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SYNTHESIS AND POLYMERIZATION OF 3,4-DIAMINOTHIOPHENE DERIVATIVES

Miss Donlaya Boontham



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

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ดลยา บุญธรรม : การสังเคราะห์และพอลิเมอไรเซชันของอนุพันธ์ 3,4-ไดแอมิโนไทโอเฟน (SYNTHESIS AND POLYMERIZATION OF 3,4-DIAMINOTHIOPHENE DERIVATIVES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.ยงศักดิ์ ศรีธนาอนันต์, 66 หน้า.

งานวิจัยนี้เป็นการนำปฏิกิริยาการแทนที่ด้วยนิวคลีโอไฟล์ลงบนวงแอโรมาติกอย่างต่อเนื่องมาสังเคราะห์คอนจูเกตพอลิเมอร์ชนิดใหม่ โดยพอลิเมอร์ 3 เกิดจากปฏิกิริยาพอลิเมอไรเซชันระหว่าง 2,5-ไดคลอโร-3,4-ไดไนโตรไทโอเฟน กับ พารา-ฟีนิลลีนไดเอมีน ได้ผลิตภัณฑ์เป็นของแข็งสีน้ำตาลแดงและไม่ละลายในตัวทำละลายอินทรีย์ในปริมาณ 61.2% พอลิเมอร์ 4 เกิดจากปฏิกิริยาพอลิเมอไรเซชันระหว่าง 2,5-ไดคลอโร-3,4-ไดไนโตรไทโอเฟน กับ เอ็น,เอ็น'-ได-เซก-บิวทิล-พารา-ฟีนิลลีนไดเอมีนที่ให้ผลิตภัณฑ์ในปริมาณ 59.3% มีลักษณะเป็นของแข็งสีดำสามารถละลายในตัวทำละลายอินทรีย์ได้บางส่วน เมื่อรีดิวซ์พอลิเมอร์ 3 ด้วยทินคลอไรด์ได้ผลิตภัณฑ์เป็นพอลิเมอร์ 5 ซึ่งประกอบด้วยหน่วยของ 3,4-ไดแอมิโนไทโอเฟนในปริมาณ 65.4% และนำพอลิเมอร์ 4 มาทำปฏิกิริยารีดักชันจะได้ผลิตภัณฑ์เป็นพอลิเมอร์ 6 ในปริมาณ 34.8% ในการศึกษาเพื่อปรับเปลี่ยนหมู่ฟังก์ชันบนพอลิเมอร์ผ่านการทำปฏิกิริยาบนหมู่แอมิโนได้ทดลองกับมอนอเมอร์ต้นแบบโดยการรีดิวซ์ 2,5-ไดโบรโม-3,4-ไดไนโตรไทโอเฟน และนำมาทำปฏิกิริยากับเบนซาลดีไฮด์ได้ผลิตภัณฑ์เป็นอนุพันธ์ของอิมิดาโซล 1 ในปริมาณ 34% และปฏิกิริยาระหว่าง 2,5-ไดคลอโร-3,4-ไดไนโตรไทโอเฟนกับซาลิไซลาลดีไฮด์ได้เป็นผลิตภัณฑ์ 2 ในปริมาณ 17% ซึ่งเป็นการพิสูจน์ว่าปฏิกิริยาสามารถเกิดขึ้นได้บนมอนอเมอร์จึงได้นำมาทำปฏิกิริยาบนพอลิเมอร์โดยมีพอลิเมอร์ 4 เป็นสารตั้งต้น ทำปฏิกิริยารีดักชันและคอนเดนเซชันตามลำดับ ได้ผลิตภัณฑ์เป็นพอลิเมอร์ 7 ในปริมาณ 40.2% คอนจูเกตพอลิเมอร์ชนิดใหม่ที่สังเคราะห์ได้มีสมบัติการดูดกลืนแสงยูวีวิสิเบิลที่ความยาวคลื่นสูงสุดอยู่ในช่วง 550-670 นาโนเมตร

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DONLAYA BOONTHAM: SYNTHESIS AND POLYMERIZATION OF 3,4-DIAMINOTHIOPHENE DERIVATIVES. ADVISOR: ASSIST. PROF. YONGSAK SRITANA-ANANT, Ph.D., 66 pp.

Repeated nucleophilic aromatic substitutions (S_NAr) were used to synthesize new conjugated polymers. Polymer 3 was obtained from S_NAr reactions of 2,5-dichloro-3,4-dinitrothiophene (DCDNT) and *p*-phenylenediamine as insoluble red-brown solid in 61.2% yield. Polymer 4 was also obtained from S_NAr reactions of DCDNT and *N,N'*-di-*sec*-butyl-*p*-phenylenediamine as partially soluble black solid in 59.3% yield. The polymer 3 was then reduced by $SnCl_2$ to obtain polymer 5 containing 3,4-diaminothiophene units in 65.4% yield. The polymer 4 was also reduced to obtain polymer 6 in 34.8% yield. To study the functionalization of the polymers through the diamino groups, the model reaction of the reduced 2,5-dibromo-3,4-dinitrothiophene (DBDNT) and benzaldehyde produced the imidazole derivative 1 in 34% yield. Similarly, reaction of the reduced DCDNT and salicylaldehyde gave the product 2 in 17% yield. With these successes on monomeric units, the polymer 7 was synthesized in 40.2% yield by consecutive reduction and condensation with benzaldehyde on polymer 4 precursor. These newly synthesized conjugated polymers exhibited the characteristic UV-Vis maximum wavelength absorptions (λ_{max}) in the bathochromic range of 550-670 nm.

Field of Study: Petrochemistry and
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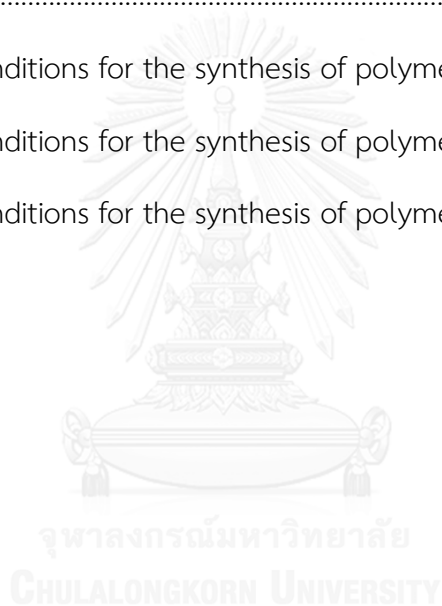


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LIST OF ABBREVIATIONS

cm^{-1}	: unit of wavenumber (IR)
CDCl_3	: deuterated chloroform
CH_2Cl_2	: dichloromethane
$^{\circ}\text{C}$: degree Celsius
^{13}C NMR	: carbon-13 nuclear magnetic resonance spectroscopy
d	: day (s), doublet (NMR)
DBDNT	: 2,5-dibromo-3,4-dinitrothiophene
DCDNT	: 2,5-dichloro-3,4-dinitrothiophene
DMSO	: dimethyl sulfoxide
$\text{DMSO-}d_6$: hexadeuterated dimethyl sulfoxide
Equiv	: equivalent (s)
Et_3N	: triethylamine
EtOAc	: ethyl acetate
g	: gram (s)
h	: hour (s)
^1H NMR	: proton nuclear magnetic resonance spectroscopy
HCl	: hydrochloric acid
HNO_3	: nitric acid
H_2SO_4	: sulfuric acid
Hz	: hertz (s)
IR	: infrared spectroscopy
M	: molar (s)
m	: multiplet (NMR)
MeOH	: methanol
MgSO_4	: anhydrous magnesium sulfate

min	: minute
mL	: milliliter (s)
mmol	: millimole (s)
Na ₂ CO ₃	: sodium carbonate
NaOH	: sodium hydroxide
nm	: nanometer (s)
ppm	: parts per million (unit of chemical shift)
q	: quartet (NMR)
rt	: room temperature
s	: singlet (NMR)
st	: stretching vibration (IR)
t	: triplet (NMR)
THF	: tetrahydrofuran
UV-Vis	: ultra-violet and visible spectroscopy
δ	: chemical shift
λ _{max}	: maximum wavelength

CHAPTER I

INTRODUCTION

1.1 Conducting polymers

The large majority of polymers, mostly known as commodity materials such as polyethylene, polypropylene, poly(ethylene terephthalate) or polystyrene, have similar electrical properties. They are insulators, i.e., they possess no mobile charges and the lowest electronic absorption are in the UV region. There exists a different class of polymers that carry conjugated double bonds of equivalences in the main chain. They are semiconductors and have unique electrical and optical properties, which called conducting polymers.

Conducting polymers are organic semiconductors that become important materials for applications in electronic and photonic devices such as electrochromic display [1], electroluminescent organic light emitting diode (OLEDs) [2], polymer-based photovoltaic cells for solar energy conversion [3], sensor [4, 5], organic thin film transistors (OTFTs) [6], etc.

Conducting polymers consist of conjugate structure with alternating single and double bonds between carbon-carbon or carbon-nitrogen atoms along their backbones as showed in **Figure 1.1**. These were conjugated sp^2 -hybridized carbons and π -electrons. Electrons can delocalize along the polymers chain through π -orbitals, which give rise to semiconducting properties. Polyacetylene was the first example that has been widely studied as a prototype for other electronic conducting polymers [7].

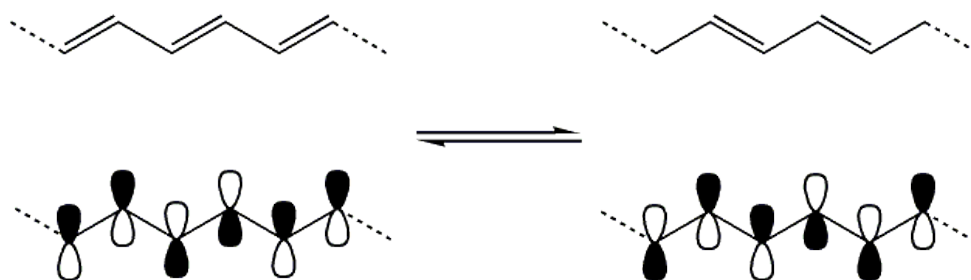


Figure 1.1 Delocalized π system of conjugated polymers

1.2 Organic versus inorganic semiconductors

Organic materials offer several major advantages over inorganic materials some potential benefits are:

Light weight. The densities of polymers are much lower than those of traditional metals (1-2 g/cm³ compared to 3-10 g/cm³).

Low cost. Inorganic semiconductors are sensitive to impurities and must be produced, handled, and assembled in specialized clean rooms. On the other hand, organic semiconductors may be synthesized in relatively unsophisticated laboratories and are much more tolerant to contaminations.

Tunability. The art of organic chemistry offers an infinite amount of chemical modifications of the active materials, which may be fine-tuned to suit each desired application.

Flexibility. Inorganic semiconductors are stiff and, therefore, useless for flexible devices. Many organic semiconductors are, on the other hand, quite flexible and useful for flexible devices.

Solubility/Processability. Many organic semiconductor materials are soluble in common organic solvents and can be applied onto the substrates by evaporation.

1.3 Band theory of conjugated polymers

The conduction of conjugated polymers can be explained by band theory. Unlike an atom where the availability of the energy states for electrons are specific or quantized, the solid materials have electronic energy states in band form because the energy states of the electrons arrange in close proximity and become overlapped. The highest range of electron energy states where electron normally exist forms the valance band (VB); while the lowest range of electron energy states which are normally empty forms the conduction band (CB) (**Figure 1.2**). The VB lies below the CB separated by a band gap (E_g) in the case of insulators and semiconductors. Electrons in the VB can be injected to the CB. The electrons injected to the CB can move freely along the atomic lattice, and provide conductivity to the material. Insulators typically have very wide band gap that inhibit electrons in the VB from crossing over, while metals and conductors have no band gap because the VB overlap the CB; providing high conductivity. In a semiconductor, electronic conductivity can be controlled by introducing small quantities of foreign atoms to the lattice of the host semiconductor. This process is known as “doping” and the foreign substance is called a “dopant”. The dopant incorporated into a semiconductor generates excess conduction electrons or holes in the semiconductor, introducing a new energy level to the band gap, and, thus, facilitates conduction. High dopant concentration generally enhances the conductivity [8].

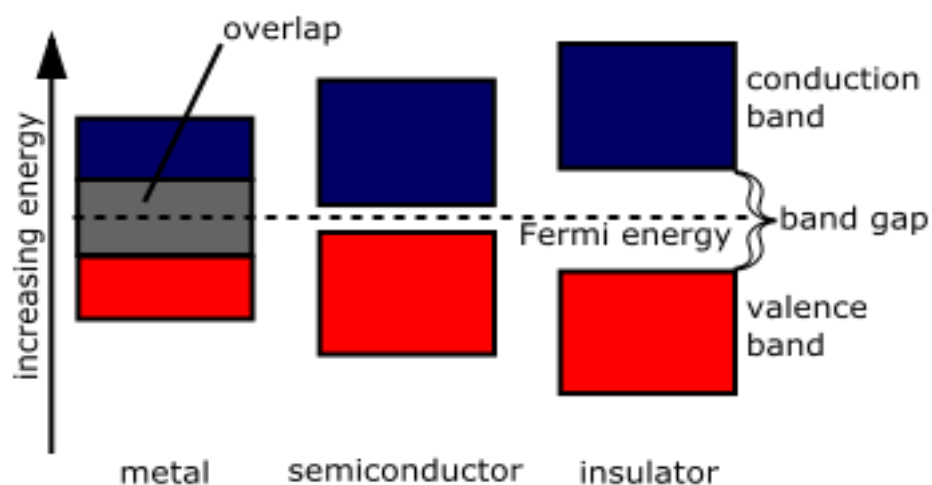


Figure 1.2 Simple band pictures of an insulator, a semiconductor and a metal

The conductivity of conducting polymers can be controlled in a similar manner. Doping a conducting polymer involves adding mobile charge carriers to the conjugated backbone by oxidation or reduction of the polymer, called p-doping and n-doping, respectively. Counter ions must also be incorporated to maintain electro-neutrality. **Figure 1.3** shows the structures of some common conducting polymers in their neutral forms. In these forms, conducting polymers have band gaps of a few electron volts (eV), resulting in conductivity range 10^{-10} S/cm, but doping can increase their conductivity in a metallic conducting regime of 1 to 10^4 S/cm [9].

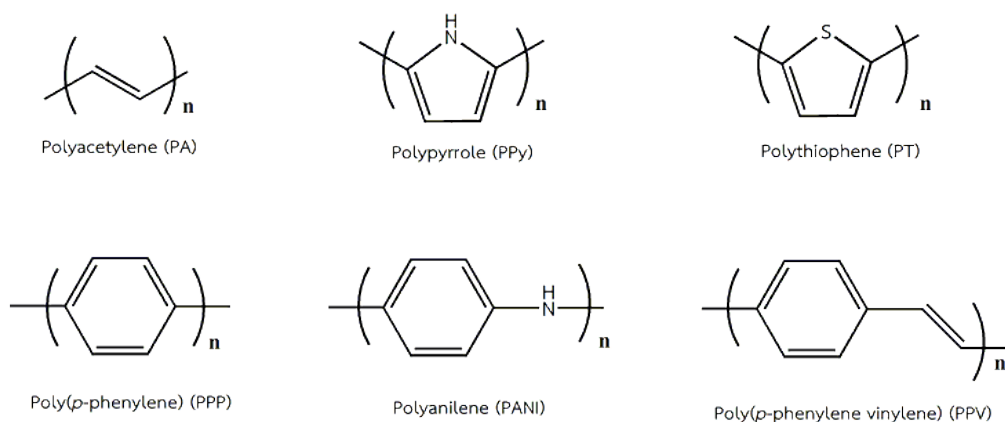


Figure 1.3 Structure of some conducting polymers in their neutral forms

1.4 Types of conjugated polymers

Conjugated polymers can be classified according to the types of electrons transfer as:

Donor (p-type) polymer:

The main chains of the polymers were constructed from connections of donor or electron-rich units. The hydrocarbon-based polymers were substituted with electron-donating groups such as hydroxyl or alkyl groups such as Poly(3,4-ethylenedioxythiophene) (PEDOT) [10], Poly(3-hexylthiophene) [11]. **(Figure 1.4)**

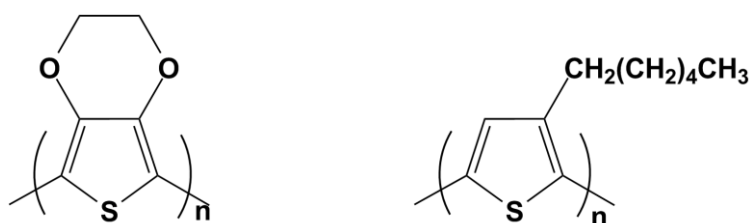


Figure 1.4 Examples of donor (p-type) polymers

Donor units refer to an electron-rich unit. Thiophene and benzene are the two most basic donor units, and they are also the main primary blocks to modify other new donor units such as fluorine (F), carbazole (Cz), cyclopentadithiophene (CPDT), dithienosilole (DTS), *etc.* The basic donor units that were widely used were presented in **Figure 1.5** [12].

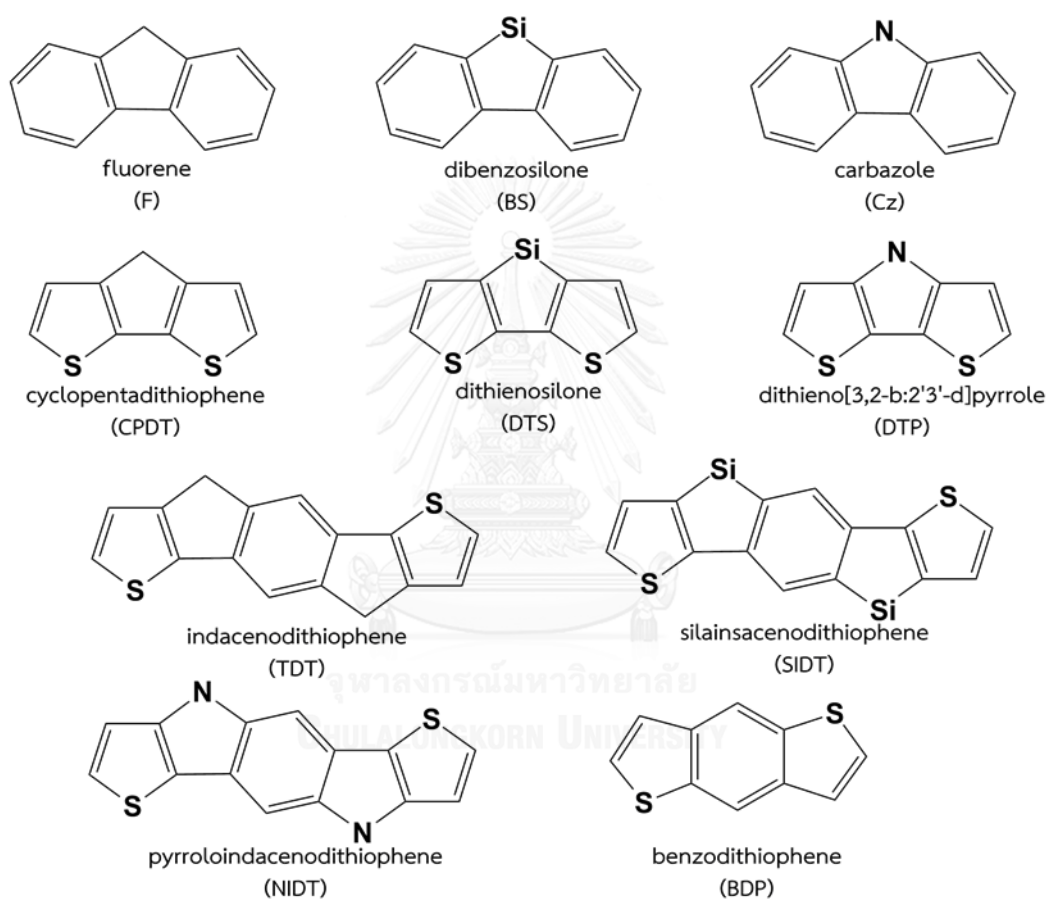


Figure 1.5 The basic donor units

Acceptor (*n*-type) polymers

The main chains of the polymers were constructed from connections of acceptor or electron-poor units. The hydrocarbon-base polymers were substituted with electron-withdrawing groups such as cyano or nitro groups such as Poly(3,3'-dicyanobithiophene) [13], β,β' -diperfluorohexyl-substituted oligothiophene [14]. (Figure 1.6)

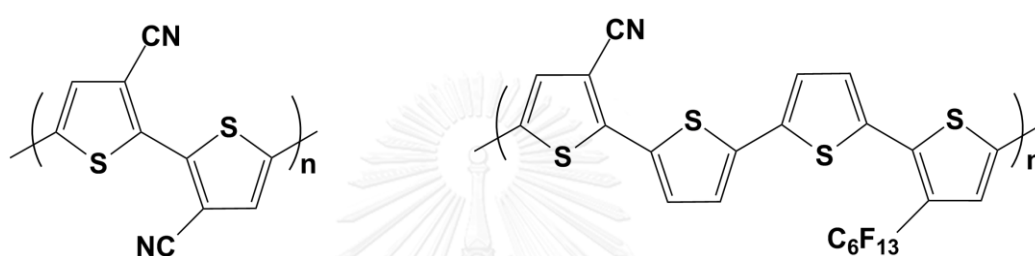


Figure 1.6 Examples of acceptor (*n*-type) polymers

Acceptor units refer to electron poor groups that usually contain electron withdrawing groups such as carbonyl nitro and cyano groups. However, several well-known acceptor units contains the electron withdrawing nitrogen hetrocycles such as bencothiadiazole (BT), quinoxaline (QA), thienopyrazine (TP), bithiazole (BTz), thiazolothiazole (TTz), benzobisthiazole (BBTz), benzotriazole (BTA), *s*-tetrazine (STTz), naphtha[1,2-*c*:5,6-*c'*]bis[1,2,5]thiadiazole (NT). The chemical structures of some of these acceptor unit are shown in Figure 1.7 [12].

