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นางสาวปรียานุช ตรีวิทยากุล

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CONJUGATED POLYMER SYNTHESIS FROM 2,5-DICHLORO-3,4-DINITROTHIOPHENE

Miss Preeyanuch Treewittayakul

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title	CONJUGATED POLYMER SYNTHESIS FROM 2,5-DICHLORO-3,4-DINITROTHIOPHENE
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Field of Study	Petrochemistry and Polymer Science
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ปรียานุช ตรีวิทยากุล : การสังเคราะห์คอนจูเกตพอลิเมอร์จาก 2,5-ไดคลอโร-3,4-ไดไนโตรไทโอฟีน (CONJUGATED POLYMER SYNTHESIS FROM 2,5-DICHLORO-3,4-DINITROTHIOPHENE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.ยงศักดิ์ ศรีธนาอนันต์, 93 หน้า.

งานวิจัยนี้เป็นการศึกษาการสังเคราะห์คอนจูเกตพอลิเมอร์ชนิดใหม่ผ่านปฏิกิริยาพอลิเมอไรเซชันด้วยการแทนที่ด้วยนิวคลีโอไฟล์ลงบนวงแอโรมาติกจาก 2,5-ไดคลอโร-3,4-ไดไนโตรไทโอฟีน ซึ่งเป็นมอนอเมอร์หลักและทำหน้าที่เป็นหน่วยรับอิเล็กตรอนในสายโซ่พอลิเมอร์ โดยทำการเกิดพอลิเมอร์ร่วมกับนิวคลีโอไฟล์ในกลุ่มต่างๆ ซึ่งจะทำหน้าที่เป็นหน่วยให้อิเล็กตรอนในสายโซ่พอลิเมอร์ จากการศึกษาในการสังเคราะห์มอนอเมอร์บางชนิด 2,5-ไดคลอโร-3,4-ไดไนโตรไทโอฟีนสังเคราะห์ได้ในปริมาณ 78% และออกทิลพีโรล (1) *เอ็น*^{1},*เอ็น*^{4}-ไดออกทิลเบนซีน-1,4-ไดเอมีน (2) และ 2-เฮปทิลเบนซิมิดาโซล (4) ได้ในปริมาณ 75%, 54% และ 33% ตามลำดับ เมื่อนำมอนอเมอร์มาพอลิเมอไรซ์ร่วมกับ 2,5-ไดคลอโร-3,4-ไดไนโตรไทโอฟีน พบว่า สาร 1 สารนอร์มอล-บิวทิลามีน และสาร 4 ไม่ประสบความสำเร็จ โดยสาร 1 และ นอร์มอล-บิวทิลามีนไม่ได้ผลิตภัณฑ์เป็นพอลิเมอร์ ในขณะที่สาร 3,4-เอทิลีนไดออกซีไทโอฟีน (อีดอท) 3,4-ไดเมทอกซีไทโอฟีน (ดีเอ็มที) โซเดียมซัลไฟด์ ไฮดราซีน *พารา*-ฟีนิลลีนไดเอมีน *เอ็น,เอ็น'*-ได-*เซก*-บิวทิล-*พารา*-ฟีนิลลีนไดเอมีน และสาร 2 สามารถสังเคราะห์พอลิเมอร์ 7, 8, 9, 12, 13, 15 และ 17 ได้ตามลำดับ โดยพอลิเมอร์เหล่านั้นไม่สามารถละลายได้ในตัวทำละลายอินทรีย์ทั่วไป ซึ่งสมบัติการดูดกลืนแสงของคอนจูเกตพอลิเมอร์เหล่านี้มีค่าความความยาวคลื่นสูงสุดของการดูดกลืนแสงอยู่ในช่วง 540-690 นาโนเมตร

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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PREEYANUCH TREEWITTAYAKUL: CONJUGATED POLYMER SYNTHESIS FROM 2,5-DICHLORO-3,4-DINITROTHIOPHENE. ADVISOR: ASST. PROF. YONGSAK SRITANA-ANANT, Ph.D., 93 pp.

New conjugated polymers were synthesized via nucleophilic aromatic substitution (S_NAr) polymerizations. 2,5-dichloro-3,4-dinitrothiophene (DCDNT) as a main acceptor monomer was polymerized together with varieties of nucleophilic monomers as donor units. For some of the monomers: DCDNT was synthesized in 78% yield, and 1-*n*-octyl-*1H*-pyrrole (1), N^1,N^4-dioctylbenzene-1,4-diamine (2) and 2-heptylbenzimidazole (4) were also synthesized in 75%, 54% and 33% yields, respectively. The reactions of DCDNT with compound 1, *n*-butylamine, and compound 4 were unsuccessful, in which the reactions with compound 1 and *n*-butylamine did not give any polymeric products. However, the reactions with 3,4-ethylenedioxythiophene (EDOT), 3,4-dimethoxythiophene (DMT), sodium sulfide, hydrazine, *p*-phenylenediamine, *N,N'*-di-*sec*-butyl-*p*-phenylenediamine and compound 2 yielded polymers 7, 8, 9, 12, 13, 15 and 17, respectively. The polymers were insoluble in common organic solvents. They exhibited the characteristic absorptions in the visible region of conjugated polymers with a maximum wavelength absorption (λ_{max}) in the range of 540-690 nm.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature	....
		Advisor's Signature	....
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$AlCl_3$: aluminum chloride
cm^{-1} : unit of wavenumber (IR)
$CDCl_3$: deuterated chloroform
CH_2Cl_2 : dichloromethane
°C : degree Celsius
^{13}C NMR : carbon-13 nuclear magnetic resonance spectroscopy
d : doublet (NMR), day (s)
DCDNT : 2,5-dichloro-3,4-dinitrothiophene
DMT : 3,4-dimethoxythiophene
DMSO : dimethyl sulfoxide
DMSO-d_6 : hexadeuterated dimethyl sulfoxide
EDOT : 3,4-ethylenedioxythiophene
equiv : equivalent (s)
Et_3N : triethylamine
EtOAc : ethyl acetate
g : gram (s)
h : hour (s)
^{1}H NMR : proton nuclear magnetic resonance spectroscopy
HCl : hydrochloric acid
HNO_3 : nitric acid
H_2SO_4 : sulfuric acid
Hz : hertz (s)
IR : infrared spectroscopy
J : coupling constant
M : molar (s)
m : multiplet (NMR)
MeOH : methanol
MgSO4 : anhydrous magnesium sulfate
min : minute
mL : milliliter (s)
mmol : millimole (s)
m.p. : melting point
m/z : mass per charge ratio (s)
MS : mass spectrometry

MSA	: methanesulfonic acid
$NaBH_4$	: sodium borohydride
$NaCNBH_3$	: sodium cyanoborohydride
Na_2CO_3	: sodium carbonate
NaH	: sodium hydride
NaOH	: sodium hydroxide
Na_2S	: sodium sulfide
nm	: nanometer (s)
ODCB	: *o*-dichlorobenzene
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
TLC	: thin layer chromatography
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 absorptions are in the UV region. There exists a different class of polymers that carry conjugated double bonds or 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 polymer chain through π-orbitals, which give rise to semiconducting properties [7]. Polyacetylene was the first example that has been widely studied as a prototype for other electronic conducting polymers [8].

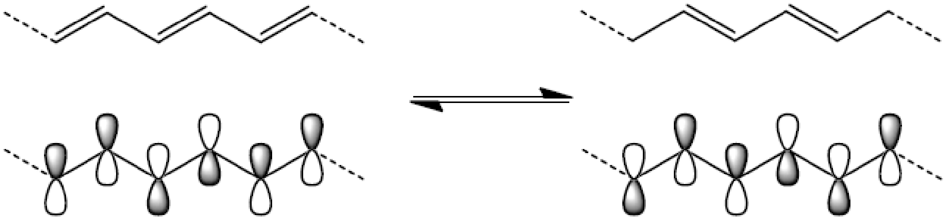


Figure 1.1 The delocalized π system of conjugated polymers

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/cm^3 compared to 3-10 g/cm^3).
- *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 electrons normally exist forms the valence 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; if there is sufficient energy (e.g. thermal energy) to overcome the band gap of a material. 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 overlaps 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. Higher dopant concentration generally enhances the conductivity [9].

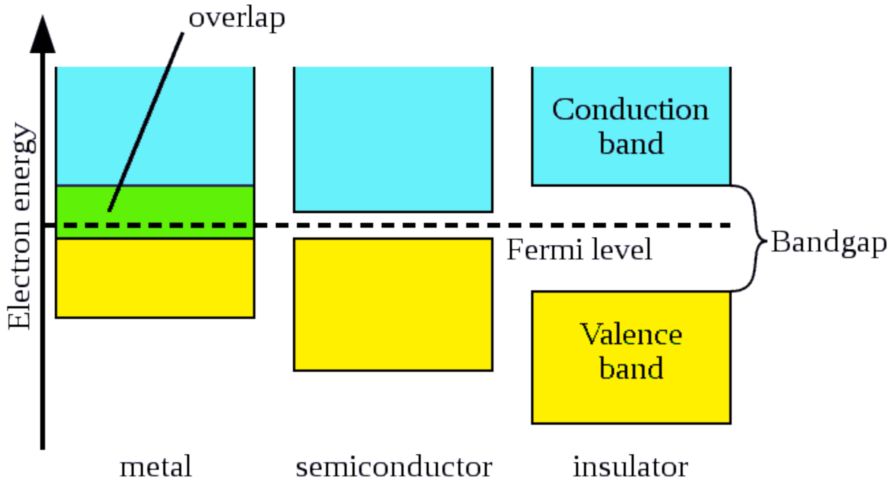


Figure 1.2 Simple band pictures of an insulator, a semiconductor and a metal

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 of 10^{-10} S/cm to 10^{-5} S/cm, but doping can increase their conductivity in a metallic conducting regime of 1 to 10^{4} S/cm [10].

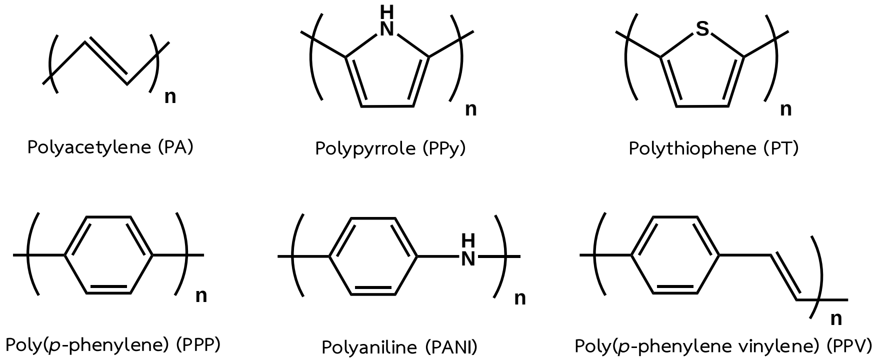


Figure 1.3 Structure of some conducting polymers in their neutral forms

1.4 Types of conjugated polymers

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

1) *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) (EDOT) [11], Poly(3-hexylthiophene) [12], Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]. **(Figure 1.4)**

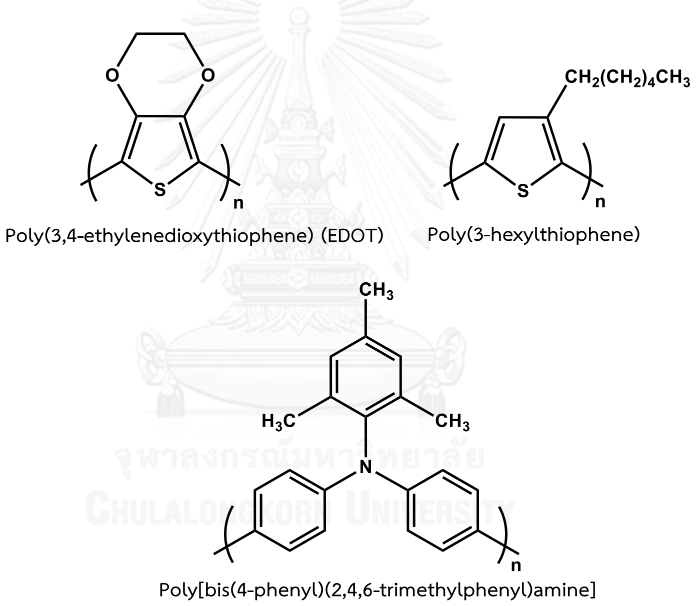
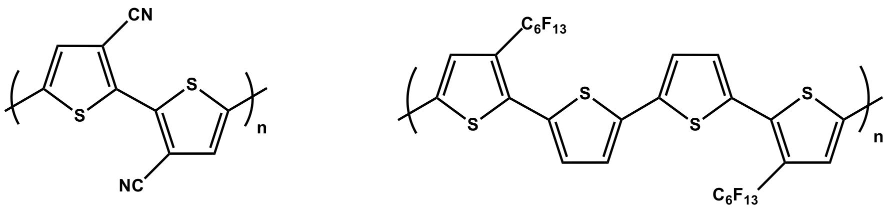


Figure 1.4 Examples of donor (p-type) polymers

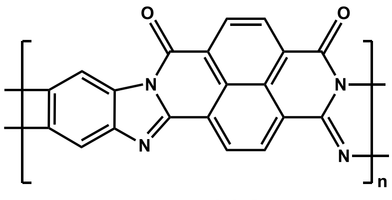
2) *Acceptor (n-type) polymer*:

The main chains of the polymers were constructed from connections of acceptor or electron-poor units. The hydrocarbon-based polymers were substituted with electron-withdrawing groups such as cyano or nitro groups such as Poly(3,3'-dicyanobithiophene) [13], β,β'-diperfluorohexyl-substituted oligothiophenes [14], Poly(benzimidazobenzophenanthroline) [6], *etc*. **(Figure 1.5)**



Poly(3,3'-dicyanobithiophene)

diperfluorohexyl-substituted oligothiophenes



Poly(benzimidazobenzophenanthroline)

Figure 1.5 Examples of acceptor (n-type) polymers

These n-type semiconductors are formed to be difficult to reduce or n-dope, leading to redox properties that often makes them unstable in air [15]. Furthermore, all the current n-type materials are difficult to process, and some of them are difficult to synthesize. As a result, the use of n-type conducting polymers has so far been of academic interest in contrast to the already commercially used p-type semiconductors. Incorporations of electron-poor acceptor units were mostly part of the systems designed to carry both types together known as donor-acceptor or push-pull polymer [16].

1.5 Donor-acceptor or push-pull polymer

The donor–acceptor concept is one of the most successful approaches to tailoring band gaps of conjugated polymers for applications in organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic photovoltaic devices (OPVs) [17]. Donor–acceptor (D-A) or push-pull semiconducting polymers, in which the backbone consists of alternating electron rich (donor) and electron-deficient (acceptor) units, are emerging materials that promote intermolecular interactions and offer desirable electronic structures, in turn leading to high charge carrier transport [18]. The higher energy of the donor group and the lower energy of the acceptor unit results in a reduced band gap. For example, donor–acceptor polymer in **Figure 1.6** was synthesized from benzodithiophene as donor unit and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) as acceptor unit [19].

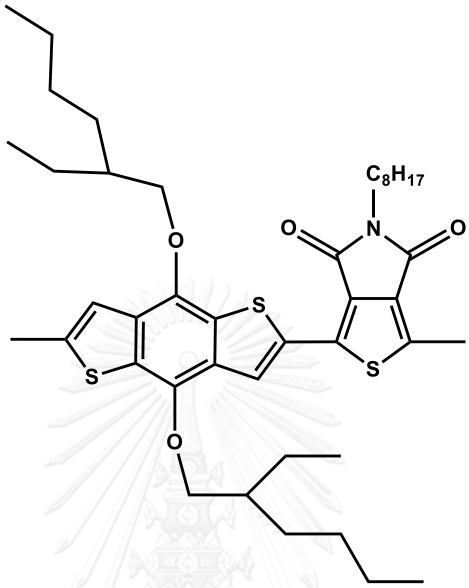


Figure 1.6 An example of donor–acceptor polymer

Donor units refer to an electron-rich unit. Thiophene and benzene are the two most basic donor units, and they are also the main fundamental blocks to construct other new donor units such as fluorene (F), carbazole (Cz), cyclopentadithiophene (CPDT), dithienosilole (DTS), *etc*. The basic donor units that were widely used were presented in **Figure 1.7** [20].

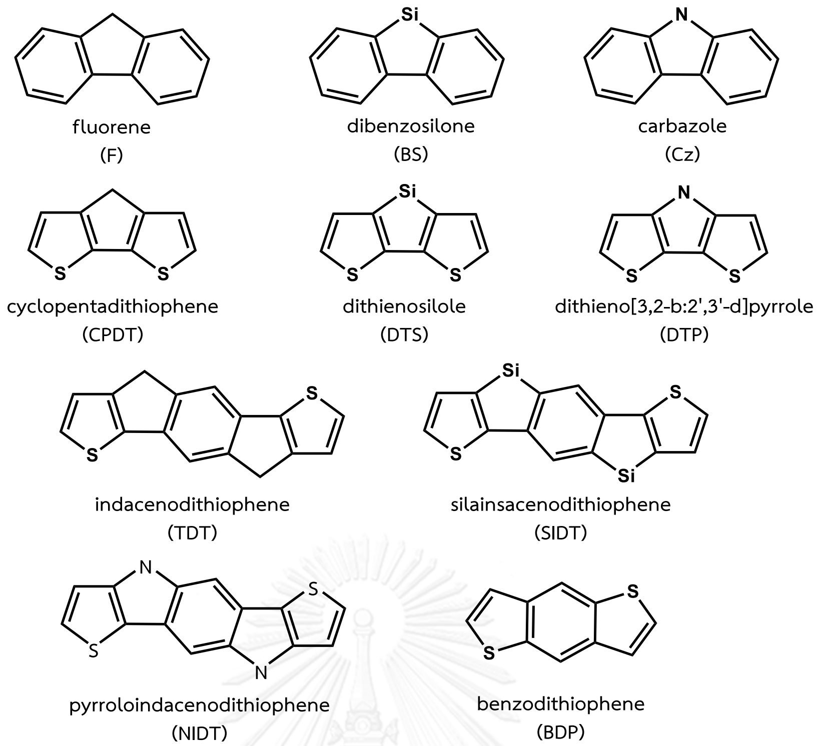
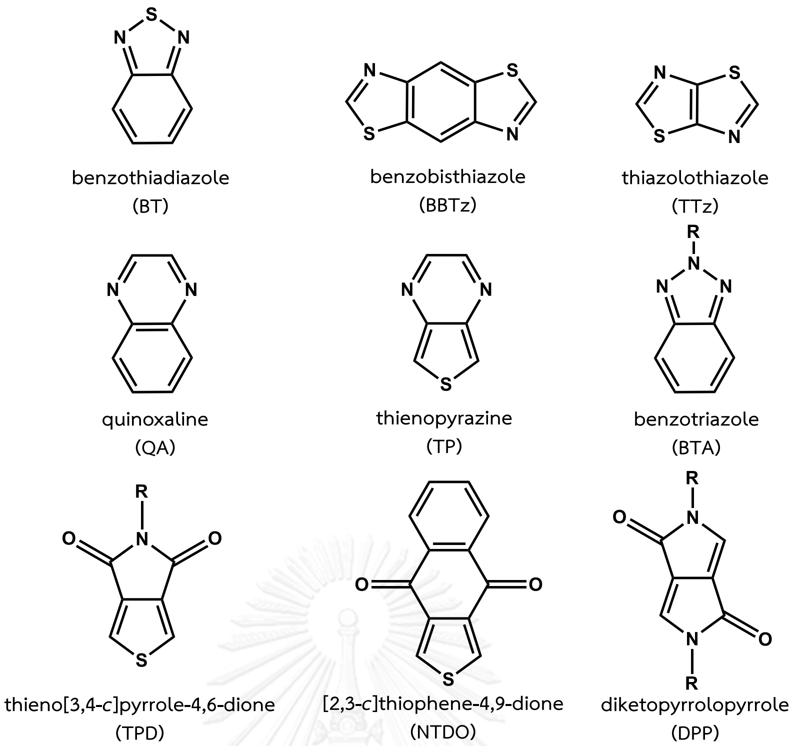


Figure 1.7 The basic donor units

Acceptor units refer to electron deficient (or 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 benzothiadiazole (BT), quinoxaline (QA), thienopyrazine (TP), bithiazole (BTz), thiazolothiazole (TTz), benzobisthiazole (BBTz), benzotriazole (BTA), s-tetrazine (STTz), naphtho[1,2-*c*:5,6-*c*]bis[1,2,5]thiadiazole (NT) The chemical structures of some of these acceptor units are shown in **Figure 1.8** [20].



benzothiadiazole (BT)

benzobisthiazole (BBTz)

thiazolothiazole (TTz)

quinoxaline (QA)

thienopyrazine (TP)

benzotriazole (BTA)

thieno[3,4-*c*]pyrrole-4,6-dione (TPD)

[2,3-*c*]thiophene-4,9-dione (NTDO)

diketopyrrolopyrrole (DPP)

Figure 1.8 The basic acceptor units

1.6 The band gaps of donor–acceptor conjugated polymers

As showed in **Figure 1.9**, the HOMO of the donor segment will interact with that of the acceptor segment to generate two new occupied molecular orbitals after covalent bond connection of two different moieties, one of them is higher and the other one is lower than the two initial HOMOs before molecular orbital hybridization. Two new unoccupied molecular orbitals would also be generated in a similar manner after molecular orbital hybridization, where one is lower and the other is higher than the two initial LUMOs of the two moieties. Hence, the overall effect of this redistribution of frontier molecular orbitals is the formation of a higher-positioned HOMO and a lower-positioned LUMO in the whole conjugated main chain, and this accordingly leads to the narrowing of the band gap [21].

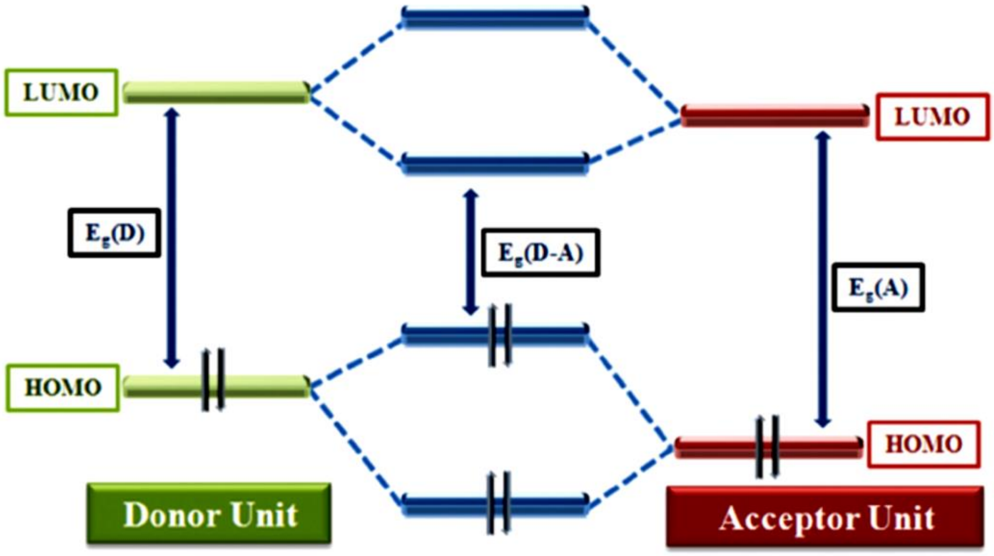


Figure 1.9 Molecular orbital interactions of donor and acceptor units, resulting in a narrowing of the band gap in donor-acceptor conjugated polymers

The alternation of the electron donating and the electron withdrawing components also increases the double bond character between each unit. Thus, the conjugated polymer backbone adopts a more planar configuration, which facilitates π-electron delocalization along the polymer backbone, and decreases the band gap. This class of donor-acceptor or D–A polymers, where the HOMO is mainly located on the donor unit and the LUMO is located on the acceptor unit, is susceptible to tuning of the HOMO and LUMO energy levels by attaching electron withdrawing groups on the acceptor and electron donating groups on the donor unit [22].

1.7 Polymerization of donor-acceptor conjugated polymers

The syntheses of donor-acceptor conjugated polymers were usually achieved through metal-catalyzed cross coupling reactions, as demonstrated in the following examples:

Suzuki coupling: the coupling partners are a boronic acid with a halide catalyzed by a palladium complex [23].

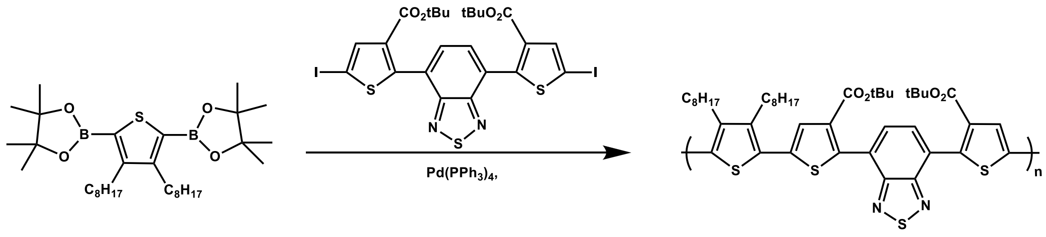


Figure 1.10 Donor-acceptor conjugated polymer by Suzuki coupling

Yamamoto coupling: the coupling of two organohalides with nickel or palladium catalyst [24].

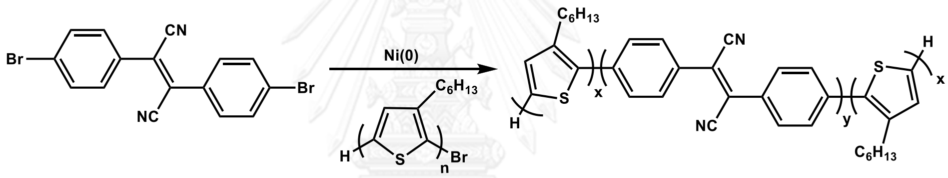


Figure 1.11 Donor-acceptor conjugated polymer by Yamamoto coupling

Stille coupling: the reaction of an organohalide with an organostannane compound gives the coupled product using a palladium catalyst [25].

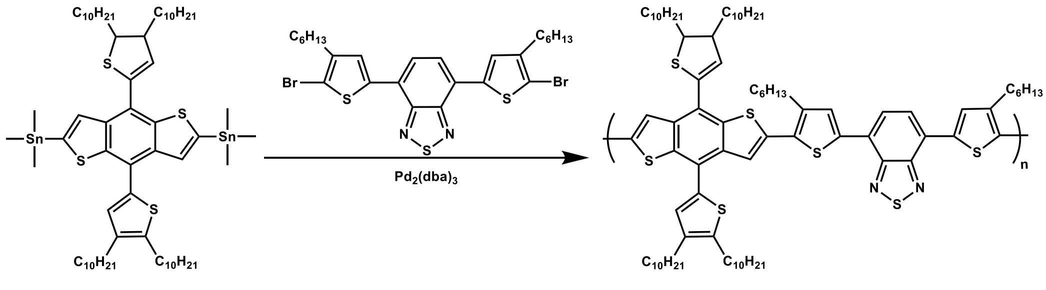


Figure 1.12 Donor-acceptor conjugated polymer by Stille coupling

1.8 Nucleophilic aromatic substitution (S_NAr) polymerization

A nucleophilic aromatic substitution is a 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 [26]. The reaction occurs repeatedly, leading to the formation of polymer.

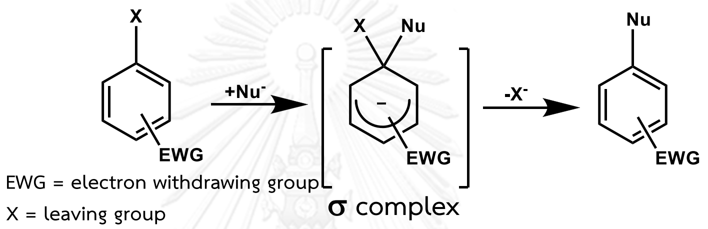


Figure 1.13 Mechanism of the S_NAr reaction

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 [27]. 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.

1.9 Literature reviews

Guo and coworkers [28] reported chemical synthesis of polyaniline (PANI) by ionic nucleophilic aromatic substitution of *p*-dichlorobenzene and sodium amide in benzene [29], which was one of the early examples of conjugated polymers synthesized by S_NAr polymerization. **(Figure 1.14)**

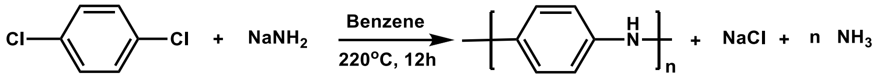


Figure 1.14 Synthesis of polyaniline by nucleophilic aromatic substitution

Herbert and coworkers [30] prepared poly(arylene pyrimidine ether)s by nucleophilic aromatic substitution reactions with 4,6-bis(4-(trimethylsiloxy)phenyl) pyrimidine and a series of activated bis(aryl fluoride)s using a catalytic amount of cesium fluoride in diphenyl sulfone. **(Figure 1.15)** The products were prepared in medium to high molecular weights with good thermal stability.

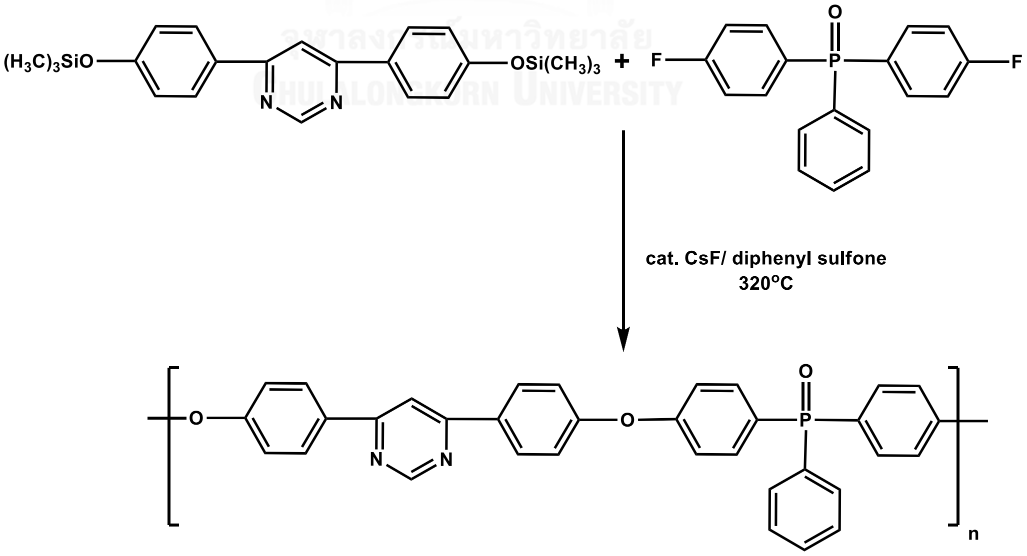


Figure 1.15 Synthesis of poly(arylene pyrimidine ether)s

Weckerly and coworkers [31] showed that nucleophilic aromatic substitution polymerization can be used to generate poly(*m*-phenylene oxide) and minimize cyclooligomer (oxacalixarene) production **(Figure 1.16)**. The synthesized poly(*m*-phenylene oxide) displayed a wide range of thermal behavior, including in several cases high thermal stabilities, and robust resistance to aqueous basic conditions.

