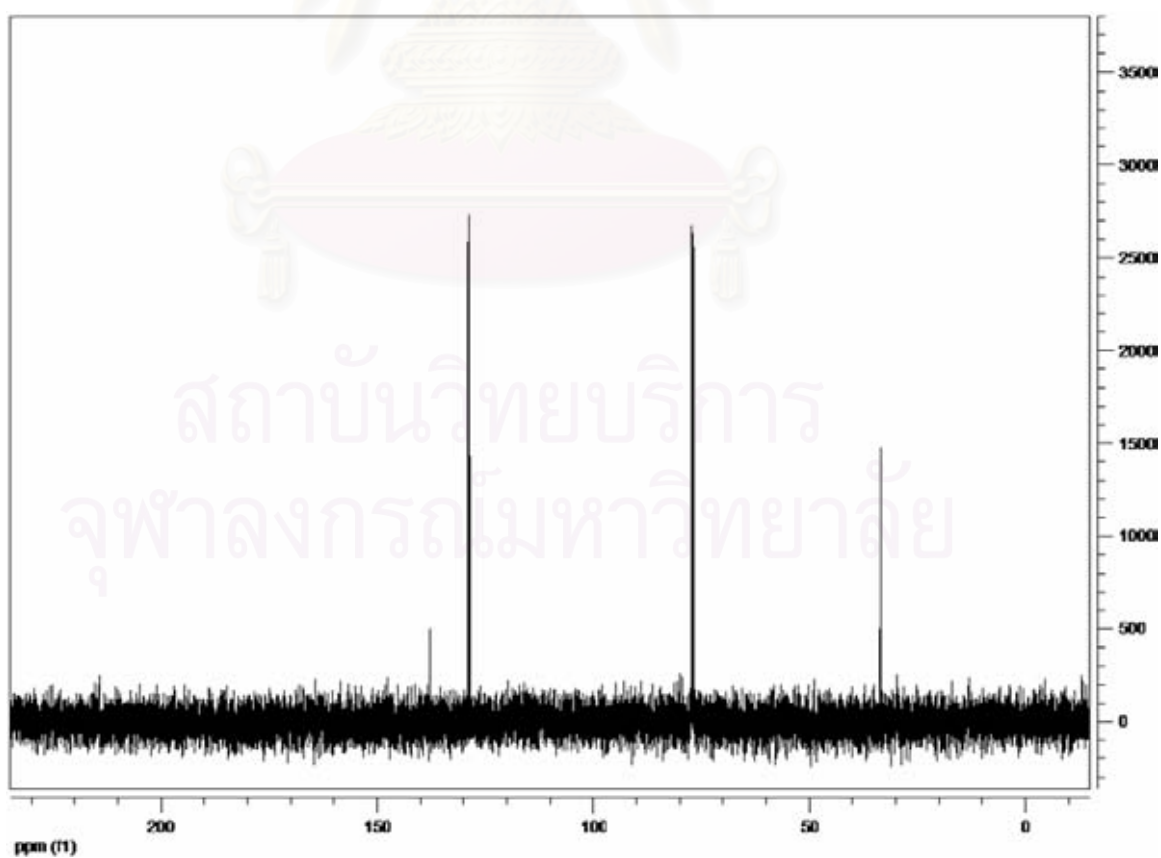


Figure A-25 The $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of dibenzylether