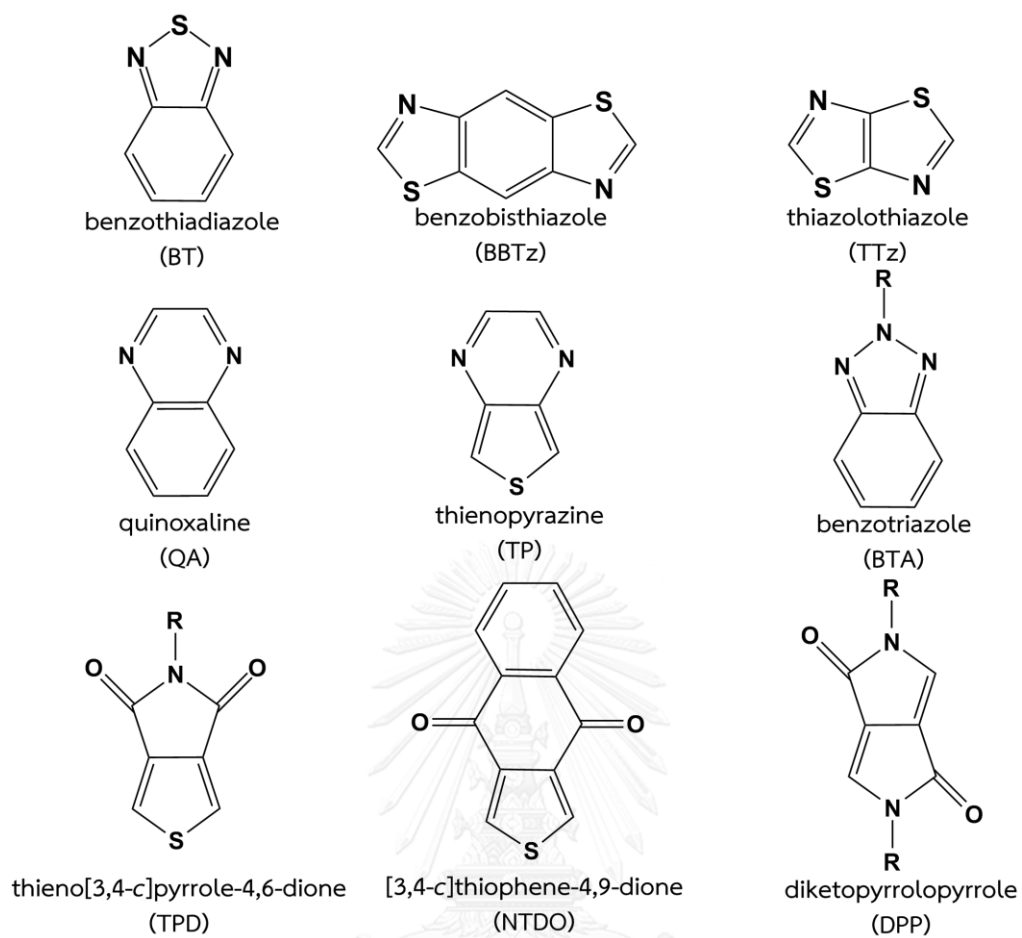


Figure 1.7 The basic acceptor units

1.5 Nucleophilic aromatic substitution (S_NAr) polymerization

A nucleophilic aromatic substitution reaction in which the nucleophile displaces a good leaving group on an aromatic ring with an aid of electron withdrawing group as activator. The nucleophilic displacement of a halogen from an activated aryl halide system occurs in a two-step addition-elimination reaction (S_NAr). The nucleophile adds to the electron-deficient aryl halide, forming a negatively charged Meisenheimer complex from which the halide is eliminated [15]. The reaction occurs repeatedly, leading to the formation of polymer.

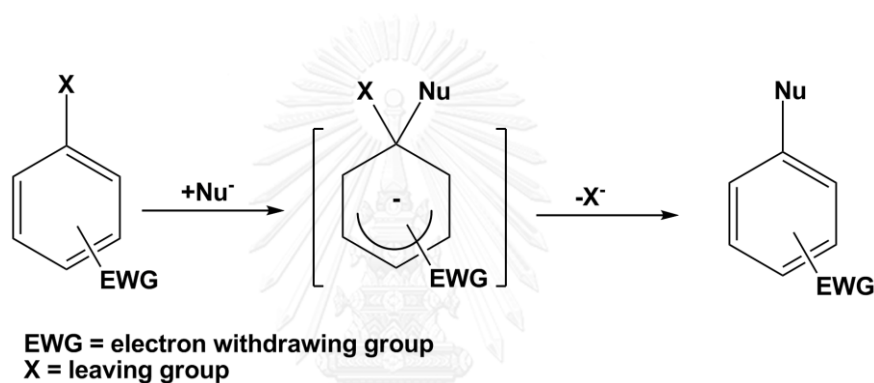


Figure 1.8 Mechanism of the S_NAr reaction

The activating group presented in the aryl halide serves two purposes. The group may be an electron-withdrawing moiety such as nitro or cyano groups, which decrease the electron density at the site of the reaction. Second, it makes the aryl ring behave as acceptor unit. Its presence lower the energy of the transition state for the reaction by stabilizing the anionic intermediate formed [16]. In principle, connecting acceptors into conjugated polymers could go through repeated nucleophilic aromatic substitutions using binucleophiles. When then binucleophiles are electron-rich aromatic species, the products would form new type of donor-acceptor conjugated polymers.



1.6 Literature reviews

Guo and coworkers [17] reported chemical synthesis of polyaniline (PANI) by ionic aromatic substitution of *p*-dichlorobenzene and sodium amide in benzene, which was one of the early examples of conjugated polymers synthesized by S_NAr polymerization. (Figure 1.9)

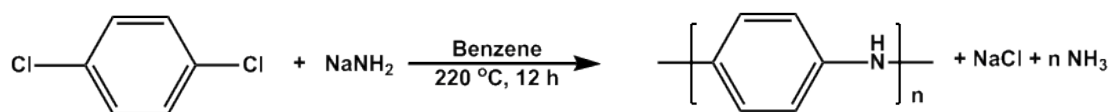


Figure 1.9 Synthesis of polyaniline by nucleophilic aromatic substitution

Preeyanuch [18] synthesized new conjugated polymer which contained 2,5-dichloro-3,4-dinitrothiophene (DCDNT) and diamine derivatives as electron acceptors and electron donors units, respectively. (Figure 1.10) They polymerization by nucleophilic aromatic substitution (S_NAr).

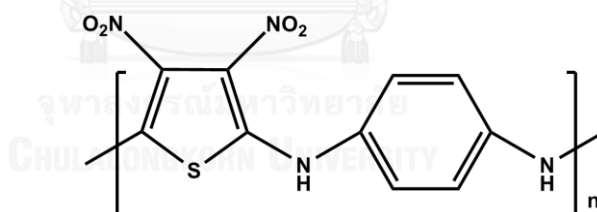


Figure 1.10 DCDNT and *p*-phenylenediamine polymerization by S_NAr

Zhang and Tour [19] synthesized polythiophene which contained amino groups and nitro groups as electron donors and electron acceptors units, respectively. (Figure 1.11) Stille polymerizations using Pd(0)/CuI catalyst systems were used to couple aryl dibromides with aryl distannanes. The polythiophene has λ_{max} at 676 nm (THF) and 768 nm (film). The optical band gaps of the substituted polythiophene in solution and solid-state were 1.4 and 1.1 eV. Respectively, unusually small values for undoped polythiophenes.

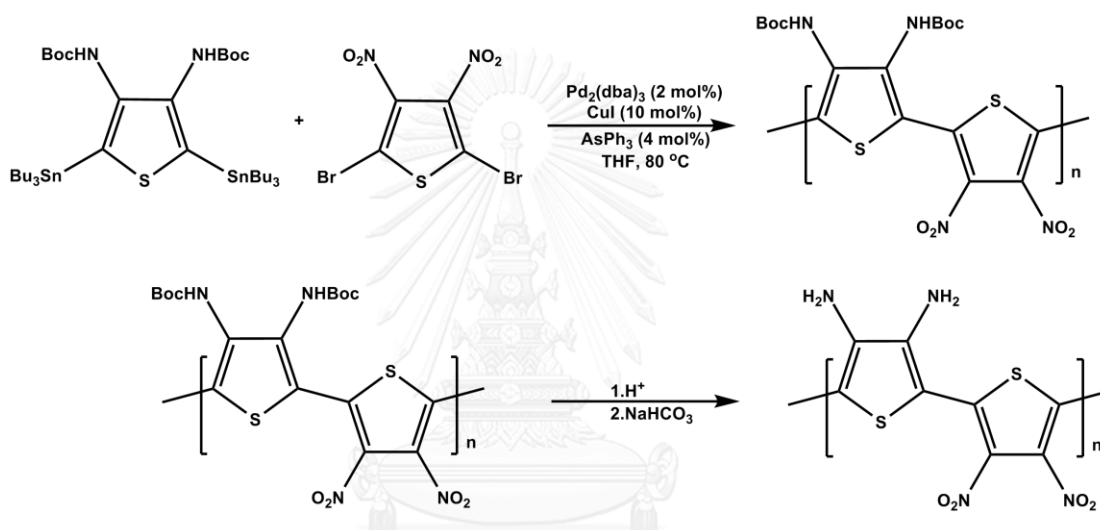


Figure 1.11 Synthesis of donor-acceptor conjugated polythiophene

Kenning and coworkers [20] reported a general synthetic route which was developed for the efficient preparation of 2,3-disubstituted thieno[3,4-*b*]pyrazines. (Figure 1.12) The precursor 2,5-dibromo-3,4-dinitrothiophene was used, in which the nitro groups were reduced to amino groups, and then condensed with α -diones to obtain 2,3-disubstituted thieno[3,4-*b*]pyrazines which were excellent precursors for production of narrow band gap conjugated polymers.

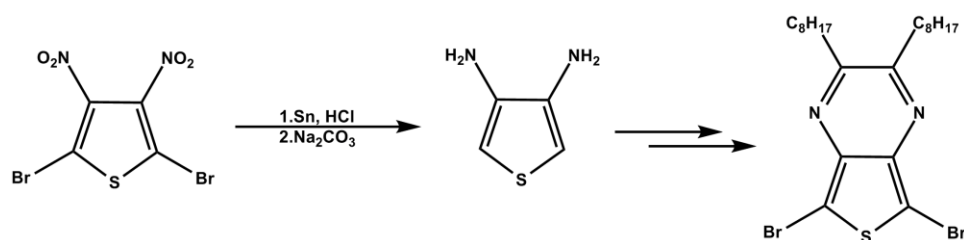


Figure 1.12 Synthesis of thieno[3,4-b]pyrazines

Yamishita and Tanaka [21] presented the new narrow band gap copolymer consisting of aromatic thiophene and nonclassical thiophene repeat units. The monomer molecule was synthesized from 3,4-diaminothiophene.

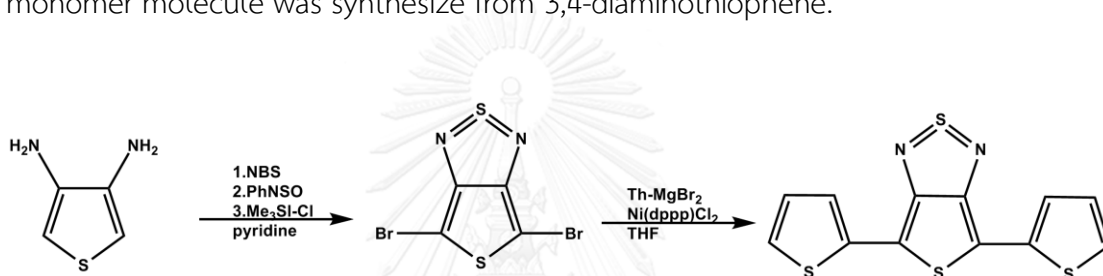


Figure 1.13 Synthesis route to 4,6-di(2-thienyl)thieno[3,4-c][1,2,5]thiadiazole

Rasmussen and coworkers [22] was researching about Thieno pyrazine differential at position 3,4 to comparing optical and electro chemistry property. The result shows that the close loop replacement group has absorption quality higher than alkyl replacement group, because it has more resonance system which help sending the electron to main chain.

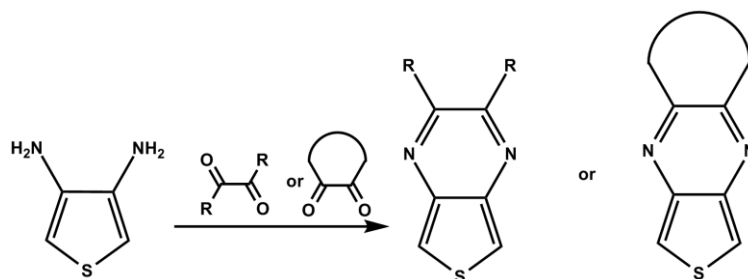


Figure 1.14 Synthesis of thieno[3,4-b]pyrazine derivatives

Creencia and coworkers [23] reported synthesis of nitrogen containing heterocycles is modified by using microwave radiation of heat instead by reflux for several hours. Synthesizes 96%yield of benzimidazoles. The results shown that microwave-asissted cadogan reaction gave better product yields at shorter reaction times.

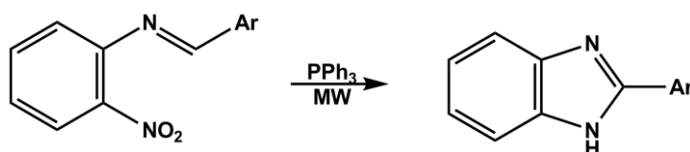


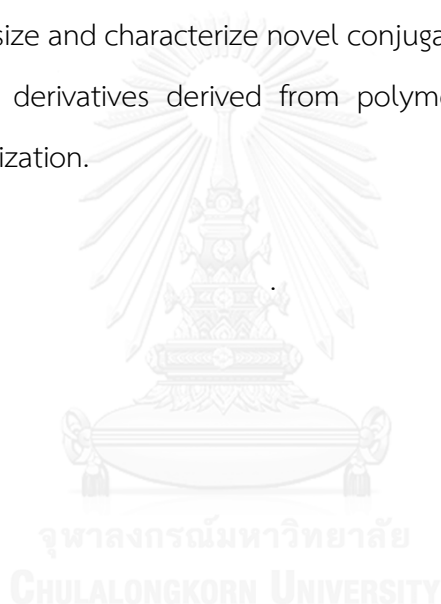
Figure 1.15 Synthesis of benzimidazoles by microwave radiation



Herein, we attempted to prepare novel conjugated polymers containing units of diaminothiophene derivatives. Because the amino groups (-NH_2) generally provide high density of electrons into π -conjugated system and potentially reduce its band gap, such polymer should have improved conductive property. Moreover, the easily functionalized amino groups into various functional groups would expand possibility to create many new types of polymers for varieties of applications.

1.7 Objective

To synthesize and characterize novel conjugated polymers containing units of diaminothiophene derivatives derived from polymer precursor that was made through $\text{S}_{\text{N}}\text{Ar}$ polymerization.



CHAPTER II

EXPERIMENTS

2.1 Chemicals

Thin layer Chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck Kieselgel 60 F₂₅₄, Merck KGaA, Darmstadt, Germany). Column chromatography was performed using 0.063-0.200 mm or 70-230 mesh ASTM silica gel 60 (Merck Kieselgel 60 G, Merck KGaA, Darmstadt, Germany). Solvents used in column chromatography were distilled from commercial grade prior to use. Other reagents were purchased from the following vendors:

- RCI Labscan (Bangkok, Thailand): acetone, acetonitrile, chloroform, dichloroethane, dichloromethane, dimethylsulfoxide (DMSO), 1,4-dioxane, ethanol (EtOH), sodium hydrogen carbonate (NaHCO₃), sodium hydroxide (NaOH), tetrahydrofuran (THF)
- Acrös Organic (New Jersey, USA): *o*-phenylenediamine, potassium tert-butoxide, trifluoroacetic acid (TFA), triethylamine (Et₃N)
- Fluka Chemical (Buchs, Switzerland): aluminum chloride (AlCl₃) anhydrous
- Merck Co. (Darmstadt, Germany): concentrated hydrochloric acid, concentrated sulfuric acid, methanol (MeOH), toluene
- Cambridge Isotope Laboratories (USA): deuterated acetone (acetone-*d*₆), deuterated chloroform (CDCl₃), deuterated dimethylsulfoxide (DMSO-*d*₆)
- Aldrich (USA): *N*-butylamine, *N,N'*-di-*sec*-butyl-*p*-phenylenediamine, 1,2-dichlorobenzene, deuterium oxide (D₂O), Methanesulfonic acid (MSA), octanoyl chloride, *p*-phenylenediamine, sodium hydride (NaH), propionyl chloride, oxalyl chloride
- Panreac (Spain): anhydrous magnesium sulfate (MgSO₄)
- Ajax Finechem Pty (Auckland, New Zealand): sodium carbonate

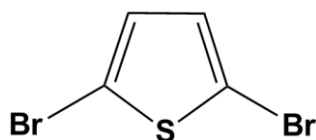
2.2 Instruments and equipment

Melting points were determined with a Stuart Scientific Melting Point SMP10 (Bibby Sterlin Ltd., Staffordshire, UK). The FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. The ^1H and ^{13}C NMR spectra were obtained using Varian Mercury NMR spectrometer operated at 400.00 MHz for ^1H and 100.00 MHz for ^{13}C nuclei (Varian company, USA). The mass spectra were recorded on Waters Micromass Quattro micro API ESCi (Waters, USA). UV-Vis absorption spectra were recorded on UV-VISIBLE Spectrometer: UV-2550 (Shimadzu Corporation, Kyoto, Japan).