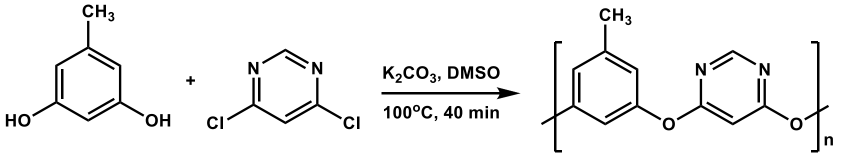


Figure 1.16 High yielding synthesis of poly(*m*-phenylene oxide)

Zhang and Tour [32] synthesized polythiophene which contained amino groups and nitro groups as electron donors and electron acceptors units, respectively. **(Figure 1.17)** Stille polymerizations using Pd(0)/CuI catalyst systems were used to couple aryldibromides with aryldistannanes. 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.

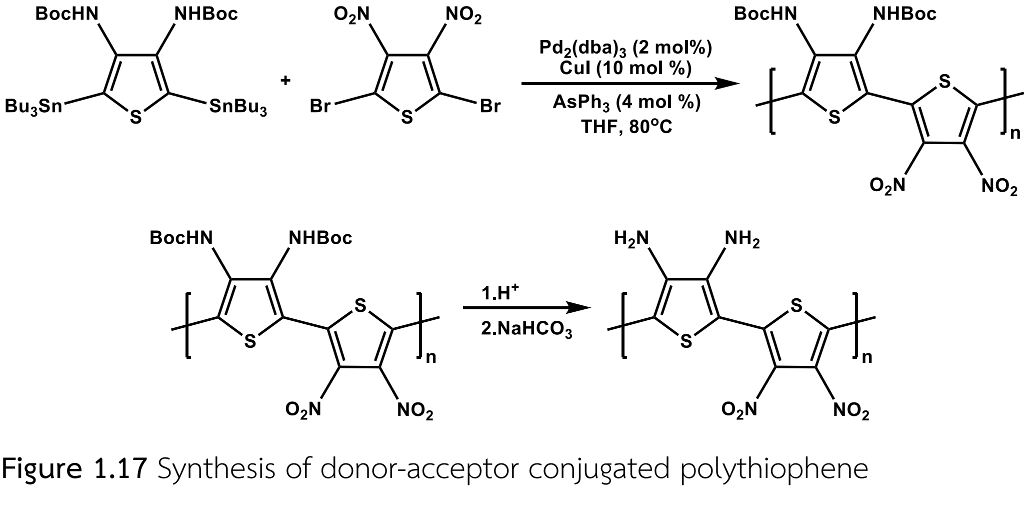


Figure 1.17 Synthesis of donor-acceptor conjugated polythiophene

Kenning and coworkers [33] reported a general synthetic route which was developed for the efficient preparation of 2,3-disubstituted thieno[3,4-*b*]pyrazines. **(Figure 1.18)** 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 obtaine 2,3-disubstituted thieno[3,4-*b*]pyrazines which were excellent precursors for production of narrow band gap conjugated polymers.

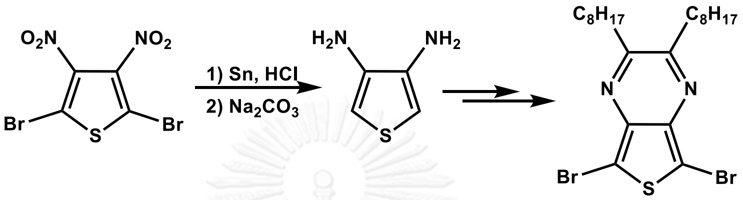


Figure 1.18 Synthesis of thieno[3,4-*b*]pyrazines compounds

Cheng and coworkers [34] successfully synthesized donor-acceptor multifused dibenzothiadiazolopyrrolothiophene (DBTPT) with benzothiadiazole as electron-deficient unit. **(Figure 1.19)** DBTPT was synthesized from 2,5-diamino-3,4-dinitrothiophene coupled with benzothiadiazole units by Suzuki coupling. The benzothiadiazole units were fused with central thiophene by double intramolecular Cadogan annulations to obtaine dipyrrolothiophene moiety. Then, *N*-Alkylations on dipyrrolothiophene resulted in DBTPT with two dodecyl side chains. Not only can the nitrogen atoms function as the bridge for covalent planarization to induce π-π interaction but also facilitate intramolecular charge transfer for better light harvesting.

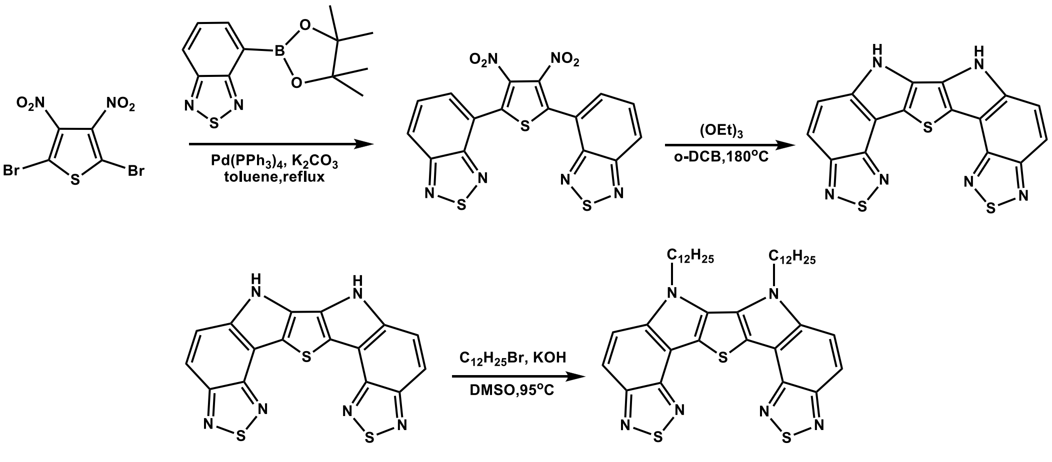


Figure 1.19 Synthesis of dibenzothiadiazolopyrrolothiophene (DBTPT)

Beaupré and coworkers [27] presented the new push-pull copolymers based on bithiophene as the "push" unit and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) as the "pull" unit, achieved by Stille cross-coupling reactions. **(Figure 1.20)** This conjugated polymers exhibited electrooptical properties that could lead to interesting bulk heterojunction plastic solar cells.

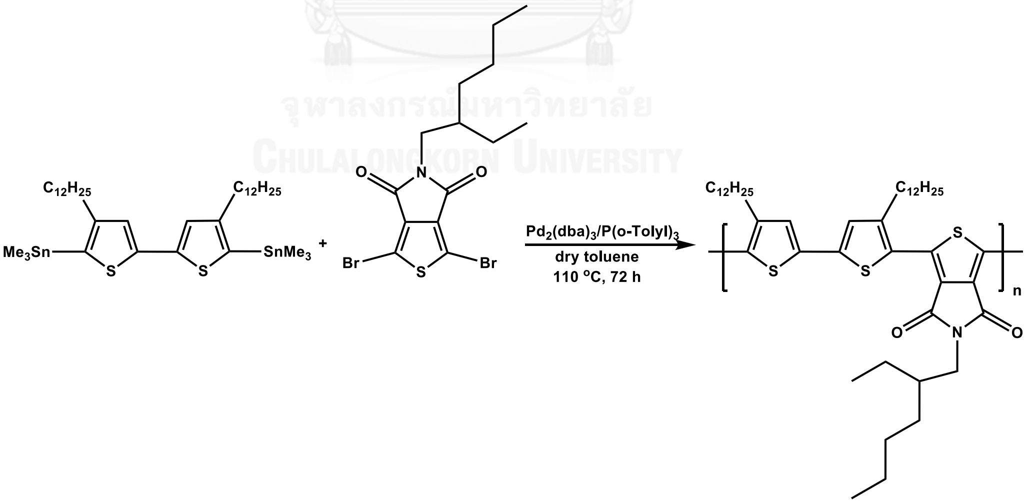


Figure 1.20 Synthesis of push-pull copolymers based on bithiophene and thieno[3,4-*c*]pyrrole-4,6-dione (TPD)

Herein, we postulated that a novel conjugated polymers could be made from S_NAr reactions on 2,5-dichloro-3,4-dinitrothiophene (DCDNT) as the acceptor units, and a variety of nucleophiles as donor units. Although DCDNT has been reported in other works, it has never been used as part of conjugated polymers prepared by this polymerization strategy. Moreover, the nitro groups of DCDNT could activate nucleophiles towards direct substitutions on thiophene rings and then post-functionalized to many other compounds such as diamines and thieno[3,4-*b*]pyrazines. The success of the synthesis would yield the first new donor-acceptor conjugated polymer of this type through this polymerization method.

1.10 Objective

The goal of this project aims to synthesize and characterize novel conjugated polymers obtained from 2,5-dichloro-3,4-dinitrothiophene (DCDNT) and a variety of nucleophiles via nucleophilic aromatic substitution polymerizations (S_NAr polymerization).

1.11 Scope of the investigation

The sequential investigation was carried out as follows:

1. Literature survey on related research

2. Synthesis of 2,5-dichloro-3,4-dinitrothiophene (DCDNT) as the main acceptor monomer unit by nitration reaction

3. Synthesis of 1-*n*-octyl-*1H*-pyrrole **(1)** via *N*-substitution reaction as one of the potential donor monomer units

4. Synthesis of N^1,N^4-dioctylbenzene-1,4-diamine **(2)** and 2-heptylbenzimidazole **(4)** as nitrogen nucleophiles to be donor units

5. Synthesis of conjugated polymers from DCDNT and three types of nucleophiles as donor units by nucleophilic aromatic substitution (S_NAr) polymerizations **(Figure 1.21)**

6. Study the optical properties of the resulted conjugated polymers

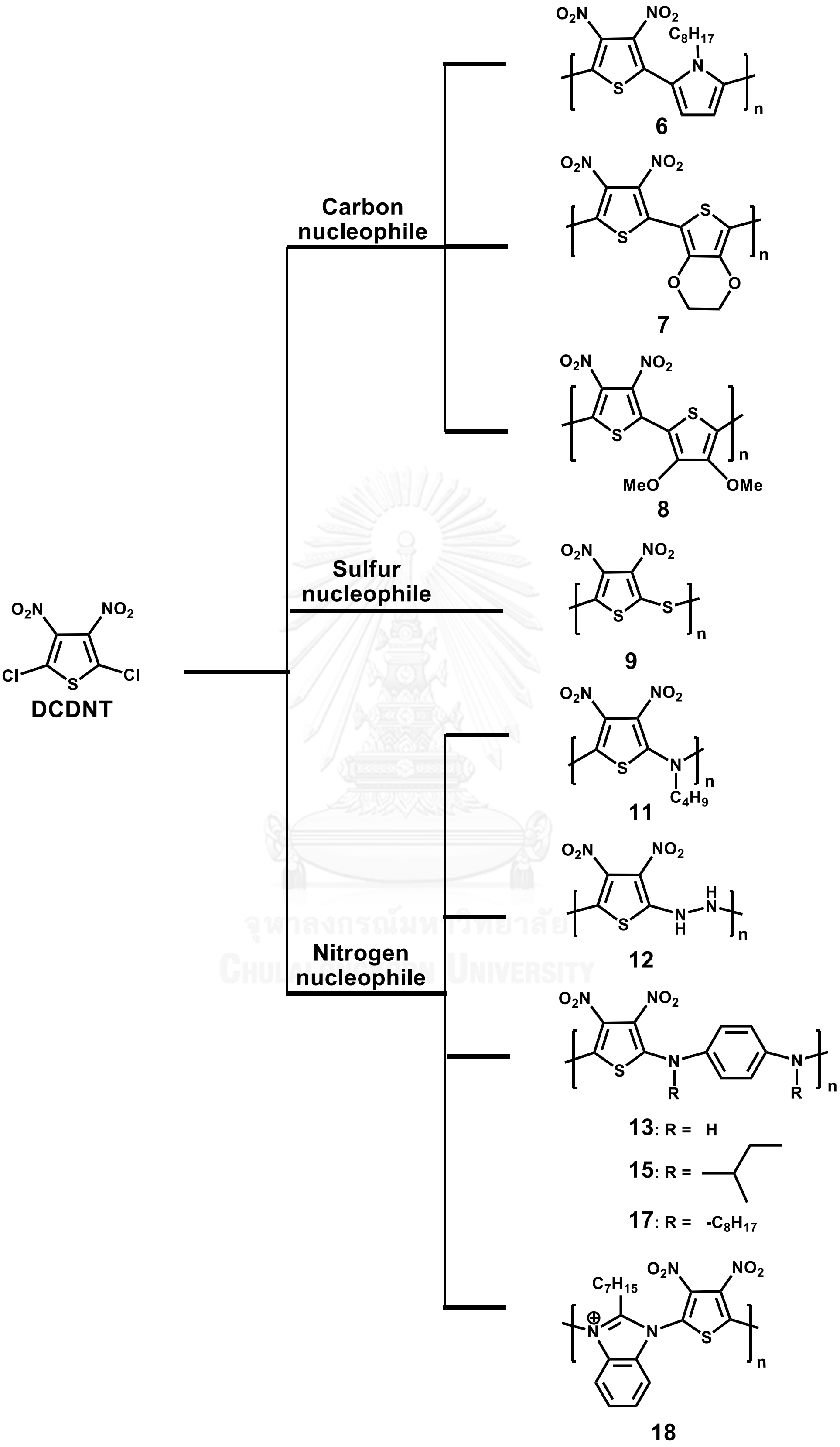


Figure 1.21 S_NAr polymerization of DCDNT and various nucleophiles

CHAPTER II

EXPERIMENTS

2.1 Chemicals

Thin layer Chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck Kieselgel 60 F_{254}, 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 synthesis were reagent or analytical grades. Solvents used in column chromatography were distilled from commercial grade prior to use. Other reagents were purchased from the following venders:

- RCI Labscan (Bangkok, Thailand): acetone, acetonitrile, chloroform, dichloroethane, dichloromethane, dimethylsulfoxide (DMSO), 1,4-dioxane, ethanol (EtOH), *N*-methyl-2-pyrrolidone (NMP), sodium hydrogen carbonate ($NaHCO_3$), sodium hydroxide (NaOH), tetrahydrofuran (THF)
- Acrös Organics (New Jersey, USA):, Boron trifluoride etherate, *o*-phenylenediamine, potassium tert-butoxide, trifluoroacetic acid (TFA)
- Carlo Erba (Milan, Italy): fuming nitric acid, pyridine, sodium sulfide nonahydrate ($Na_2S.9H_2O$), triethylamine (Et_3N)
- Fluka Chemical (Buchs, Switzerland): aluminum chloride ($AlCl_3$), Borane dimethyl sulfide,
- Merck Co. (Darmstadt, Germany): concentrated hydrochloric acid, concentrated sulfuric acid, hydrazinium dichloride, methanol (MeOH), toluene
- Cambridge Isotope Laboratories (USA): deuterated acetone (acetone-*d₆*), deuterated chloroform ($CDCl_3$), deuterated dimethylsulfoxide (DMSO-*d₆*)
- Aldrich (USA): 1-bromooctane, *N*-butylamine, *N,N'*-di-sec-butyl-*p*-phenylenediamine, 1,2-dichlorobenzene, 2,5-dichlorothiophene, 3,4-

ethylenedioxythiophene (EDOT), 3,4-dimethoxythiophene (DMT), deuterium oxide (D_2O), methanesulfonic acid (MSA), octanoyl chloride, *p*-phenylenediamine, pyrrole, sodium borohydride, sodium hydride (NaH)

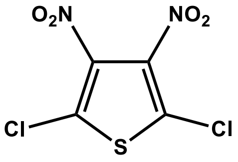
- Panreac (Spain): anhydrous magnesium sulfate ($MgSO_4$)
- Ajax Finechem Pty (Auckland, New Zealand): sodium carbonate

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 Quatto 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

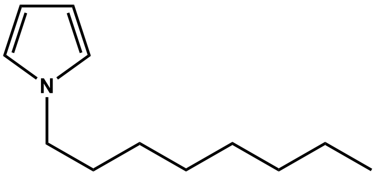
2.3.1 2,5-dichloro-3,4-dinitrothiophene (DCDNT)



DCDNT

DCDNT was prepared through the modification of the previous work described in literature [33]. 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-Dichlorothiophene (2.884 g, 18.8 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 (9:1) as eluent, affording a pale yellow solid (3.549 g, 78%). mp 81-83°C (lit. [35] 83.4-84.3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 136.8, 127.8. **(Figure A.1, Appendix)** IR (ATR, cm^{-1}): 1546, 1394 (N-O st). **(Figure A.2, Appendix)** MS: $[M+H]^+$ m/z = 241.8, 243.9, 245.7. **(Figure A.3, Appendix)** UV (CH_2Cl_2) λ_{max} = 240, 306 nm. **(Figure A.4, Appendix)**

2.3.2 1-*n*-octyl-1*H*-pyrrole (1)



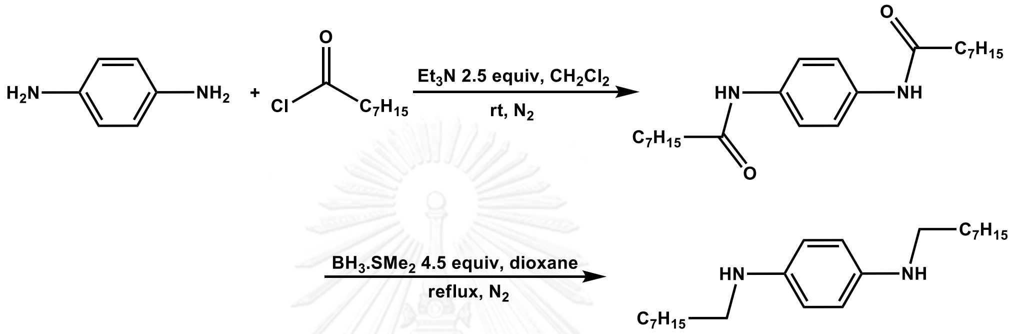
1

Compound **1** was prepared through the modification of the previous work described in literature [36]. NaH (1.4 g, 60 mmol) was stirred in DMSO (20.0 mL) at room temperature overnight. Pyrrole (0.4 mL, 6.0 mmol) and octylbromide (2.1 mL, 12.0 mmol) were added under nitrogen atmosphere. The reaction was heated to reflux for 2 h, and then quenched by the addition of H_2O. The product was extracted with EtOAc. The separated organic phase was dried over anhydrous $MgSO_4$ and filtered. The solvents were removed under reduced pressure and the crude mixture was purified on a silica column chromatography using a 9:1 hexane/EtOAc mixture. Compound **1** was obtained as pale yellow liquid (0.806 g, 74.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.64 (d, *J* = 1.95 Hz, 2H), 6.13 (d, *J* = 19.7 Hz, 2H), 3.87 (t, *J* = 7.0 Hz, 2H), 1.77 (m, 2H), 1.29 (m, 10H), 0.92 (t, *J* = 6.8 Hz, 3H). **(Figure A.5, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 120.4, 107.8, 49.6, 31.7, 31.5, 29.1, 29.1, 26.7, 22.6, 14.0. **(Figure A.6, Appendix)** IR (ATR, cm^{-1}): 2920, 2850 (C-H st). **(Figure A.7, Appendix)** UV (CH_2Cl_2) λ_{max} = 237 nm. **(Figure A.8, Appendix)**

2.3.3 N^1,N^4-dioctylbenzene-1,4-diamine (2)

Compound **2** was synthesized from two pathways: through diamide intermediate and diimine intermediate

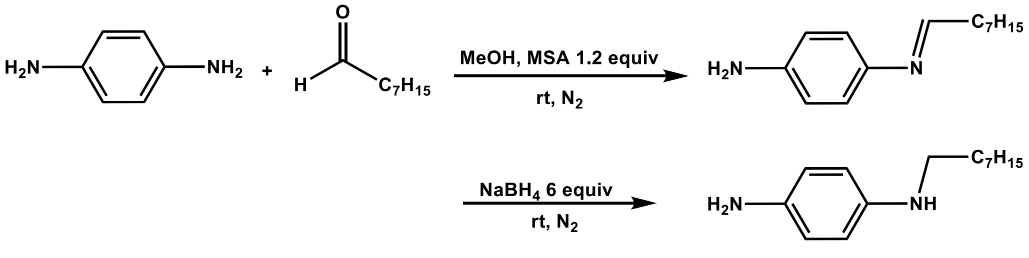
1) Diamide intermediate pathway



2

To a solution of *p*-phenylenediamine (0.541 g, 5.0 mmol) in dichloromethane (5 mL) was added dropwise octanoyl chloride (2.13 mL, 12.5 mmol) and Et_3N (1.74 mL, 12.5 mmol). The reaction mixture was stirred at room temperature until complete conversion. Then, borane dimethyl sulfide (11.30 mL, 22.6 mmol) was added. The reaction mixture was heated under reflux for 10 h and then quenched by extracted with EtOAc. The organic layer was dried with anhydrous $MgSO_4$, concentrated by rotary evaporator to give dark purple solid. The crude mixture was purified by passing through a silica gel column chromatography eluted with hexane:EtOAc (8:2) to yield compound **2** as black purple solid (0.897 g, 54.0%). mp 77-78 °C (lit. [37] 79 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.55 (s, 4H), 3.03 (t, J = 7.3 Hz, 4H), 1.57 (m, 4H), 1.41 – 1.19 (m, 20H), 0.88 (t, J = 6.2 Hz, 6H). **(Figure A.9, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 126.7, 121.9, 113.2, 112.9, 44.03, 31.6, 29.5, 29.2, 27.1, 26.8, 22.6, 14.05. **(Figure A.10, Appendix)** IR (ATR, cm^{-1}): 3360 (N-H st), 2921 (C-H st). **(Figure A.11, Appendix)** MS: $[M+H]^+$ m/z = 332.3. **(Figure A.12, Appendix)** UV (CH_2Cl_2) λ_{max} = 260, 332 nm. **(Figure A.13, Appendix)**

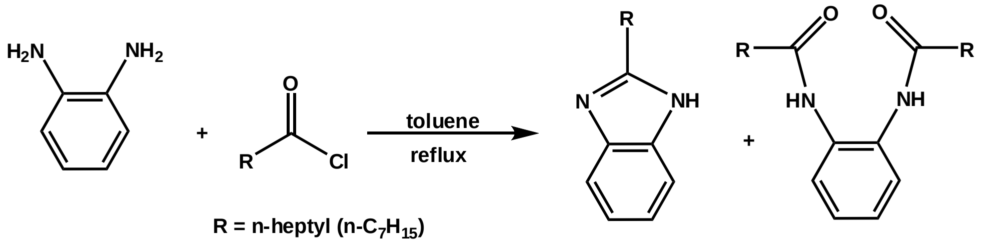
2) Diimine intermediate pathway



3

To a solution of octanal (2.35 mL, 15.0 mmol) in methanol (5 mL) was added *p*-phenylenediamine (0.541 g, 5.0 mmol) and MSA (0.32 mL, 6.0 mmol). The reaction mixture was stirred at room temperature until complete conversion. Then, $NaBH_4$ (1.130 g, 30.0 mmol) was added. The reaction mixture was stirred at room temperature for 15 h and then quenched by adding 10% HCl until acidic and extracted with EtOAc. The H_2O layer was added 2 M NaOH until basic and extracted with EtOAc. The organic layer was dried with anhydrous $MgSO_4$, concentrated by rotary evaporator to give dark purple solid. The crude mixture was purified by passing through a silica gel column chromatography eluted with hexane:EtOAc (8:2) to yield compound **3** as dark purple solid partial liquid (0.040 g, 3.64%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.64 (d, *J = 8.4 Hz*, 2H), 6.56 (d, *J = 8.4 Hz*, 2H), 3.31 (s, 2H), 3.06 (t, *J= 7.1 Hz*, 2H), 1.61 (dd, *J= 14.3, 7.3 Hz*, 2H), 1.45 – 1.17 (m, 10H), 0.91 (t, *J = 6.6 Hz*, 3H). **(Figure A.14, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 120.4, 107.8, 49.6, 31.7, 31.5, 29.1, 29.1, 26.7, 22.6, 14.0. **(Figure A.15, Appendix)** IR (ATR, cm^{-1}): 3366 (N-H st), 2917 (C-H st). **(Figure A.16, Appendix)** MS: $[M+H]^+$ m/z = 221.29. **(Figure A.17, Appendix)**

2.3.4 2-heptylbenzimidazole (4)



R = n-heptyl (n-C_7H_{15})

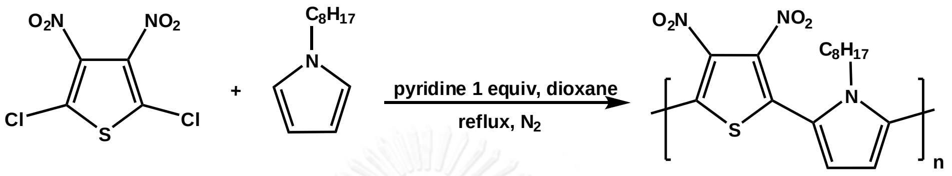
4 **5**

Compound **4** was prepared through the modification of the previous work described in literature [38]. To a solution of *o*-phenylenediamine (0.486 g, 4.5 mmol) in toluene (5 mL) was added dropwise octanoyl chloride (1.10 mL, 3.0 mmol). The reaction mixture was heated under reflux for 3 h under nitrogen atmosphere. The reaction was then quenched by adding 2 M NaOH and extracted with EtOAc. The organic layer was dried with anhydrous $MgSO_4$, concentrated by rotary evaporator to give yellow solid. The crude mixture was purified by passing through a silica gel column chromatography eluted with hexane:EtOAc (1:1) to yield compound **4** as light yellow solid (0.184 g, 28.3%). mp 139-140 °C (lit. [39] 138-140 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (m, 2H), 7.28 (m, 2H), 2.94 (dt, *J* = 10.9, 7.9 2H), 1.86 (m, 2H), 1.43 – 1.14 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H). **(Figure A.18, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 155.6, 138.1, 122.2, 114.5, 31.6, 29.3, 29.1, 28.9, 28.3, 28.30, 22.5, 13.9. **(Figure A.19, Appendix)** IR (ATR, cm^{-1}): 3081 (sp^2 C-H st), 2927, 2852 (sp^3 C-H st), 1537 (C=C st). **(Figure A.20, Appendix)** MS: $[M+H]^+$ m/z = 217.2. **(Figure A.21, Appendix)** UV (CH_2Cl_2) λ_{max} = 276, 282 nm. **(Figure A.22, Appendix)** [39] Compound **5** was also obtained as yellow solid (0.761 g, 70.3%). mp 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.34 (s, 2H), 7.30 – 7.27 (m, 2H), 7.15 – 7.12 (m, 2H), 2.28 (t, *J* = 7.6 Hz, 4H), 1.67 (m, 8H), 1.31 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 6H). **(Figure A.23, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 172.8, 130.7, 125.9, 125.5, 37.1, 31.7, 29.2, 29.0, 25.7, 22.61, 14.0. **(Figure A.24, Appendix)** IR (ATR, cm^{-1}): 3283 (N-H st), 2921, 2848 (C-H st), 1642 (C=O st). **(Figure A.25, Appendix)** MS: $[M+Na]^+$ m/z = 383.4. **(Figure A.26, Appendix)**

2.4 Polymer synthesis

2.4.1 Reaction of DCDNT with carbon nucleophiles

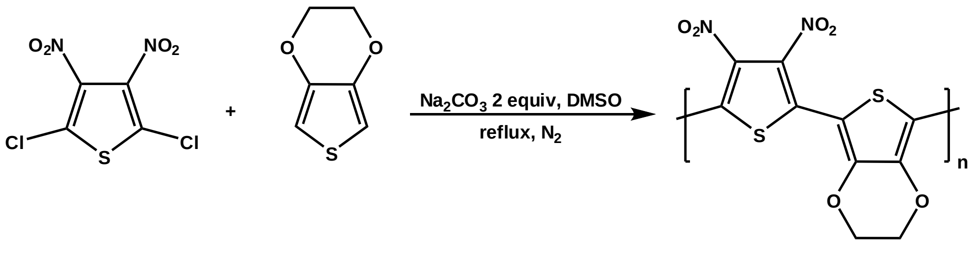
2.4.1.1 With 1-*n*-octyl-*1H*-pyrrole (1)



DCDNT 1 6

To a solution of DCDNT (0.293 g, 1.2 mmol) in dioxane (5 mL) was added pyridine (0.08 mL, 1 mmol) and compound **1** (0.179 mL, 1 mmol). After refluxing for 5 h under nitrogen atmosphere, the reaction was quenched by adding 10% HCl, and extracted by EtOAc. The separated organic layer was dried with anhydrous $MgSO_4$ and concentrated by rotary evaporator to give crude product as insoluble black solid (0.052 g, 13.5%). IR (ATR, cm^{-1}): 2923 (C-H st), 1605, 1266 (N-O st). **(Figure A.27, Appendix)**