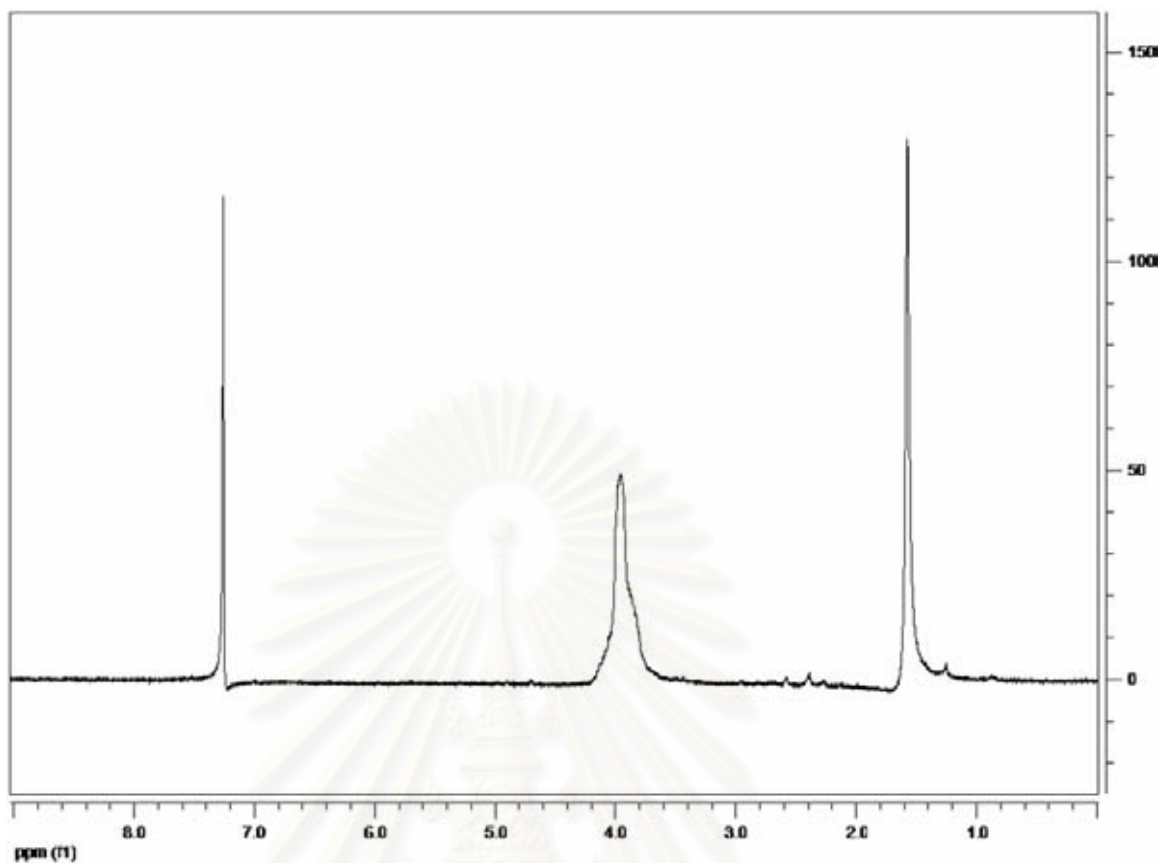


Figure A-26 The ¹H-NMR (400 MHz, CDCl₃) of Poly(3,4-dimethoxythiophene)