2.3 Monomer synthesis

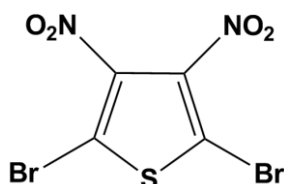
2.3.1 Bromination : 2,5-dibromothiophene



2,5-dibromothiophene was prepared following the procedure described in literature [24]. Thiophene (0.78 g, 9 mmol) in CH_2Cl_2 (10 mL) and glacial. CH_3COOH (10 mL) was added NBS (3.60 g, 18 mmol) slowly at room temperature for 30 min and then added 3M NaOH until the solution was basic. The product was extracted by EtOAc. The separated organic phase was dried over anhydrous MgSO_4 and filtered. The solvents were removed under reduced pressure. The crude mixture was purified by short column chromatography using hexane as eluent, affording yellow liquid. (1.67 g, 80.4 %yield) ^1H NMR (400MHz, CDCl_3): δ (ppm) 6.86 (s). (Figure A.1, Appendix)

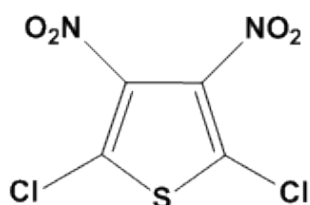
2.3.2 Nitration

2.3.2.1 2,5-dibromo-3,4-dinitrothiophene (DBDNT)



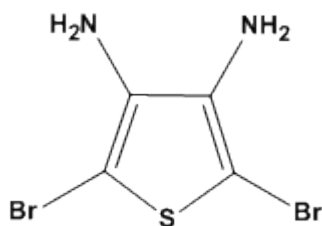
DBDNT was prepared through the modification of the procedure previous work described in literature [25]. Fuming HNO_3 (7 mL) and conc. H_2SO_4 (30 mL) were combined in a flask and cooled in an ice bath. 2,5-Dibromothiophene (0.7 mL, 19 mmol) was added dropwise and the reaction was maintained at temperature of 20-30 °C until complete conversion. The mixture was poured over ice. The solid residue was recovered by vacuum filtration. The crude product was purified by column chromatography using hexane/EtOAc (8:2) as eluent, affording a pale yellow solid (0.39 g, 23.5 %yield). mp 137-139 °C (lit. [26] 135-137 °C). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 113.8, 139.2. (Figure A.4, Appendix)

2.3.2.2 2,5-dichloro-3,4-dinitrothiophene (DCDNT)



DCDNT was prepared through the same method as above, using fuming HNO_3 (7 mL), and conc. H_2SO_4 (30 mL) and the precursor 2,5-dichlorothiophene (2.884 g, 18.8 mmol). The crude product was purified by column chromatography using hexane/EtOAc (9:1) as eluent, affording a pale yellow solid (3.45 g, 78 %yield). mp 81-83 °C (lit. [26] 83.4-84-3 °C). IR (ATR, cm^{-1}): 1546, 1394 (N-O st). (Figure A.5, Appendix); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 136.8, 127.8 (Figure A.6, Appendix),

2.3.3 reduction : 3,4-diamino-2,5-dibromothiophene

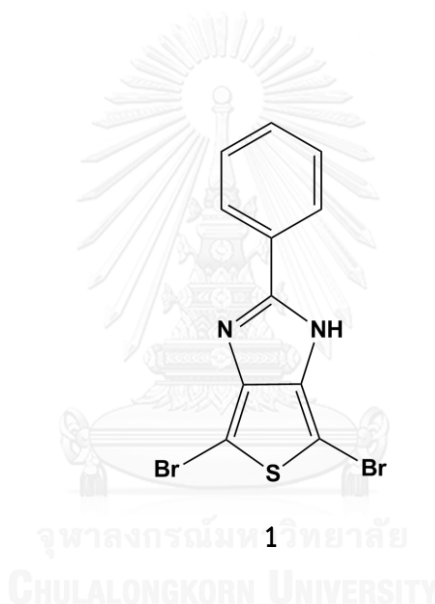


3,4-diamino-2,5-dibromothiophene using the method described in literature [20]. DBDNT (0.083 g, 1.5 mmol) in EtOH (4 mL) was added SnCl_2 (0.632 g, 4.5 mmol) at room temperature under N_2 atmosphere and stir for 24 hr. The product was extracted by CH_2Cl_2 . The separated organic phase was dried over anhydrous MgSO_4

and filtered. The solvents were removed under reduced pressure. The product was a dark yellow but after that the product have darker color and insoluble in organic solvent because product was decompose when evaporation. In case that this compound was used as the precursor in synthesis of some of other products, it was not separated nor purified and used as crude solution in the following steps.

2.3.4 Reactions with benzaldehyde derivatives

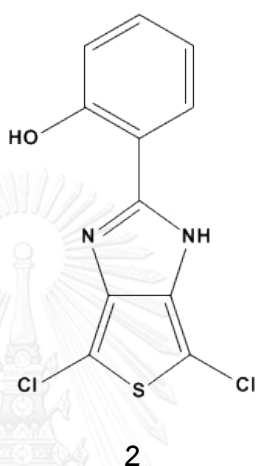
2.3.4.1 4,6-dibromo-2-phenyl-1H-thieno[3,4-d]imidazole (1)



3,4-diamino-2,5-dibromothiophene in EtOH, product in reduction, was added benzaldehyde (0.43 g, 5 mmol) and conc. H₂SO₄ 5 drops. The mixture was stirred at room temperature for 3 h and then added 2M NaHCO₃ (5 mL) and extracted with EtOAc. The separated organic phase was dried over anhydrous MgSO₄ and filtered. The solvents were removed under reduced pressure and the crude mixture was purified on silica column chromatography using a 8:2 EtOAc/hexane eluent. Compound **1** was obtained as pale yellow liquid (0.17 g, 34 %yield). ¹H NMR (400MHz, CDCl₃): δ (ppm) 9.87 (s, N-H) 7.86 (d, 2H), 7.62 (t, *J* = 1.31 2.62.6.77 Hz, 1H) 7.48 (t, 2H) (**Figure A.7**,

Appendix), ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 113.4, 128.7, 129.3, 130.2, 132.5, 134.8, 136.9. (Figure A.8, Appendix)

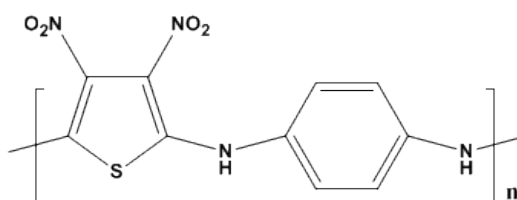
2.3.4.2 2-(4,6-dichloro-1*H*-thieno[3,4-*d*]imidazol-2-yl)phenol (2)



Dissolve DCDNT (0.243 g, 1 mmol) in THF (5 mL) and added salicylaldehyde (0.52 g, 5 mmol) and PPh_3 (0.85 g, 6 mmol) and the mixture was heated by microwave at 100°C for 30 min the solvent was removed under reduced pressure and the crude mixture was purified on silica column chromatography using a 1:1 CH_2Cl_2 /hexane eluent. Compound **2** was obtained a pale yellow liquid (0.023 g, 17%yield). ^1H NMR (400MHz, CDCl_3): δ (ppm) 7.71 (m, 1H) 7.61 (t, 1H), 7.50 (q, 1H) 7.40 (m, 1H) (Figure A.9, Appendix), ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 133.3, 132.3, 132.2, 132.1, 131.6, 128.7, 128.5, 128.4, 127.9. (Figure A.10, Appendix)

2.4 Polymer synthesis

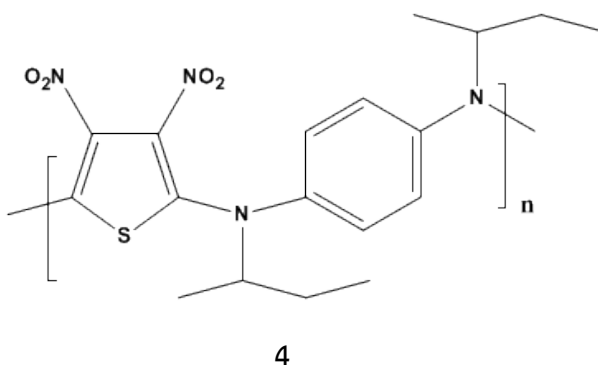
2.4.1 DCDNT with *p*-phenylenediamine (3)



3

To a solution of DCDNT (0.023 g, 0.1 mmol) in DMSO (3 mL) was added *p*-phenylenediamine (0.011 g, 0.1 mmol) and Et₃N (0.012 g, 0.1 mmol). The mixture was heated by microwave at 100 °C for 30 min and then added H₂O (2 mL) to precipitate the polymer product. The solid residue was filtered by vacuum filtration and washed with H₂O and EtOAc to get polymer **3** as insoluble red brown solid (0.019 g, 61% yield). IR (ATR, cm⁻¹): 3345 (N-H st) 1544, 1331 (N-O st), 1253 (C-N st). (Figure A.11, Appendix); UV (solid) λ_{\max} = 516 nm (Figure A.12, Appendix).

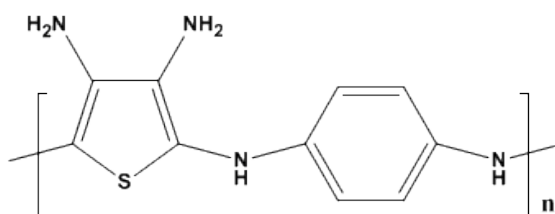
To a solution of DCDNT (0.243 g, 1 mmol) in DMSO:H₂O (4 mL) was added *p*-phenylenediamine (0.108 g, 1 mmol) and Et₃N (0.14 mL, 1 mmol). The mixture was stirred at room temperature for 6 day under nitrogen atmosphere. The solid residue was filtered by vacuum filtration and washed with H₂O and EtOAc to get polymer **3** as insoluble red brown solid (0.21 g, 70.0%). IR (ATR, cm⁻¹): 3295 (N-H st) 1560, 1320 (N-O st), 1224 (C-N st). (Figure A.13, Appendix) UV (solid) λ_{\max} = 542 nm (Figure A.14, Appendix).

2.4.2 DCDNT with *N,N'*-di-*sec*-butyl-*p*-phenylenediamine (4)

A mixture of DCDNT (0.024 g, 0.1 mmol), *N,N'*-di-*sec*-butyl-*p*-phenylenediamine (0.023 g, 0.1 mmol) and NaH (0.006 g, 0.03 mmol) in DMSO (3 mL) was heated by microwave at 80 °C for 1 h. The solid residue was filtered by vacuum filtration and washed with 2M NaOH and hexane to get polymer **4** as black solid (0.031 g, 59.3% yield). ¹H NMR (400 MHz, partially dissolved in CDCl₃): δ (ppm) 6.50 -7.54, 3.24-3.50, 0.53–1.98 (**Figure A.15, Appendix**); IR (ATR, cm⁻¹): 3345 (N-H st) 2967 (C-H st), 1605, 1376 (N-O st); (**Figure A.16, Appendix**) UV (solid) λ_{max} = 503 nm (**Figure A.17, Appendix**).

A mixture of DCDNT (0.243 g, 1 mmol), *N,N'*-di-*sec*-butyl-*p*-phenylenediamine (0.23 g, 1.1 mmol) and NaH (0.06 g, 2.5 mmol) in DMSO (3 mL) the mixture was stirred at room temperature for 6 d. The solid residue was filtered by vacuum filtration and washed with 2M NaOH and hexane to get polymer **4** as black solid (0.35 g, 75.9% yield). ¹H NMR (400 MHz, partially dissolved in CDCl₃): δ (ppm) 6.50 -7.67, 2.75-3.50, 0.43–1.97 (**Figure A.18, Appendix**); IR (ATR, cm⁻¹): 3345 (N-H st) 2967 (C-H st), 1605, 1376 (N-O st), (**Figure A.19, Appendix**) UV (solid) λ_{max} = 542 nm (**Figure A.20, Appendix**).

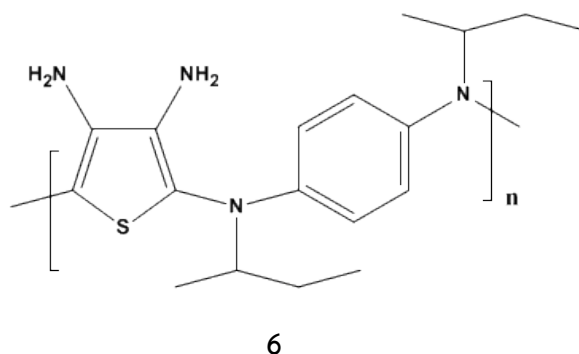
2.4.3 Synthesis of polymer 5



5

Polymer **3** (0.19 g, 0.07 mmol) in EtOH (3mL) was added SnCl₂ (0.04 g, 0.2 mmol). The mixture was heated by microwave at 100 °C for 30 min. The solid residue was filtered by vacuum filtration and washed with hexane to get polymer **5** as insoluble red brown solid (0.01 g, 65.7 %yield). IR (ATR, cm⁻¹): 3401 (N-H st) 1544, 1261 (C-N st) (**Figure A.20, Appendix**); UV (solid) $\lambda_{\text{max}} = 550 \text{ nm}$ (**Figure A.21, Appendix**).

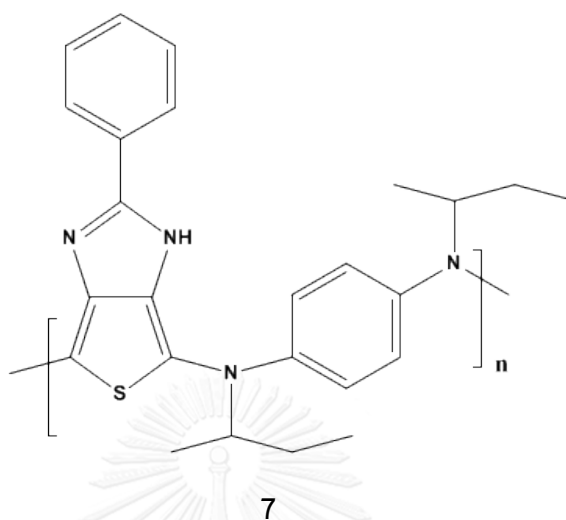
2.4.4 Synthesis of polymer 6



Polymer **5** (0.031 g, 0.05 mmol) in THF (4 mL) was added PPh₃ (0.078 g, 0.3 mmol). The mixture was heated by microwave at 120 °C for 20 min. The solid residue was filtered by vacuum filtration and washed with 2M NaOH and EtOAc to get polymer **6** as black solid (0.005 g, 34.8 %yield). ¹H NMR (400MHz, partially dissolved DMSO): δ (ppm) 0.74-1.68, 3.02-3.84, 6.23-7.02 (**Figure A.23, Appendix**); UV (solid) λ_{max} = 617 nm (**Figure A.24, Appendix**); IR (ATR, cm⁻¹): 3345 (C-H aromatic) 2950 (C-H aliphatic) (**Figure A.25, Appendix**).

Polymer **5** (0.35 g, 0.3 mmol) in EtOH (4 mL) was added SnCl₂ (0.17 g, 0.5 mmol). The mixture was stirred at room temperature for 10 d. The solid residue was filtered by vacuum filtration and washed with 2M NaOH and EtOAc to get polymer **6** as black solid (0.037 g, 42.1 %yield). ¹H NMR (400MHz, partially dissolved DMSO): δ (ppm) 0.73-2.01, 3.25-4.50, 7.00-7.72 (**Figure A.26, Appendix**); UV (solid) λ_{max} = 643 nm (**Figure A.27, Appendix**); IR (ATR, cm⁻¹): 3330 (C-H aromatic) 2978 (C-H aliphatic) (**Figure A.28, Appendix**).

2.4.5 Synthesis of polymer 7



The mixture of polymer **5** (0.35 g, 0.05 mmol) in EtOH (5 mL) was added SnCl₂ (0.34 g, 1.5 mmol) and benzaldehyde (0.026 g, 0.25 mmol). The mixture was stirred at room temperature for 5 d. The solid residue was filtered by vacuum filtration and washed with 2M NaOH and EtOAc to get polymer **7** as black solid (0.081 g, 40.2 %yield). IR (ATR, cm⁻¹): 1610 (C=N st) (**Figure A.29, Appendix**); ¹H NMR (400MHz, DMSO): δ (ppm) 0.74-1.68, 3.02-3.84, 6.02-8.23 (**Figure A.30, Appendix**); UV (solid) λ_{max} = 658 nm (**Figure A.31, Appendix**).

CHAPTER III

RESULTS AND DISCUSSION

3.1 Monomer synthesis

3.1.1 Bromination

2,5-dibromothiophene was synthesized from thiophene by electrophilic bromination reaction using NBS. The conditions of the reactions were varied according to **Table 3.1**.

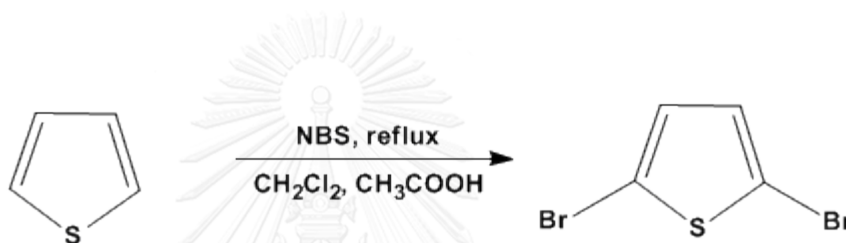


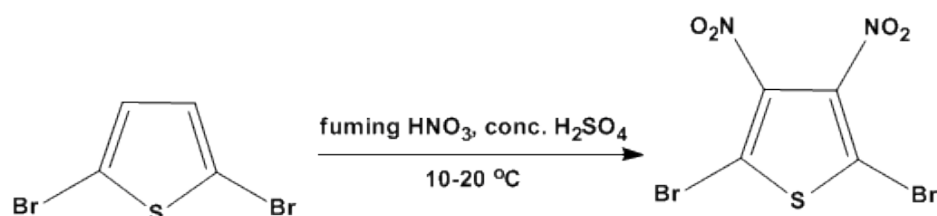
Table 3.1 Various conditions for the bromination of thiophene

Entry	Thiophene (mmol)	NBS (eqv)	Time (min)	% Yield
1	9 mmol	2	20	74.1
2	36 mmol	2	30	80.4

Following **Table 3.1**, high yields of the α -disubstituted product were obtained even at larger scale of the reaction. The results could be improved if slightly excess of NBS was used. The ¹H NMR spectrum clearly showed the singlet signal at 6.82 ppm of the β -protons of the thiophene ring. (**Figure A.1, Appendix**). The spectrum matched well with the information from literature [24].

3.1.2 Nitration

3.1.2.1 2,5-Dibromo-3,4-dinitrothiophene (DBDNT)



DBDNT was synthesized from 2,5-dibromothiophene through highly vigorous electrophilic nitration reaction. The conditions of the reactions were varied according to **Table 3.2**.

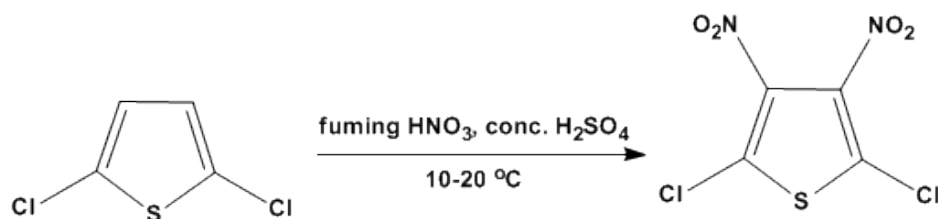
Table 3.2 Various conditions for the synthesis of DBDNT

Entry	2,5-dibromothiophene (mmol)	conc. H ₂ SO ₄ (mL)	fuming HNO ₃ (mL)	Time (h)	Product (%yield)
1	6.2	30	7.0	3.0	7.5
2	10.0	30	7.0	3.0	23.1
3	20.0	30	7.0	3.5	23.8

The nitration reactions appeared to give low product yields. Several by-products were detected. Two of the major by-products were those from acid-catalyzed debrominations, giving 2-bromo-3,4-dinitrothiophene in which its ¹H NMR spectrum clearly showed the singlet signal at 7.82 ppm. (**Figure A.2, Appendix**), and 3,4-dinitrothiophene from the loss of both bromine atoms where its ¹H NMR spectrum clearly showed the singlet signal at 8.23 ppm (**Figure A.3, Appendix**). Nevertheless, the desired product as yellow solid was obtained up to 23.8 %yield in large scale. The ¹³C NMR spectrum showed both carbon signals at 114.1, 141.2 ppm. (**Figure A.4, Appendix**). The losing of bromine atoms was assumed to occur under strong acidic

condition at relatively high temperature. Heat generated from the reaction may have warmed the reaction enough to trigger the side reaction.

3.1.2.2 2,5-Dichloro-3,4-dinitrothiophene (DCDNT)



DCDNT was synthesized from commercially available 2,5-dichlorothiophene through electrophilic nitration reaction. The conditions of the reactions were varied according to **Table 3.3**.