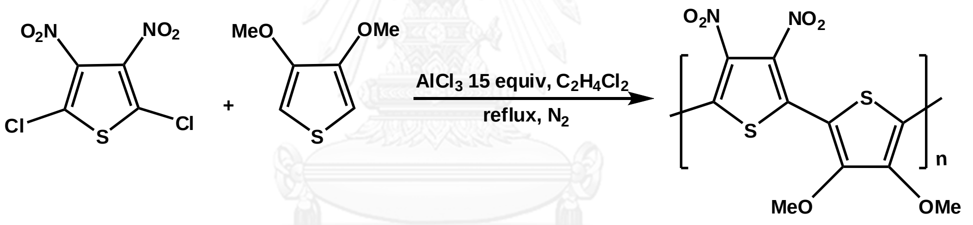
2.4.1.2 With 3,4-ethylenedioxythiophene (EDOT)



DCDNT EDOT 7

To a solution of DCDNT (0.243 g, 1 mmol) in DMSO (2 mL) was added Na_2CO_3 (0.212 g, 2 mmol) and EDOT (0.142 mL, 1 mmol). After refluxing for 15 h under nitrogen atmosphere, the reaction was quenched by adding H_2O and extracted by EtOAc. The organic layer was dried with anhydrous $MgSO_4$, and concentrated by rotary evaporator. The crude product was purified by column chromatography using hexane/EtOAc (1:1) as eluent to obtain black solid (0.032 g, 9.2%) ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.59 (s, 2H), 6.37 (s, 2H), 4.27 (m, 16H). **(Figure A.28, Appendix)** IR (ATR, cm^{-1}): 3056 (=C-H st), 1927, 2855 (C-H st), 1598, 1366 (N-O st), 1093 (C-O st). **(Figure A.29, Appendix)**

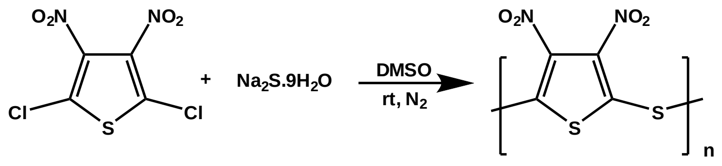
2.4.1.3 With 3,4-dimethoxythiophene (DMT)



DCDNT DMT 8

To a solution of DCDNT (0.486 g, 2 mmol) in 1,2-dichloroethane (5 mL) was added $AlCl_3$ (2.0 g, 15 mmol) and DMT (0.12 mL, 1 mmol). The reaction mixture was heated under reflux for 16 h under nitrogen atmosphere. The reaction was quenched by adding H_2O and 2 M NaOH until basic. The resulted precipitate was filtered and washed with 1,2-dichloroethane and H_2O to give polymer **8** as insoluble black solid (0.438 g, 67.5%). IR (ATR, cm^{-1}): 3362 (O-H st), 1639, 1423 (N-O st), 1091 (C-O st). **(Figure A.30, Appendix)** UV (solid) λ_{max} = 541 nm. **(Figure A.31, Appendix)**

2.4.2 Reaction of DCDNT with sulfur nucleophile

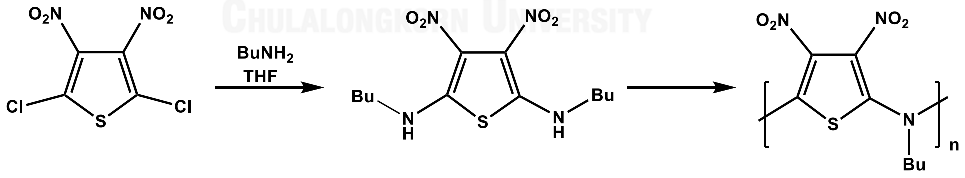


DCDNT 9

To a solution of DCDNT (0.389 g, 1.6 mmol) in DMSO (3 mL) was added Na_2S (0.360 g, 1.5 mmol). The mixture was stirred at room temperature for 2 days under nitrogen atmosphere and then quenched by adding H_2O. The resulted black precipitate was collected by vacuum filtration and washed with H_2O to give polymer **9** as insoluble black solid (0.226 g, 62.7%). IR (ATR, cm^{-1}): 1513, 1227 (N-O st). **(Figure A.32, Appendix)**. UV (solid) λ_{max} = 542 nm. **(Figure A.33, Appendix)**

2.4.3 Reaction of DCDNT with nitrogen nucleophiles

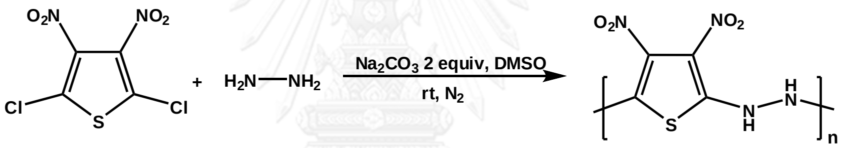
2.4.3.1 With *n*-butylamine



DCDNT 10 11

To a solution of DCDNT (0.365 g, 1.5 mmol) in THF (2 mL) was added butylamine (0.05 mL, 0.5 mmol). The mixture was stirred at room temperature for 50 minutes under nitrogen atmosphere. The reaction was quenched by adding 10% HCl until acidic. The separated aqueous layer was neutralized by 2 M NaOH and extracted repeatedly with EtOAc. The combined organic layer was dried with anhydrous $MgSO_4$, concentrated by rotary evaporator, and purified on a silica column chromatography using a 6:4 of hexane/CH_2Cl_2 as eluent mixture. N^2,N^5-dibutyl-3,4-dinitrothiophene-2,5-diamine (compound **10**) was obtained as a yellow solid (0.120 g, 75.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.55 (s, 2H), 3.35 (dd, *J* = 13.0, 7.0 Hz, 4H), 1.77 (dt, *J* = 19.9, 7.2 Hz, 4H), 1.48 (dt, *J* = 15.0, 7.4 Hz, 4H), 1.00 (t, *J* = 7.4 Hz, 6H). **(Figure A.34, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.5, 47.8, 30.5, 19.9, 13.4. **(Figure A.35, Appendix)** IR (ATR, cm^{-1}): 3289 (N-H st), 2927, 2867 (C-H st), 1582, 1343 (N-O st). **(Figure A.36, Appendix)** $[M+Na]^+$ m/z = 339.2. **(Figure A.37, Appendix)** UV (CH_2Cl_2) λ_{max} = 215, 386 nm. **(Figure A.38, Appendix)**

2.4.3.2 With hydrazine

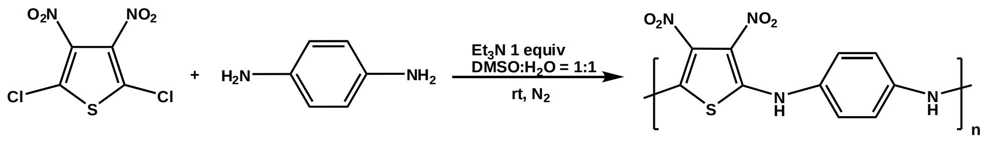


DCDNT

12

To a solution of DCDNT (0.243 g, 1 mmol) in DMSO (2 mL) was added hydrazine dihydrochloride (0.157 g, 1.5 mmol) and Na_2CO_3 (0.212 g, 2 mmol). The mixture was stirred at room temperature for 3.5 h under nitrogen atmosphere. The solid residue was filtered by vacuum filtration and washed with H_2O and EtOAc to obtain polymer **12** as insoluble black solid (0.091 g, 38.0%). IR (ATR, cm^{-1}): 3404 (N-H st), 1532, 1303 (N-O st). **(Figure A.39, Appendix)** UV (solid) λ_{max} = 634 nm. **(Figure A.40, Appendix)**

2.4.3.3 With *p*-phenylenediamine

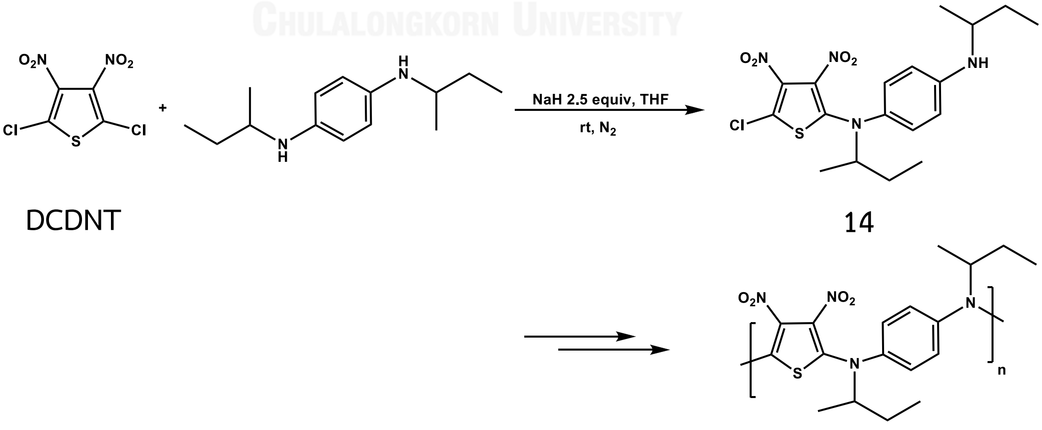


DCDNT

13

To a solution of DCDNT (0.243 g, 1 mmol) in DMSO:H_2O (4 mL) was added *p*-phenylenediamine (0.108 g, 1 mmol) and Et_3N (0.14 mL, 1 mmol). The mixture was stirred at room temperature for 6 d under nitrogen atmosphere. The solid residue was filtered by vacuum filtration and washed with H_2O and EtOAc to get polymer **13** as insoluble brown solid (0.220 g, 70.0%). IR (ATR, cm^{-1}): 3345 (N-H st) 1544, 1331 (N-O st), 1253 (C-N st). **(Figure A.41, Appendix)** UV (solid) λ_{max} = 542 nm. **(Figure A.42, Appendix)**

2.4.3.4 With *N,N'*-di-*sec*-butyl-*p*-phenylenediamine



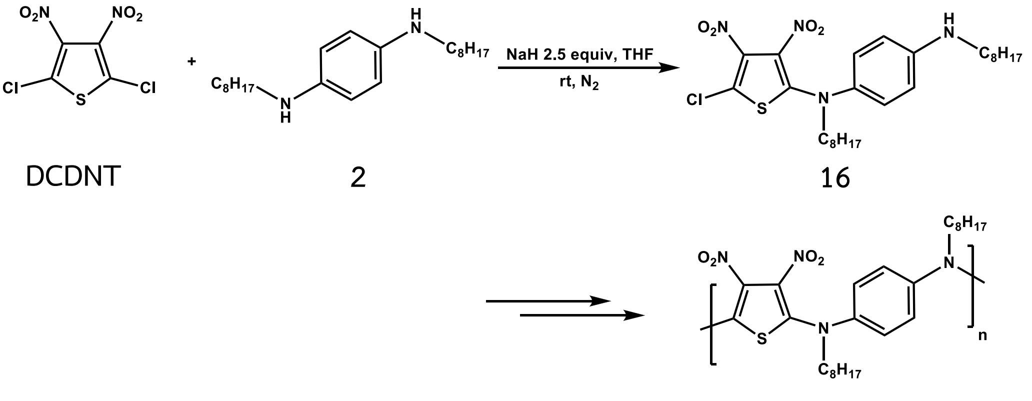
DCDNT

14

15

To a solution of DCDNT (0.243 g, 1 mmol) in THF (7 mL) was added *N,N'*-di-*sec*-butyl-*p*-phenylenediamine (0.25 mL, 1.1 mmol) and NaH (0.065 g, 2.5 mmol). The reaction mixture was stirred at room temperature for 11 d under nitrogen atmosphere. The reaction was then quenched by an addition of H_2O and extracted by EtOAc. The combined organic phase was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The crude product was obtained as black solid and purified by trituration from dichloromethane solution with an addition of hexane to obtain polymer **15** as black precipitate (0.789 g, 78.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (m), 6.74 (m), 3.40 (m), 2.37 – 0.19 (m). **(Figure A.43, Appendix)** IR (ATR, cm^{-1}): 3400 (N-H st), 2967 (C-H st), 1605, 1376 (N-O st). **(Figure A.44, Appendix)** UV (solid) λ_{max} = 668 nm. **(Figure A.45, Appendix)** The filtrate from trituration was evaporated and separated by column chromatography using hexane/CH_2Cl_2 (6:4) as eluent, affording yellow liquid of compound **14** (0.007 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, *J* = 8.7 Hz, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 4.05 – 3.79 (m, 1H), 3.51 – 3.23 (m, 1H), 1.73 (dt, *J* = 14.1, 7.3 Hz, 1H), 1.60 (td, *J* = 13.4, 6.8 Hz, 1H), 1.55 – 1.45 (m, 1H), 1.46 – 1.34 (m, 1H), 1.20 (dd, *J* = 16.8, 11.6 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H). **(Figure A.46, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 147.7, 138.8, 129.6, 129.3, 120.3, 113.7, 113.2, 29.5, 28.8, 20.0, 18.8, 11.3, 10.3. **(Figure A.47, Appendix)** IR (ATR, cm^{-1}): 3400 (N-H st), 2965 (C-H st), 1515, 1308 (N-O st). **(Figure A.48, Appendix)** MS: $[M+H]^+$ m/z = 427.0, 429.03. **(Figure A.49, Appendix)** UV (CH_2Cl_2) λ_{max} = 264, 409 nm. **(Figure A.50, Appendix)**

2.4.3.5 With N^1,N^4-dioctylbenzene-1,4-diamine (2)



DCDNT

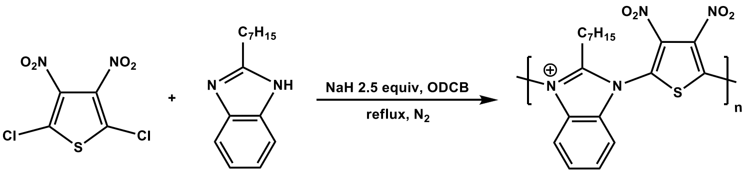
2

16

17

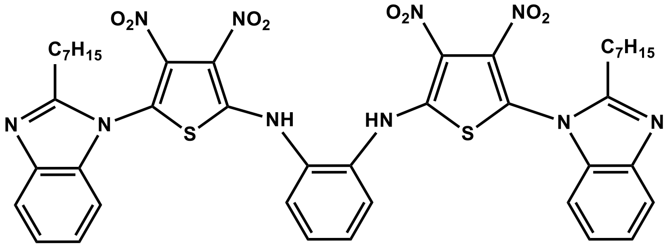
To a solution of DCDNT (0.122 g, 0.5 mmol) in THF (5 mL) was added compound **2** (0.183 g, 0.55 mmol) and NaH (0.051 g, 1.25 mmol). The reaction mixture was stirred at room temperature for 8 d under nitrogen atmosphere. The reaction was then quenched by an addition of H_2O and extracted by EtOAc. The combined organic phase was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The crude product was obtained as black brown liquid and purified on a silica column chromatography using a 8:2 hexane/EtOAc as eluent mixture to obtain polymer **17** as dark yellow liquid (0.007 g, 2.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (m), 6.56 (m), 3.66 (m), 3.09 (m), 1.60 (m), 1.30 (m), 0.86 (m). **(Figure A.52, Appendix)** IR (ATR, cm^{-1}): 3372 (N-H st), 2918 (C-H st), 1510, 1331 (N-O st). **(Figure A.53, Appendix)** UV (CH_2Cl_2) λ_{max} = 261, 405 nm. **(Figure A.54, Appendix)** Compound **16** was also obtained as dark yellow liquid (0.039 g, 14.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 1H), 3.77 (t, *J* = 7.9 Hz, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.73 – 1.52 (m, 6H), 1.35 – 1.17 (m, 18H), 0.87 (dd, *J* = 11.5, 4.7 Hz, 6H). **(Figure A.55, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 148.6, 138.3, 134.3, 126.6, 113.7, 113.2, 112.6, 57.8, 28.8, 20.0, 18.8, 11.3, 10.3. **(Figure A.56, Appendix)** IR (ATR, cm^{-1}): 3388 (N-H st), 2924 (C-H st), 1544, 1381 (N-O st). **(Figure A.57, Appendix)** MS: $[M+H]^+$ m/z = 539.5, : $[M+Na]^+$ m/z = 561.4, : $[M+K]^+$ m/z = 577.4. **(Figure A.58, Appendix)** UV (CH_2Cl_2) λ_{max} = 259, 419 nm. **(Figure A.59, Appendix)**

2.4.3.6 With 2-heptylbenzimidazole (4)



DCDNT 4 18

To a solution of DCDNT (0.073 g, 0.3 mmol) in *o*-dichlorobenzene (ODCB, 5 mL) was added compound **4** (0.074 g, 0.33 mmol) and NaH (0.036 g, 0.75 mmol). The mixture was heated under reflux for 20 h under nitrogen atmosphere. The solid residue was filtered by vacuum filtration and washed with H_2O and EtOAc to obtain partly dissolving dark brown solid of mixture products of polymer **18** (and possibly compound **19)** (0.020 g, 15.7 %). IR (ATR, cm^{-1}): 2936 (C-H st), 1525, 1328 (N-O st). **(Figure A.60, Appendix)** UV (solid) λ_{max} = 681 nm. **(Figure A.61, Appendix)**. The mixture products were partly dissolved in chloroform with 3 drops of trifluoroacetic acid to obtain as brown solution. ^{1}H NMR of this solution (400 MHz, $CDCl_3$+TFA): δ 7.65 (dd, *J = 6.1, 3.3 Hz*, 4H), 7.59 – 7.55 (m, 4H), 7.44 (dd, *J = 6.0, 3.6 Hz*, 2H), 7.22 – 7.18 (m, 2H), 3.19 – 3.10 (m, 4H), 1.85 (d, *J = 7.6 Hz*, 4H), 1.31 (d, *J = 47.1 Hz*, 16H), 0.88 – 0.78 (m, 6H). **(Figure A.62, Appendix)** ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.5, 129.9, 127.6, 127.2, 113.5, 31.2, 28.7, 28.4, 26.9, 26.5, 22.3, 13.5. **(Figure A.63, Appendix)**



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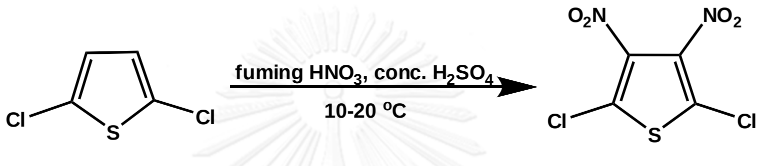
CHAPTER III

RESULTS AND DISCUSSION

3.1 Monomer synthesis

3.1.1 2,5-dichloro-3,4-dinitrothiophene (DCDNT)

DCDNT was synthesized from 2,5-dichlorothiophene through highly vigorous nitration reaction. The conditions of the reactions were varied according to **Table 3.1**:



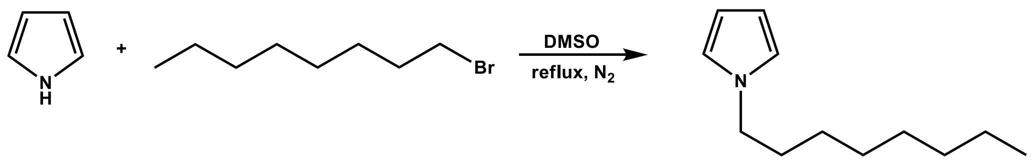
DCDNT

Table 3.1 Various conditions for the synthesis of DCDNT

Entry	2,5-dichlorothiophene (mmol)	conc. H_2SO_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 3.1**, the optimized time for this reaction was 3.5 h, leading to the highest yields of DCDNT (Entry 3). High yields of the product were also 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 either the starting material or the product under such harsh conditions. The product was characterized by the presence of strong, sharp bands of nitro groups at 1549, 1309 cm^{-1} in IR spectrum. **(Figure A.2, Appendix)** Both ^{13}C NMR **(Figure A.1, Appendix)** and MS **(Figure A.3, Appendix)** methods confirmed that all the details matched well with the expected structure and the corresponding information from the literature [35].

3.1.2 1-*n*-octyl-*1H*-pyrrole (1)



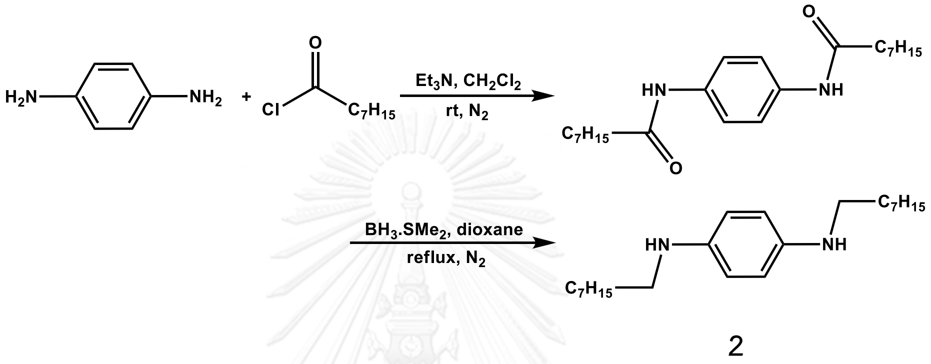
1

Compound **1** was synthesized from pyrrole and *n*-octylbromide through direct nucleophilic substitution reaction. After completion, compound **1** as pale yellow liquid was obtained in 74.9% yield. The ^{1}H NMR spectrum clearly showed the triplet signal at 3.90 ppm of α-proton adjacent to the nitrogen atom from pyrrole ring together with the pyrrole protons at 6.68 and 6.17 ppm. **(Figure A.5, Appendix)** IR spectrum illustrated medium C-H stretching signals of the alkyl group at 2920, 2850 cm^{-1}. **(Figure A.7, Appendix)** [36]

3.1.3 N^1,N^4-dioctylbenzene-1,4-diamine (2)

Compound **2** was synthesized from two pathways: through diamide intermediate or diimine intermediate by reactions with corresponding acid chloride or aldehyde, respectively, followed by reductions.

1) Diamide intermediate pathway



For diamide intermediate pathway, *p*-phenylenediamine was condensed together to prepare the corresponding diamide, which was then reduced with borane dimethyl sulfide to obtain compound **2** as black purple solid in 54% yield. In ^{1}H NMR, there were one singlet signal of protons on the aromatic ring at 6.55 ppm and a set of signals that matched well with the octyl groups. **(Figure A.9, Appendix)** The ^{13}C NMR spectrum showed two signals of carbons on aromatic ring and eight signals of octyl groups. **(Figure A.10, Appendix)** The N-H and C-H stretching signals were observed in IR spectrum at 3360 and 2921 cm^{-1}, respectively. **(Figure A.11, Appendix)** In mass spectrum, the molecular peaks at 332.57 matched with the calculated molecular weights of compound **2** as well. **(Figure A.12, Appendix)**

2) Diimine intermediate pathway (reductive amination)

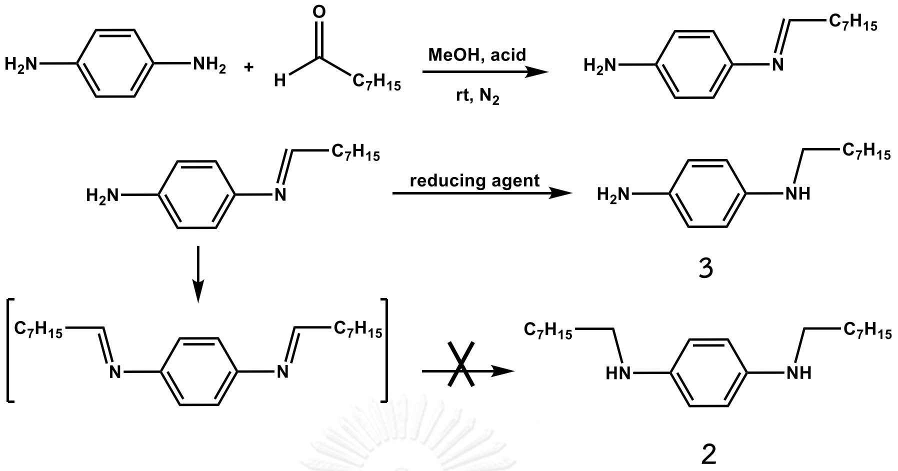


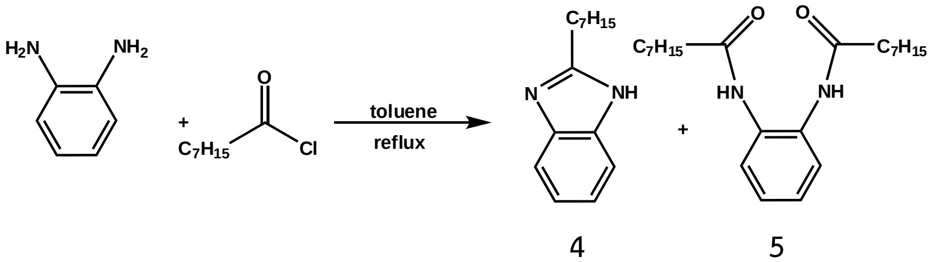
Table 3.2 Various conditions for the synthesis of compound **2** through diimine intermediate

Entry	*p*-phenylenediamine (mmol)	Octanal (mmol)	Acid (mmol)	Reducing agent (mmol)	Reduction condition	
					temp	time
1	1.0	2.5	-	$NaBH_4$ (2.5)	rt	10 min
2	0.8	1.0	-	$NaBH_4$ (1.0)	rt	2.0 h
3	5.0	15.0	MSA (5)	$NaBH_4$ (30.0)	rt	15.0 h
4	5.0	15.0	MSA (5)	$NaBH_4$ (50.0)	reflux	45 min
5	5.0	15.0	MSA (10)	$NaCNBH_3$ (15.0)	rt	2.0 h

From various conditions shown in **Table 3.2**, whether using higher *p*-phenylenediamine (Entry 1), higher equivalence of octanal (Entry 2), using $NaBH_4$ as reducing agent of the imine intermediate at room temperature (Entry 3), or at reflux temperature (Entry 4), or using $NaCNBH_3$ as reducing agent (Entry 5), no sign of compound **2** was observed in all cases. Instead, only the monosubstituted compound **3** was obtained, together with recovered diamine starting material. It was assumed that the protonated form of diimine intermediate was poorly soluble in MeOH and precipitated out of the solution as yellow solid and could not be reduced. Only the partially soluble protonated monoimine was reduced to give compound **3**. The remaining diimine was then by hydrolyzed back to the diamine starting material after workup.

The ^{1}H NMR spectrum of compound **3** clearly showed the two doublet signals of aromatic ring at 6.61 and 6.52 ppm, the proton signal of amino group at 3.23 ppm and a set of signals of the octyl group on nitrogen atom. **(Figure A.14, Appendix)** In ^{13}C NMR spectrum, there were four signals of the aromatic ring and eight signals of the octyl group. **(Figure A.15, Appendix)** IR spectrum presented medium N-H stretching of the amino group and C-H stretching of octyl group signals at 3366, 2917 cm^{-1}, respectively. **(Figure A.16, Appendix)** Moreover, the calculated molecular weight of compound **3** matched with the observed molecular ion peak at 221.2 in the mass spectrum. **(Figure A.17, Appendix)**

3.1.4 2-heptylbenzimidazole (4)



4 5

Table 3.3 Various conditions for the synthesis of compound **4**

Entry	*o*-phenylenediamine (mmol)	Octanoyl chloride (mmol)	Time (h)	%Yield*	
				Compound **4**	Compound **5**
1	1.0	1.5	2.5	22.2	44.4
2	3.0	4.5	5.5	26.3	35.8
3**	3.0	2.0	1.5	24.0	21.0
4	4.5	3.0	3.0	28.3	70.3
5	7.5	5.0	4.5	33.0	57.8

* % Yield were calculated from the limiting agent.

** Entry 3 was added 1 equiv of pyridine as base.

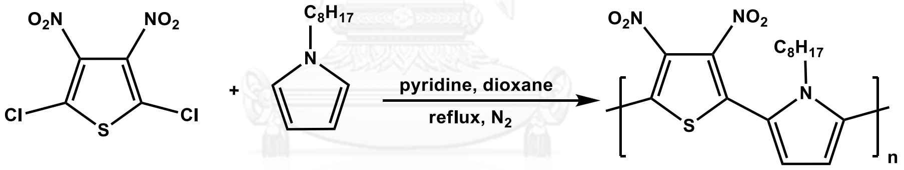
Compound **4** was obtained as light yellow solid from *o*-phenylenediamine and octanoyl chloride via substitution followed by cyclization reaction. In ^{1}H NMR, there were two signals of protons on the aromatic ring at 7.57 and 7.28 ppm and a set of signals that matched well with the heptyl group on the imidazole ring. **(Figure A.18, Appendix)** IR spectrum showed the characteristic C-H stretching peaks of alkyl group at 2927, 2852 cm^{-1}. **(Figure A.20, Appendix)** [39] However, compound **5** was instead obtained as the major product. Its IR spectrum showed N-H and C=O stretching signals of amide groups at 3283 and 1642 cm^{-1}, respectively **(Figure A.25, Appendix)**, and its NMR spectra also matched well with the expected structure. **(Figure A.23-24, Appendix)**

From **Table 3.3**, the equivalence of octanoyl chloride in entries 1 and 2 was higher than that of *o*-phenylenediamine. The results indicated that there were only small differences on yields and ratios of the products when using larger scale of the starting materials and longer reaction time. An addition of pyridine as an external base in entry 3 did not improve the reaction. In entries 4 and 5, the reactions seemed to proceed better without base and higher equivalence of the diamine. The results showed that the combined yields of compounds **4** and **5** of the last two entries were relatively high, though the undesired compound **5** was still found to be the major product.

3.2 Polymer synthesis

3.2.1 Reaction of DCDNT with carbon nucleophiles

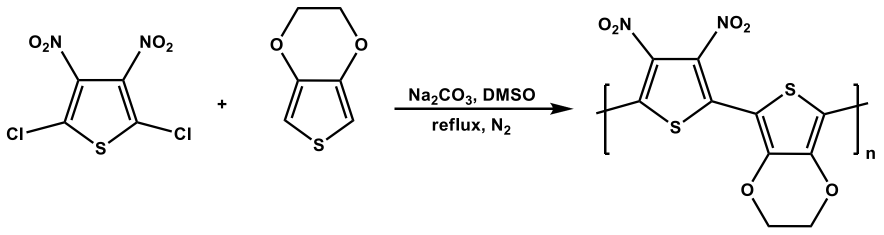
3.2.1.1 With 1-*n*-octyl-*1H*-pyrrole (1)



DCDNT 1 6

Compound **1** was substituted with the octyl group on the nitrogen atom to potentially increase the electron density of the ring as the nucleophile and solubility of the expected polymer. After its reaction with DCDNT, polymer **6** was obtained as insoluble black solid. In IR spectrum, it showed C-H stretching signal of octyl group at 2923 cm^{-1} and probable N-O stretching signals of nitro groups at 1605 and 1266 cm^{-1}. **(Figure A.27, Appendix)** The polymer was obtained in very small amount and because of its insolubility; it could not be further characterized to confirm whether polymer **6** was actually obtained.