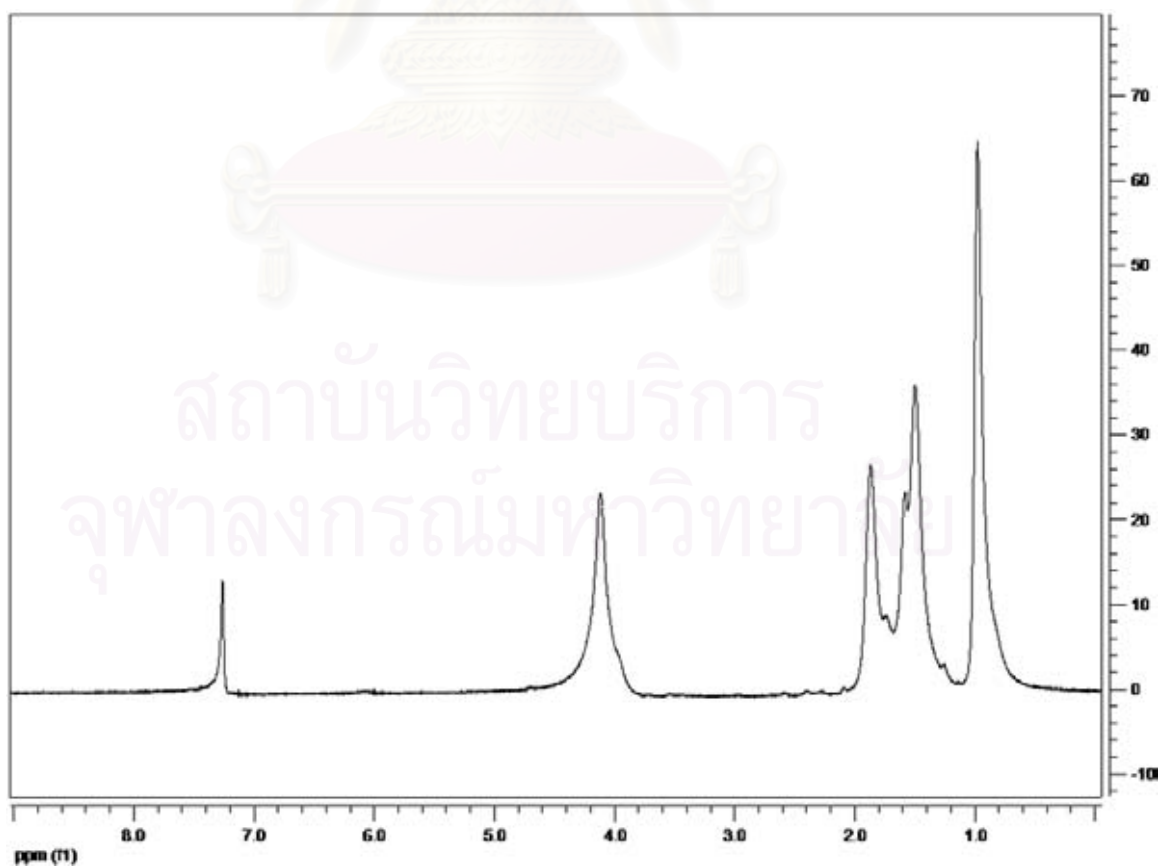


Figure A-27 The ¹H-NMR (400 MHz, CDCl₃) of Poly(3,4-dibutoxythiophene)