Table 3.3 Various conditions for the synthesis of DCDNT

Entry	2,5-dichlorothiophene (mmol)	conc. H ₂ SO ₄ (mL)	fuming HNO ₃ (mL)	Time (h)	Product (%yield)
1	3.7	6	1.5	3.0	55.6
2	18.8	30	7.0	3.0	61.9
3	18.8	30	7.0	3.5	77.5
4	18.8	30	7.0	4.0	70.9

Following **Table 3.3**, the optimized time for this reaction was 3.5 h, leading to the highest yield of DCDNT (Entry 3). High yields of the product were obtained at larger scale of the reaction. Short reaction time resulted in low yield could be due to incomplete reaction. Nevertheless, longer reaction time might cause decomposition of the starting material or the product, perhaps through dechlorinations similar to what have been found in the previous sections. Although in this case, the amounts of by-

products were small and not isolate nor identified. The expected product was characterized by the presence of strong, sharp bands of nitro groups at 1549, 1309 cm^{-1} in IR spectrum. (Figure A.5, Appendix) The ^{13}C NMR spectrum (Figure A.6, Appendix) confirmed the signal details that matched with information from literature [26].

3.1.3 Reduction : 3,4-diamino-2,5-dibromothiophene

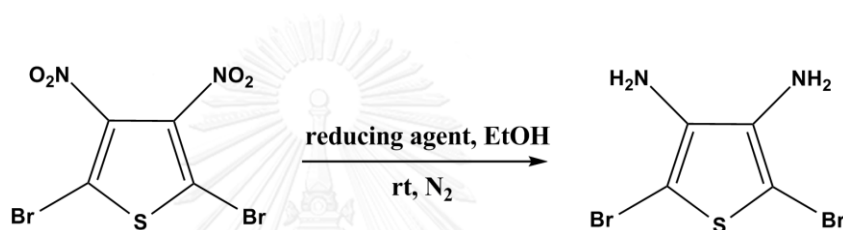


Table 3.4 Various conditions for the synthesis of 3,4-diamino-2,5-dibromothiophene

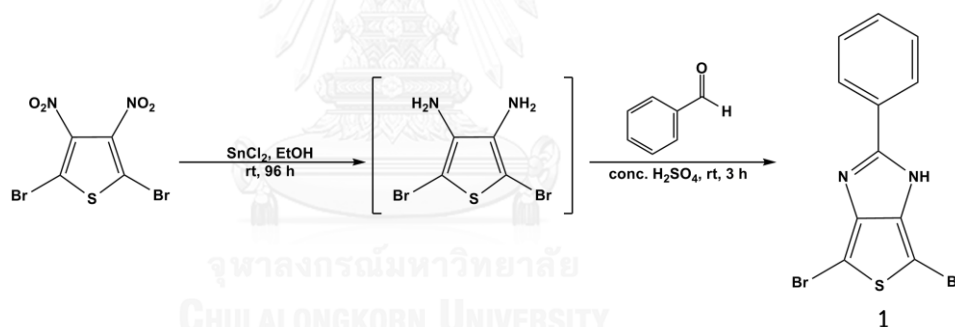
Entry	DBDNT (mmol)	Reagent (equiv)	conc. HCl (mL)	Time (h)	Crude yield (%)
1	0.3	Sn (5)	20	24	-
2	1.0	Zn dust (18)	7	24	-
3	1.0	SnCl_2 (9)	7	36	13

The 3,4-diamino-2,5-dibromothiophene synthesis was carried out as shown in **Table 3.4**. Tin metal was first chosen as the reducing agent following a reported procedure. (entry 1) [20] During the process, a mixture turned black with some precipitates formed. After filtering and evaporating the solvent, highly polar, inseparable solid black polymer was obtained, which could not be further identified. From this point, the reducing agent was changed to Zn dust (entry 2) and reduce the amount of HCl. However, the same unidentifiable tar was still obtained. At last, the

reducing agent was changed again to SnCl_2 . [27] The reaction was more slowly proceed and did not produce any solid black tar. Yet, after working up, only 13% yield of crude product could be obtained. Furthermore, after the solvent was removed, the crude product could not be redissolved in any organic solvents. The possible explanation for this result is that the product any decompose after evaporation. The newly formed diamino group may not be stable enough in the air and was oxidized into insoluble polymer. Because of this potential instability of the product during the quenching process, the diamino product preferably should be used in subsequent reactions without isolation.

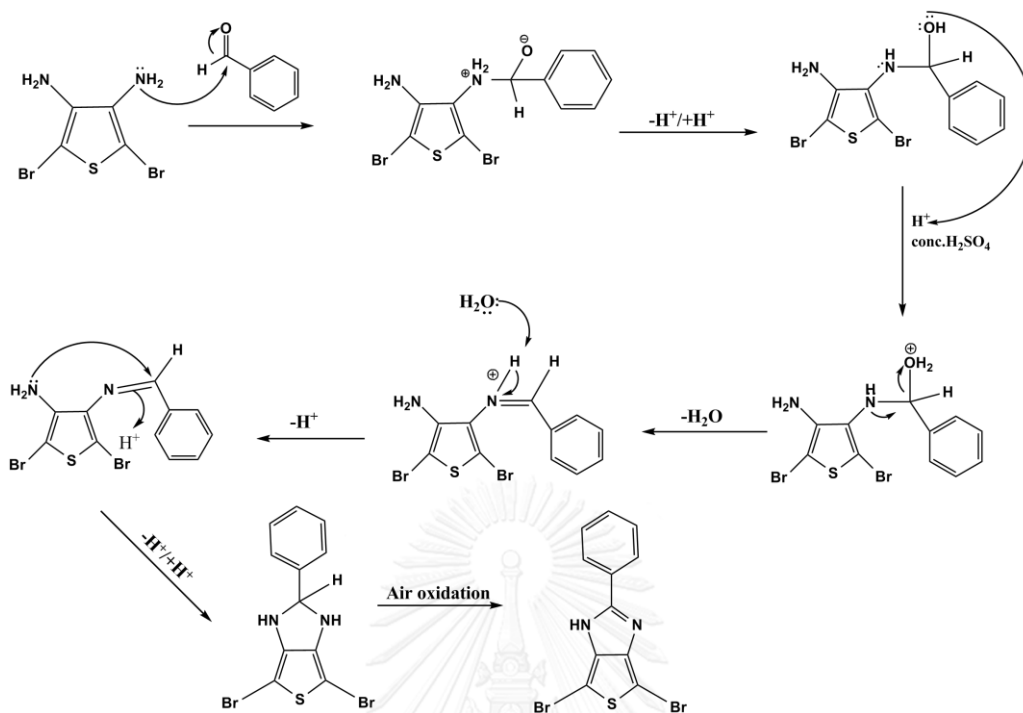
3.1.4 Reactions with aldehydes

3.1.4.1 4,6-dibromo-2-phenyl-1H-thieno[3,4-*d*]imidazole (1)



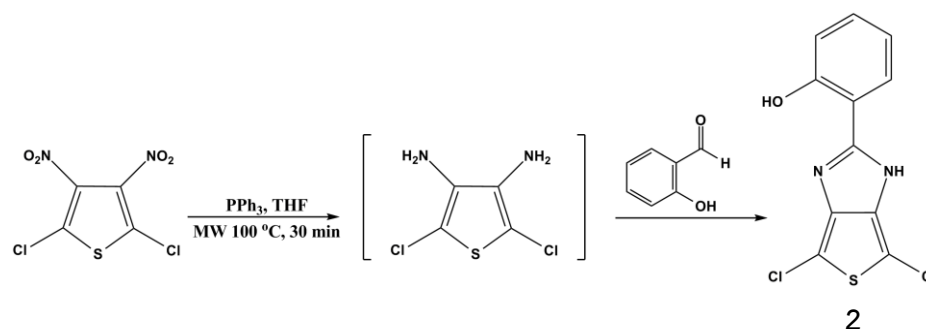
The 4,6-dibromo-2-phenyl-1H-thieno[3,4-*d*]imidazole (**1**) was produced from a reaction between benzaldehyde and the crude solution of 3,4-diamino-2,5-dibromothiophene from section 3.1.3 without product isolation. The initial imine formation with one of the amino group reacted further with the adjacent free amino

group and become the fused thieno-imidazole bicycle (**Scheme 3.1**).



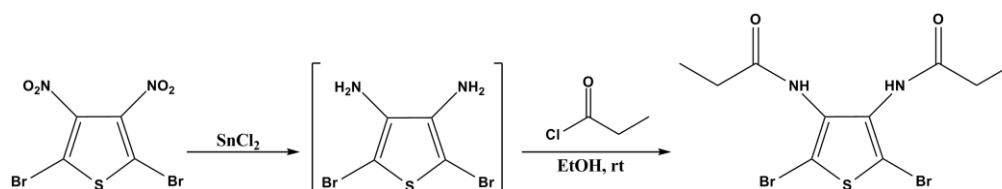
Scheme 3.1 Mechanism for the synthesis of compound 1

The ^1H NMR spectrum showed the expected signals of monosubstituted aromatic ring (**Figure A.7, Appendix**), which corresponded to ^{13}C NMR spectrum with seven peaks of different carbons. (**Figure A.8, Appendix**) The light yellow solid product was obtained in 34% yield based on two-step processes starting from DBDNT.

3.1.4.2 2-(4,6-Dichloro-1*H*-thieno[3,4-*d*]imidazol-2-yl)phenol (2)

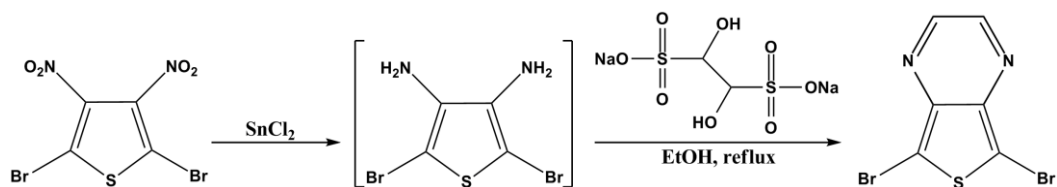
Following the reaction with benzaldehyde in the previous, we continued the reaction with salicylaldehyde, but using DCDNT as a precursor and PPh_3 as the reducing agent for DCDNT in a hope that this condition could give better yield of expected product. [23] The corresponding imidazole derivative was obtained as light yellow solid in 17% yield based on two-step process. When comparing this reaction and that in section 3.1.4.1, we found out that the synthesis gave less yield because it is the two step reaction by microwave which is reduction DCDNT. After diamine was produced, we continue the reaction with salicylaldehyde and got the second product. The reaction at high temperature cause the diamine to be losing from and it is the small scale reaction that produce less result. ^1H NMR spectrum shown the multiplet signals at 7.2-7.8 ppm of *o*-disubstituted aromatic ring. (Figure A.9, Appendix) ^{13}C NMR spectrum shown the expected carbon nine signals. (Figure A.10, Appendix)

3.1.5 Reaction with acid chloride



The reaction between the crude 3,4-diamino-2,5-dibromothiophene and propionyl chloride did not come out as we hoped for *N,N'*-(2,5-dibromothiophene-3,4-diyl)dipropionamide. It is possible that the unstable diamino precursor decomposed during the quenching before the second reaction proceeds. The acid chloride would then react with residual EtOH leftover from the reduction step. In this experiment, two less reactive acid chlorides, octanoyl chloride and benzoyl chloride, were used but also not successful, confirming that the diamino precursor completely decomposed before the reaction with acid chlorides.

3.1.6 Reaction with glyoxal sodium bisulfite



The reaction between the crude 3,4-diamino-2,5-dibromothiophene and glyoxal sodium bisulfite did not come out as we hoped for 5,7-dibromothieno[3,4-*b*]pyrazine. There were a problem from this reaction between DBDNT and glyoxal sodium bisulfite by having EtOH as a solvent, the glyoxal sodium bisulfite is a salt form and cannot be dissolve in EtOH and the unstable diamino precursor decomposed during the quenching before the second reaction proceeds.

3.2 Polymer Synthesis

3.2.1 DCDNT with *p*-phenylenediamine

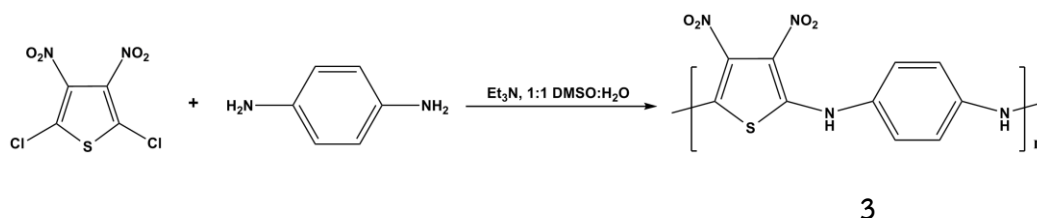


Table 3.5 Various conditions for the synthesis of polymer **3**

Entry	Δ	Time	Yield	λ_{\max}
1	rt	6 day	70.3%	542
2	MW 100 °C	1 h	61.6%	516

Polymer **3** was synthesized from series of nucleophilic aromatic substitutions (S_NAr) reaction of DCDNT and *p*-phenylenediamine using microwave heating or being stirred at RT for several days (**Table 3.5**). The desired product was obtained as a chocolate brown solid which could not be dissolved in any organic solvents. The N-H stretching signal of amino groups and N-O stretching signals of nitro group were showed at 3345 and 1544, 1331 cm^{-1} in IR spectrum, respectively. (**Figure A.11 and A.13, Appendix**) The optical property of polymer **3** from the reaction stirred at room temperature for 6 days exhibited a characteristic absorption in the visible region of a conjugated polymer, with a maximum wavelength absorption (λ_{\max}) at 542 nm. (**Figure A.14, Appendix**) On the other hand, the optical property of pressed pellet of polymer **1** from microwave heating at 100 °C for 1 h exhibited a lower maximum wavelength absorption (λ_{\max}) at 516 nm. (**Figure A.12, Appendix**) It is assumed that the much longer reaction time and lower reaction temperature allowed the monomers to react on the growing polymeric chain more than initiate new chains. The reaction at room temperature should then contain longer conjugated polymeric chain length, as reflected by the appeared longer λ_{\max} .

3.2.2 DCDNT with *N,N'*-di-*sec*-butyl-*p*-phenylenediamine

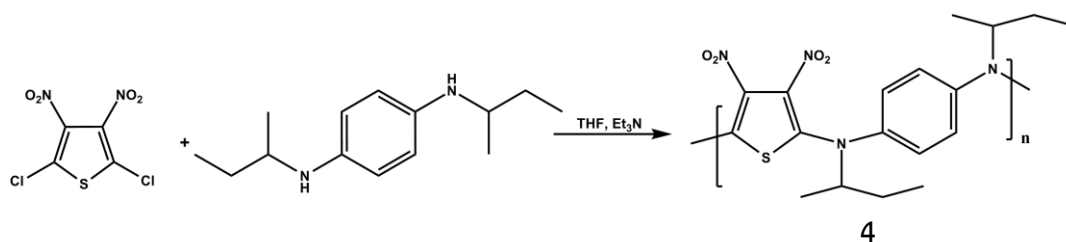
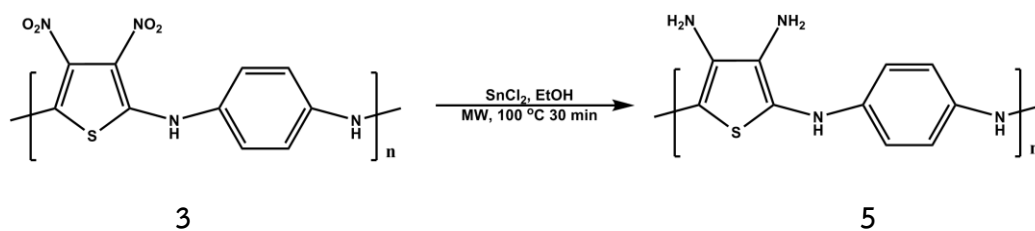


Table 3.6 Various conditions for the synthesis of polymer **4**

Entry	condition	Time	Yield	λ_{\max}
1	rt	6 d	75.9%	542
2	MW 100 °C	15 min	59.3%	503

Polymer **4** was synthesized from series of nucleophilic aromatic substitutions (S_NAr) reaction of DCDNT and *N,N'*-di-*sec*-butyl-*p*-phenylenediamine using either microwave heating or being stirred at RT for several days (**Table 3.6**). The obtained black solid product was found to partly dissolve in some organic solvents. IR spectrum of the polymer showed the strong broad signals of N-O stretching of nitro groups at 1350, 1590 cm^{-1} and C-H stretching of butyl and aromatic groups at 2945-3107 cm^{-1} . (**Figure A.18, A.21 Appendix**) The ^1H NMR spectrum of polymer **4** showed broad peaks at 6.49–7.52 ppm for aromatic protons, 3.05-3.80 ppm and 1.25–1.87 ppm for ethyl groups. (**Figure A.17, A.20 Appendix**) The NMR results should measure only the fractions of short chain polymers that could be dissolved in the solvent. Longer chains were characterized by UV-Vis spectroscopy showing the maximum wavelength absorptions (λ_{\max}) at over 500 nm. (**Figure A.19, A.22, Appendix**) Once again, the polymer obtained at room temperature which contains longer conjugated polymeric chain length showed longer λ_{\max} , as observed earlier with polymer **3**.

3.2.3 Synthesis of polymer 5



Polymer **5** was synthesized from reduction of polymer **3** in 65% yield by tin (II) chloride modified from the procedure in section 3.1.3. The obtained red brown solid could not be dissolved in common organic solvents similar to its precursor. The strong N-H stretching signal of amino groups appeared at 3350 cm^{-1} in IR spectrum. However, some residual N-O stretching signals of nitro groups were still observed, indicating that the reduction was incompletely. (**Figure A.21, Appendix**) The optical property of polymer **5** measured as pressed solid film exhibited an absorption in the visible region of a conjugated polymer with a maximum wavelength absorption (λ_{max}) at 550 nm. (**Figure A.22, Appendix**)

3.2.4 Synthesis of polymer 6

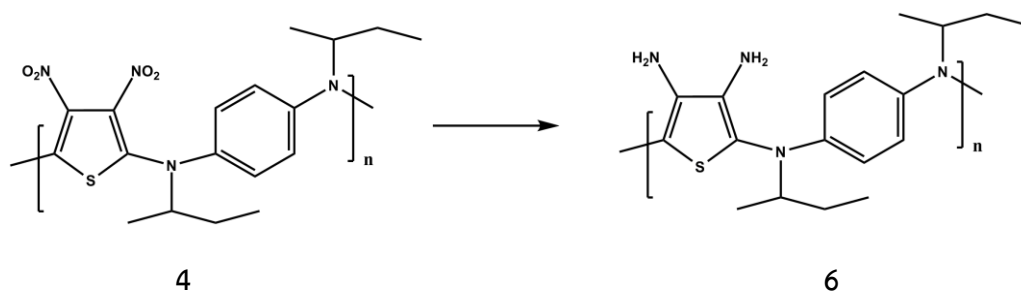


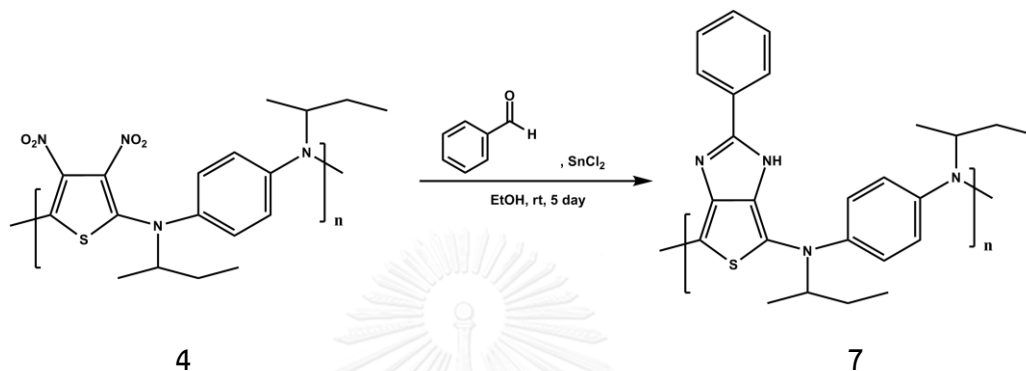
Table 3.7 Various conditions for the synthesis of polymer 6

Entry	Reducing agent (eqv)	Solvent	condition	Time	λ_{\max} (nm)
1	SnCl ₂ (2.5)	EtOH	rt	11 d	643
2	PPh ₃ (6)	THF	MW 80 °C	30 min	617

Polymer **6** was synthesized from Polymer **4** through excessive reduction of NO₂ groups, potentially converting the donor-acceptor polymer to the donor-donor polymer. The obtained black solid product partly dissolved in some organic solvents, probably due to the compact size and the presence of branched butyl groups along the chains that reduced chain aggregation. The ¹H NMR spectrum of polymer **6** showed broad peaks of aromatic protons at 6.17-7.29 ppm. (Figure A.23 and A.26, Appendix) IR spectrum of the polymer showed the strong broad signals of C-H stretching of butyl and aromatic groups at 2945-3107 cm⁻¹ and broad signals of N-H stretching at 3330 cm⁻¹. (Figure A.24 and A.27, Appendix) The UV-vis absorption of the solid film exhibited a maximum wavelength absorption (λ_{\max}) over 643 nm (Figure A.28, Appendix) and 617 nm (Figure A.25, Appendix) for entries 1 and 2 (Table 3.7) respectively. Clearly, the presence of amino groups decrease the band gap of the conjugated polymer and shift its λ_{\max} to longer wavelength compared to the nitro precursor. The longer reduction time at room temperature for entry 1 (Table 3.7) may

have produced more amino groups on the polymer chains and further increased the λ_{\max} value.