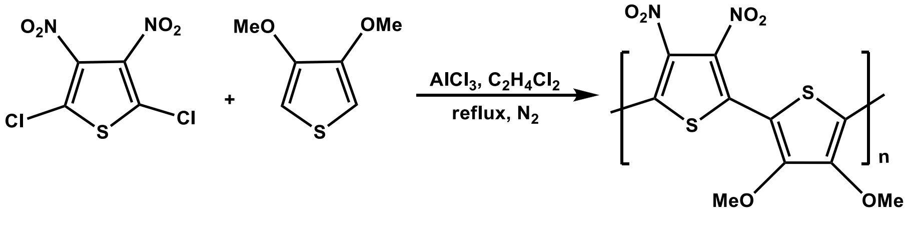
3.2.1.2 With 3,4-ethylenedioxythiophene (EDOT)



DCDNT EDOT 7

Following the procedure, the product of this reaction was postulated to be a short-chain oligomer of polymer **7** from the reactions of the two precursors. There was a singlet signal at 6.59 ppm which could be the α-proton of the terminal EDOT in the oligomer, more downfield than the similar protons on the EDOT starting material found at 6.37 ppm. **(Figure A.28, Appendix)** A group of multiplet signals was also found at 4.27 ppm that corresponded to the ethylene bridge of the EDOT units in the chain. The fact that the signal of the α-proton of the terminal EDOT unit was still strongly visible indicated that the reaction, though successful, was rather slow and only short oligomers was obtained.

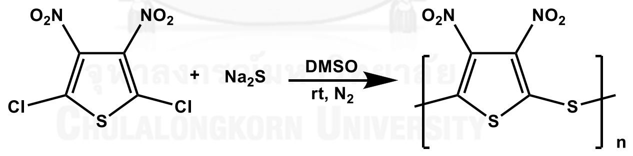
3.2.1.3 With 3,4-dimethoxythiophene (DMT)



DCDNT DMT 8

Due to the inefficiency of the previous basic condition, the synthesis of polymer **8** from DCDNT and DMT was attempted in acidic condition. The product obtained in this reaction was a black polymer which, unfortunately, could not be dissolved in any common organic solvents. Hence, the polymer was characterized only by IR and UV-Vis spectroscopy. The IR spectrum exhibited the very broad signal, potentially be hydroxyl groups at 3362 cm^{-1}, which could arise from partial demethylations of the DMT units. **(Figure A.30, Appendix)** Optical property of polymer **8** measured as pressed solid film showed a characteristic absorption of conjugated polymer at long wavelength in the visible region with a maximum wavelength absorption (λ_{max}) at 541 nm. **(Figure A.31, Appendix)** In acidic condition, some methoxy groups could be protonated by the Lewis acid and activated the removal of methyl groups by nucleophiles. Because of this incident, the thiophene ring increased its nucleophilicity and reacted more efficiently on DCDNT to yield the desired longer-chain polymer. However, the presence of the highly polar hydroxyl groups might be the reason for the insolubility of the polymer and prevented it from being fully characterized in solution.

3.2.2 Reaction of DCDNT with sulfur nucleophile

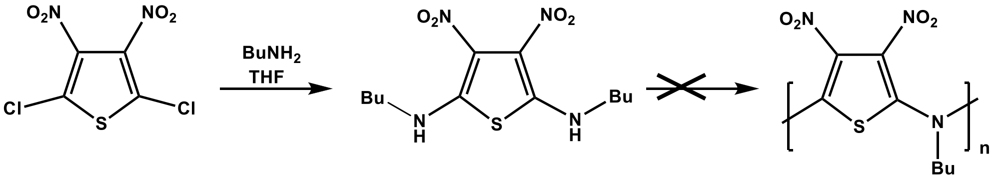


DCDNT **9**

Polymer **9** was synthesized from DCDNT using sodium sulfide as the nucleophile. The presumed product was a black powder which could not be dissolved in any common organic solvents. In IR spectrum, the N-O stretching signals of nitro groups were found at 1513 and 1227 cm^{-1}. **(Figure A.32, Appendix)** The optical property of polymer **9** measured as pressed solid film showed a characteristic absorption of conjugated polymer at long wavelength in the visible region with a maximum wavelength absorption (λ_{max}) at 542 nm. **(Figure A.33, Appendix)**

3.2.3 Reaction of DCDNT with nitrogen nucleophiles

3.2.3.1 With *n*-butylamine



DCDNT 10 11

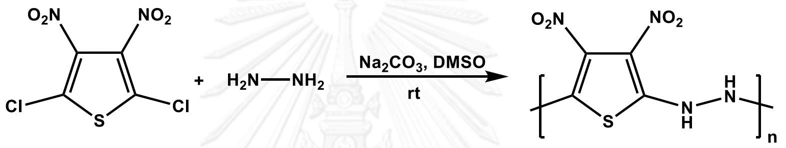
Table 3.4 Various conditions for the reaction of DCDNT and $BuNH_2$

Entry	DCDNT (mmol)	*n*-butylamine (mmol)	Solvent	Temp	Time (h)	Compound **10** (%yield)
1	1.0	1.0	ACN	reflux	6	9.8
2	1.5	0.5	THF	rt	1	75.1

DCDNT was reacted with *n*-butylamine as the nitrogen nucleophile in attempts to form polymer. Unfortunately, only the complete S_NAr substituted intermediate compound **10** was isolated. The presence of compound **10** was confirmed by NMR, IR, and MS spectroscopy. The ^1H NMR spectrum of compound **10** exhibited the singlet signal of N-H protons at 8.55 ppm and one set of the signals of the butyl groups. **(Figure A.34, Appendix)** The ^{13}C NMR spectrum also matched well with the expected structure. **(Figure A.35, Appendix)** The N-H and N-O stretching signals were observed in their IR spectrum as well. **(Figure A.36, Appendix)** Finally, the calculated molecular weights of the products matched with molecular peaks at 339.2 in the mass spectrum **(Figure A.37, Appendix)**.

In Entry 1, compound **10** was obtained in only 9.8% yield presumably because the condition used in this reaction was too harsh for the product compound **10** that led to its partial decomposition when the condition was altered to room temperature, compound **10** could be obtained up to 75.1%. As mentioned above, only compound **10** was isolated without any other longer chain polymer products. It is assumed that after butylamine substituted on to both α positions of DCDNT to generate the intermediate **10**, the strong electron-withdrawing nitro groups would reduce the reactivity of the substituted amino groups and prevent them from further reaction as nucleophiles. The reaction then stopped at this intermediate and did not progress to the desired polymer.

3.2.3.2 With hydrazine

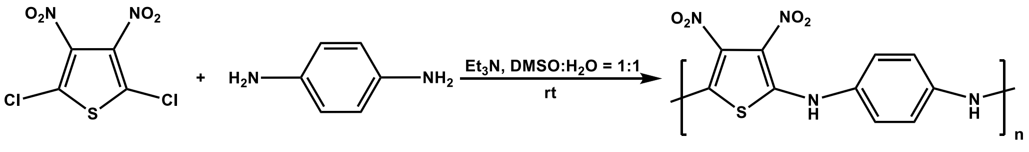


DCDNT

12

To solve the problem of unreactive nitrogen after the first substitution, the simple mono amine was replaced by hydrazine that had two nitrogen nucleophilic sites. The product from the reaction with DCDNT, probably polymer **12** was obtained as a black polymer which could not be dissolved in common organic solvents. In IR spectrum of the product, the N-H stretching signal of amino groups and N-O stretching signals of nitro group were found at 3404, and 1532, 1303 cm^{-1}, respectively. **(Figure A.39, Appendix)** The optical property of polymer **12** showed a maximum wavelength absorption (λ_{max}) at 634 nm in the visible region. **(Figure A.40, Appendix)** This demonstrated that the polymer could carry a well-ordered, highly conjugated structure, which tightly aggregated and made it insoluble.

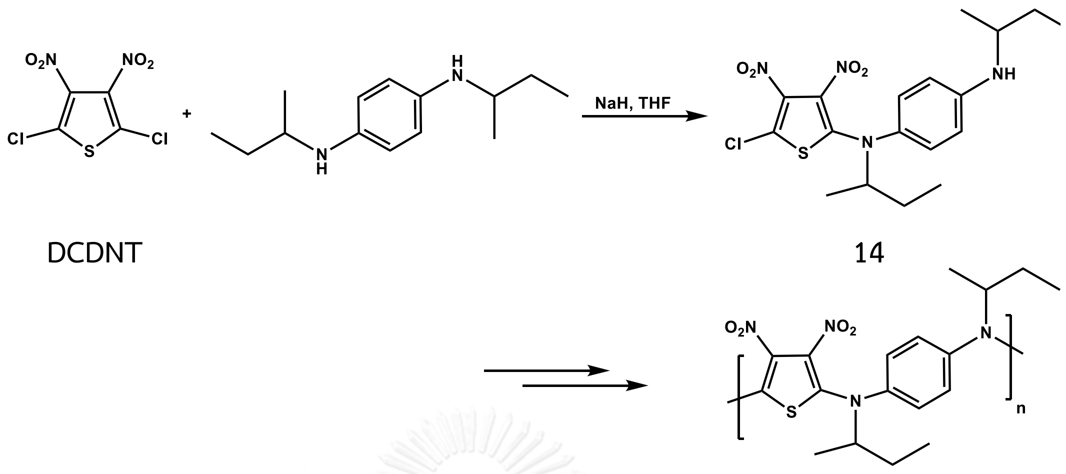
3.2.3.3 With *p*-phenylenediamine



DCDNT **13**

Polymer **13** could be synthesized from DCDNT and *p*-phenylenediamine as another nucleophile containing two nucleophilic sites. The desired product was obtained as a chocolate brown polymer which could not be dissolved in simple organic solvents. The N-H stretching signal of amino groups and N-O stretching signals of nitro groups were showed at 3345 and 1544, 1331 cm^{-1} in IR spectrum, respectively. **(Figure A.41, Appendix)** The optical property of polymer **13** measured as pressed solid film exhibited a characteristic absorption in the visible region of a conjugated polymer with a maximum wavelength absorption (λ_{max}) at 542 nm. **(Figure A.42, Appendix)** Once again, its highly aggregated nature would probably be the reason for its insolubility.

3.2.3.4 With *N*,*N'*-di-*sec*-butyl-*p*-phenylenediamine



DCDNT

14

15

Table 3.5 Various conditions for the synthesis of polymer **15**

Entry	DCDNT (mmol)	Diamine (mmol)	Temp	Time (d)	Polymer **15** (%yield)	λ_{max} (nm)
1	1.0	1.1	rt	11	78.6	668
2	1.0	1.1	reflux	4	12.2	656

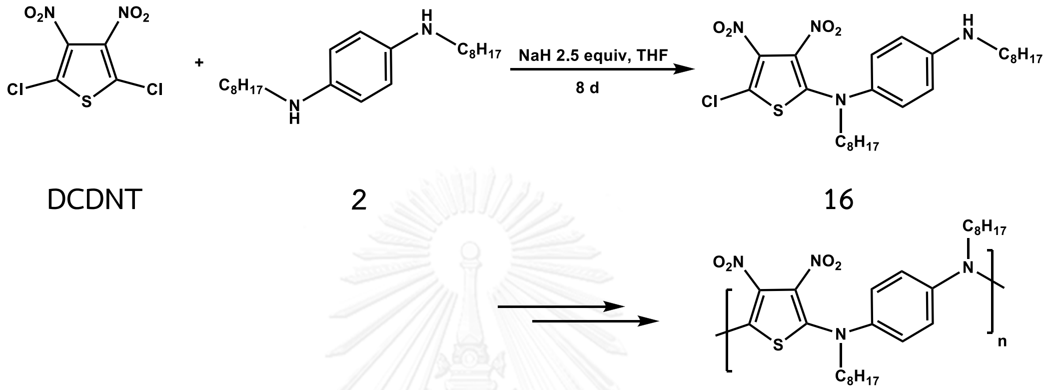
Similar to the previous section, polymer **15** was synthesized from DCDNT and *N*,*N'*-di-*sec*-butyl-*p*-phenylenediamine by nucleophilic aromatic substitution where the diamine was the nucleophile. The reaction was rather slow, but able to use up the DCDNT precursor. The obtained black solid product partly dissolved in some organic solvents, probably due to the presence of the branched butyl groups along the chains that reduced chain aggregation. Trituration of the CH_2Cl_2 solution of the crude product by an addition of hexane removed most of the smaller oligomers, including the 1:1 mono-S_NAr intermediate **14** present as a byproduct.

From the characterizations of compound **14**, its ^1H NMR spectrum clearly showed the two doublet signals of protons of the unsymmetrical phenylene ring at 6.96 and 6.55 ppm. Moreover, two different sets of signals of butyl groups were present **(Figure A.46, Appendix)** in comparison to only one set of these similar signals from the precursor *N*,*N'*-di-*sec*-butyl-*p*-phenylenediamine. **(Figure A.51, Appendix)** The ^{13}C NMR spectrum also matched well with the expected structure of this product derived from single S_NAr reaction. **(Figure A.47, Appendix)** Finally, the mass spectrum showed two molecular peaks of 427.02 and 429.03 in approximately 3:1 ratio that matched with the calculated molecular weights of the products with two different isotopes of chlorine. **(Figure A.49, Appendix)** IR spectrum **(Figure A.48, Appendix)** showed the expected C-H stretching signals of the butyl groups, N-O stretching signals of the nitro groups, and N-H stretching signal of the secondary amine. The presence of this intermediate confirmed that the S_NAr reaction of the two precursors successfully occurred, and should be able to propagate towards the polymer, albeit at the relatively slow rate.

The ^{1}H NMR spectrum of the polymer **15** corresponded to the expected structure with broadened peaks. **(Figure A.43, Appendix)** Its molecular weight was determined by gel permeation chromatography (GPC), yielding number average molecular weight (M_n) of 1628, with polydispersity index (PDI) of 2.86. The rather small M_n value corresponds to relatively short oligomeric chains with an average of approximately 8 aromatic units. High PDI number indicates that the product is a heterogeneous mixture of wide range of oligomers in various sizes. The rate of growing these oligomeric chains was probably much slower than the rate of initiating new chains, resulting from lower nucleophilicity of the second amino group of the already substituted diamines, and lower electrophilicity of the monochlorothiophene intermediates. The UV-vis absorption of the oligomer **(Figure A.45, Appendix)** measured as solid film exhibited a maximum wavelength absorption (λ_{max}) over 650 nm, **(Table 3.5)** indicating strong π-conjugation within the oligomeric chain. IR spectrum (**Figure A.44, Appendix**) of the oligomer showed the strong broad signals of C-H stretching of butyl groups, and N-O stretching signals of nitro groups at 1515 and 1308 cm^{-1}.

From **Table 3.5**, the reflux condition of entry 2 significantly decreased the reaction time compared to room temperature as in entry 1. However, the high temperature condition gave much lower product yield while the maximum wavelength absorptions (λ_{max}) of the products from both entries were not much different.

3.2.3.5 With N^1,N^4-dioctylbenzene-1,4-diamine (2)



DCDNT **2** **16**

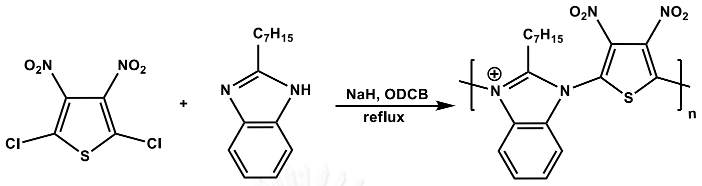
17

To further increase the nucleophilicity of the intermediates and polymer, compound **2** was used as the nucleophile to make polymer **17** from reaction with DCDNT. The polymer was obtained in the presence of the 1:1 intermediate **16** obtained as dark yellow liquid in 14.4% yield. The ^{1}H NMR spectrum of compound **16** clearly showed the two doublet signals of protons of the unsymmetrical phenylene diamine ring at 7.01 and 6.58 ppm. There were also two sets of octyl group signals. **(Figure A.55, Appendix)** ^{13}C NMR spectrum also matched well with the expected structure. **(Figure A.56, Appendix)** In IR spectrum, there were signals at 3388 cm^{-1} (N-H st), 2924 cm^{-1} (C-H st), and 1544, 1381 cm^{-1} (N-O st). **(Figure A.57, Appendix)** The occurrence of compound **16** confirmed that the S$_N$Ar reaction of DCDNT and compound **2** was successful although the reaction rate was quite.

Polymer **17** was a brown liquid which could be only slightly dissolved in some organic solvents. The IR spectrum of polymer **17** was similar to compound **16** showing signals of N-H stretching (3372 cm^{-1}), C-H stretching of octyl groups (2918 cm^{-1}), and N-O stretching of nitro groups (1510, 1331 cm^{-1}). (**Figure A.53, Appendix**)

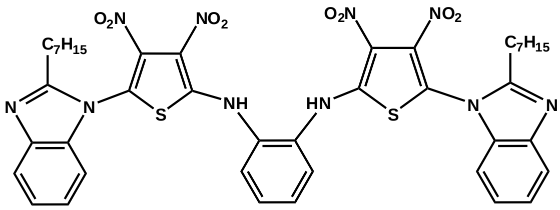
The UV-Vis absorption spectrum of polymer **17** could not show maximum wavelength absorption (λ_{max}), indicating the conjugated polymer was grown in short chain.

3.2.3.6 With 2-heptylbenzimidazole (4)



DCDNT **4** **18**

DCDNT was polymerized with imidazole compound **4** as the nucleophile to obtain black solid which could not be soluble in common organic solvents. In IR spectrum, it showed C-H stretching signal of the heptyl groups at 2936 cm^{-1}, and N-O stretching signals of the nitro groups at 1525, 1328 cm^{-1}. (**Figure A.60, Appendix**) The UV-Vis absorption spectrum (**Figure A.61, Appendix**) of the solid showed a maximum wavelength absorption (λ_{max}) at 681 nm, indicating the presence of long conjugated polymer chains. Although these data still were insufficient to confirm the structure of polymer **18**. However, some parts of the product mixture could be dissolved in chloroform in the presence of a few drops of trifluoroacetic acid. Hence, the soluble part was characterized by ^{1}H NMR and ^{13}C NMR. There were four multiplet peaks of aromatic protons and a set of heptyl signals appeared in ^{1}H NMR spectrum. (**Figure A.62, Appendix**) In ^{13}C NMR spectrum, some assumably quaternary carbon signals were still absent, probably due to the relatively poor solubility of the solid. (**Figure A.63, Appendix**) Based on these available information, the acid-soluble compound might be deduced to be compound **19** as one of the possibility, consisting of two units from DCDNT alternated with three units from compound **4**. The imidazole ring of the center unit of compound **19** was perhaps more efficiently hydrolyzed to octanoic acid and free diamine unit as shown during the quenching step. The small quantity and low solubility of this compound prevented it to be further characterized. Therefore, the structure of this intermediate is yet to be confirmed.



19

CHAPTER IV

CONCLUSION

Designs and synthesis of new conjugated polymers via nucleophilic aromatic substitution (S_NAr) polymerization had been accomplished. 2,5-dichloro-3,4-dinitrothiophene (DCDNT) as used as the main electron-poor acceptor monomer to be, alternately incorporated with a variety of electron-rich nucleophilic units. The DCDNT was prepared from dinitration of 2,5-dichlorothiophene with fuming HNO_3 in 78% yield. Some of the nucleophiles were made to be subsequently react with DCDCT. For carbon nucleophile, 1-*n*-octyl-*1H*-pyrrole **(1)** was synthesized via direct nucleophilic substitution reaction in 74.9% yield. The nitrogen nucleophiles N^1,N^4-dioctylbenzene-1,4-diamine **(2)** and 2-heptylbenzimidazole **(4)** were also synthesized. Compound **2** was successfully obtained in 54% yield through condensation of *p*-phenylenediamine and octanoyl chloride followed by reduction reaction. Reaction of *o*-phenylenediamine and octanoyl chloride provided compound **4** in 33% yield with 57.8% of the diamide compound **5** as the major product.

The rather slow reaction of DCDNT with EDOT gave the short-chain oligomers polymer **7** which was insoluble in common organic solvents. With DMT nucleophile in acidic condition, the possibly removed methyl groups by the Lewis acid increased its nucleophilicity and reacted more efficiently on DCDNT to yield the polymer **8**, which exhibited a maximum wavelength absorption (λ_{max}) at 541 nm.

The reaction of DCDNT with sodium sulfide as the nucleophile yielded polymer **9**, which could not be dissolved in any common organic solvents. Polymer **9** showed a maximum wavelength absorption (λ_{max}) at 542 nm.

For nitrogen nucleophiles: The reaction with *n*-butylamine only gave the double S_NAr intermediate **10** in 75.1% yield. The strong electron withdrawing nitro groups decreased the reactivity of the nitrogen atoms of **10**. The reaction with hydrazine obtained polymer **12** in 38% yield with λ_{max} at 634 nm, while the reaction with *p*-phenylenediamine obtained polymer **13** in 70% yield with λ_{max} 542 nm. Both polymers were insoluble in common organic solvents. *N*,*N'*-di-*sec*-butyl-*p*-phenylenediamine could be successfully used to react with DCDNT to yield the polymer **14** in 78.6% yield with λ_{max} at 668 nm. Similarly, reaction with compound **2** gave the relatively short-chain polymer **17** in 2.6% yield.