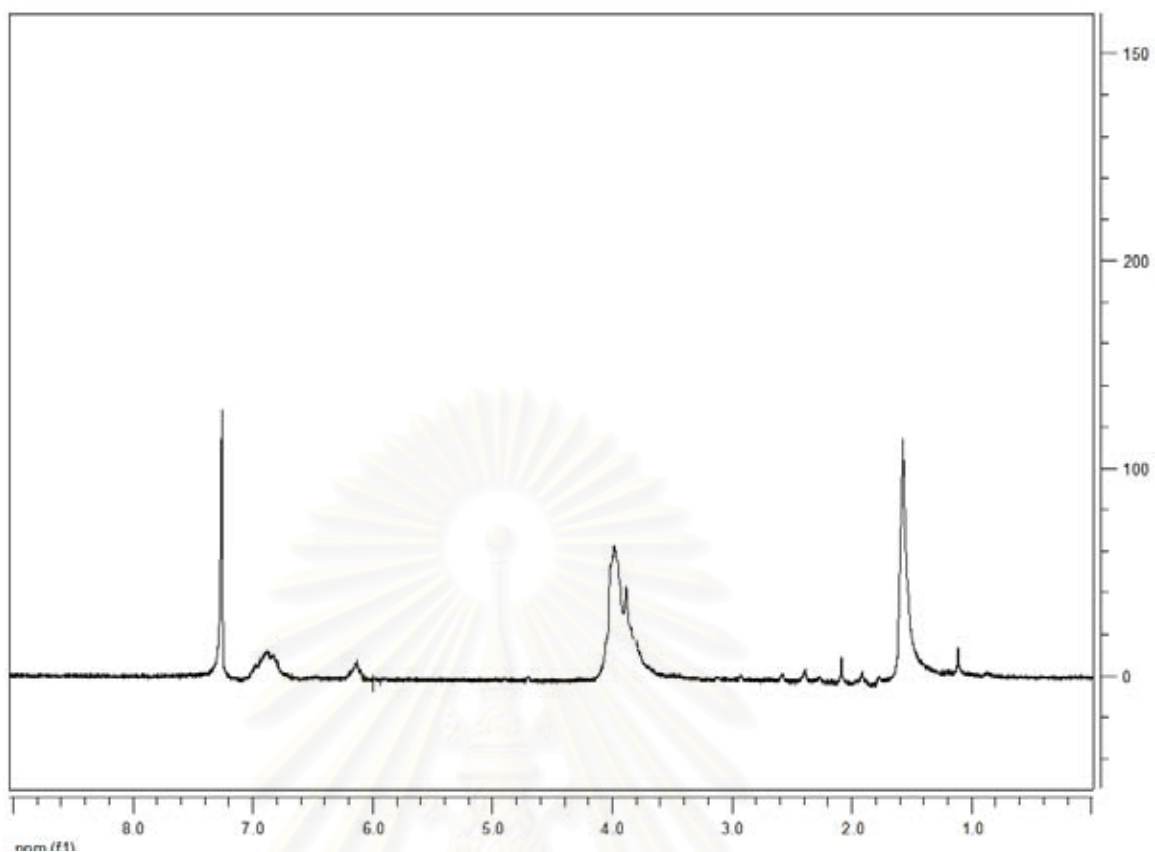


Figure A-28 The ^1H -NMR (400 MHz, CDCl_3) of Poly(3-methoxythiophene)

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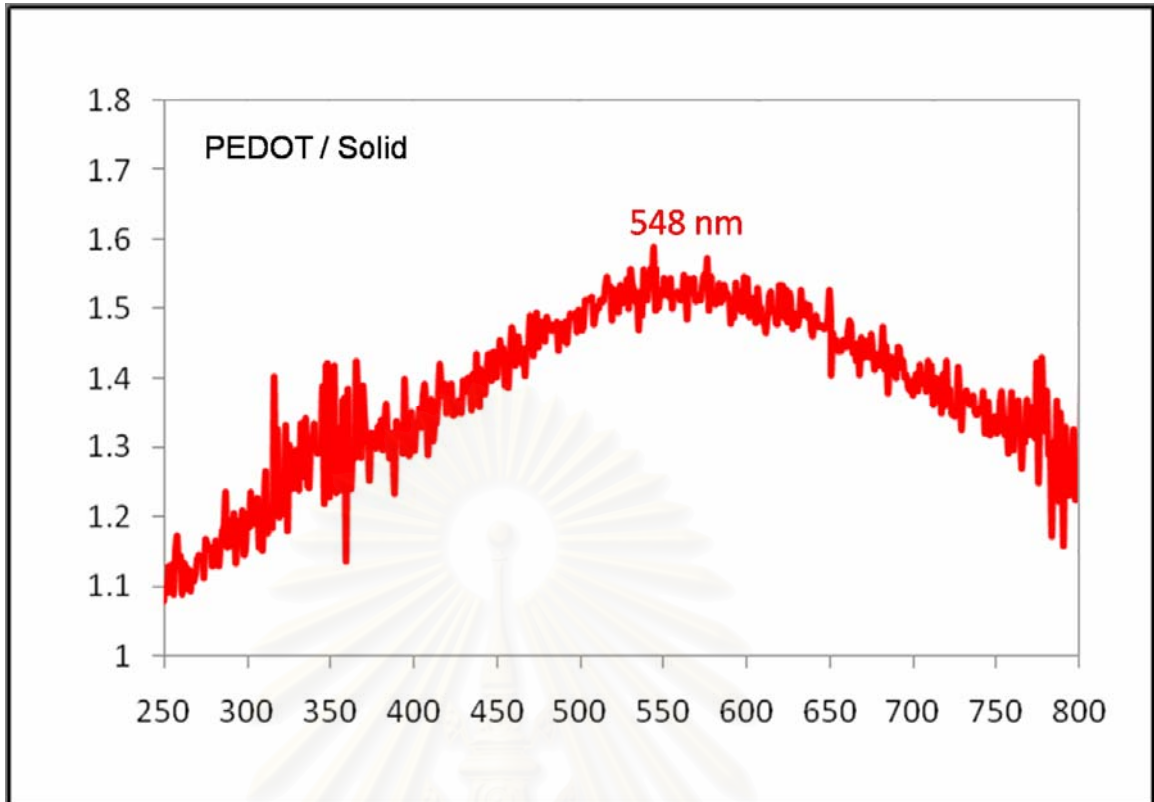