3.2.5 Synthesis of polymer 7



From the successful reaction of reduced DBDNT and benzaldehyde in section 3.1.4.1, polymer **4** was also used as a starter. Though in this case, one pot reduction and condensation with benzaldehyde was carried out to prevent losing the diamino intermediate before condensation. The reaction was tracked by following the nitro group signals from IR spectra of the sampled solutions withdrawn from the ongoing reaction until they became steady or disappeared, which can be assumed as completion. The new polymer was obtained as black solid in 40.2% yield. Its IR spectrum (**Figure A.29, Appendix**) no longer showed the nitro peaks that was obvious with the starter polymer. The ¹H NMR spectrum of polymer **7** showed broad peaks of aromatic protons at 6.00-8.59 ppm. (**Figure A.30, Appendix**) The UV-Vis absorption of the solid film exhibited a maximum wavelength absorption (λ_{\max}) over 658 nm. (**Figure A.31, Appendix**) Polymer **7** has higher λ_{\max} than polymer **4** precursor may arise from higher electron density in the polymer chain from better electron donating groups than the nitro groups, similar to what observed with polymer **6**, which is the reduced intermediate prior to polymer **7**.

CHAPTER IV

CONCLUSION

The synthesis of new conjugated polymers containing units of 2,5-diaminothiophene derivatives had been accomplished. For monomer synthesis, 2,5-dibromothiophene was prepared from thiophene and NBS in 80.4% yield. 2,5-Dibromo-3,4-dinitrothiophene (DBDNT) and 2,5-dichloro-3,4-dinitrothiophene (DCDNT) were synthesized from 2,5-dibromothiophene and 2,5-dichlorothiophene using fuming HNO_3 in 23.8% and 77.5% yields, respectively.

Compound **1** was synthesized from DBDNT and benzaldehyde in 34% yield. The $^1\text{H-NMR}$ spectrum showed the expected signals of monosubstituted aromatic ring. The structure also corresponded to ^{13}C NMR spectrum with seven peaks of different carbons.

Compound **2** was synthesized from DCDNT and salicylaldehyde in 34% yield. The $^1\text{H-NMR}$ spectrum showed the expected signals of disubstituted aromatic ring. Its ^{13}C NMR spectrum also showed the expected nine peaks of different carbons.

For polymer synthesis, polymer **3** was synthesized from DCDNT and *p*-phenylenediamine in 61.2% and 65.7% yields from microwave heating and room temperature reactions, respectively. Because of its insolubility in common organic solvents, polymer **3** was characterized by IR and solid UV-Vis spectroscopy, which showed a maximum wavelength absorption (λ_{max}) at 516 nm and 542 nm for microwave synthesis and room temperature reaction, respectively.

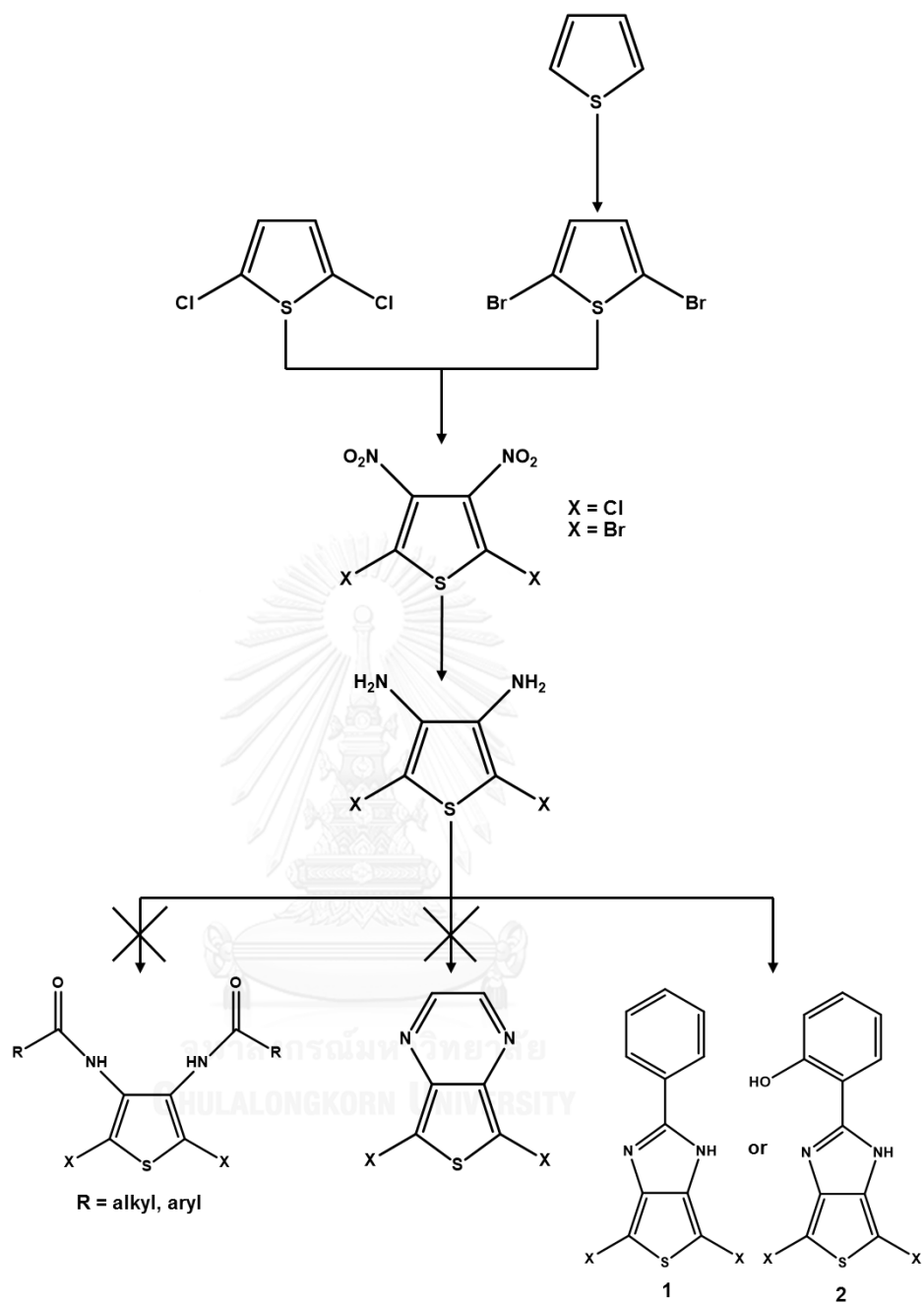
Polymer **4** was synthesized from DCDNT and *N,N'*-di-*sec*-butyl-*p*-phenylenediamine in 75.9% and 59.3% yields for microwave synthesis and room temperature reactions, respectively. The ^1H NMR spectrum of the partly dissolved polymer **4** showed the expected broadened signals of aromatic and alkyl protons and showed a maximum wavelength absorption (λ_{max}) in the UV-Vis spectrum at 503 nm and 542 nm for microwave synthesis and room temperature reactions, respectively.

Polymer **5** was synthesized from excessive reduction of polymer **3** in 65.4% yield. It was also insoluble in common organic solvents. It was characterized by IR and solid UV-Vis spectroscopy, which showed a maximum wavelength absorption (λ_{max}) at 550 nm.

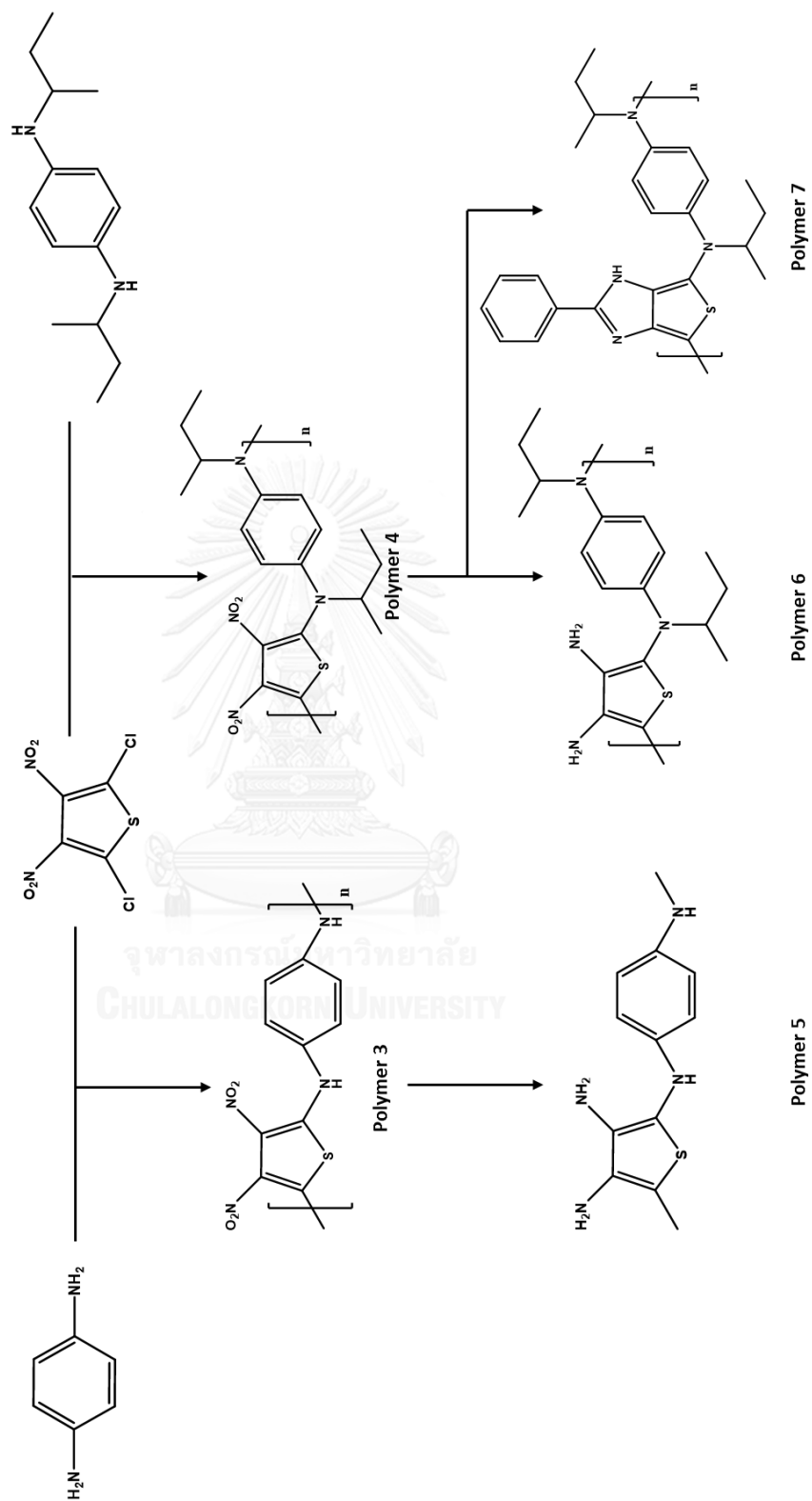
Polymer **6** was synthesized from reduction of polymer **4** in 34.8% and 42.1% yield for microwave synthesis and room temperature reactions, respectively. It was partly soluble in some organic solvents. It showed a maximum wavelength absorption (λ_{max}) in the UV-Vis spectrum at 617 nm and 643 nm for microwave synthesis and room temperature reactions, respectively.

Polymer **7** was synthesized in 40.2% yield from polymer **4** via consecutive reduction with PPh_3 followed by condensation with benzaldehyde. The ^1H NMR spectrum of the partly dissolved polymer **7** showed the expected broadened signals of aromatic and alkyl protons and showed a maximum wavelength absorption (λ_{max}) at 658 nm.

In conclusion, we have synthesized two groups of polymers. The first group is insoluble in organic solvents, which are polymer **3** and polymer **5**. The other group can be partly dissolved in organic solvents, which are polymer **4**, polymer **6** and polymer **7**. The presence of butyl groups on the polymer chain helps improve the solubility property, though not yet sufficient. They still need more restructuring process to further improve their solubility such as attaching aliphatic side chains longer than butyl group, or other groups containing highly polar functionality like carboxylic acid or amino groups.



Scheme 4.1 Summary of monomer synthesis



Scheme 4.2 Summary of polymer synthesis

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APPENDIX

The logo of Chulalongkorn University, featuring a central emblem with a sunburst and a tiered structure, resting on a base with wheels.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

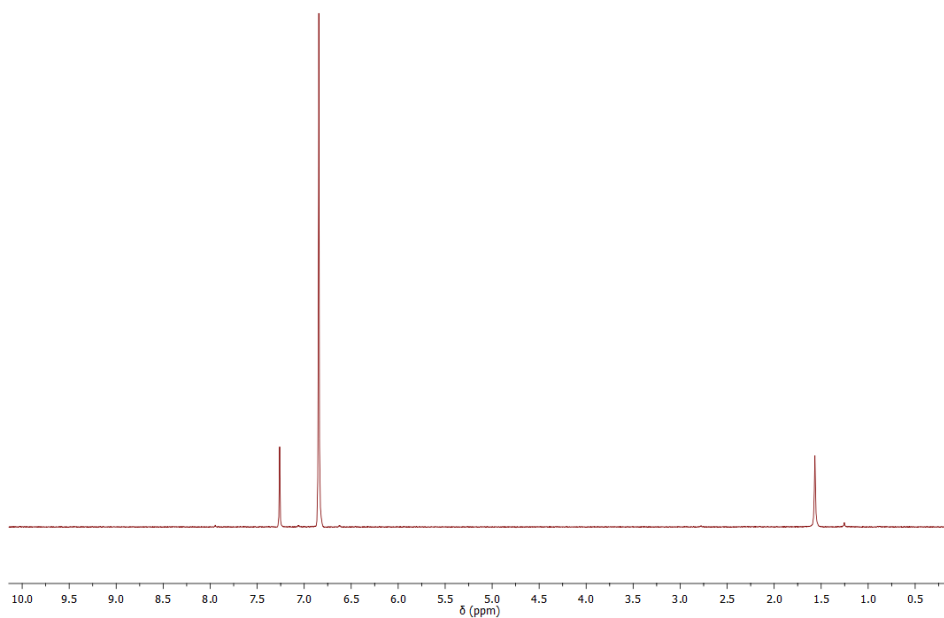


Figure A.1 ^1H NMR (CDCl_3) spectrum of 2,5-dibromothiophene

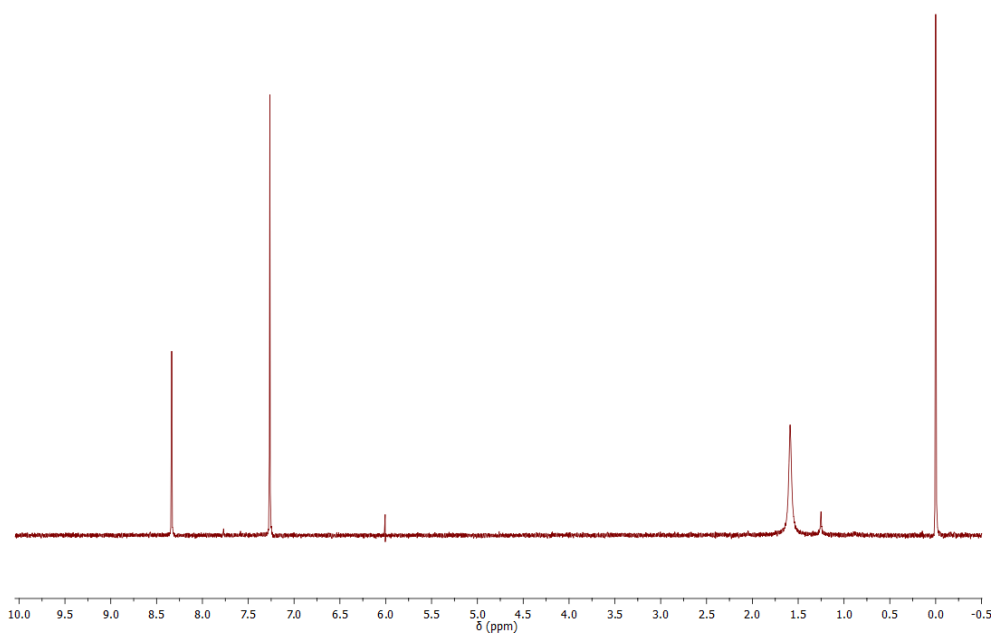


Figure A.2 ^1H NMR (CDCl_3) spectrum of 2-bromo-3,4-dinitrothiophene

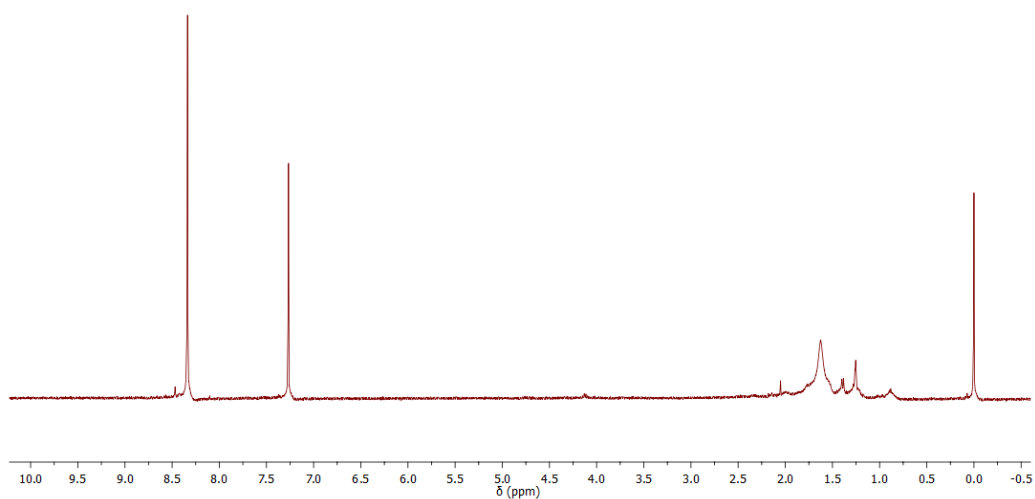


Figure A.3 ^1H NMR (CDCl_3) spectrum of 3,4-dinitrothiophene

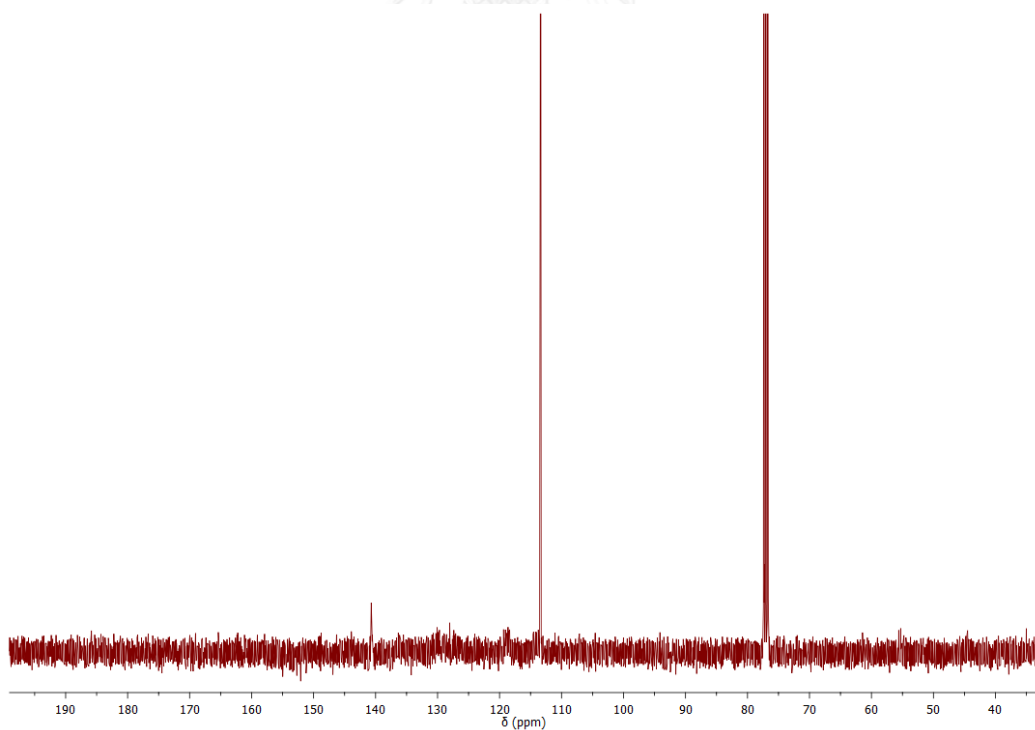


Figure A.4 ^{13}C NMR (CDCl_3) spectrum of 2,5-dibromo-3,4-dinitrothiophene (DBDNT)