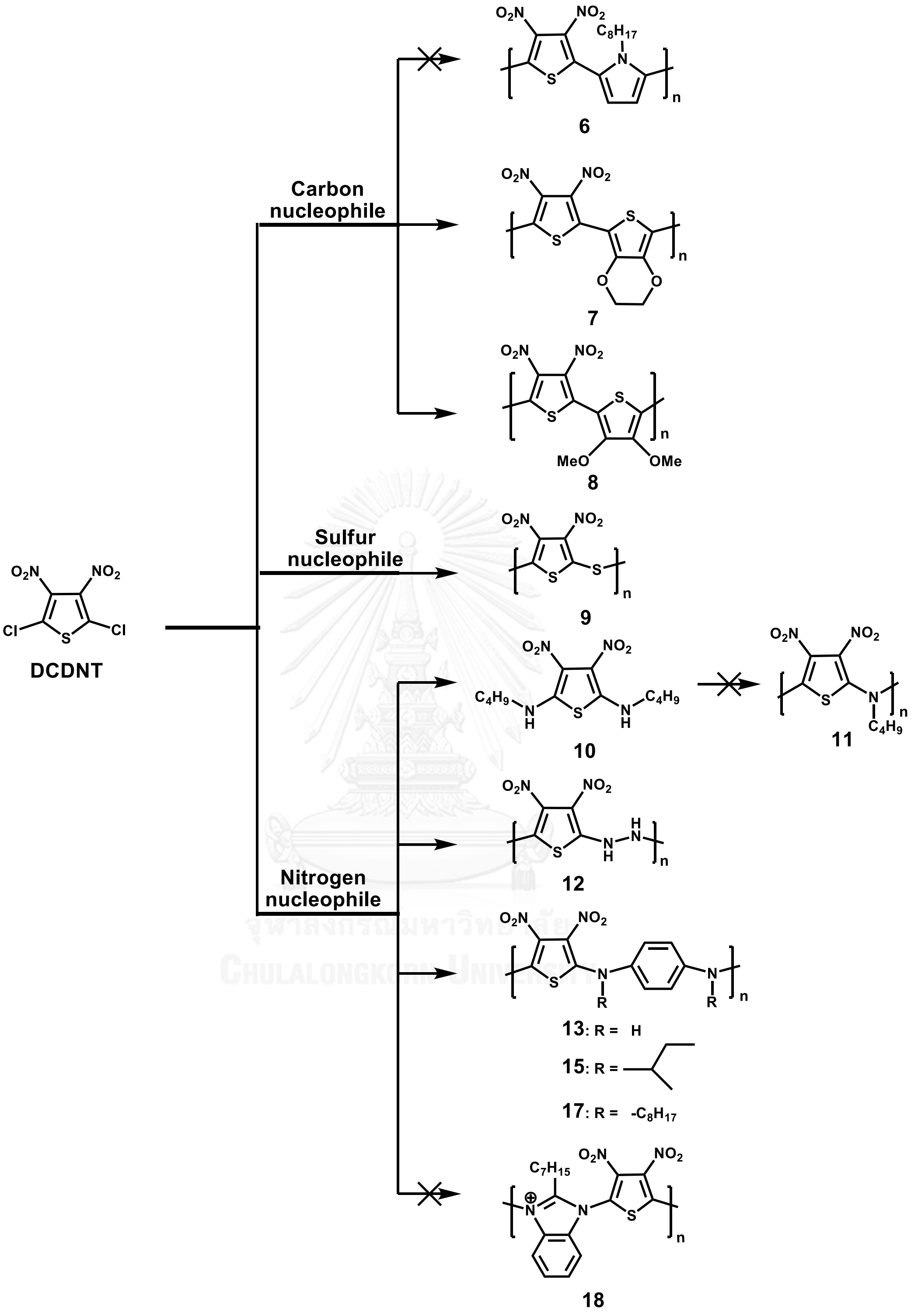


Figure 4.1 Complete synthetic scheme

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APPENDIX

APPENDIX

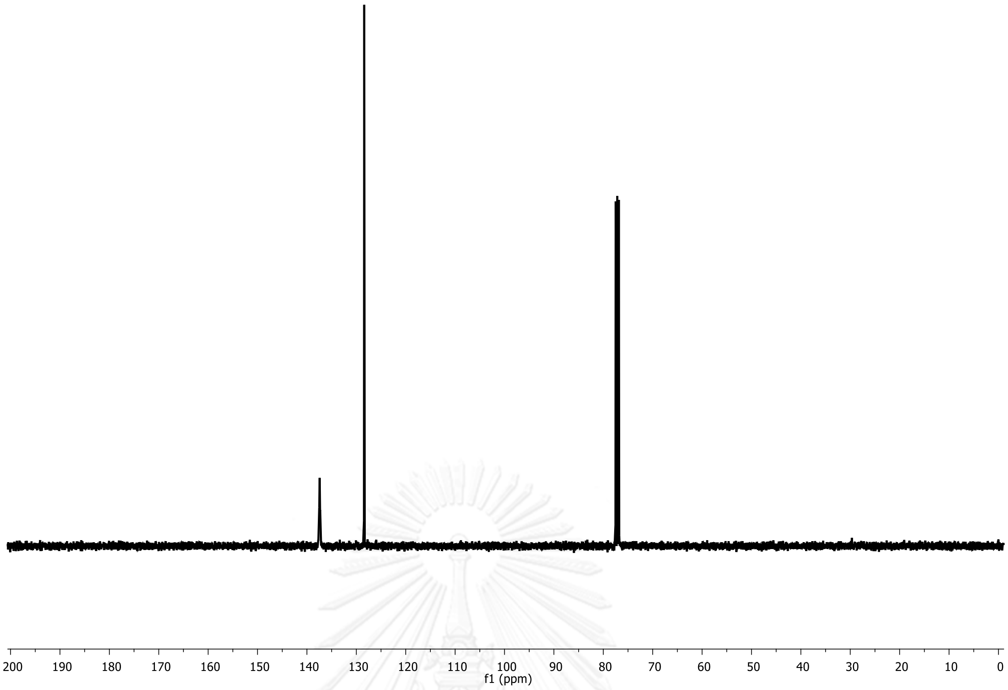

Figure A.1 ^{13}C NMR ($CDCl_3$) spectrum of DCDNT

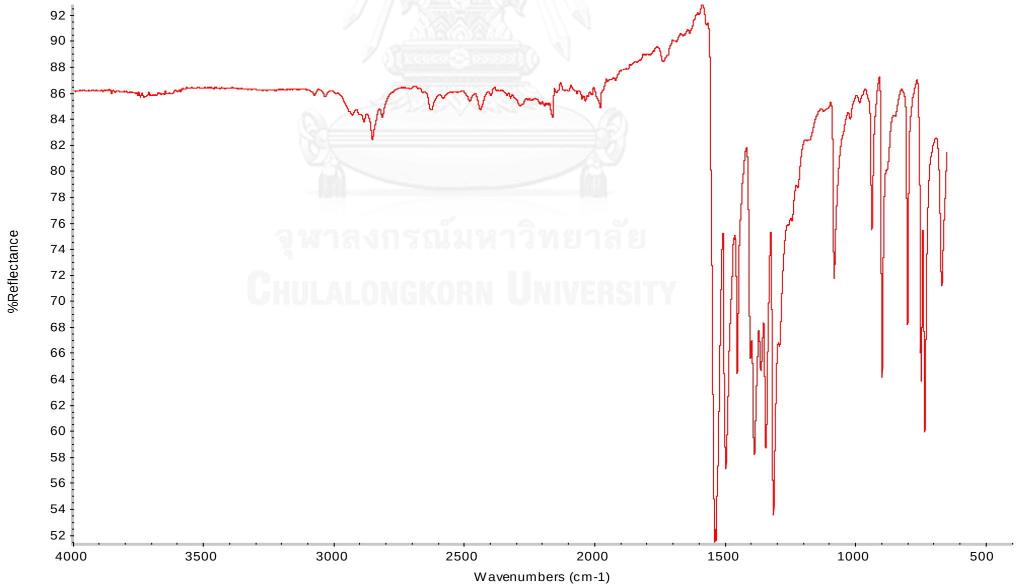

Figure A.2 IR spectrum of DCDNT

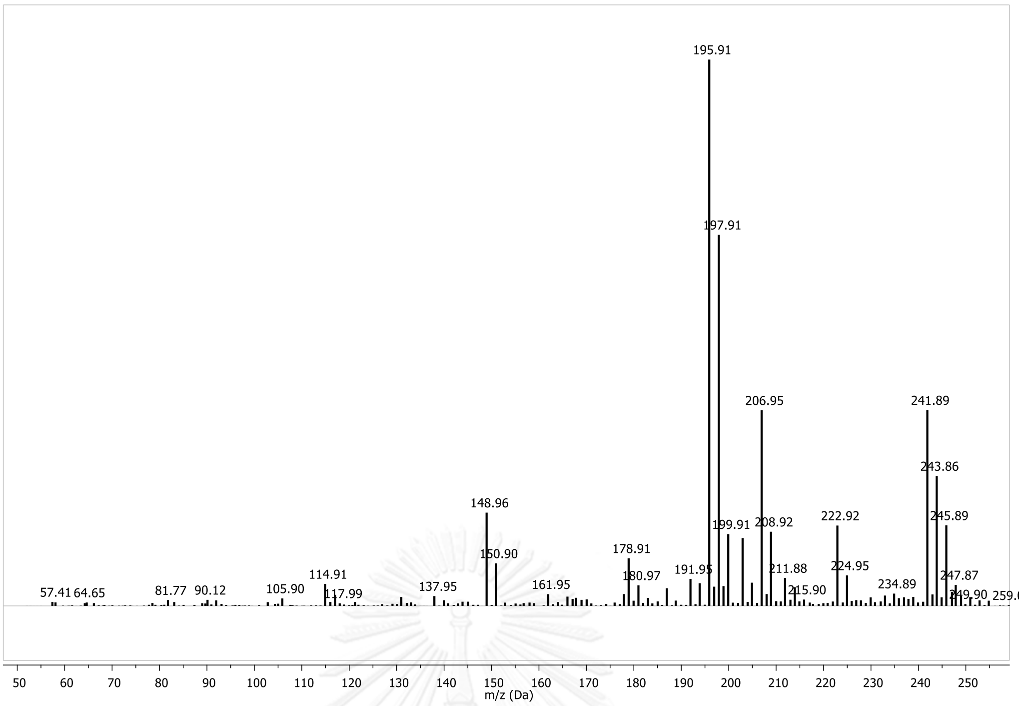

Figure A.3 Mass spectrum of DCDNT

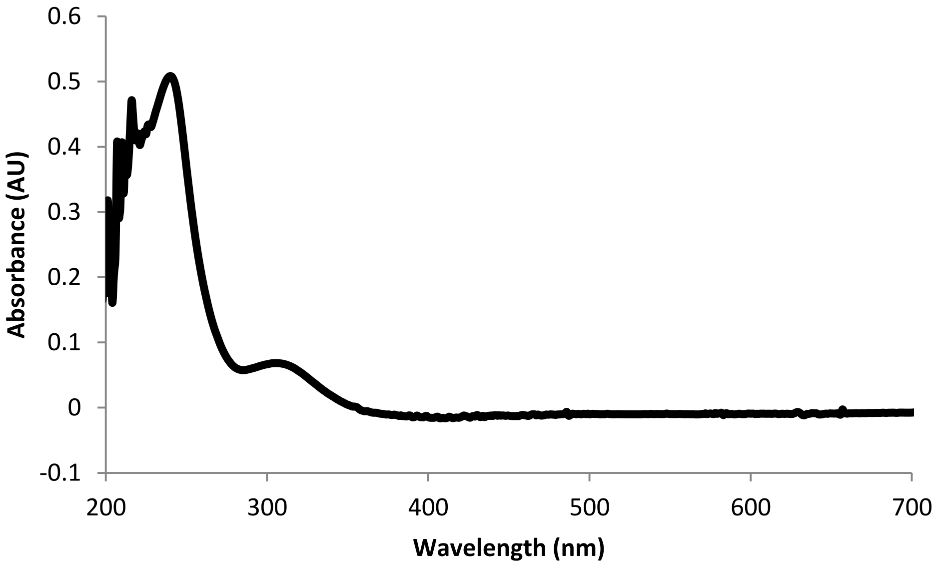

Figure A.4 Solution UV-Vis absorption spectrum of DCDNT

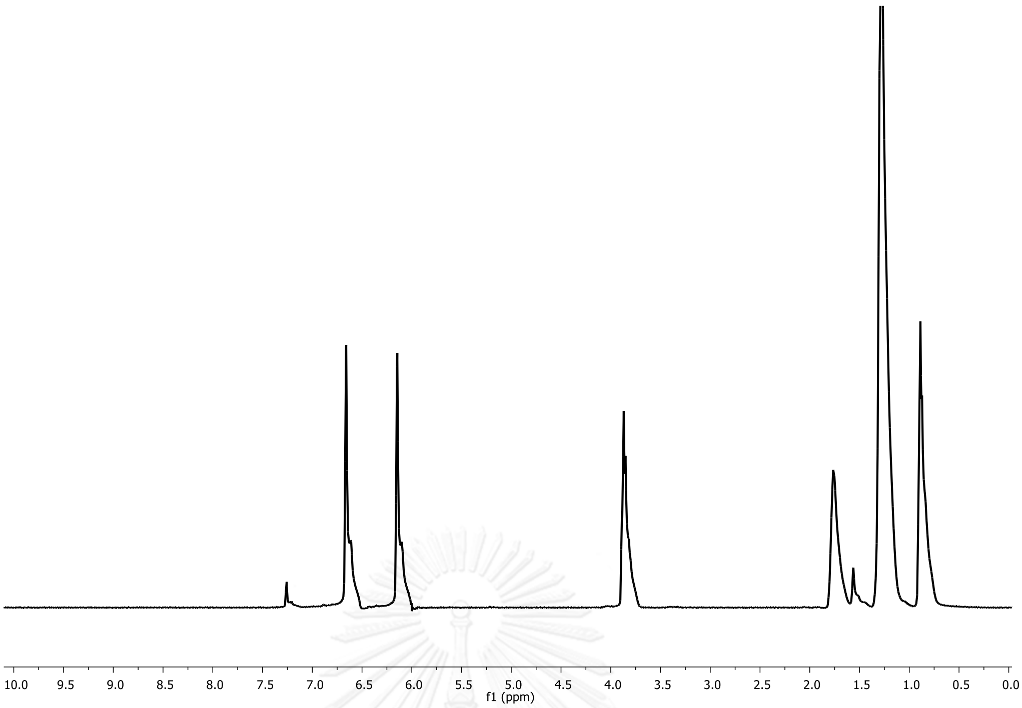

Figure A.5 ^{1}H NMR ($CDCl_3$) spectrum of compound **1**

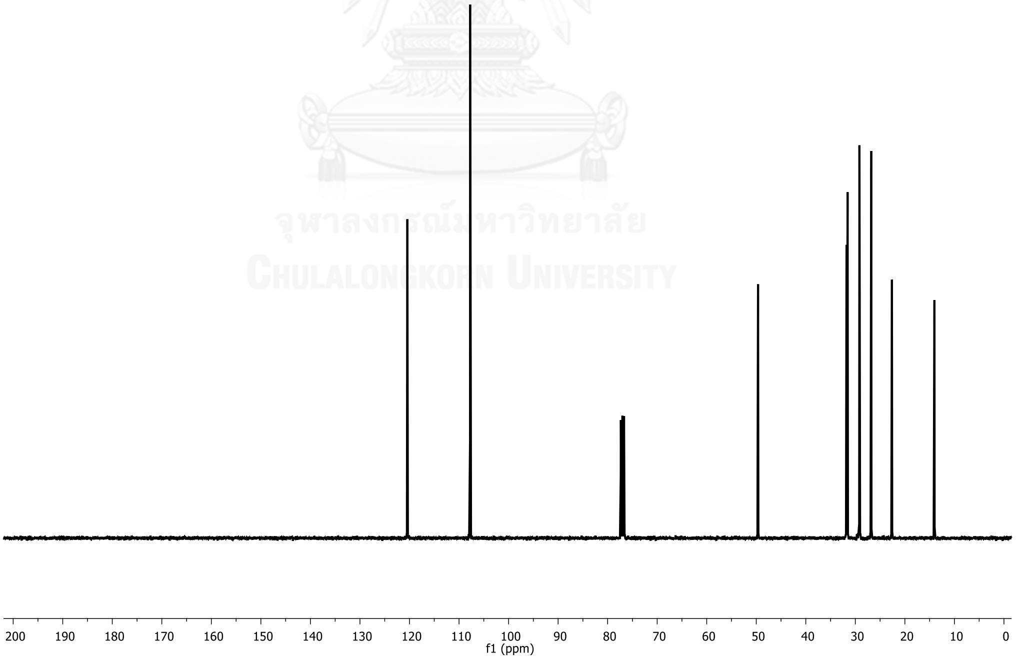

Figure A.6 ^{13}C NMR ($CDCl_3$) spectrum of compound **1**

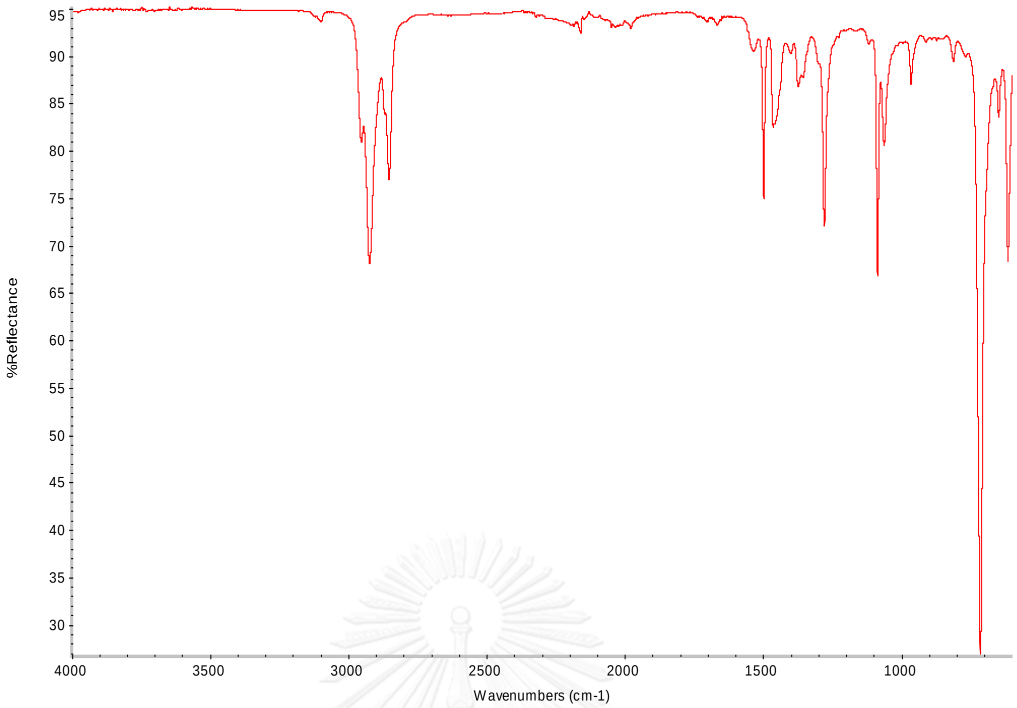

Figure A.7 IR spectrum of compound **1**

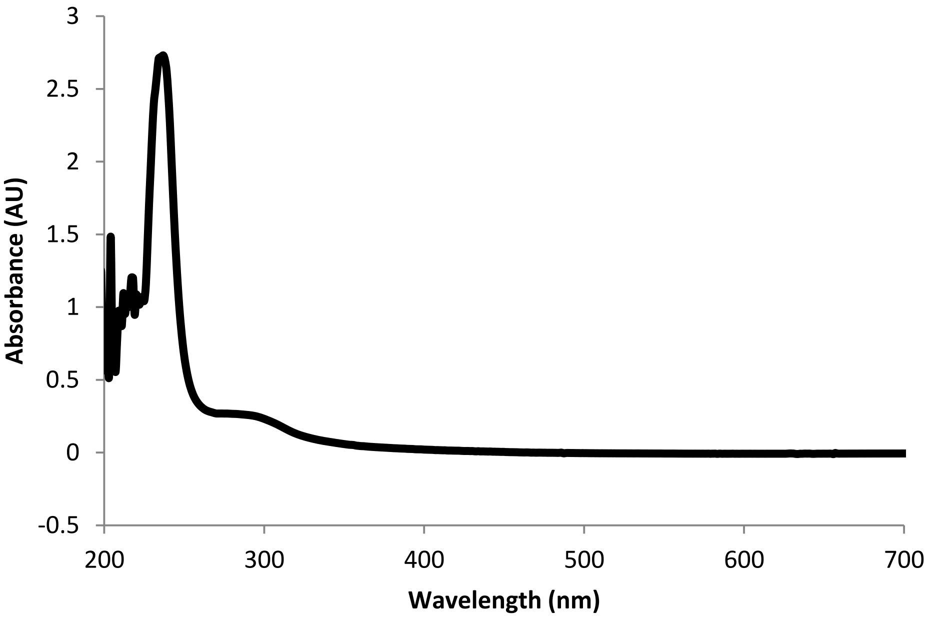

Figure A.8 Solution UV-Vis absorption spectrum of compound **1**

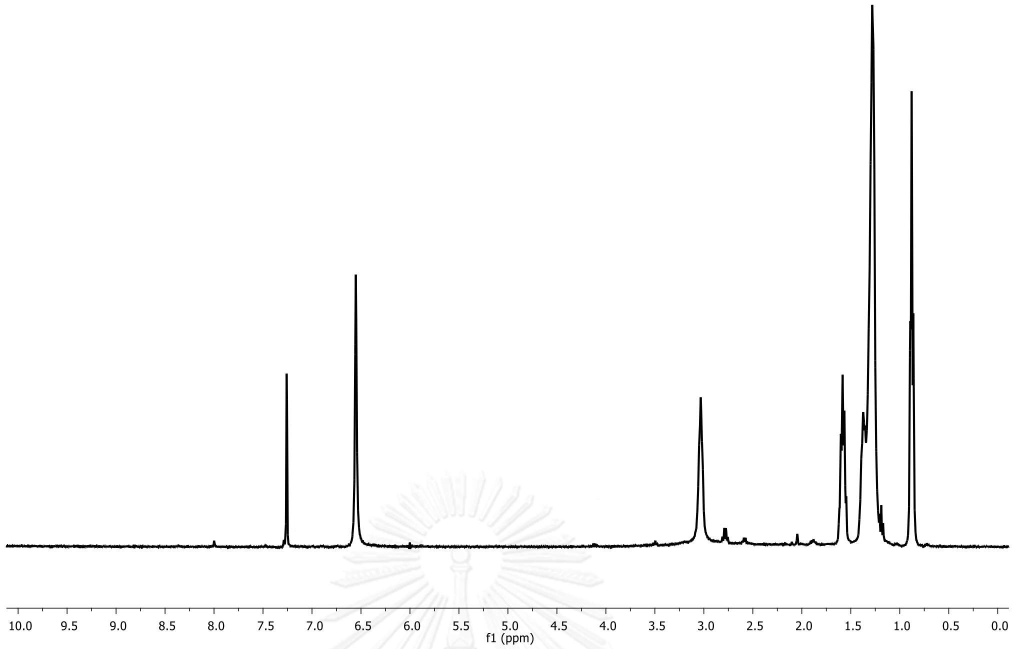

Figure A.9 ^{1}H NMR ($CDCl_3$) spectrum of compound **2**

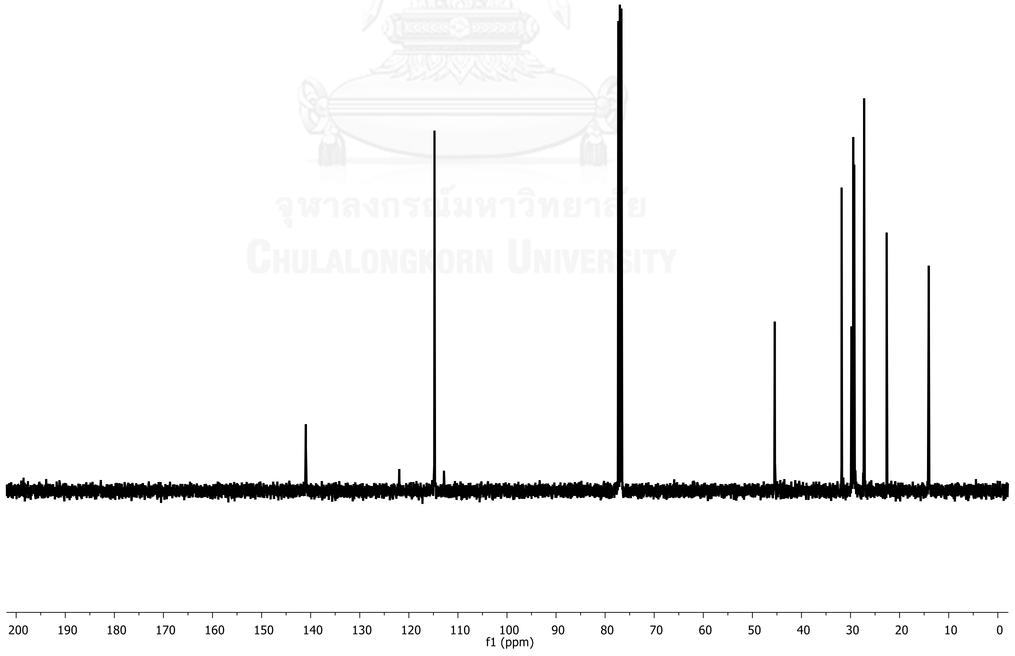

Figure A.10 ^{13}C NMR ($CDCl_3$) spectrum of compound **2**

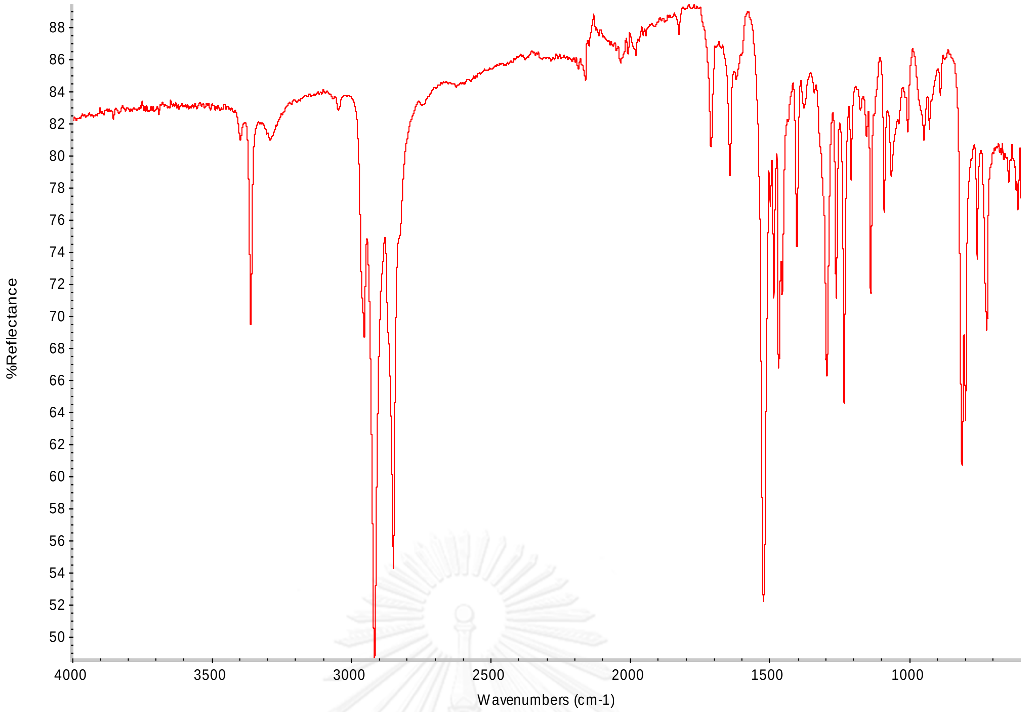

Figure A.11 IR spectrum of compound **2**

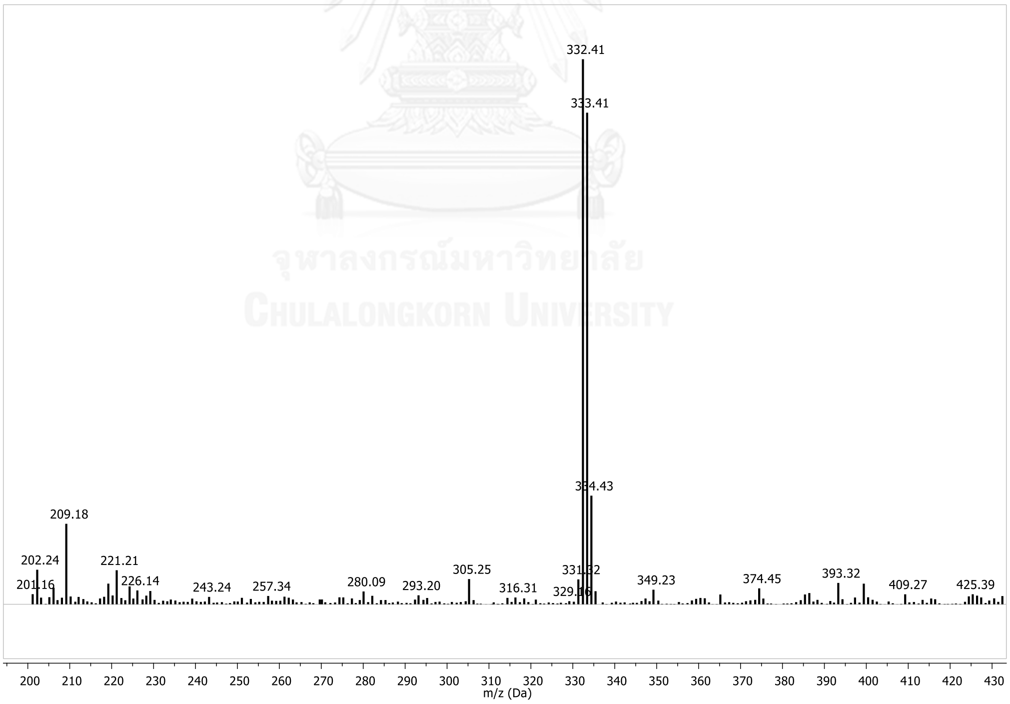

Figure A.12 Mass spectrum of compound **2**

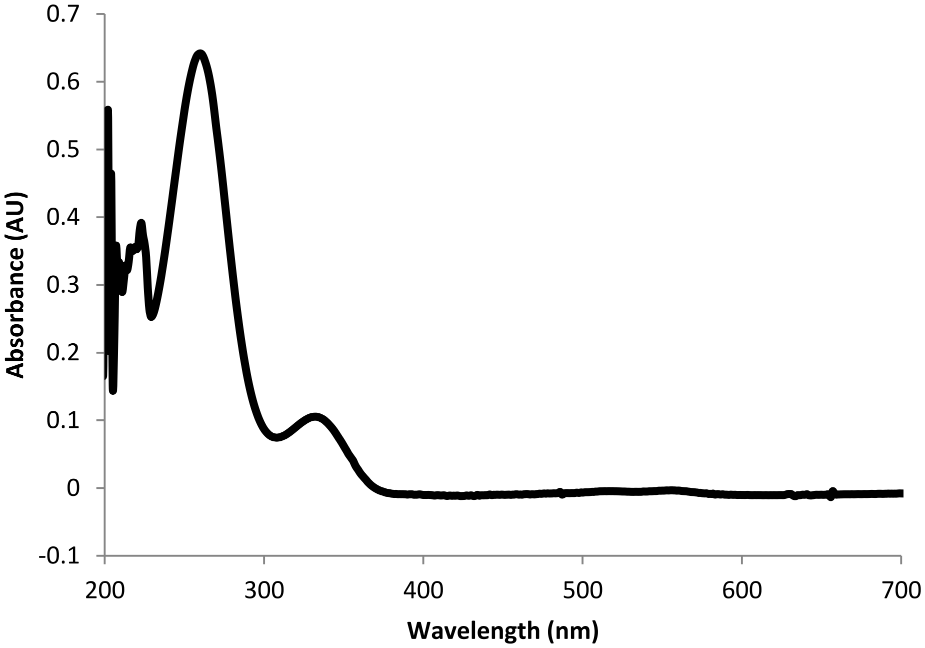

Figure A.13 Solution UV-Vis absorption spectrum of compound **3**