Figure A-29 UV-visible spectra of poly(3,4-ethylenedioxythiophene); PEDOT

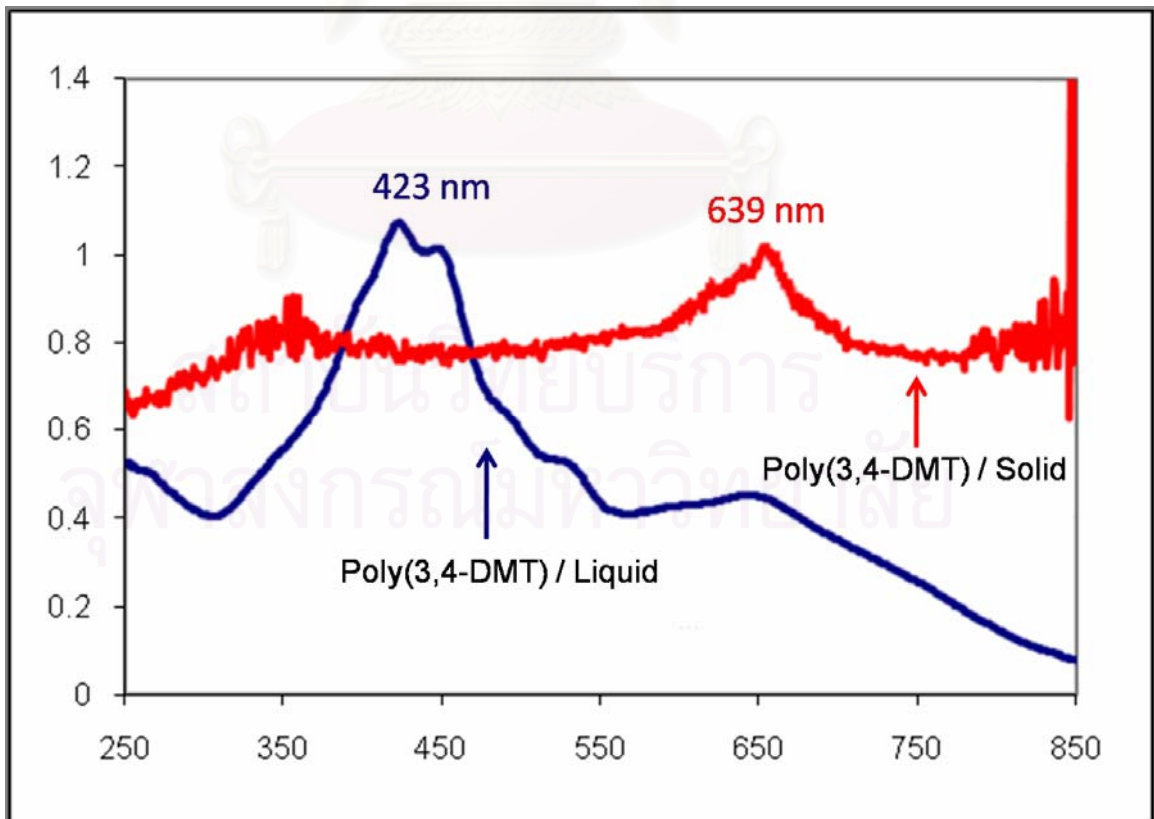


Figure A-30 UV-visible spectra of poly(3,4-dimethoxythiophene); PDMT

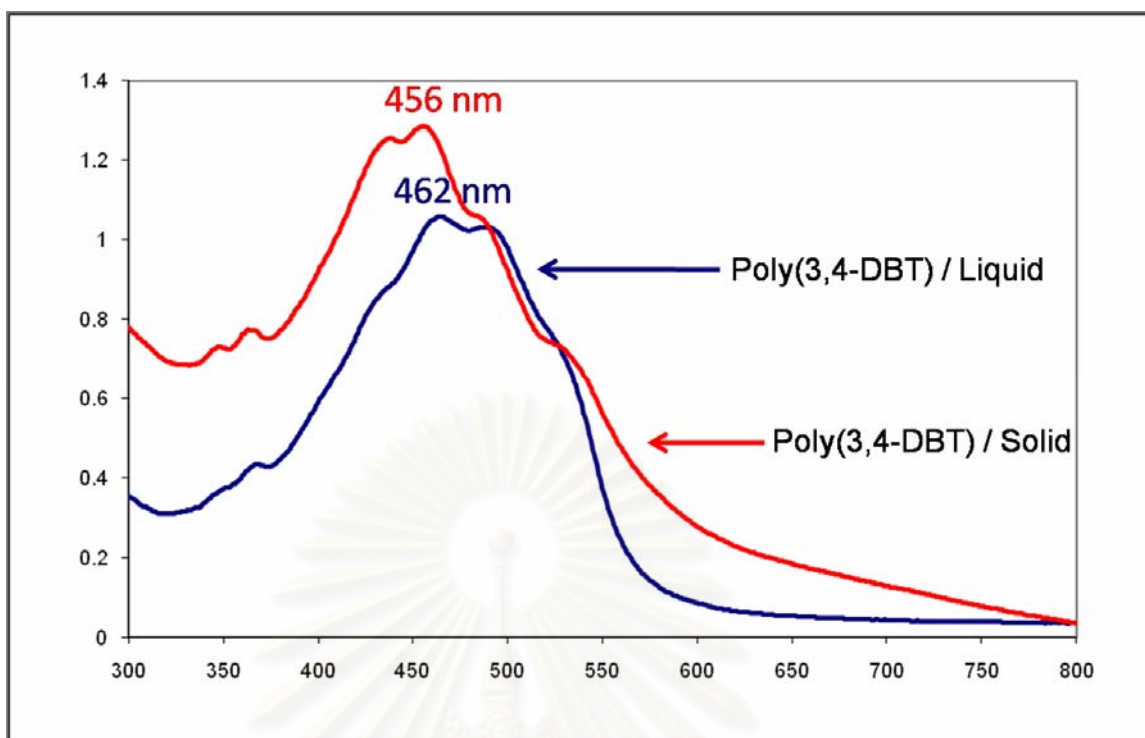


Figure A-31 UV-visible spectra of poly(3,4-dibutoxythiophene); PDBT

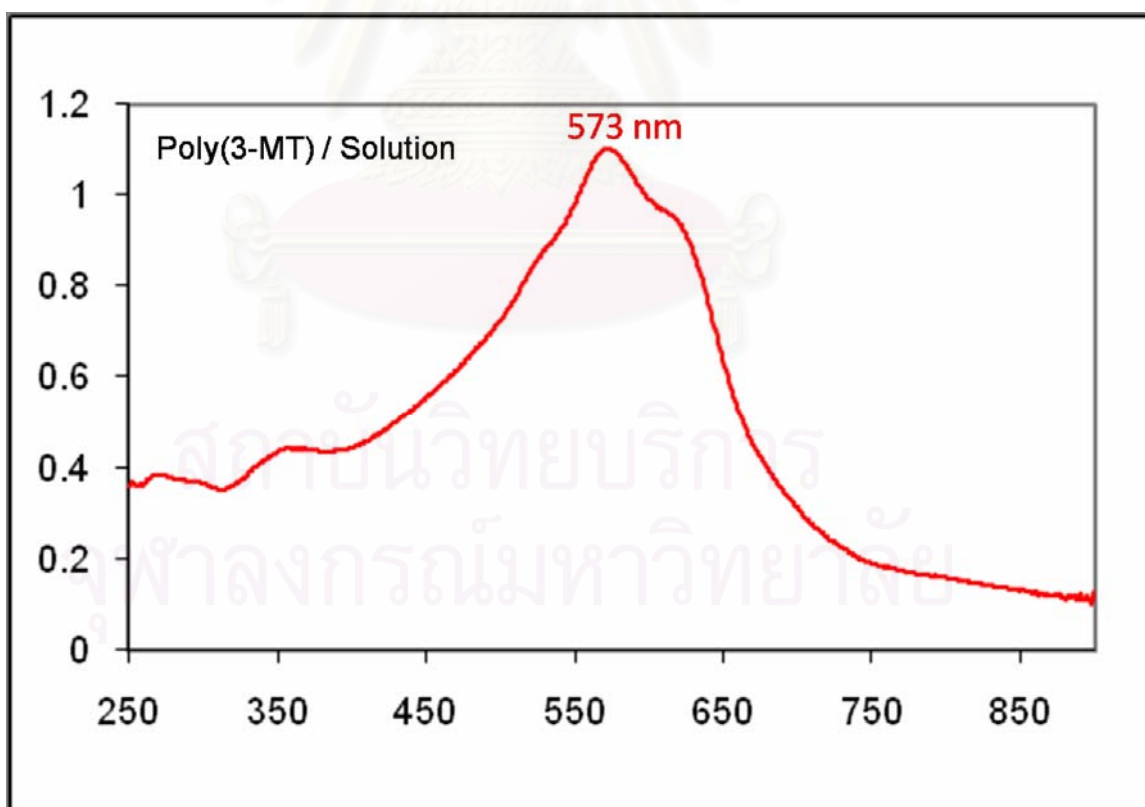


Figure A-32 UV-visible spectra of poly(3-methoxythiophene); PMT



APPENDIX B

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The Four-point Probe Method for Electrical Conductivity Measurement [37-39]

Four tiny electrodes are arranged in straight line separated at exactly equal distances (d) and touched the surface of the sample to be measured. Then the electrodes are further connected with an electrical circuit equipped with an Amp meter (A) and a Voltmeter (V) (**Figure B-1**). Contacts between the 4 electrodes and the sample surface must be equal. During the measurement, the current (I) is applied through electrode contact 1 to 4, and the potential difference (ΔV) across electrode contacts 2 and 3 is measured. The resistivity and conductivity of the sample can be calculated from the equation **B-1** and **B-2**, respectively.

$$\text{Resistivity } (\Omega \cdot \text{cm}); \quad \rho = (\pi t / \ln 2)(V/I) = 4.53(R \cdot t) \quad \dots\dots (\mathbf{B-1})$$

$$\text{Conductivity } (\text{S} \cdot \text{cm}^{-1}); \quad \sigma = 1/\rho \quad \dots\dots\dots (\mathbf{B-2})$$

Where I is current (A)

V is voltage (volt)

R is resistant (ohm)

t is film thickness (cm)