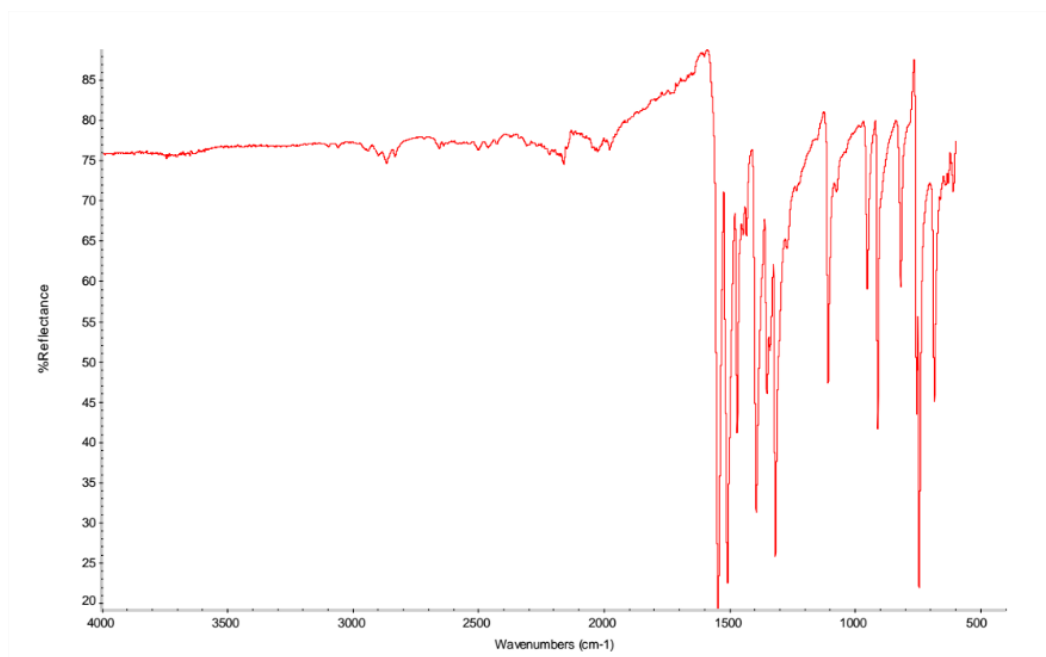


Figure A.5 IR spectrum of DCDNT

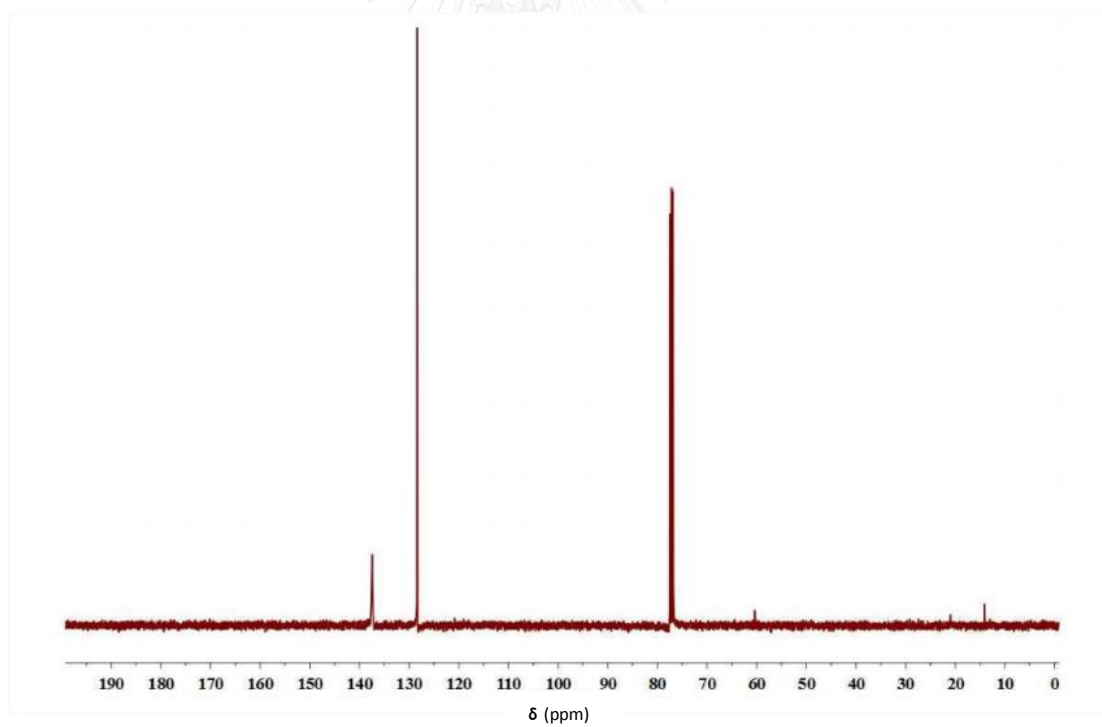


Figure A.6 ¹³C NMR (CDCl₃) spectrum of DCDNT

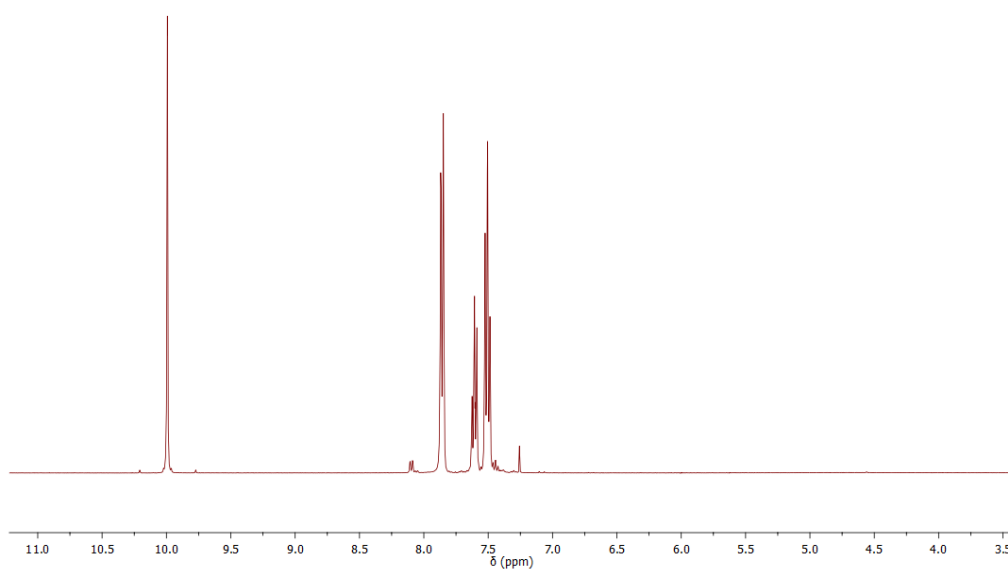


Figure A.7 ^1H NMR (CDCl_3) spectrum of compound **1**

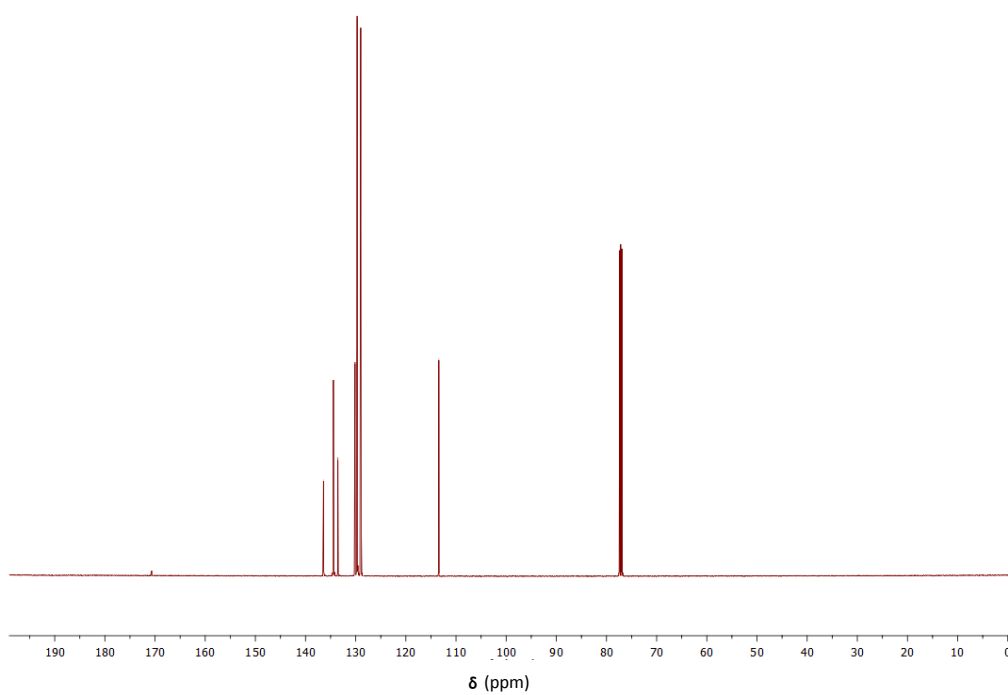


Figure A.8 ^{13}C NMR (CDCl_3) spectrum of compound **1**

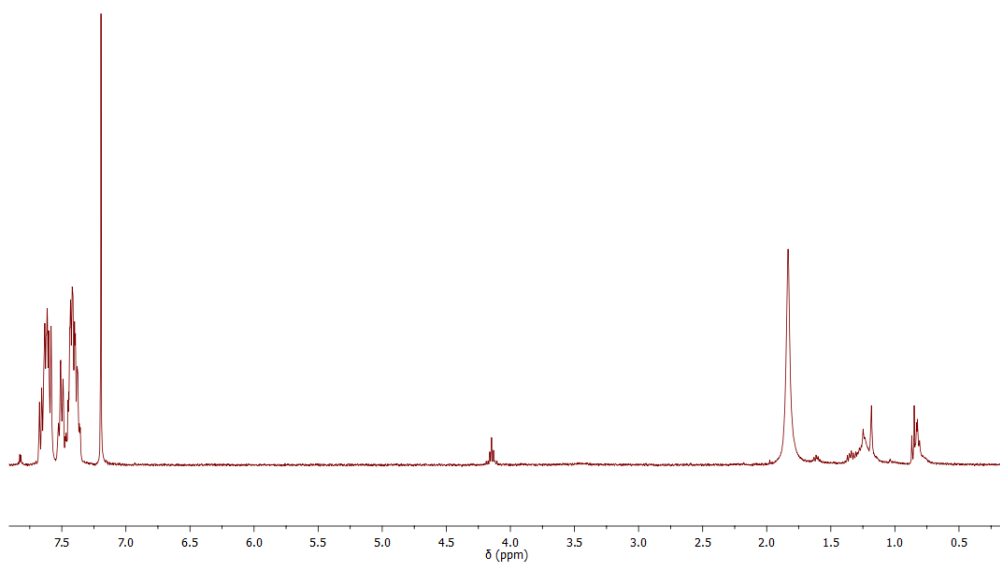


Figure A.9 ^1H NMR (CDCl_3) spectrum of compound 2

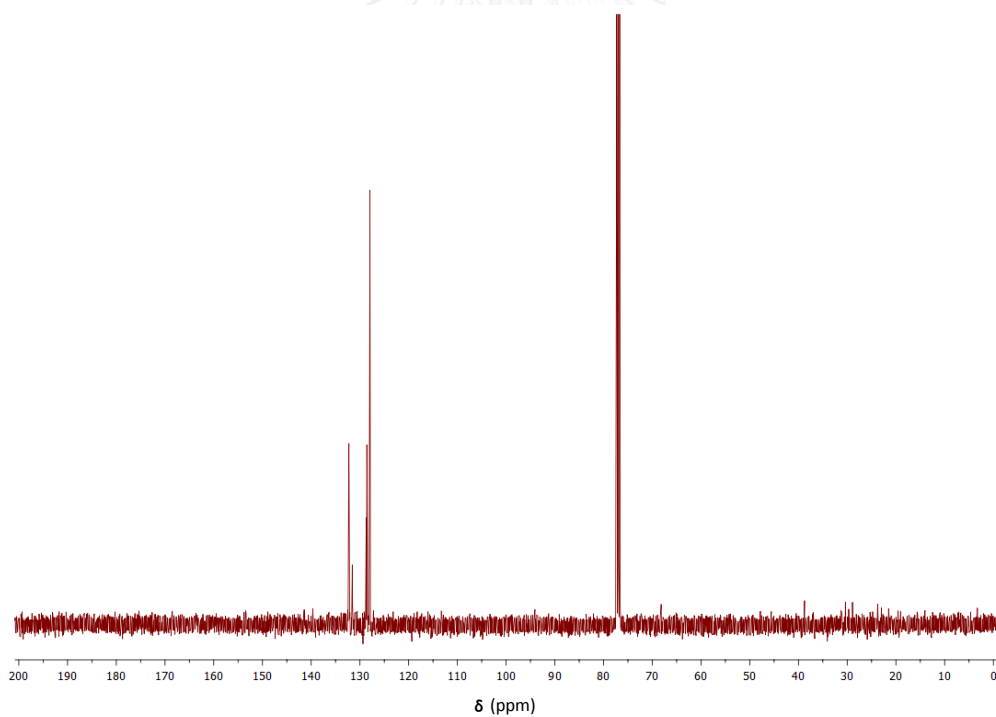


Figure A.10 ^{13}C NMR (CDCl_3) spectrum of compound 2

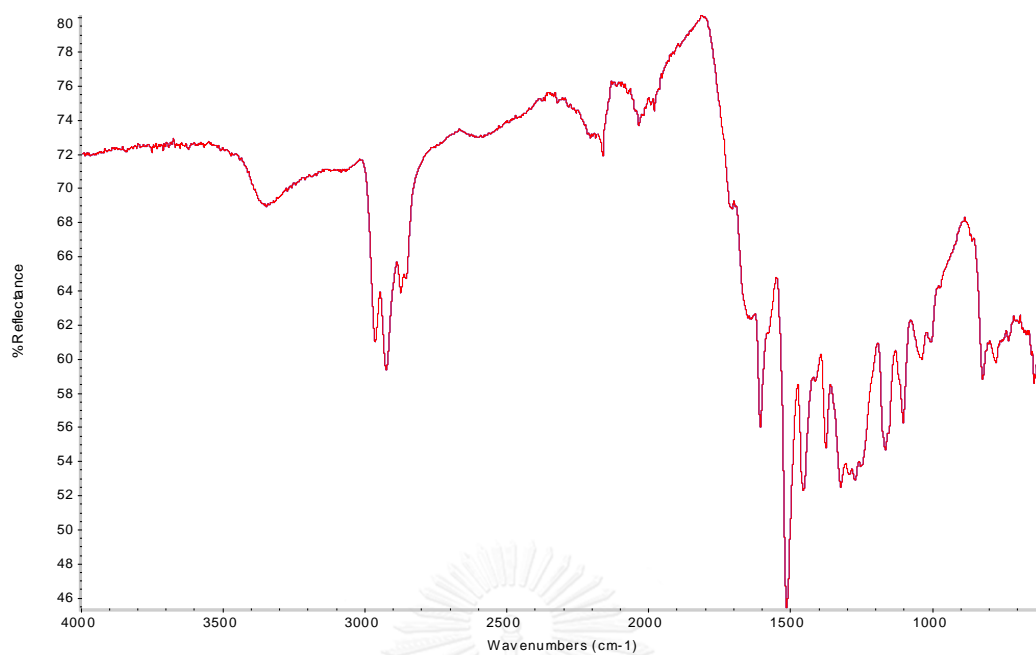


Figure A.11 IR spectrum of polymer **3** from microwave reaction

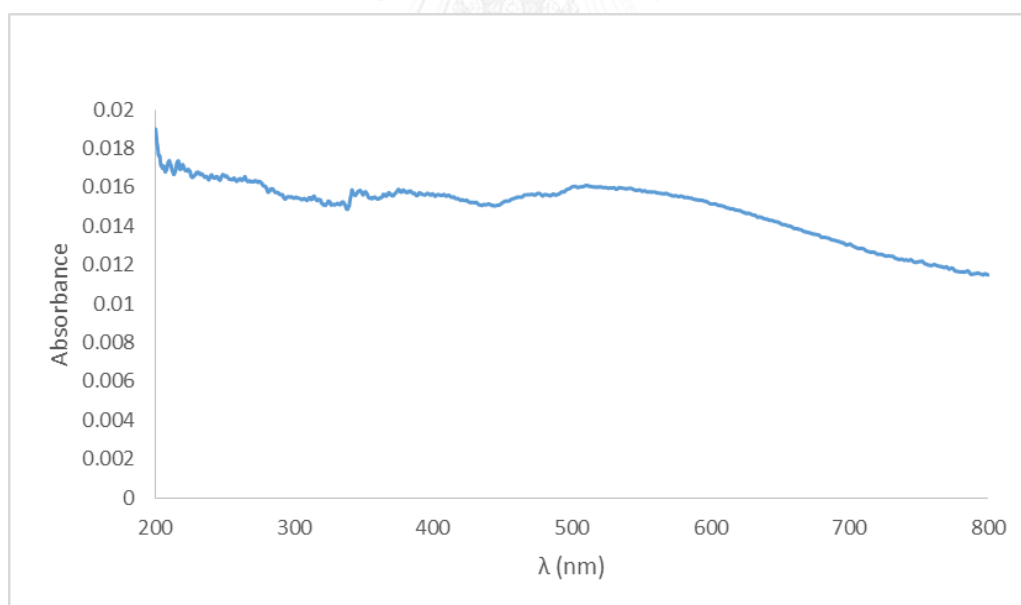


Figure A.12 Solid UV-Visible spectrum of polymer **3** from microwave reaction

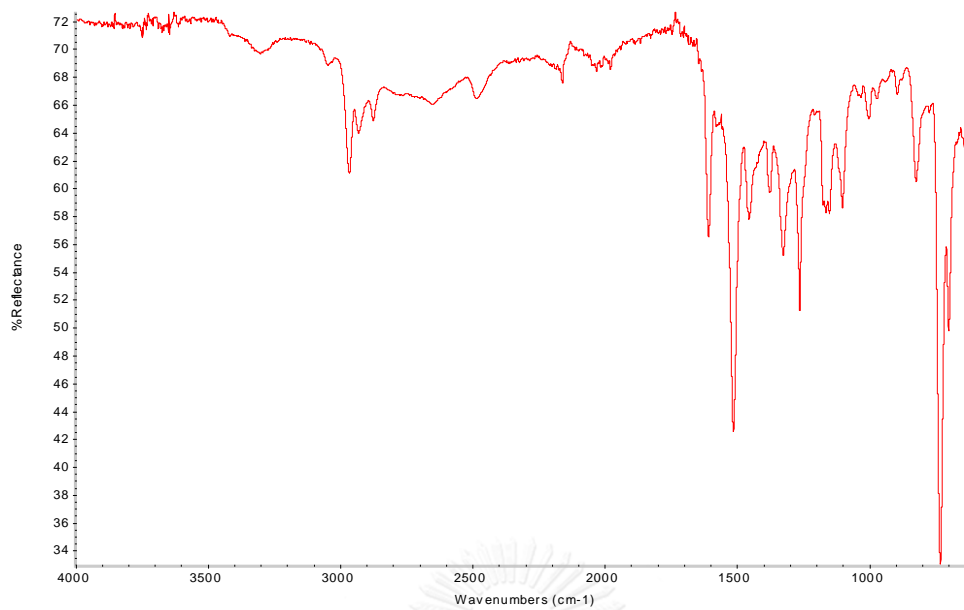


Figure A.13 IR spectrum of polymer **3** from reaction at room temperature