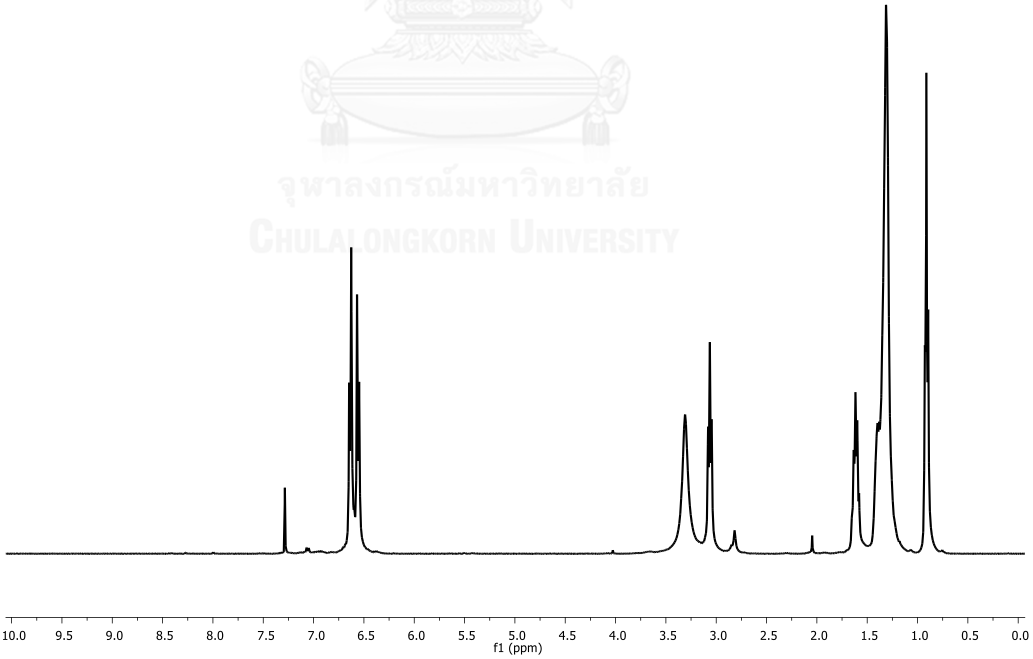

Figure A.14 ^{1}H NMR ($CDCl_3$) spectrum of compound **3**

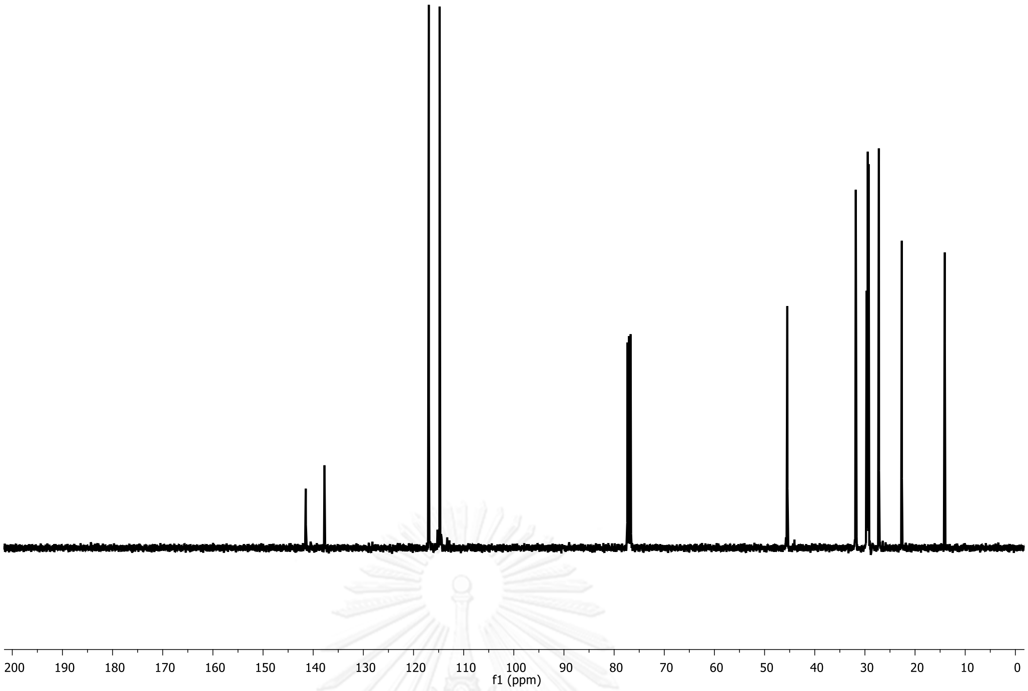

Figure A.15 ^{13}C NMR ($CDCl_3$) spectrum of compound **3**

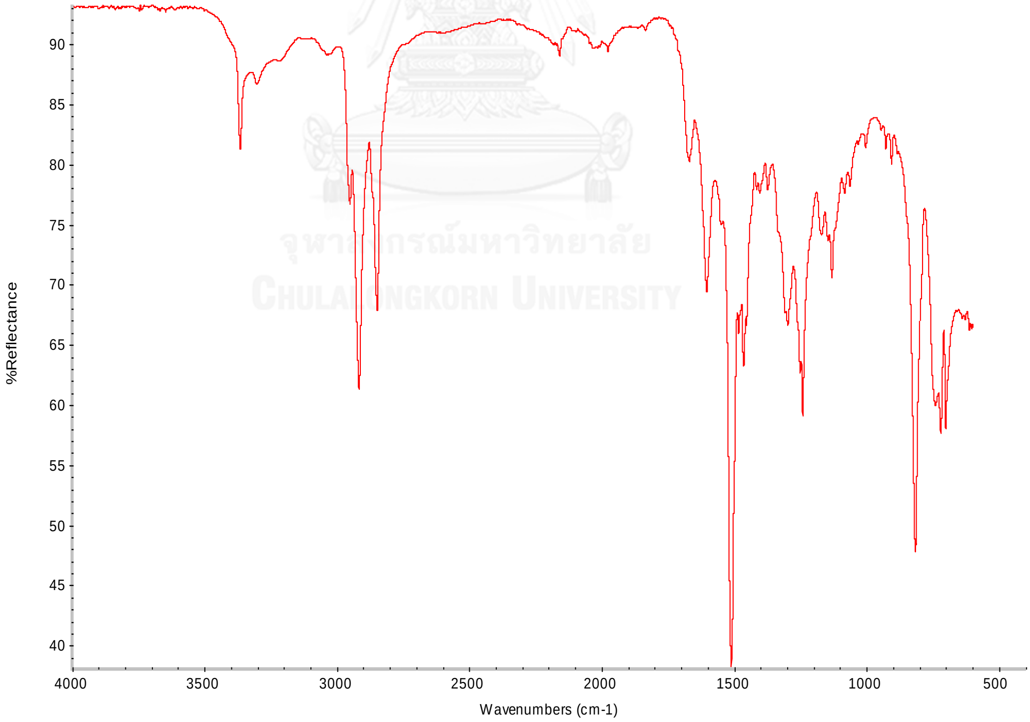

Figure A.16 IR spectrum of compound **3**

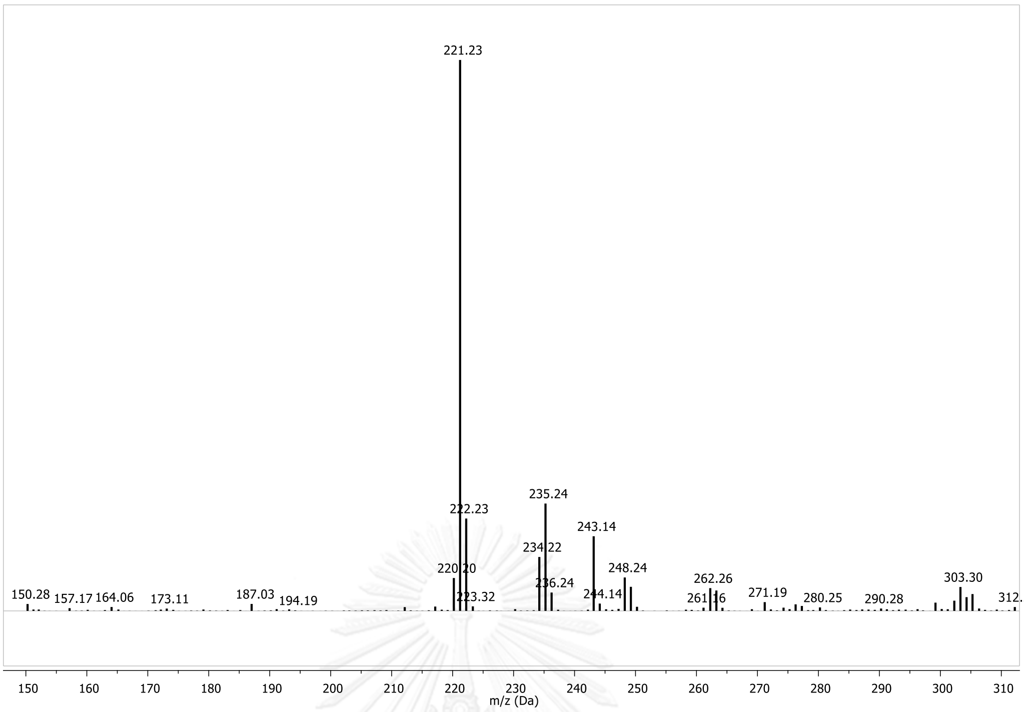

Figure A.17 Mass spectrum of compound **3**

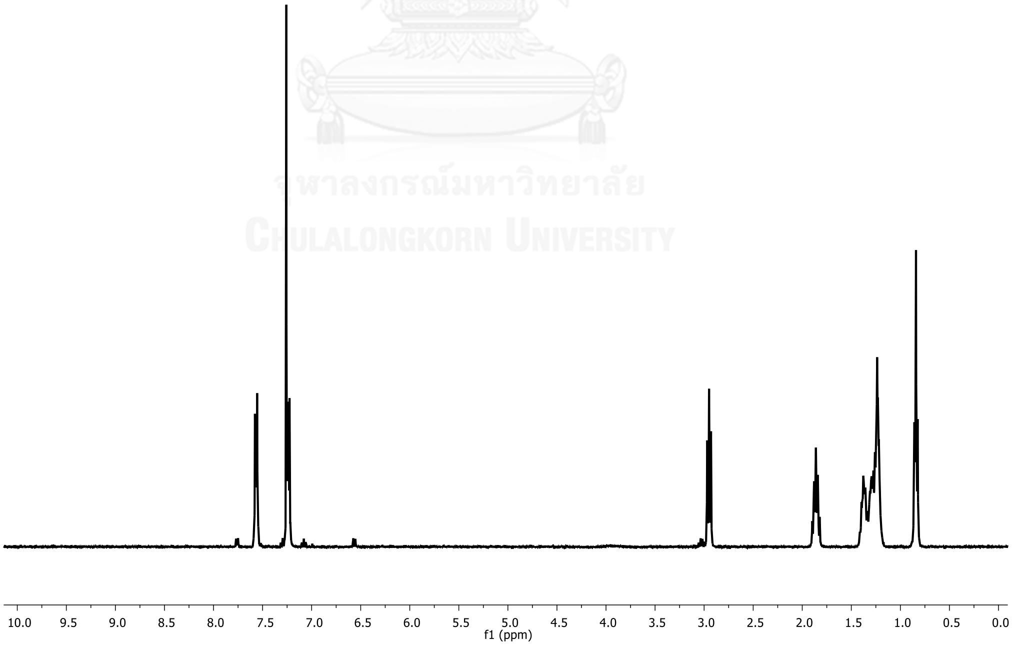

Figure A.18 ^{1}H NMR (CDCl$_3$) spectrum of compound **4**

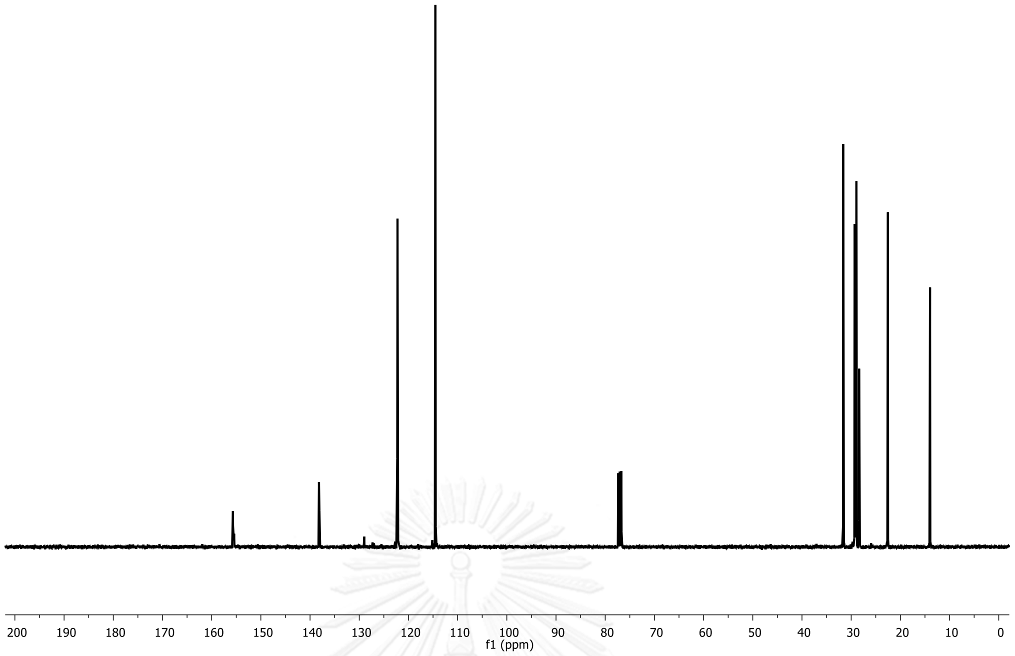

Figure A.19 ^{13}C NMR ($CDCl_3$) spectrum of compound **4**

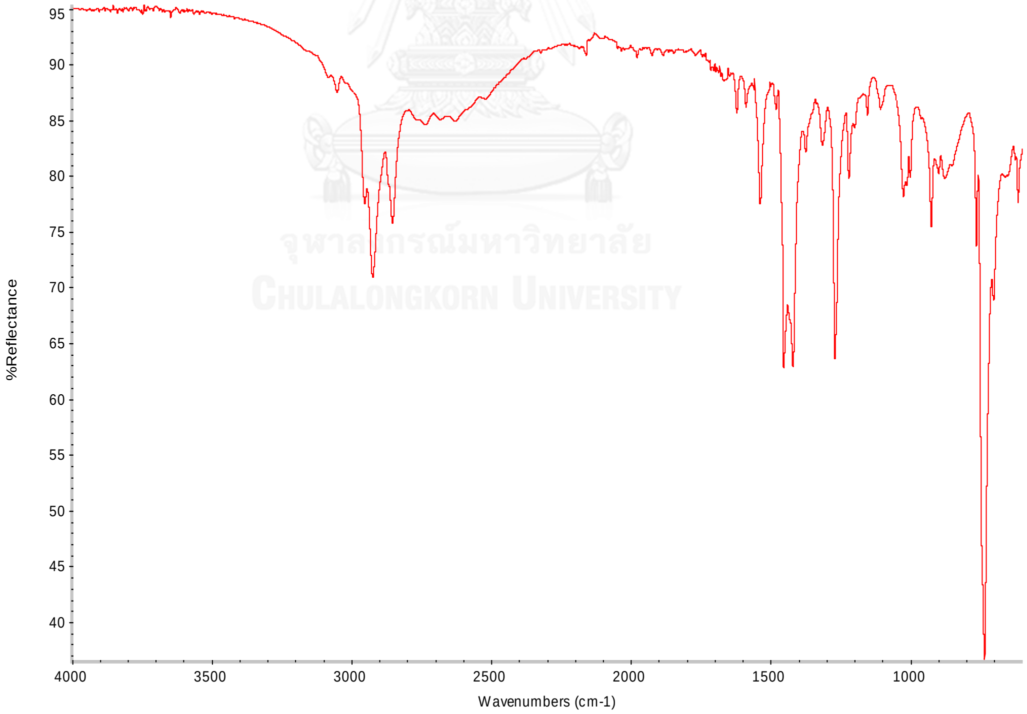

Figure A.20 IR spectrum of compound **4**

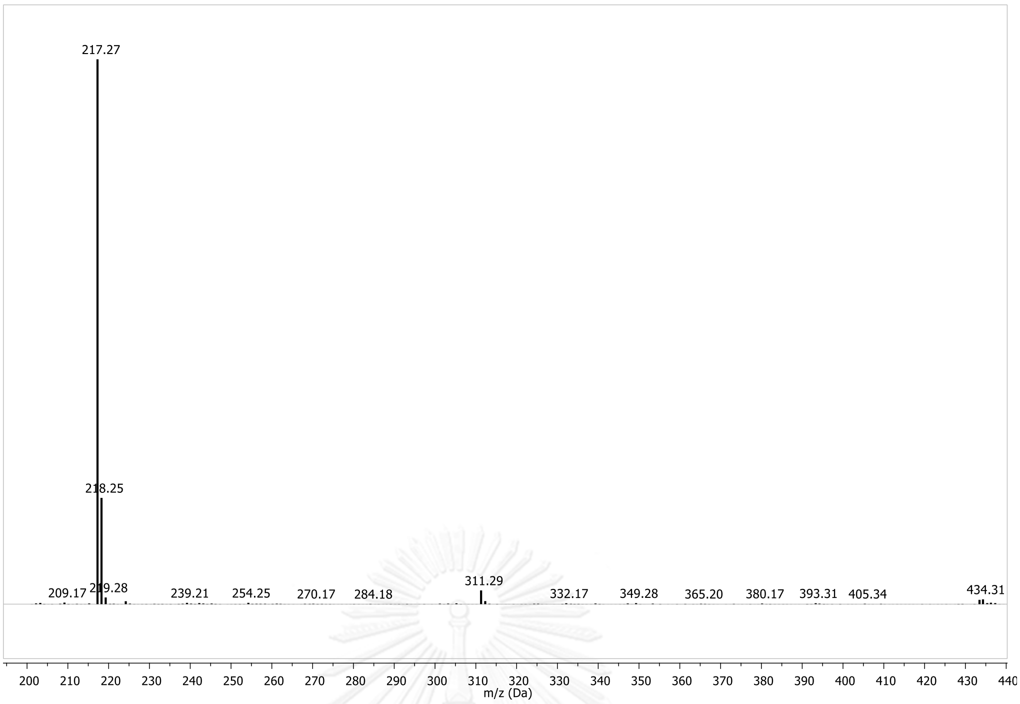

Figure A.21 Mass spectrum of compound **4**

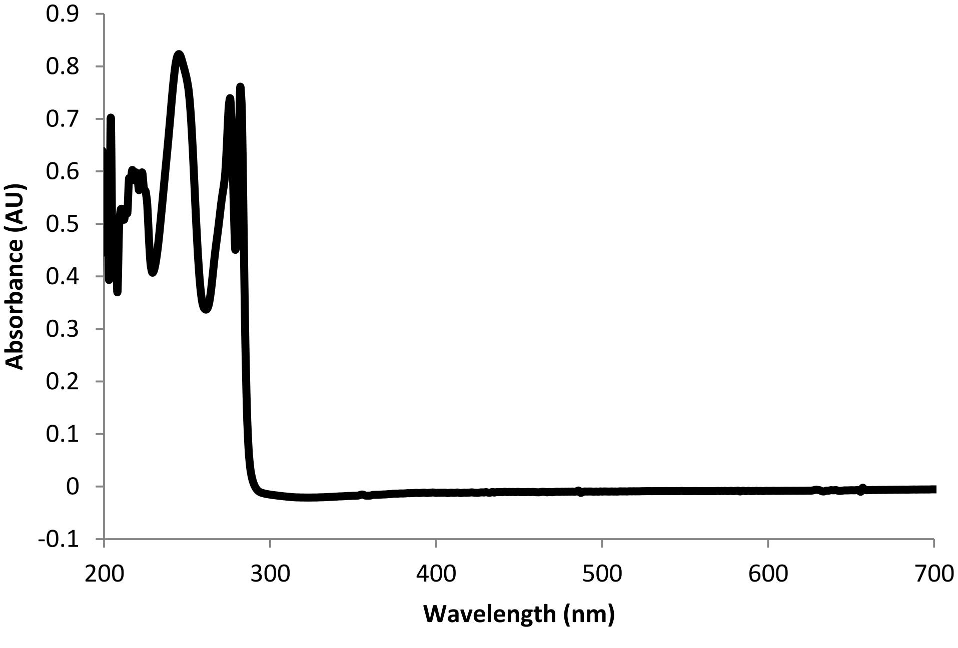

Figure A.22 Solution UV-Vis absorption spectrum of compound **4**

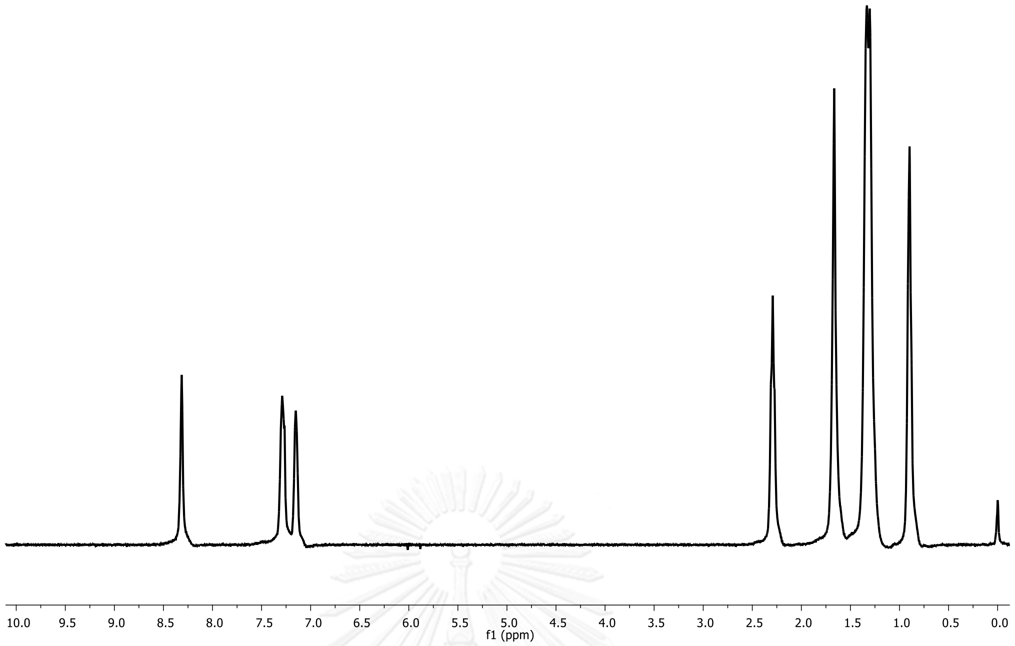

Figure A.23 ^{1}H NMR ($CDCl_3$) spectrum of compound **5**

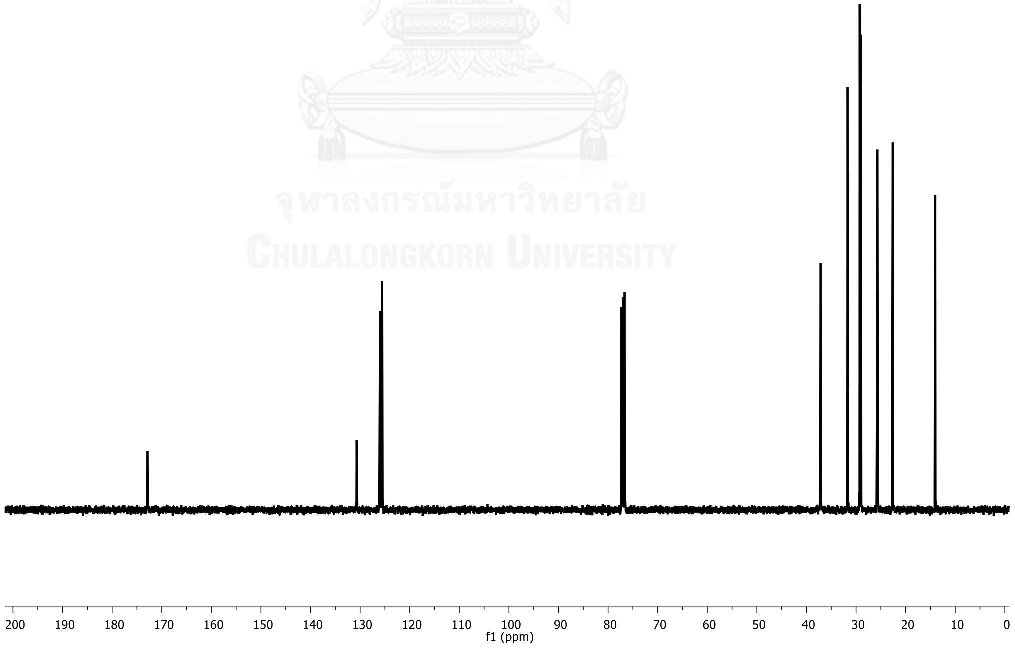

Figure A.24 ^{13}C NMR ($CDCl_3$) spectrum of compound **5**

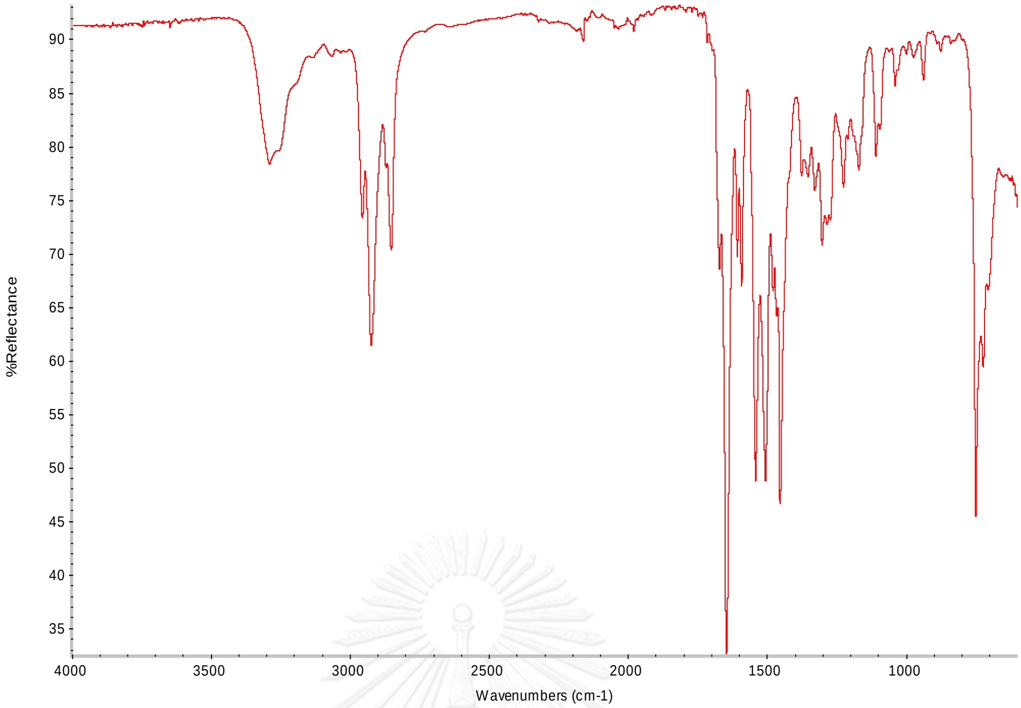

Figure A.25 IR spectrum of compound **5**

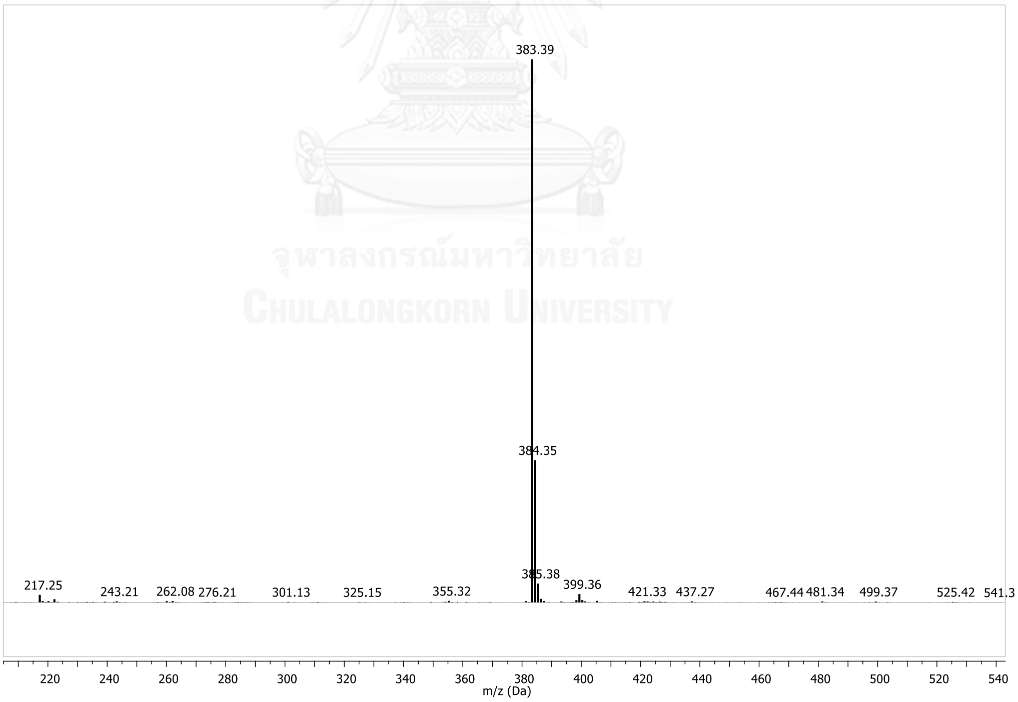

Figure A.26 Mass spectrum of compound **5**

Figure A.27 IR spectrum of polymer **6**

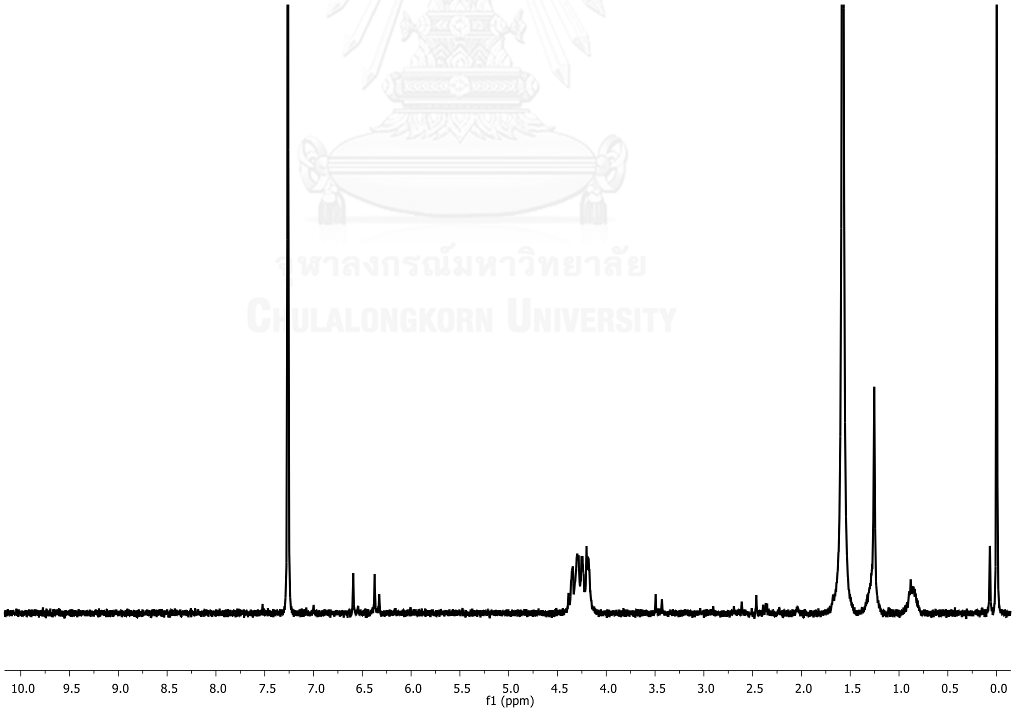

Figure A.28 ^{1}H NMR (CDCl$_3$) spectrum of polymer **7**

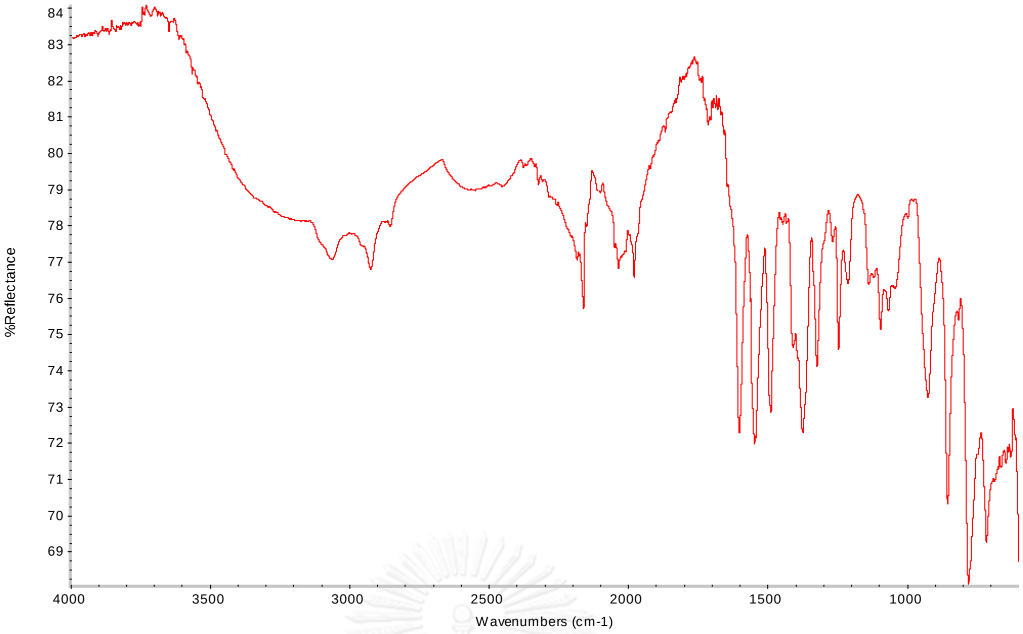