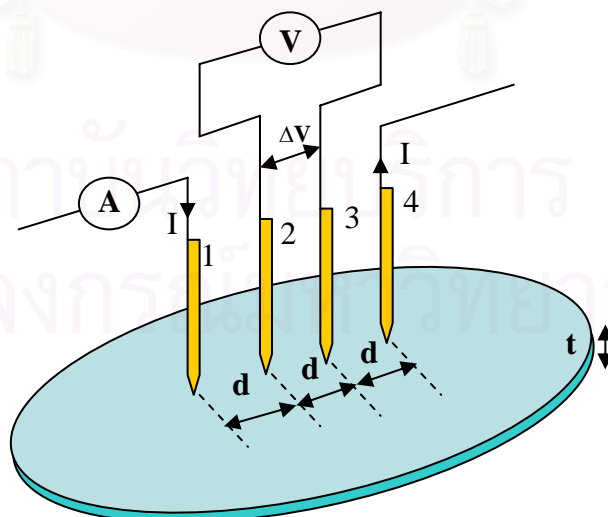


Figure B-1 Conductivity measurement by Four-point Probe method

The accuracy of the conductivity measurement by this method depends on:

i) the size of the sample, which must be very large compared to the separation distances (d) between the electrodes.

ii) thickness of the sample, which must be very small compared to the separation distances (d) between the electrodes.

Table B-1 Examples of the calculations of conductivity

Entry	Polymer	State	Current (amp)	Thickness (cm)	Resistance (Ω)
1	PEDOT	neutral	0.086 – 0.010	0.022	2.54
				0.020	2.59
				0.019	2.56
2	PEDOT	doped	0 - 0.010	0.019	0.642
				0.019	0.652
				0.021	0.650
3	SSP-PEDOT	neutral	0 – 0.010	0.019	1.51
				0.021	1.53
				0.019	1.50
4	SSP-PEDOT	doped	0 – 0.010	0.020	0.234
				0.020	0.228
				0.021	0.229
5	PDBT	neutral	$1 \times 10^{-8} - 1 \times 10^{-7}$	0.019	3.71×10^8
				0.019	3.78×10^8
				0.021	3.76×10^8
6	PDBT	doped	$8.4 \times 10^{-8} - 1 \times 10^{-7}$	0.021	3.33×10^6
				0.020	3.34×10^6
				0.020	3.33×10^6
7	PDMT	neutral	0 – 1×10^{-7}	0.021	1.55×10^8
				0.020	1.53×10^8
				0.020	1.58×10^8
8	PDMT	doped	0 – 9×10^{-5}	0.021	9.81×10^3
				0.019	9.81×10^3
				0.020	9.82×10^3
9	PMT	neutral	0 – 1×10^{-7}	0.021	6.67×10^7
				0.021	6.67×10^7
				0.019	6.64×10^7
10	PMT	doped	$8.1 \times 10^{-6} - 1 \times 10^{-5}$	0.020	1.70×10^4
				0.019	1.74×10^4
				0.020	1.69×10^4

In entry 1 :

$$\text{Average resistance } (\Omega) = \frac{2.54+2.59+2.56}{3} = 2.56$$

$$\text{Average thickness (cm)} = \frac{0.022+0.020+0.019}{3} = 0.020$$

$$\begin{aligned} \text{Resistivity } (\Omega.\text{cm}) &= 4.53 \times R \times t = 4.53 \times 2.56 \times 0.020 \\ &= 0.232 \end{aligned}$$

$$\text{Conductivity } (\text{S}.\text{cm}^{-1}) = \frac{1}{\text{Resistivity}} = \frac{1}{0.232} = 4.31$$

In entry 8 :

$$\text{Average resistance } (\Omega) = \frac{(9.81+9.81+9.82) \times 10^3}{3} = 9.81 \times 10^3$$

$$\text{Average thickness (cm)} = \frac{0.021+0.019+0.020}{3} = 0.020$$

$$\begin{aligned} \text{Resistivity } (\Omega.\text{cm}) &= 4.53 \times R \times t = 4.53 \times 9.81 \times 10^3 \times 0.020 \\ &= 888.786 \end{aligned}$$

$$\text{Conductivity } (\text{S}.\text{cm}^{-1}) = \frac{1}{\text{Resistivity}} = \frac{1}{888.786} = 1.12 \times 10^{-3}$$

VITA

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