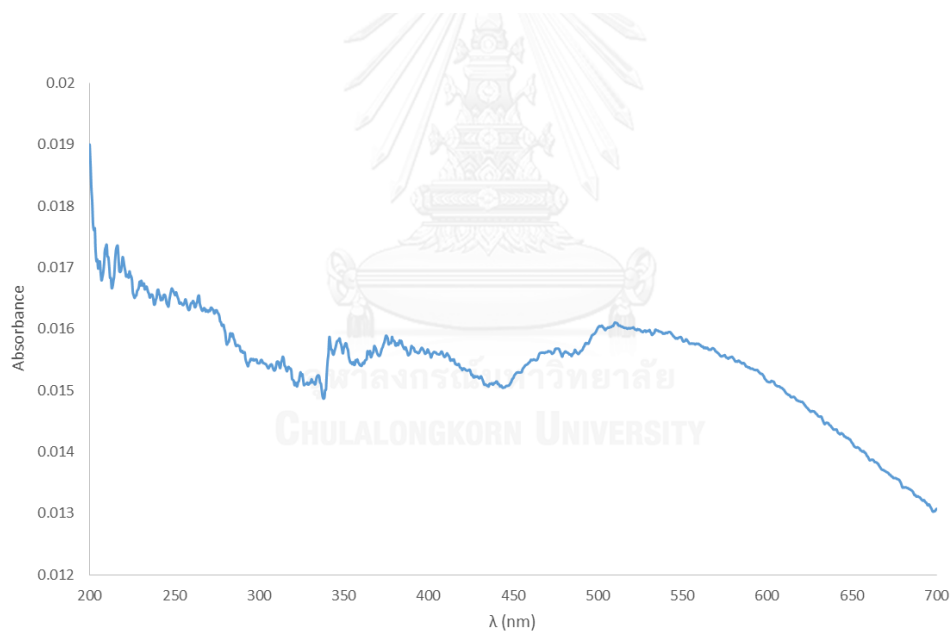


Figure A.14 Solid UV-Visible spectrum of polymer **3** from reaction at room temperature

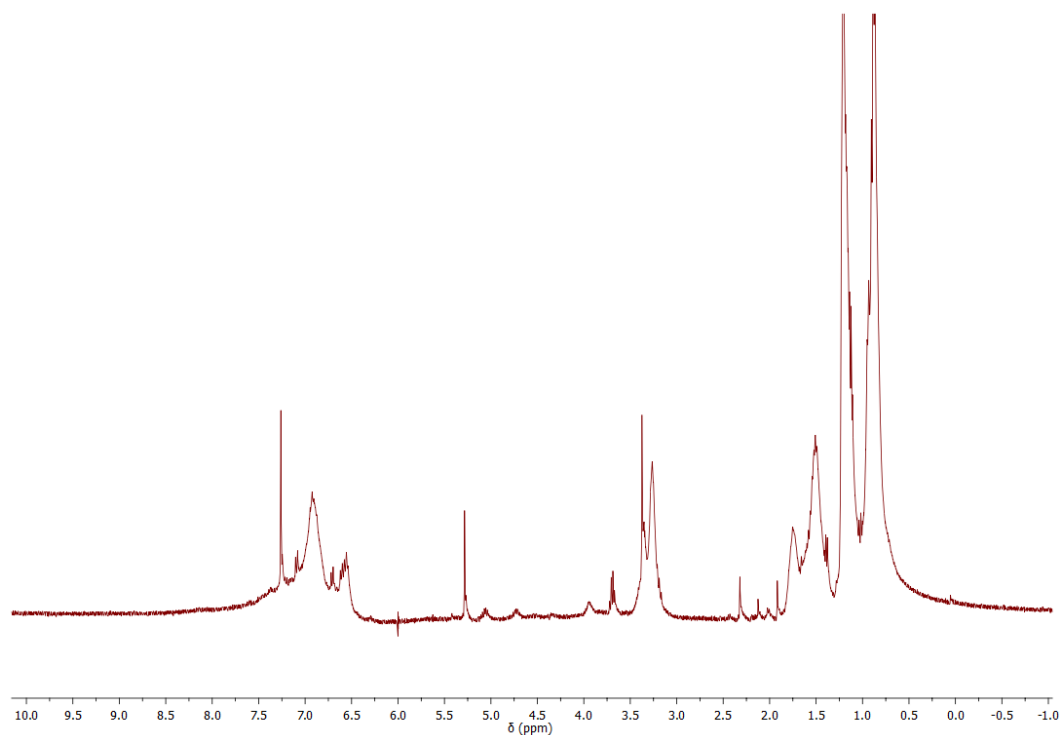


Figure A.15 ^1H NMR (CDCl_3) of polymer **4** from microwave reaction

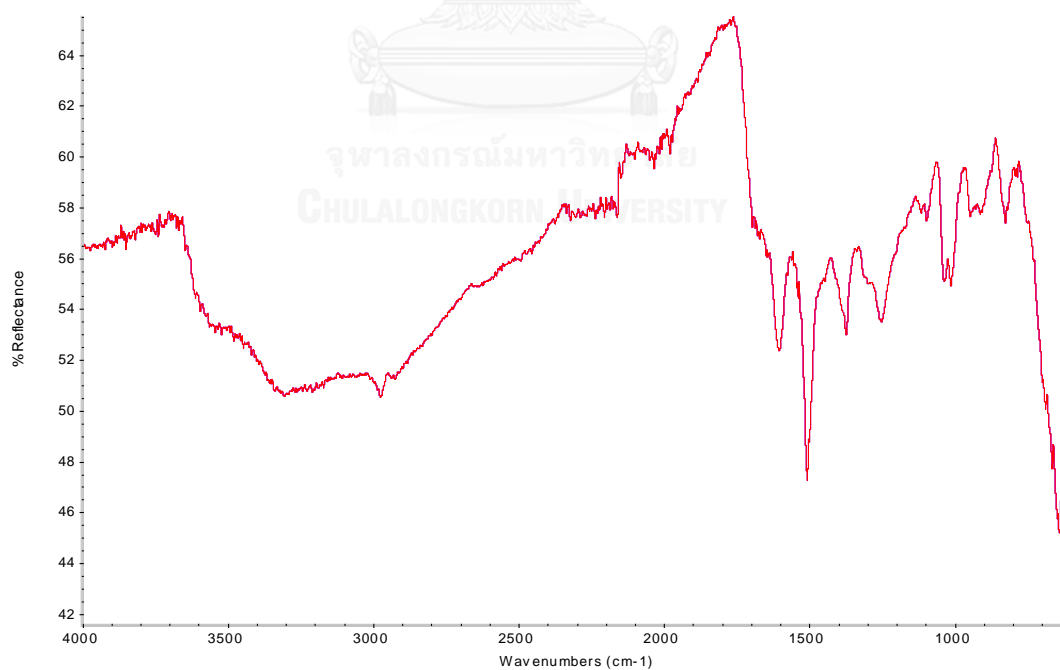


Figure A.16 IR spectrum of polymer **4** from microwave reaction

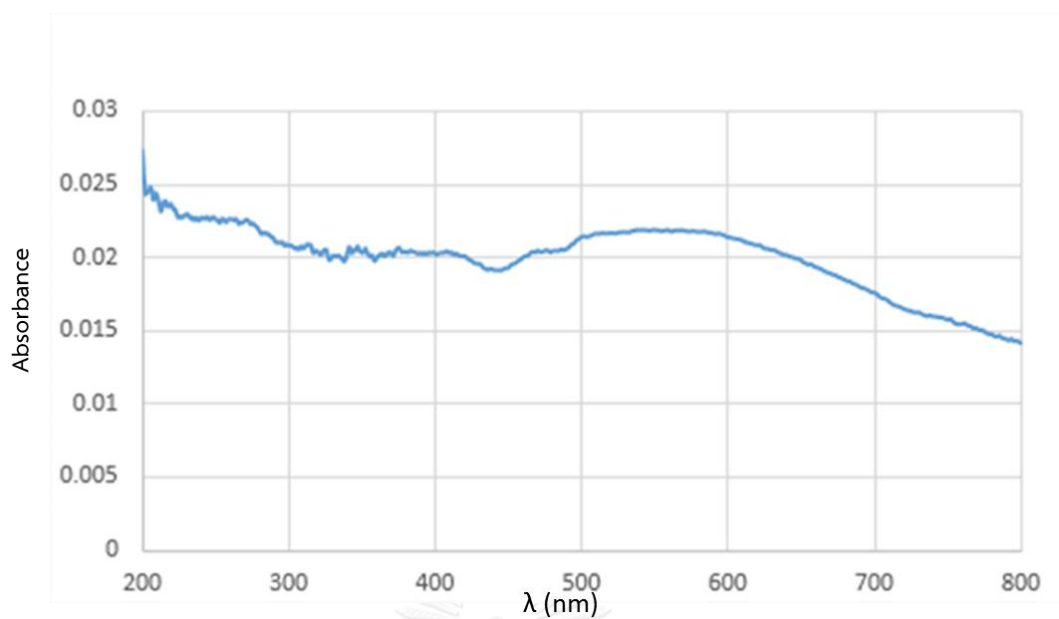


Figure A.17 Solid UV-Visible spectrum of polymer **4** from microwave reaction

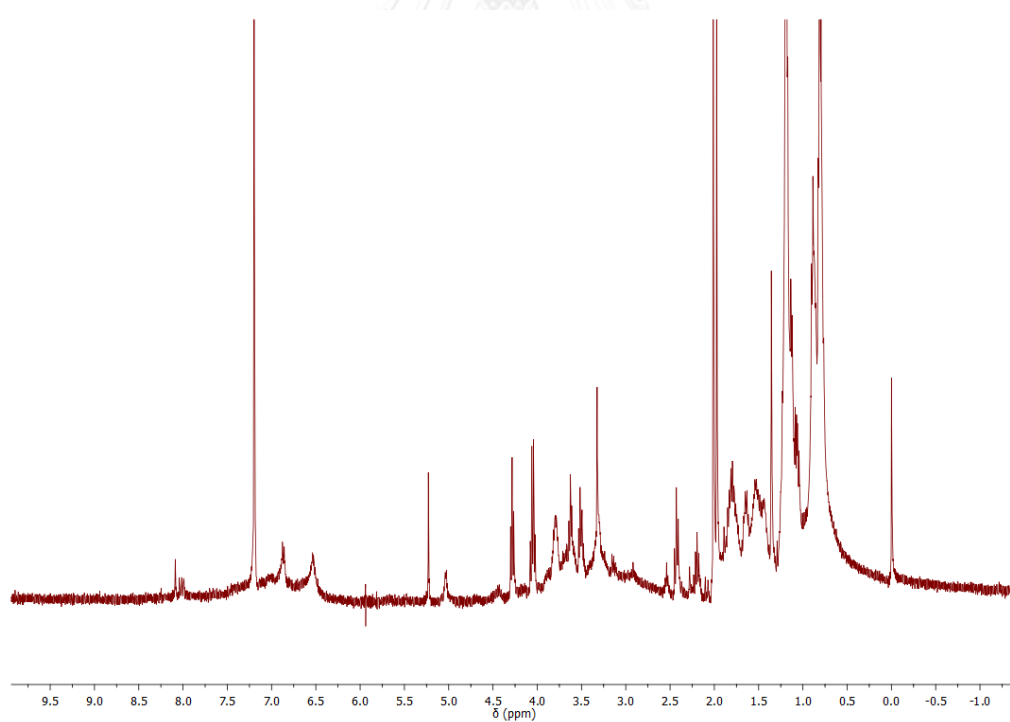


Figure A.18 ^1H NMR (CDCl_3) of polymer **4** from reaction at room temperature

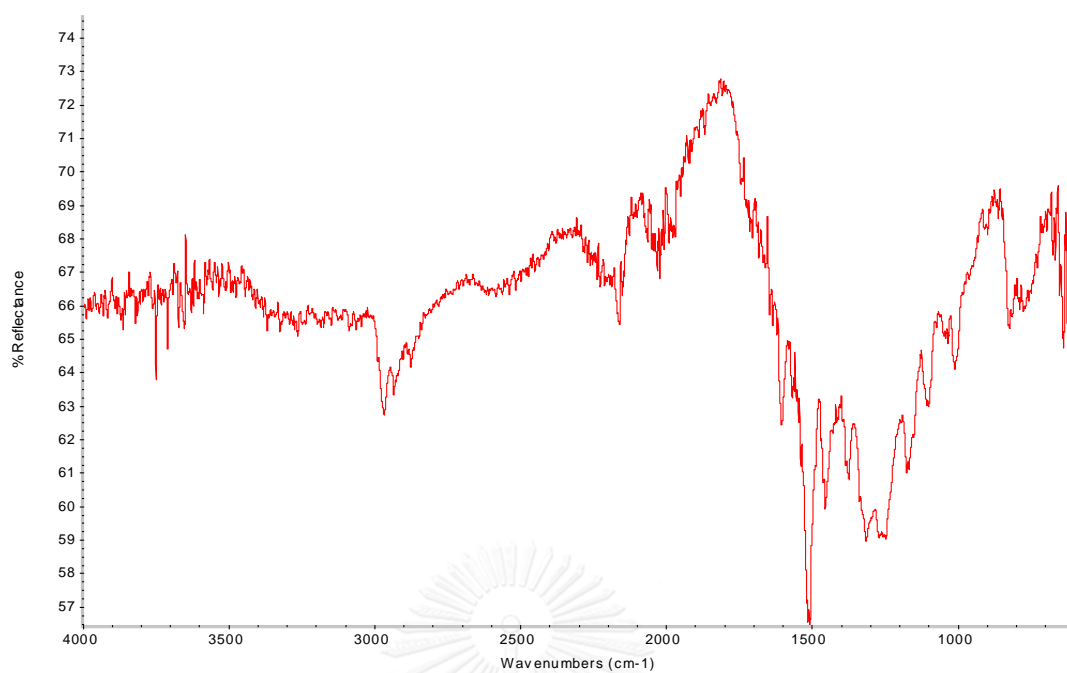


Figure A.19 IR spectrum of polymer **4** from reaction at room temperature

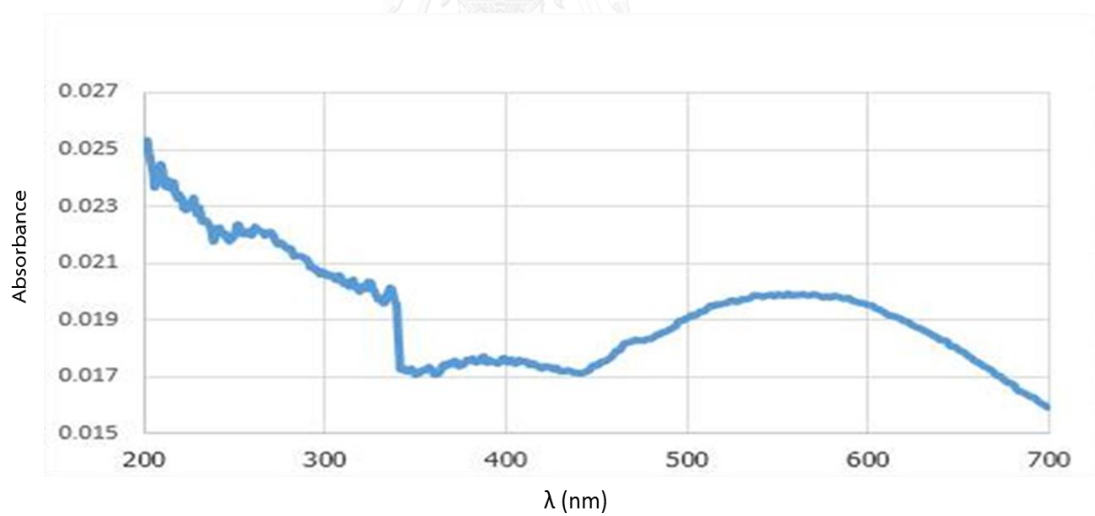


Figure A.20 Solid UV-Visible spectrum of polymer **4** from reaction at room temperature