Figure A.29 IR spectrum of polymer **7**

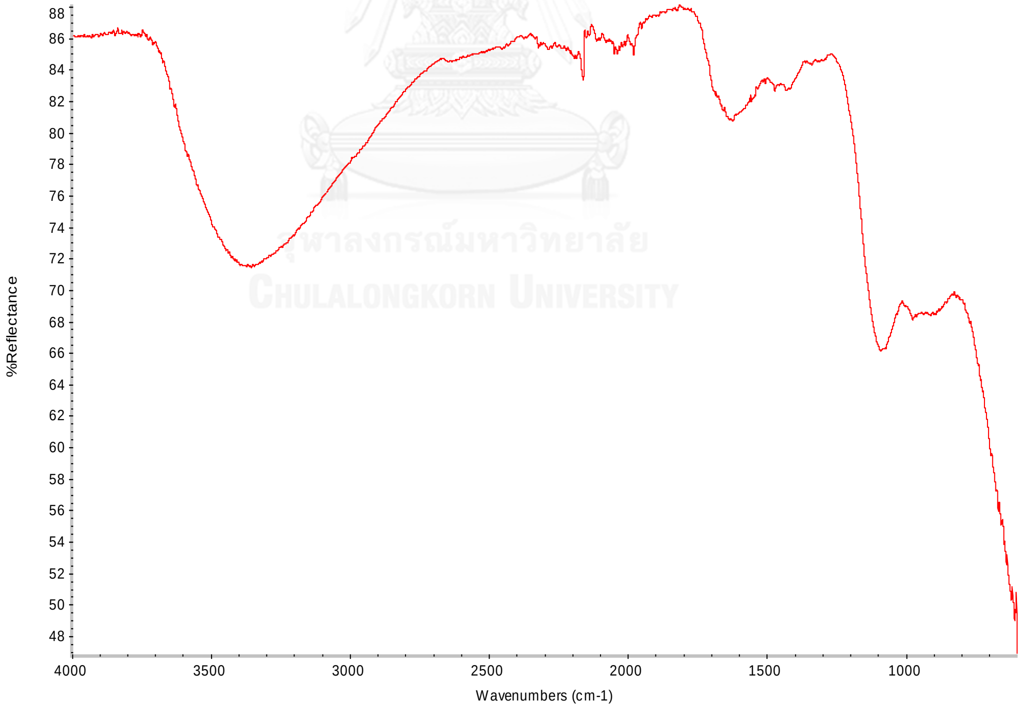

Figure A.30 IR spectrum of polymer **8**

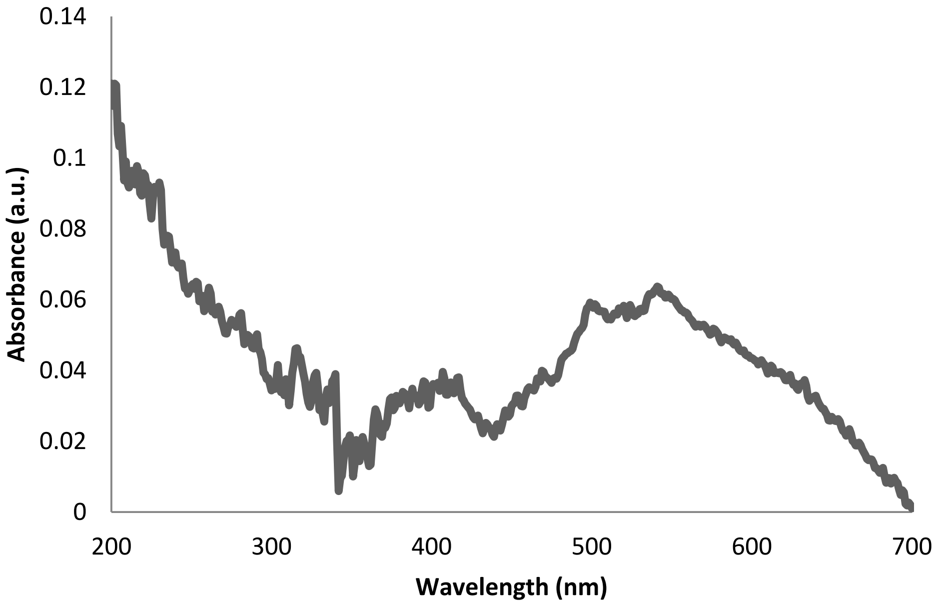

Figure A.31 Solid UV-Vis absorption spectrum of polymer **8**

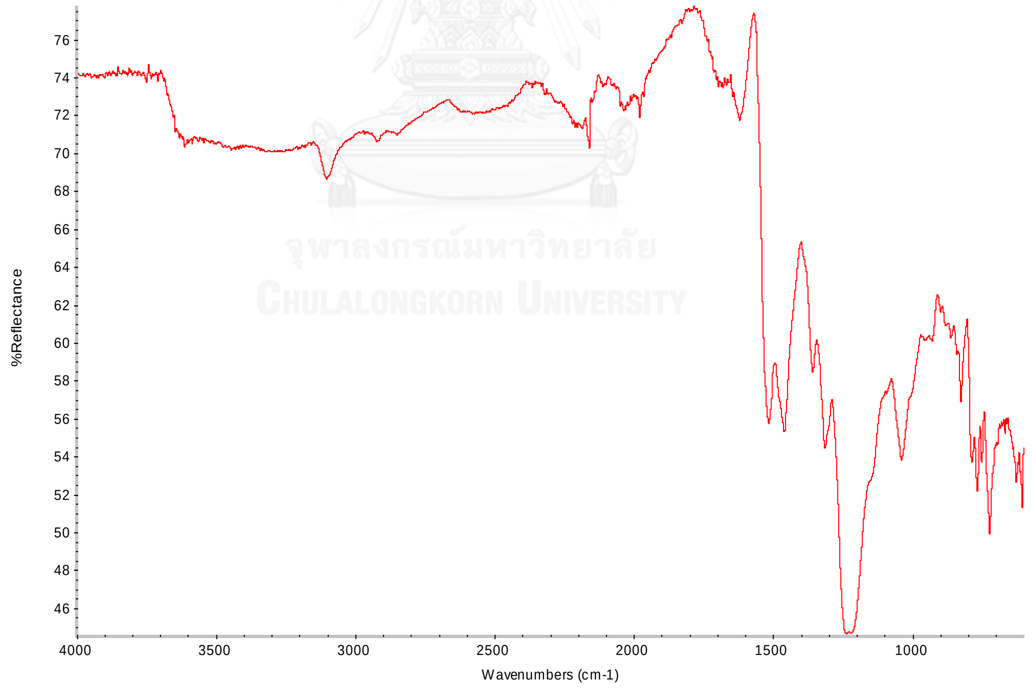

Figure A.32 IR spectrum of polymer **9**

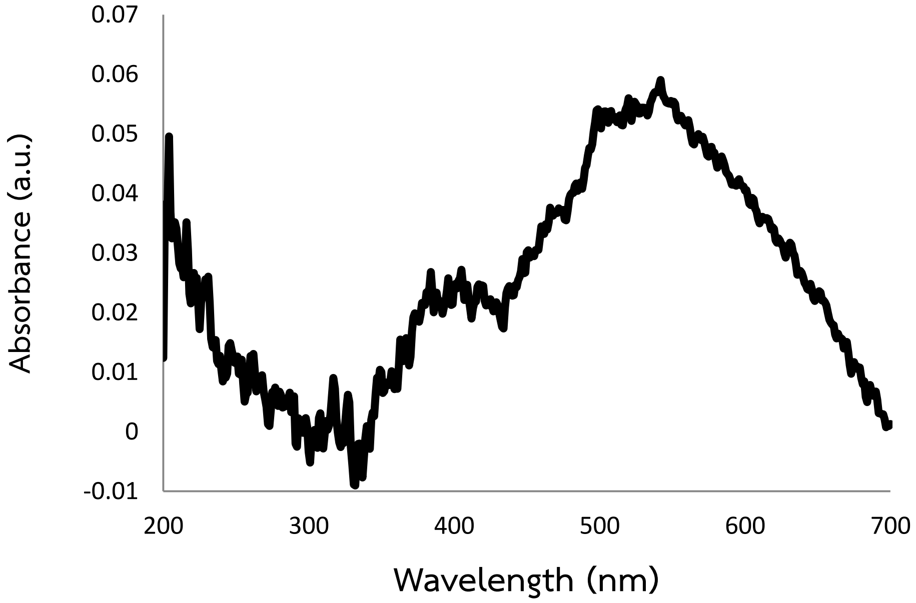

Figure A.33 Solid UV-Vis absorption spectrum of polymer **9**

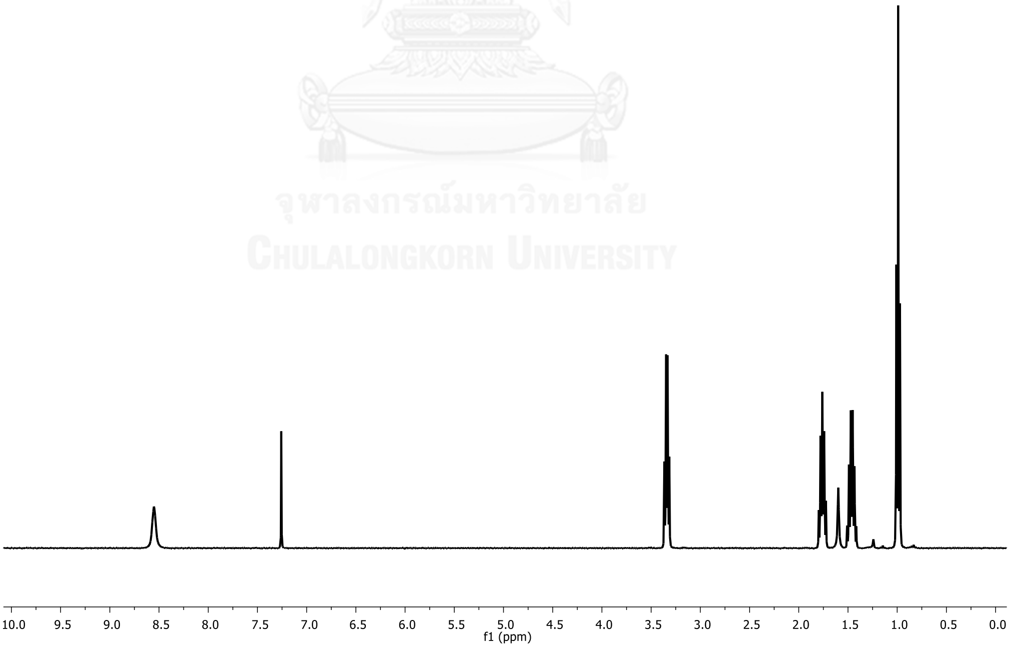

Figure A.34 ^{1}H NMR ($CDCl_3$) spectrum of compound **10**

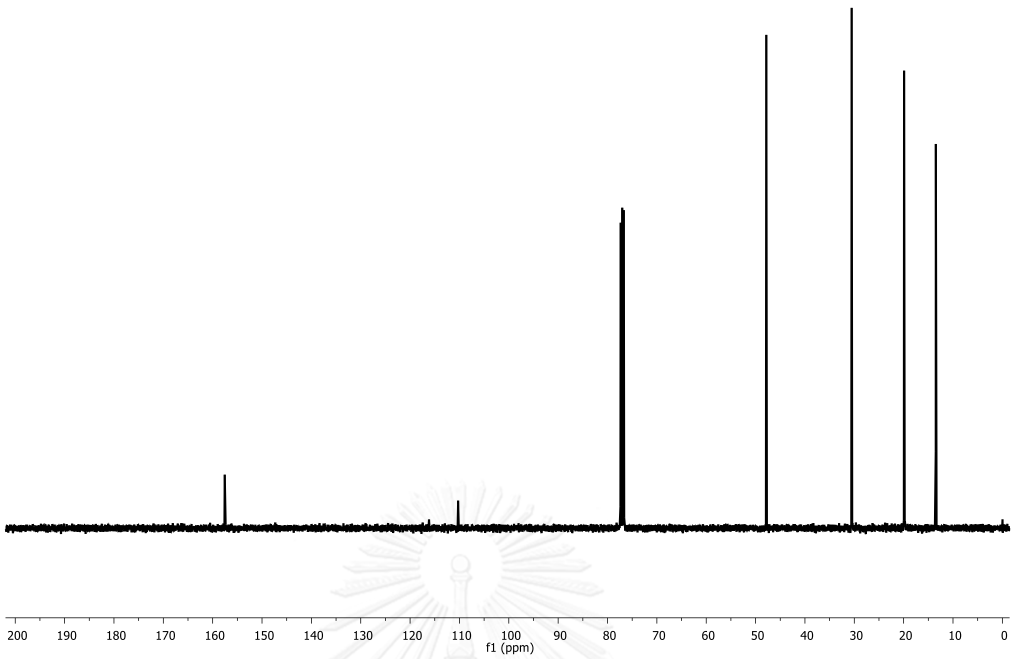

Figure A.35 ^{13}C NMR ($CDCl_3$) spectrum of compound **10**

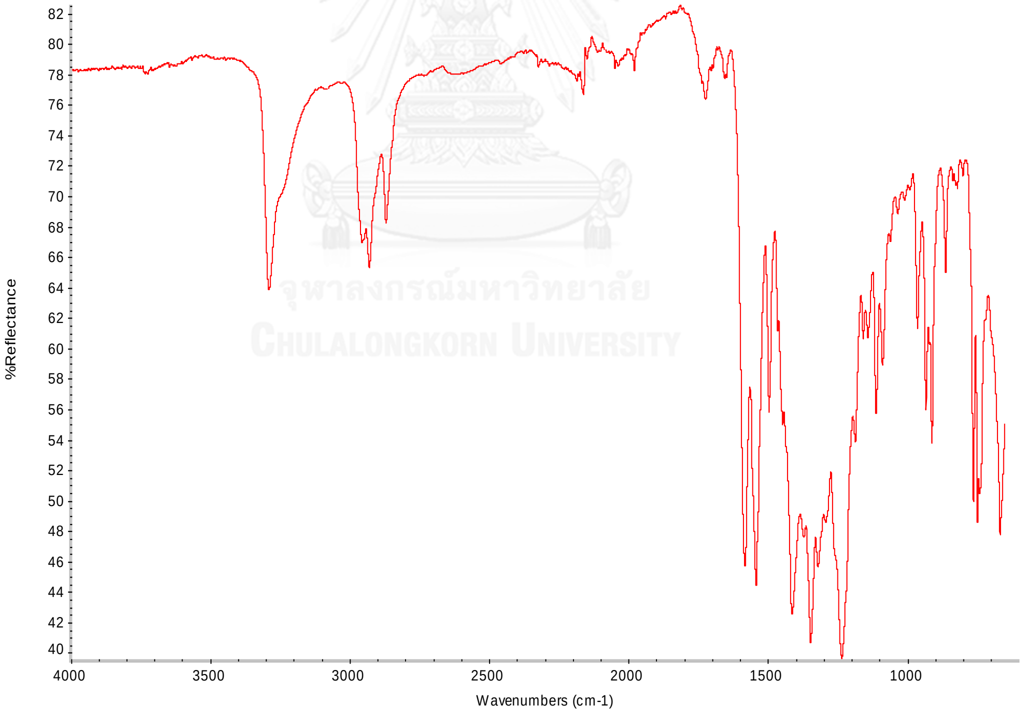

Figure A.36 IR spectrum of compound **10**

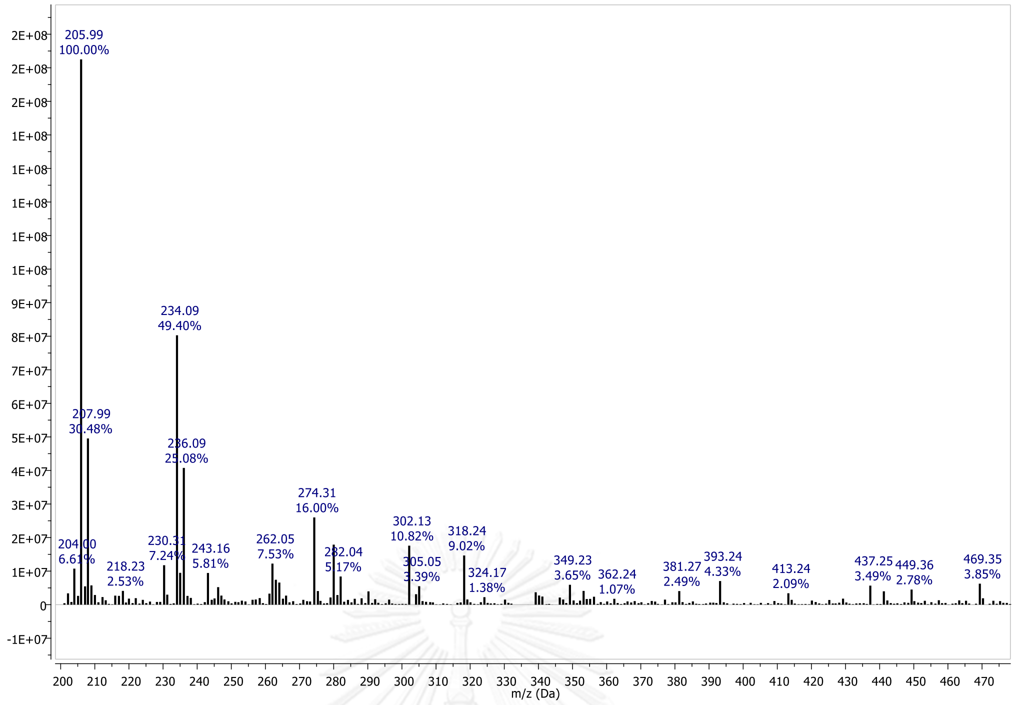

Figure A.37 Mass spectrum of compound **10**

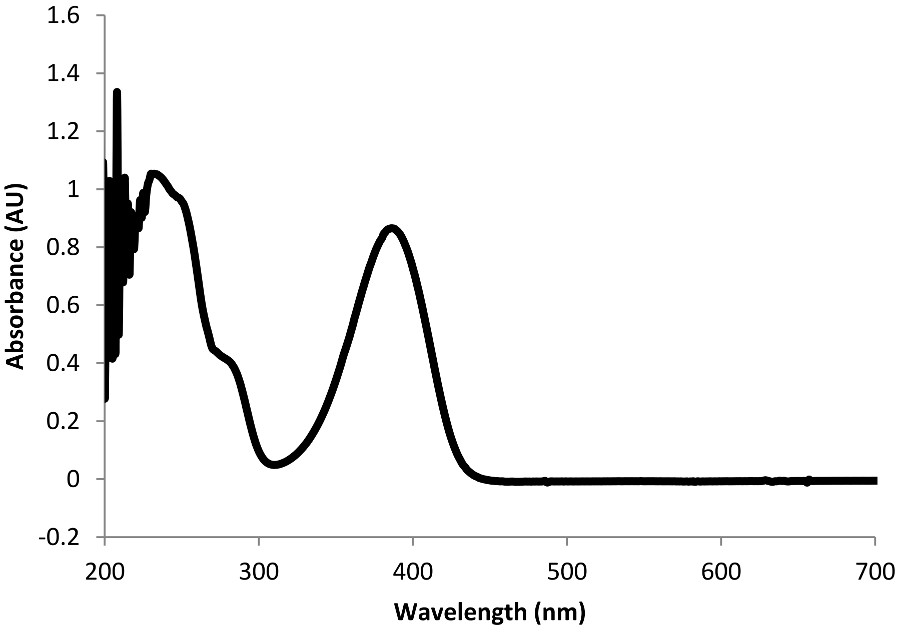

Figure A.38 Solution UV-Vis absorption spectrum of compound **10**

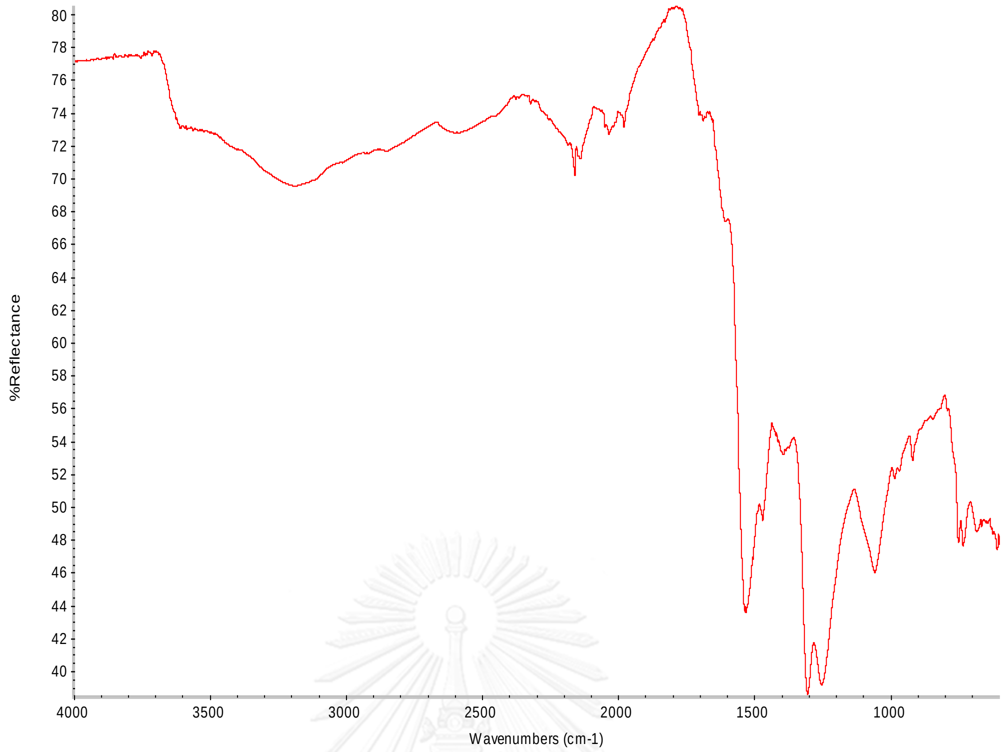

Figure A.39 IR spectrum of polymer **12**

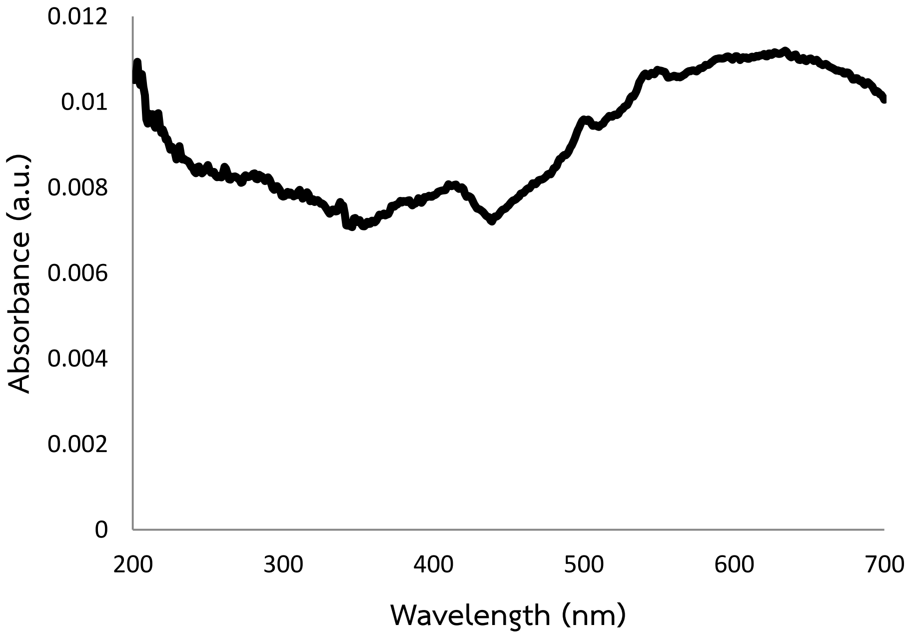

Figure A.40 Solid UV-Vis absorption spectrum of polymer **12**

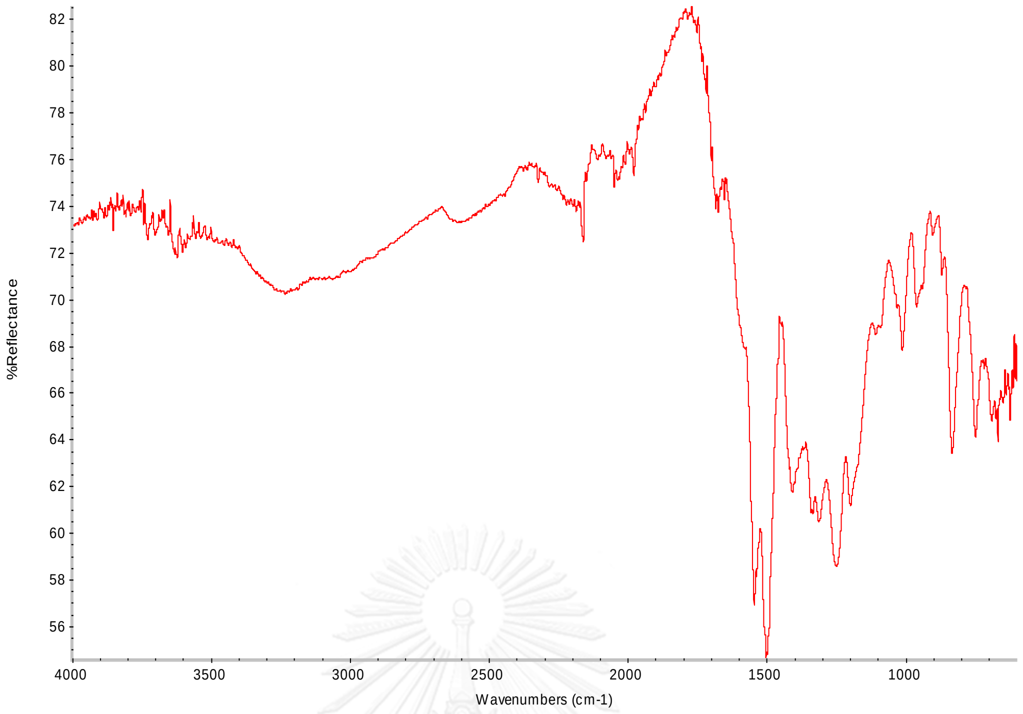

Figure A.41 IR spectrum of polymer **13**

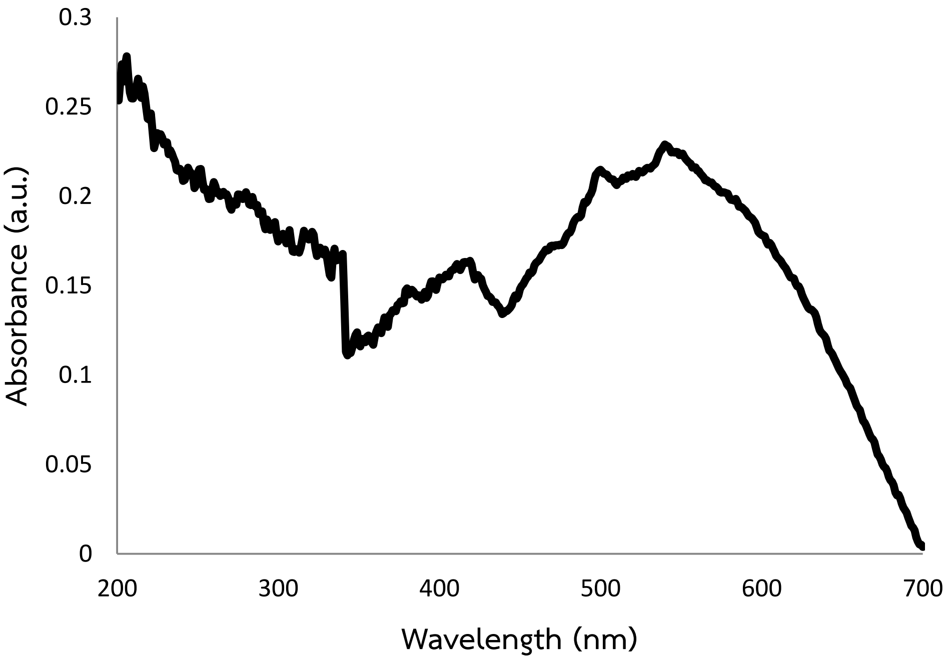

Figure A.42 Solid UV-Vis absorption spectrum of polymer **13**

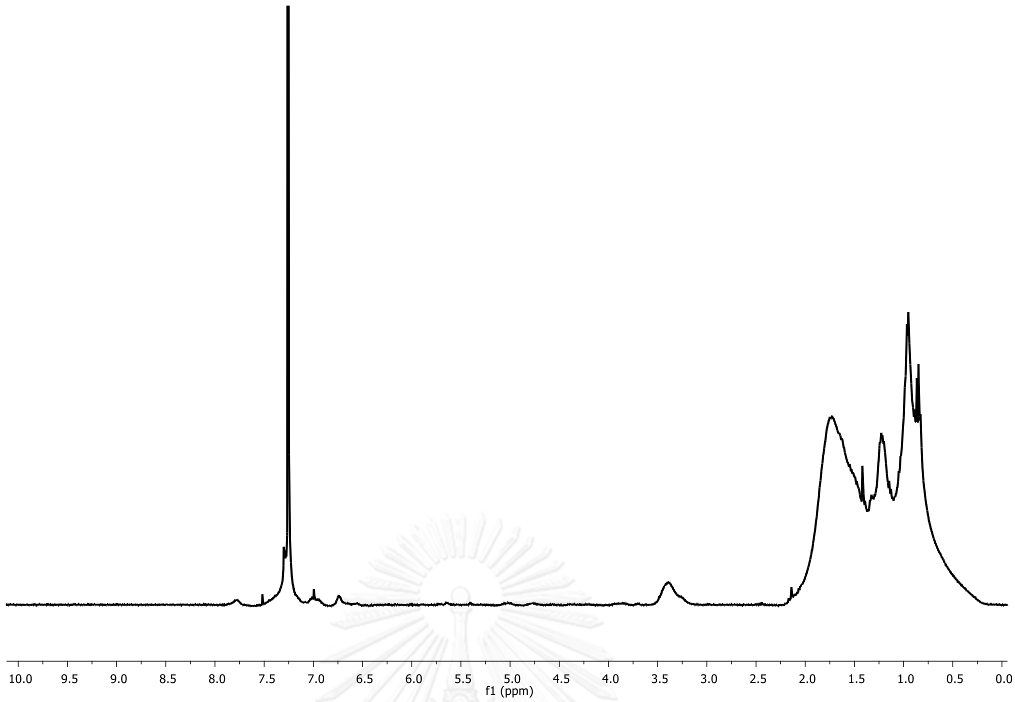

Figure A.43 ^{1}H NMR ($CDCl_3$) spectrum of polymer **15**