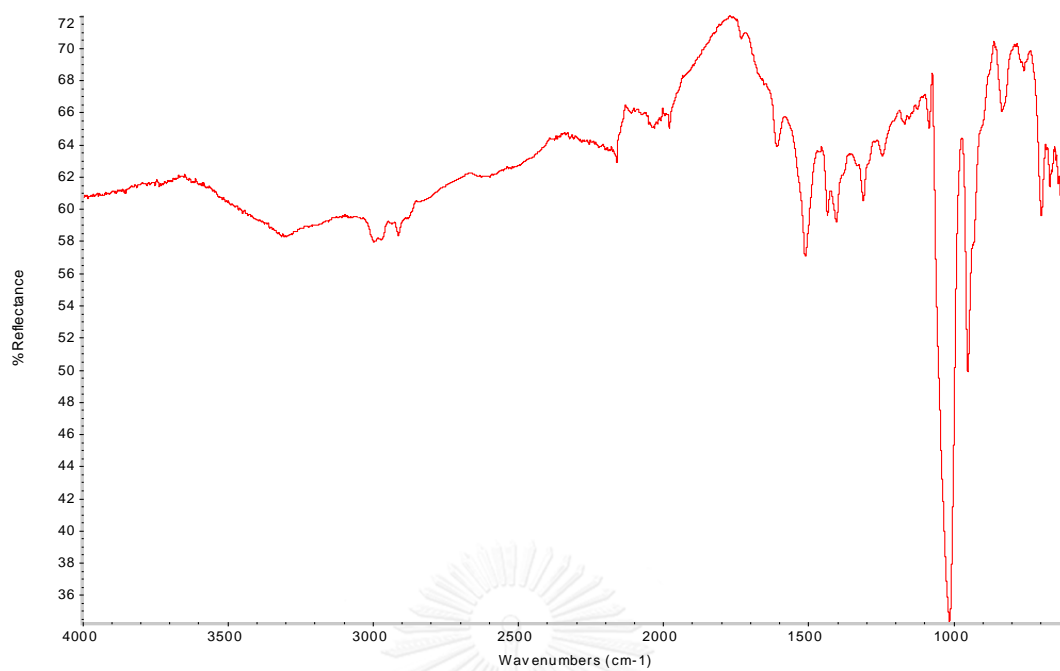


Figure A.21 IR spectrum of polymer 5

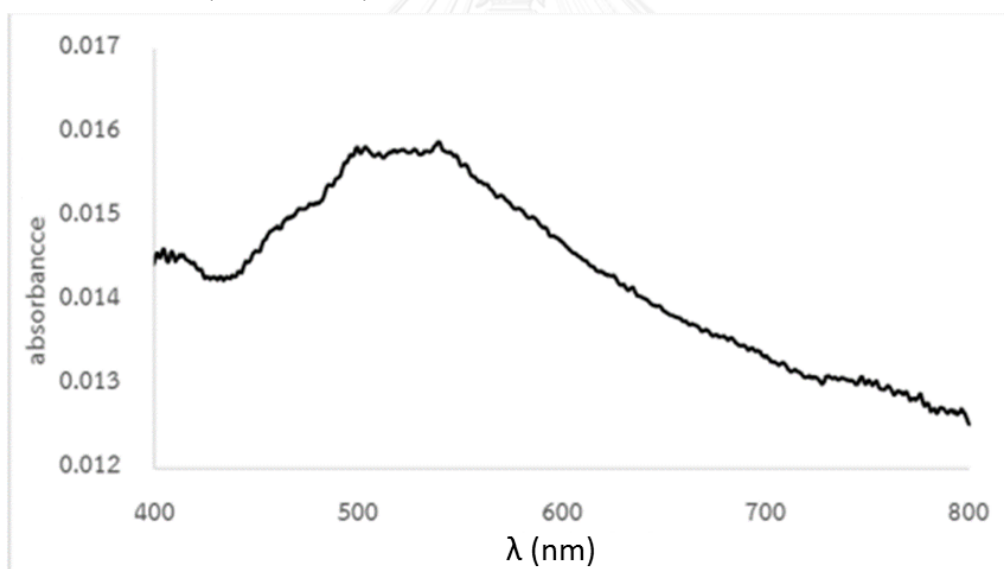


Figure A.22 Solid UV-Visible spectrum of polymer 5

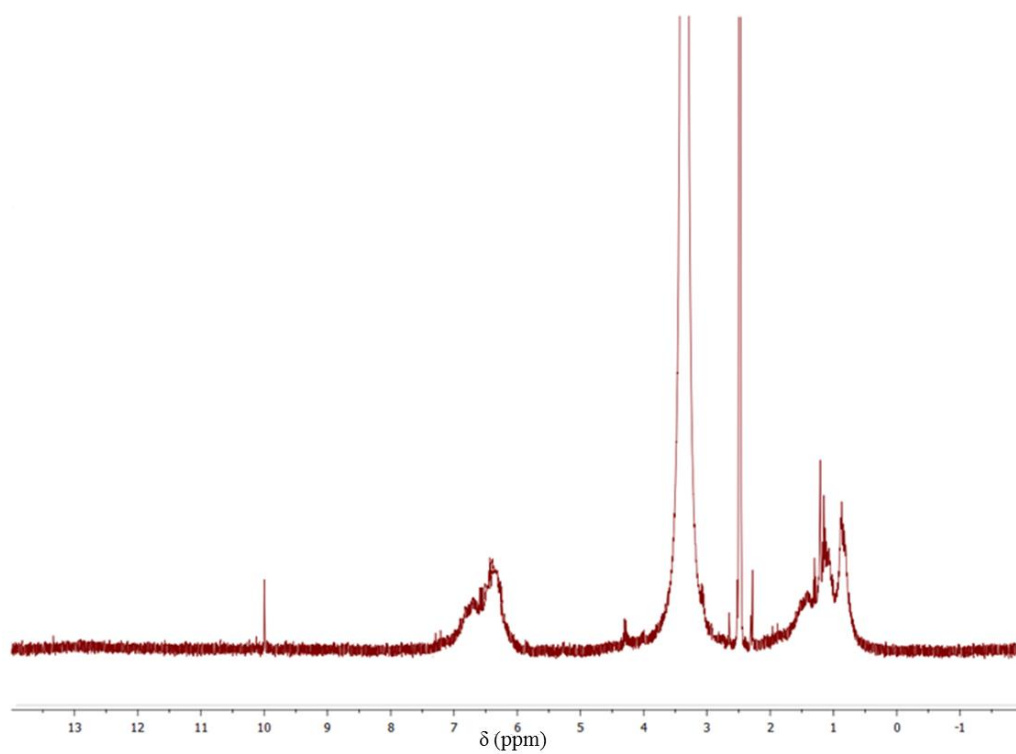


Figure A.23 ^1H NMR (DMSO) of polymer 6 from microwave reaction

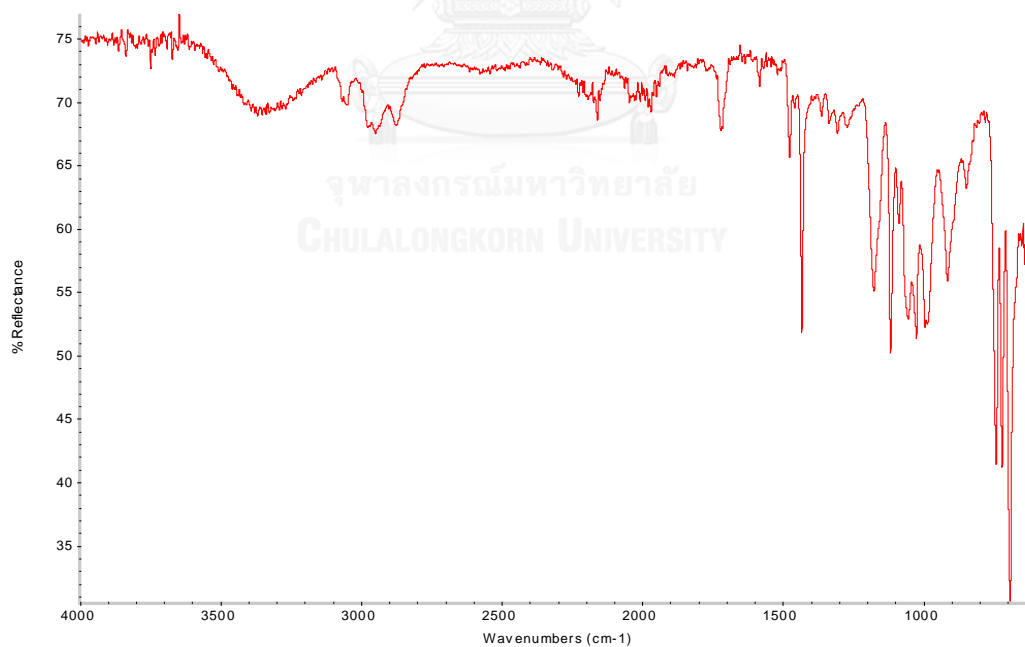


Figure A.24 IR spectrum of polymer 6 from microwave reaction

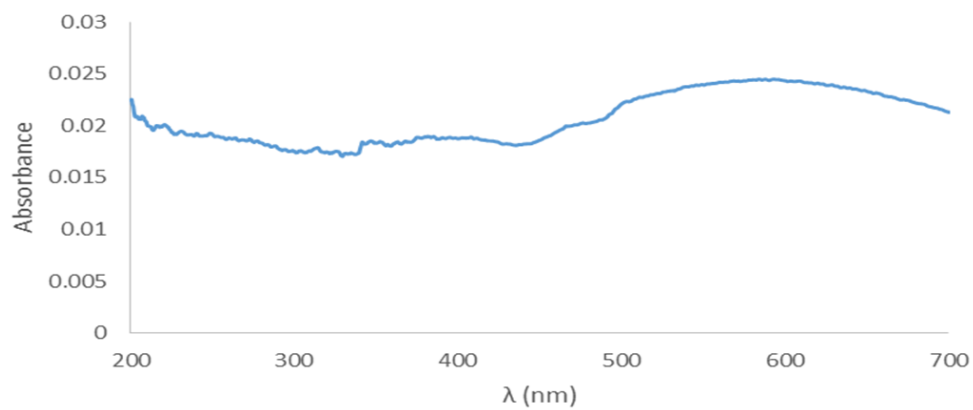


Figure A.25 Solid UV-Visible spectrum of polymer **6** from microwave reaction

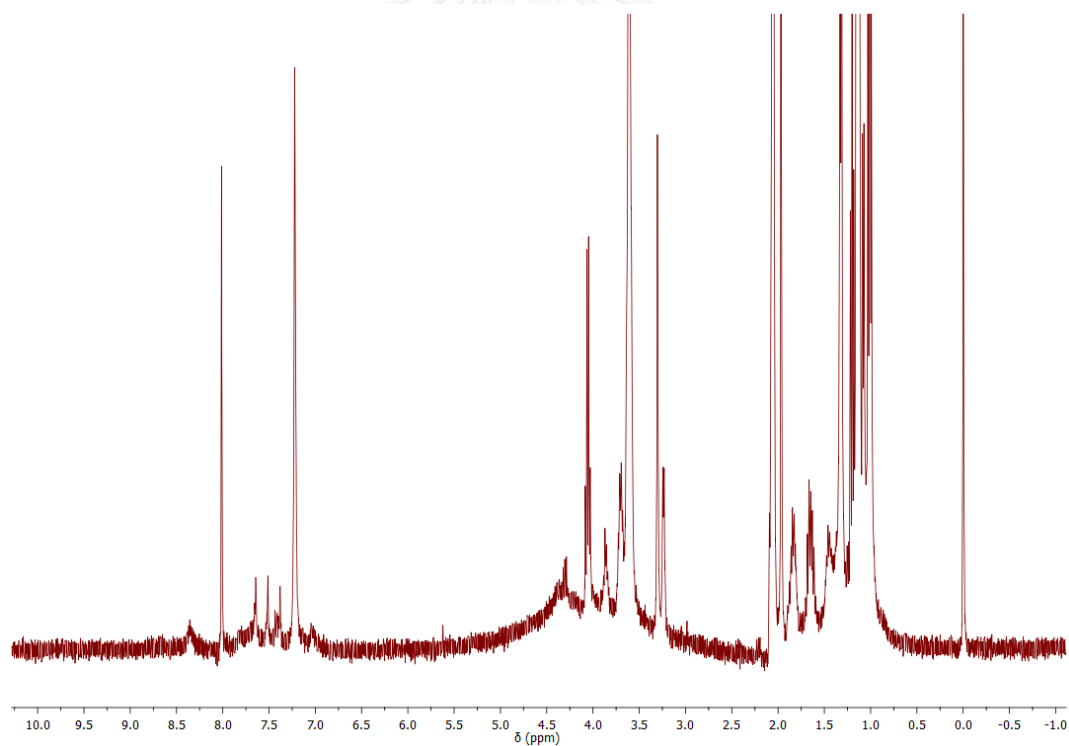


Figure A.26 ^1H NMR (CDCl_3) of polymer **6** from reaction at room temperature

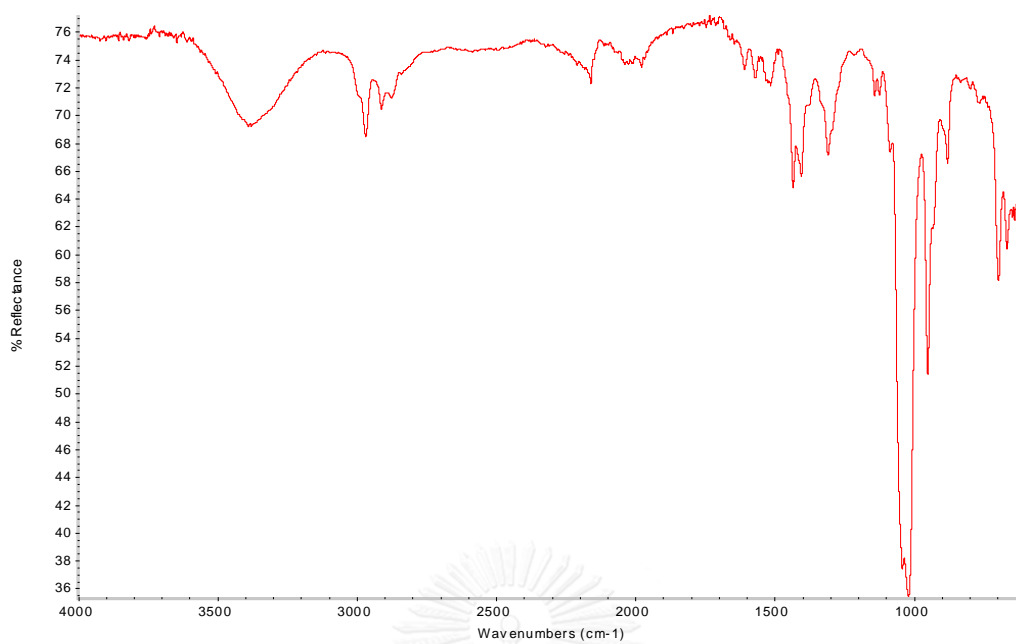


Figure A.27 IR spectrum of polymer **6** from reaction at room temperature

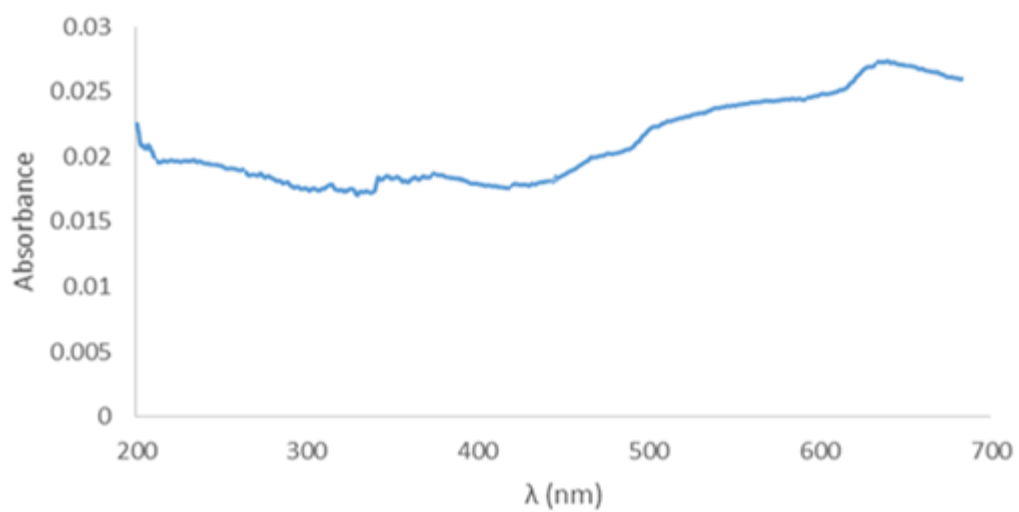


Figure A.28 Solid UV-Visible spectrum of polymer **6** from reaction at room temperature

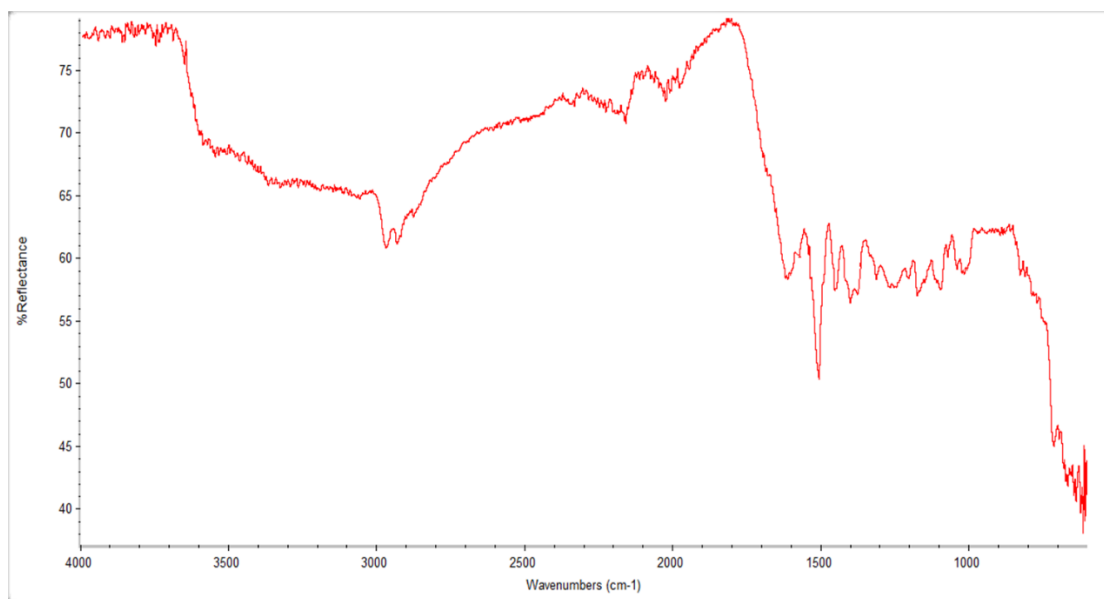


Figure A.29 IR spectrum of polymer 7 from reaction at room temperature

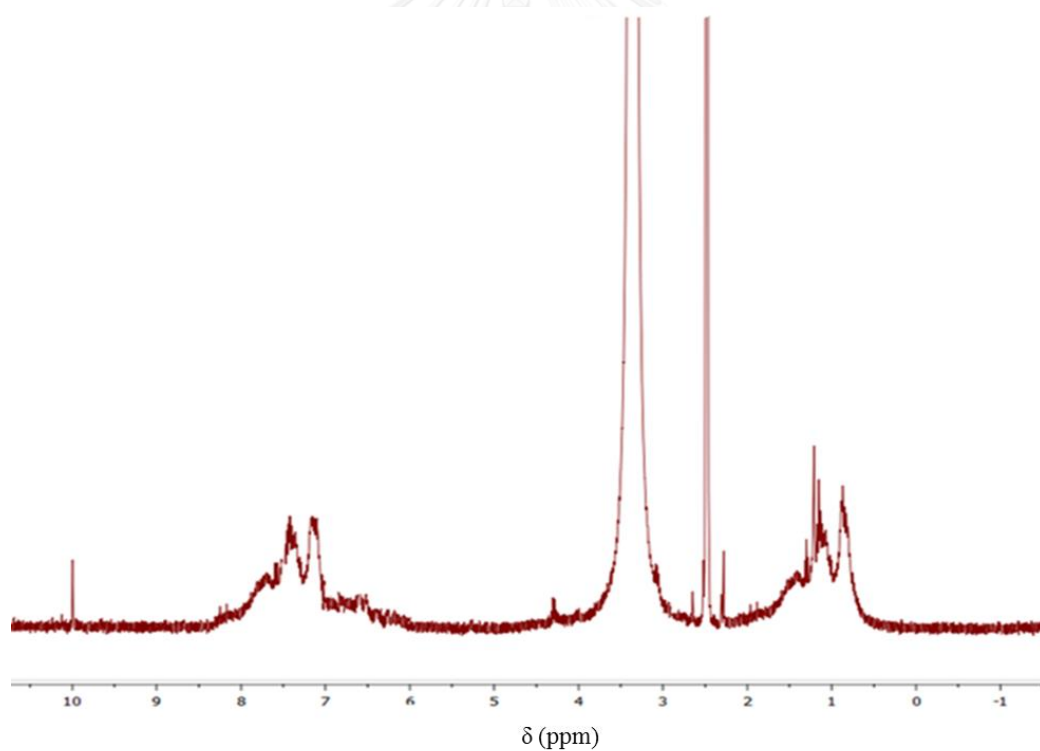


Figure A.30 ^1H NMR (DMSO) of polymer 7 from microwave reaction

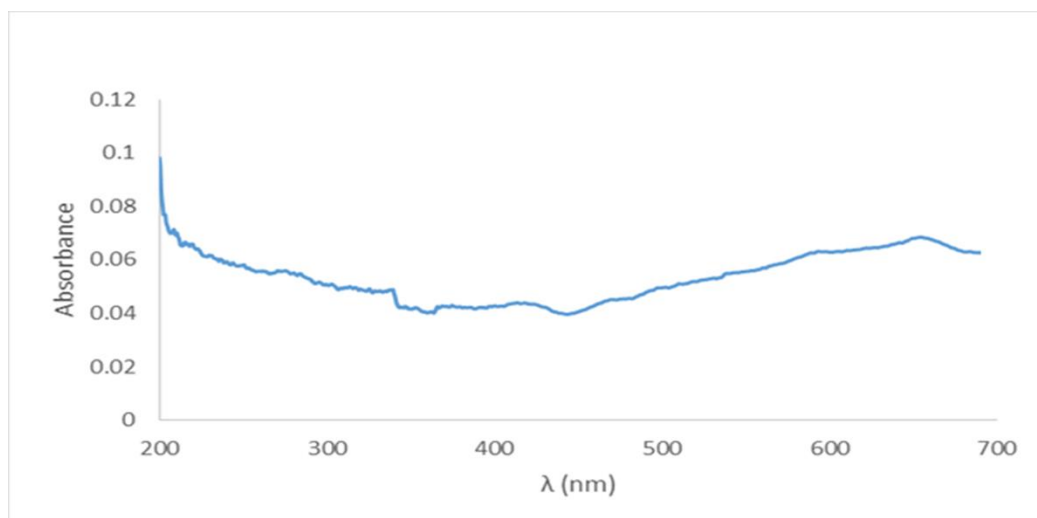


Figure A.31 Solid UV-Visible spectrum of polymer **7** from reaction at room temperature



VITA

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