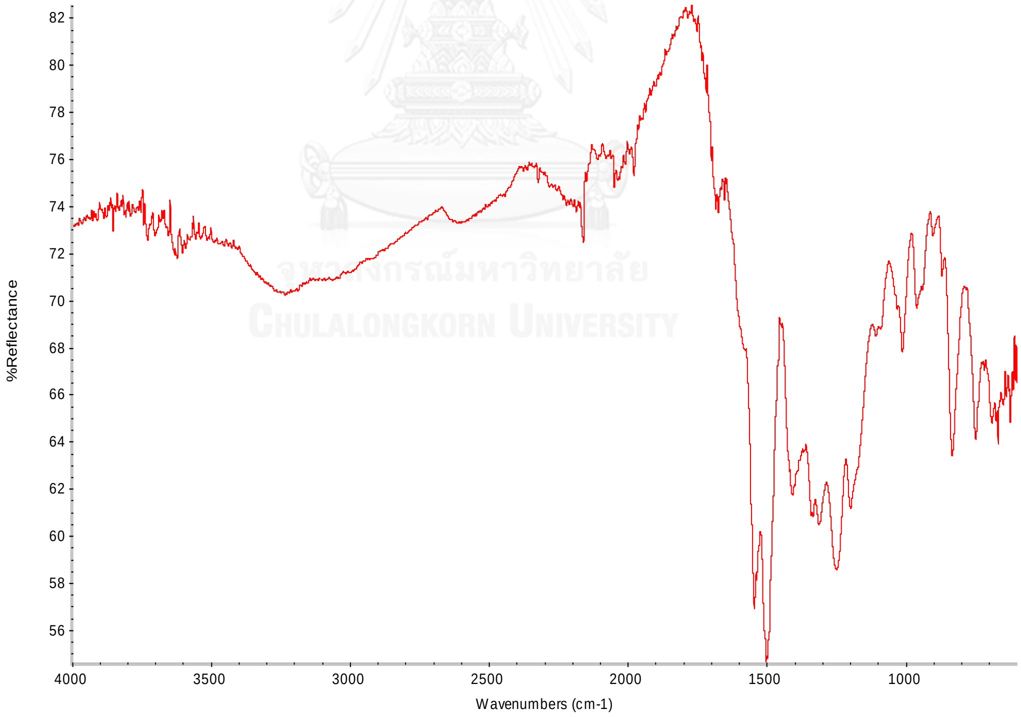

Figure A.44 IR spectrum of polymer **15**

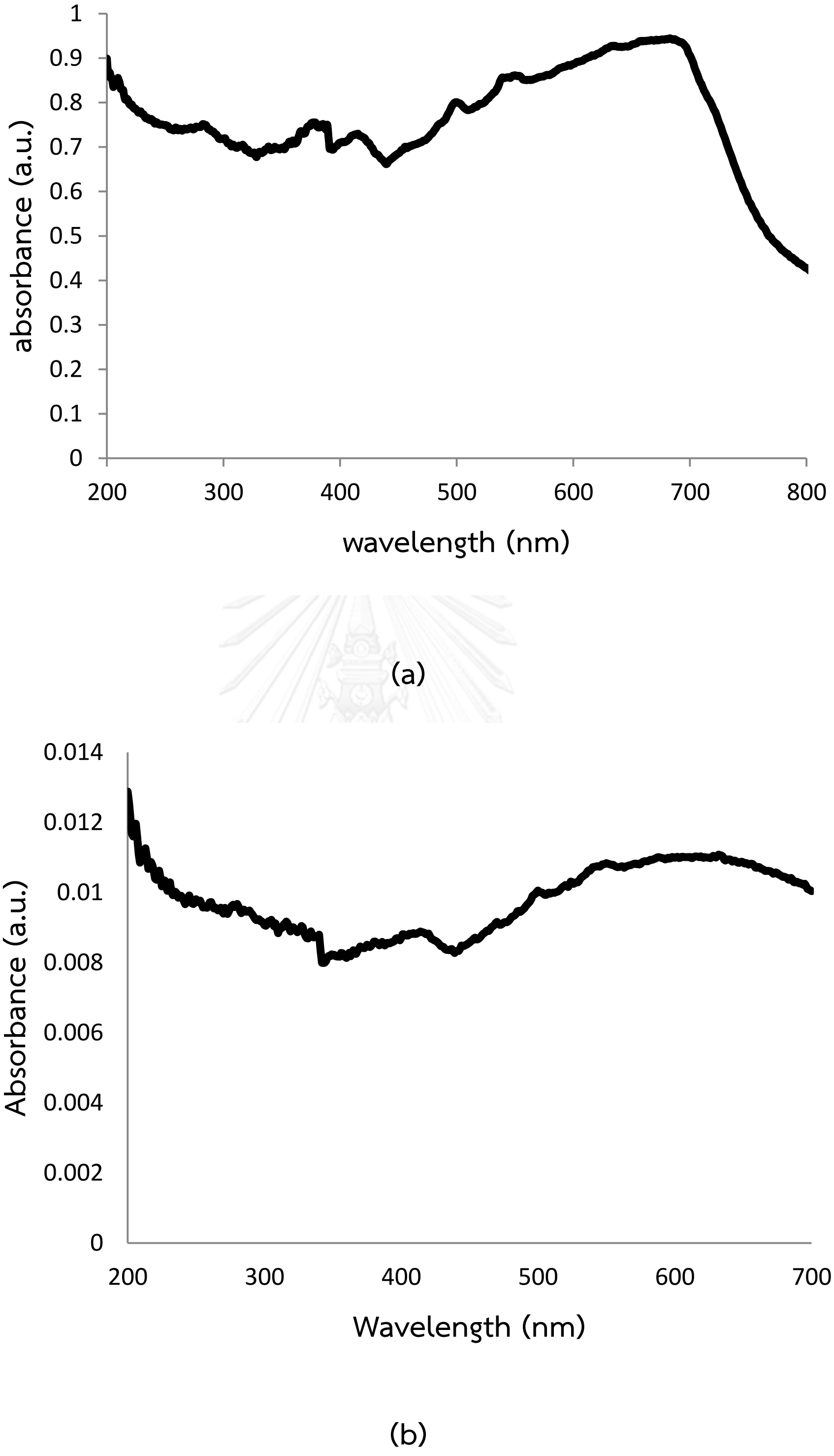

Figure A.45 Solid UV-Vis absorption spectra of polymer **15** from (a) entry 1, Table 3.5 and (b) entry 2, Table3.5

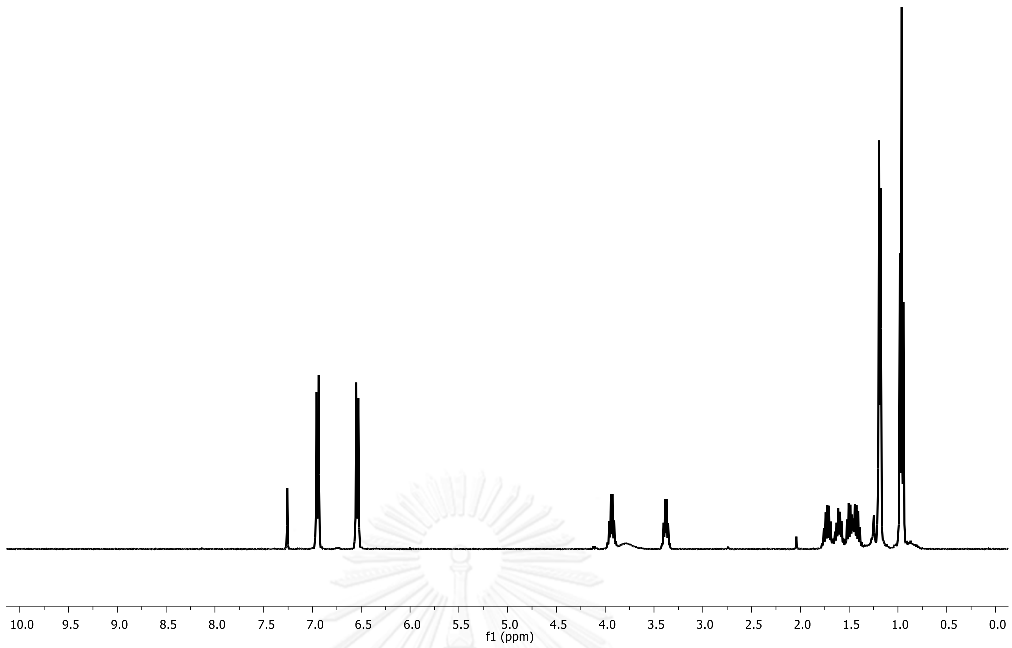

Figure A.46 ^{1}H NMR (CDCl$_3$) spectrum of compound **14**

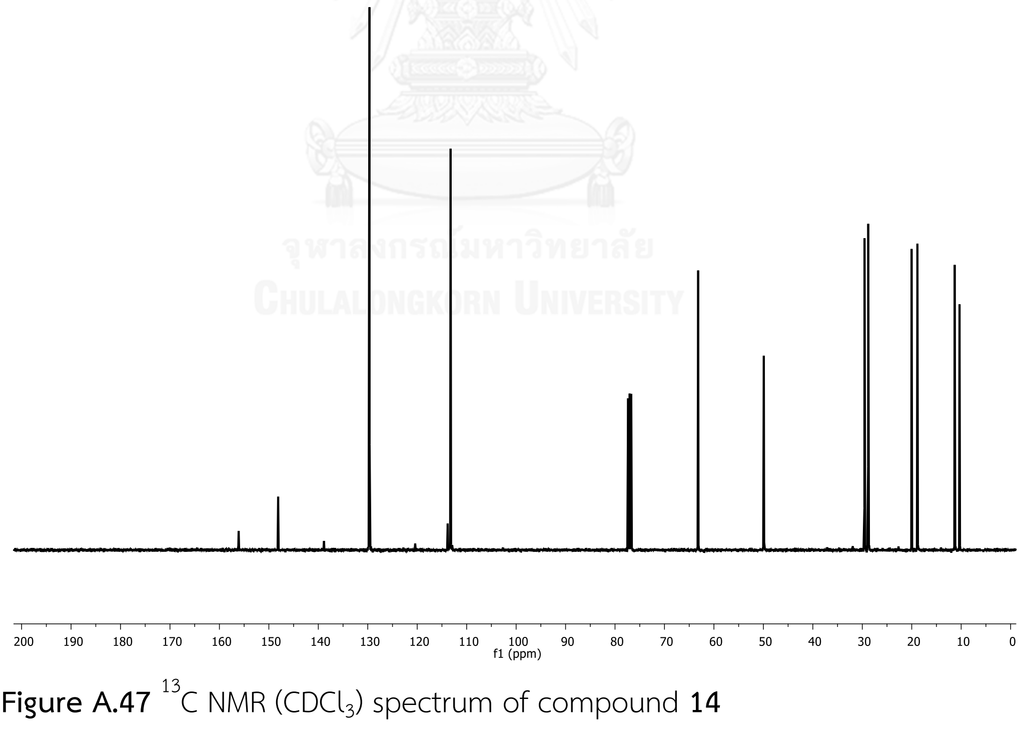

Figure A.47 ^{13}C NMR (CDCl$_3$) spectrum of compound **14**

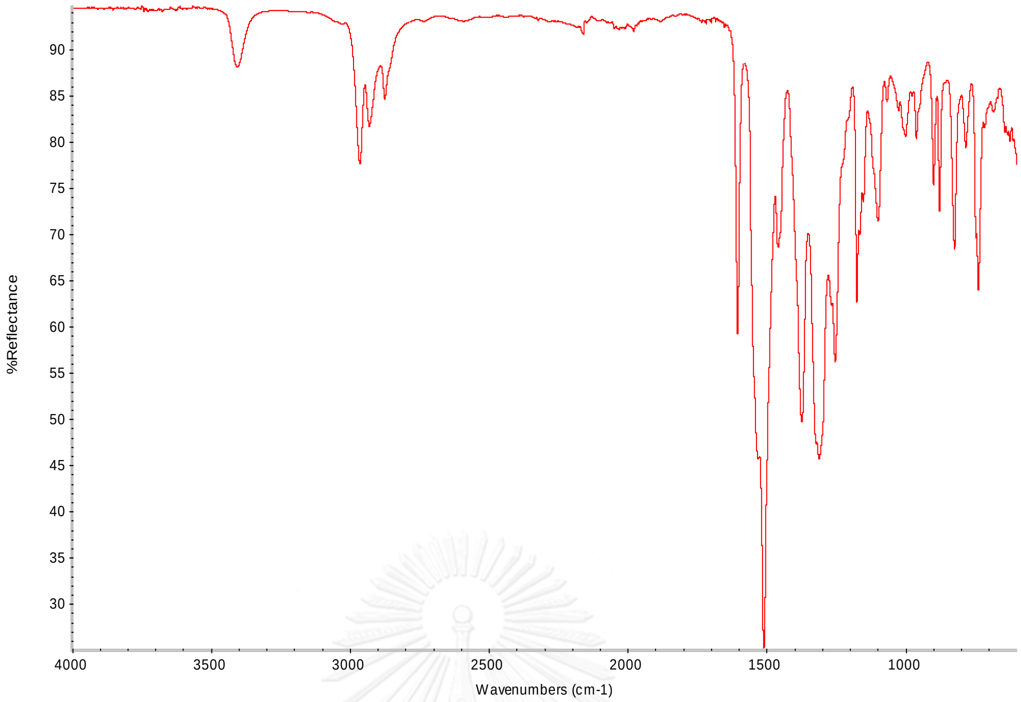

Figure A.48 IR spectrum of compound **14**

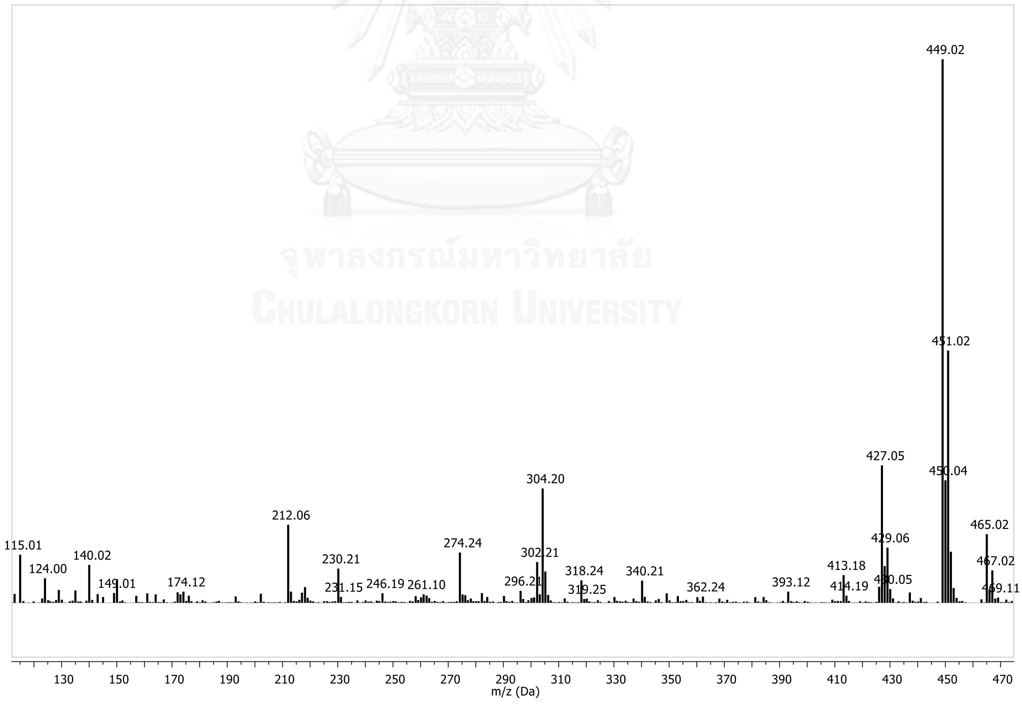

Figure A.49 Mass spectrum of compound **14**

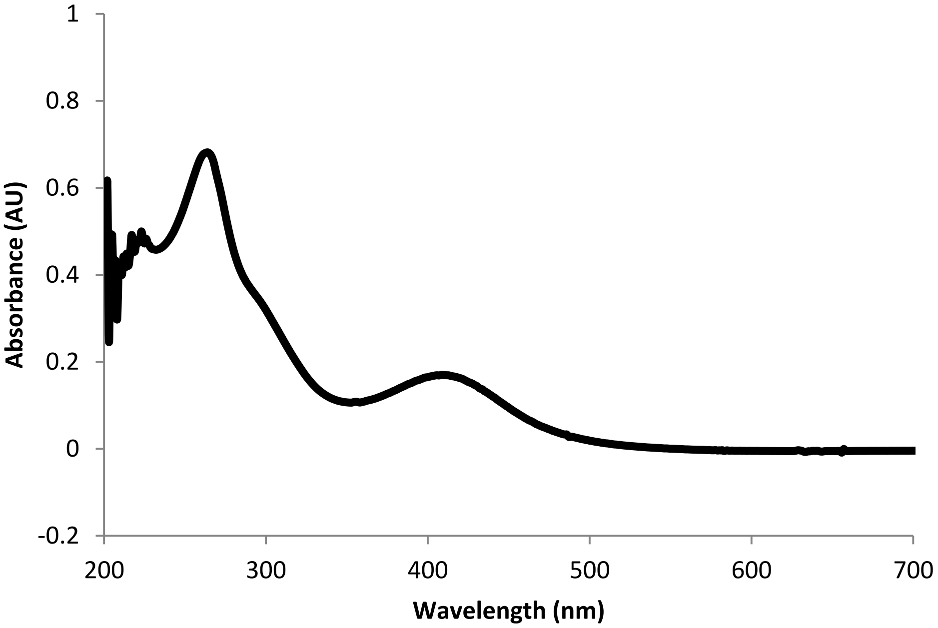

Figure A.50 Solution UV-Vis absorption spectrum of compound **14**

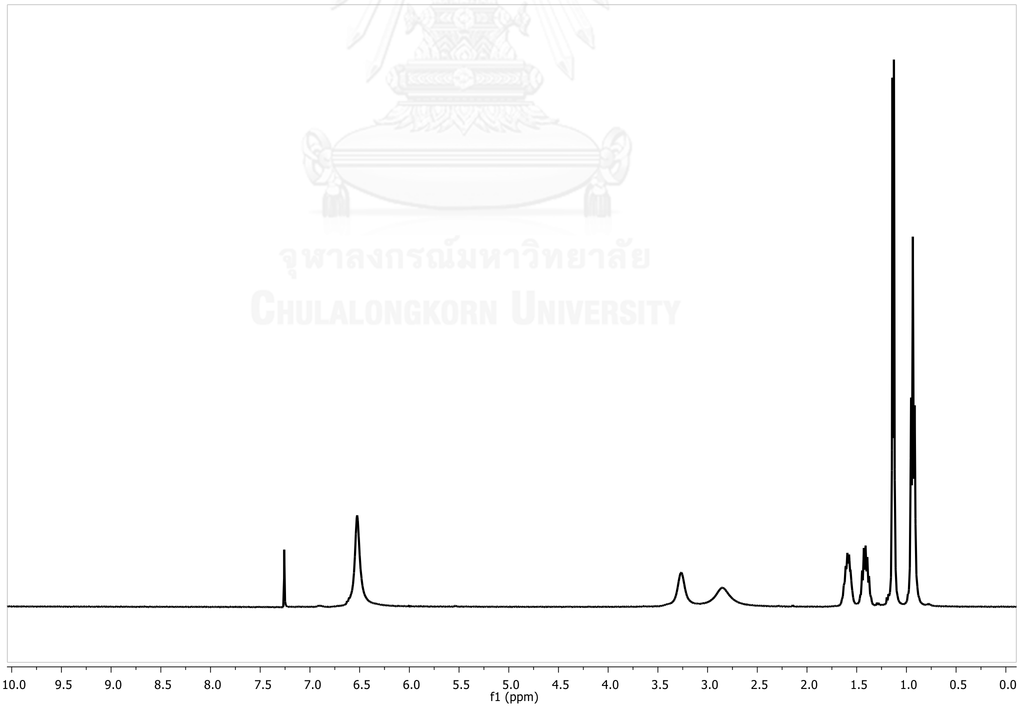

Figure A.51 ^{1}H NMR ($CDCl_3$) spectrum of *N*,*N'*-di-*sec*-butyl-*p*-phenylenediamine

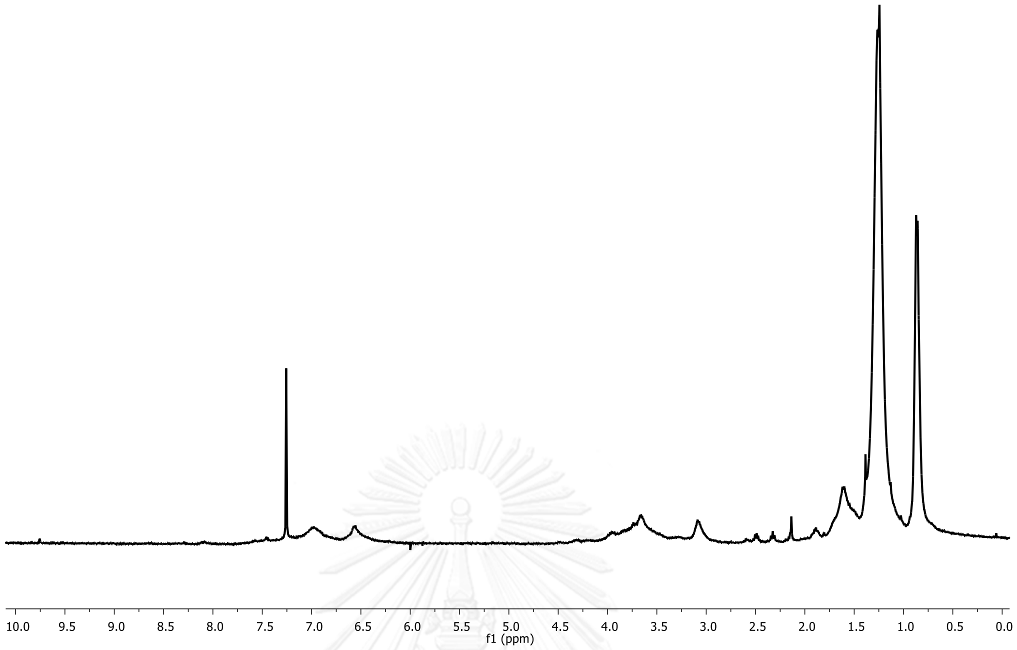

Figure A.52 ^{1}H NMR (CDCl$_3$) spectrum of polymer **17**

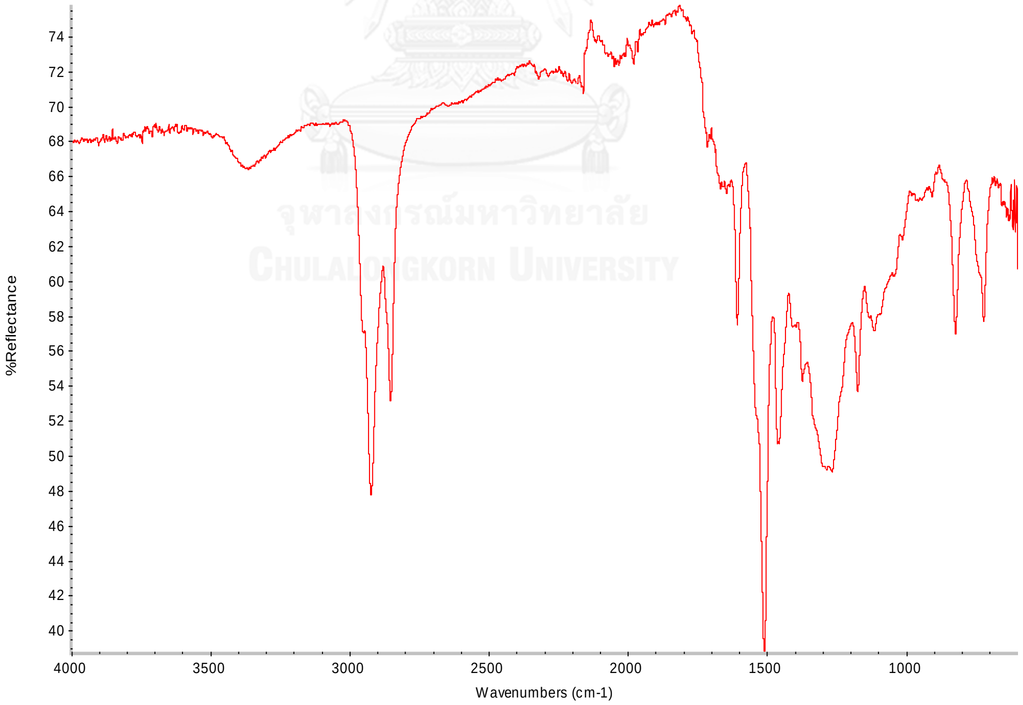

Figure A.53 IR spectrum of polymer **17**

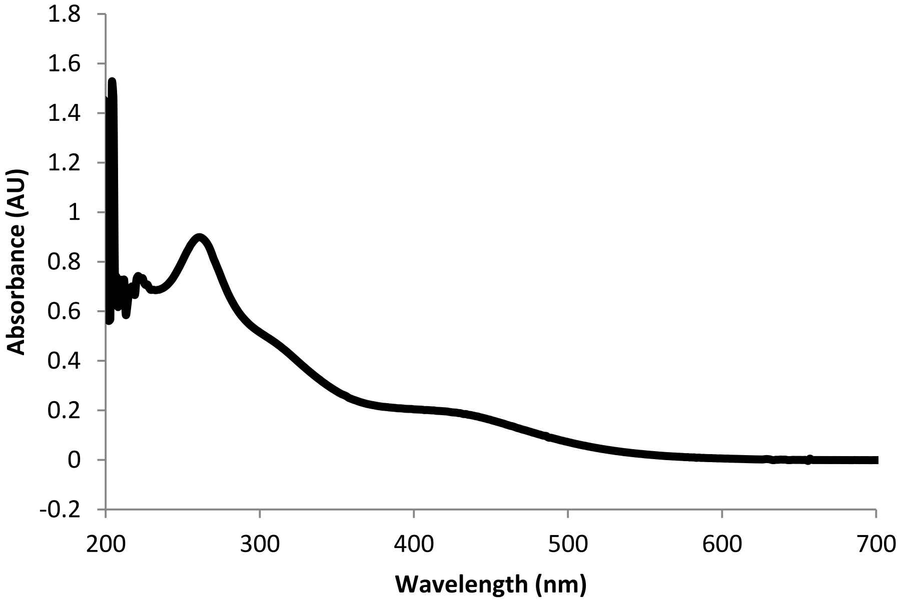

Figure A.54 Solution UV-Vis absorption spectrum of polymer **17**

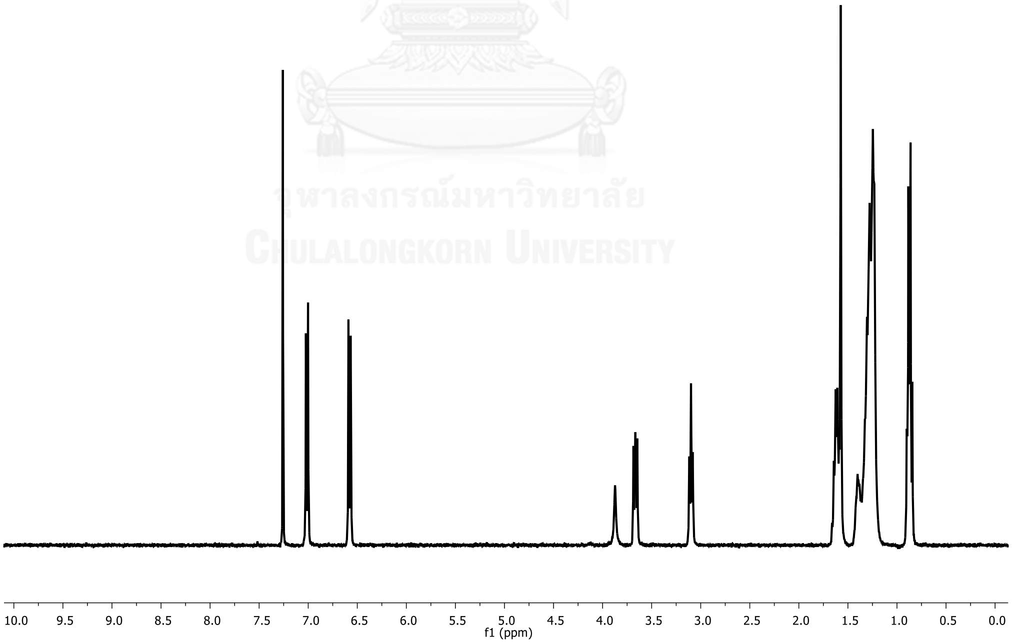

Figure A.55 ^{1}H NMR ($CDCl_3$) spectrum of compound **16**

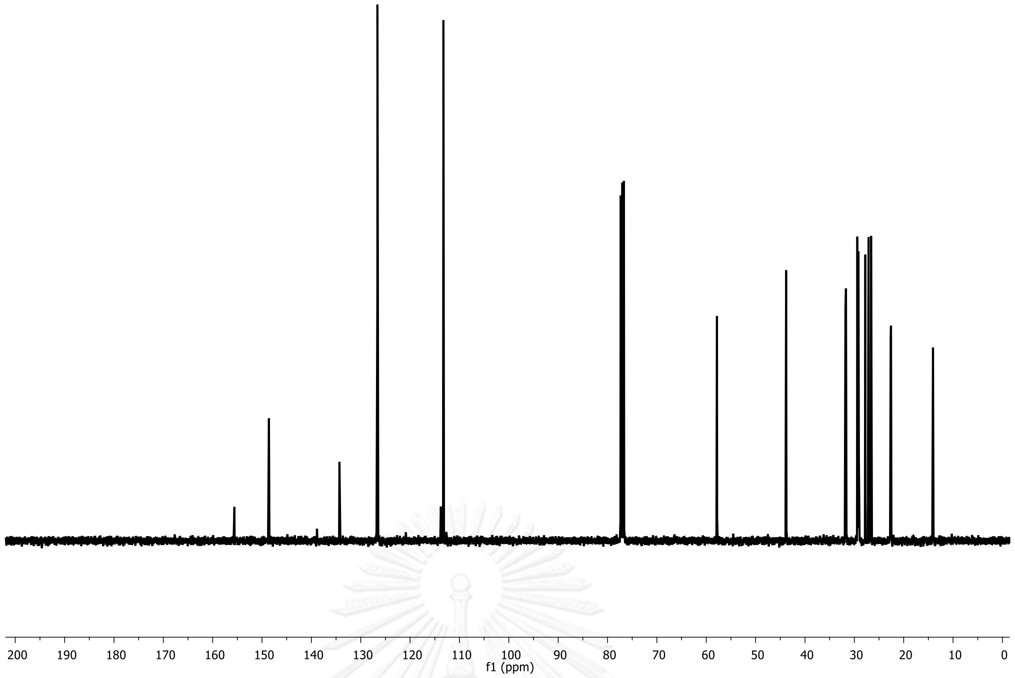

Figure A.56 ^{13}C NMR ($CDCl_3$) spectrum of compound **16**

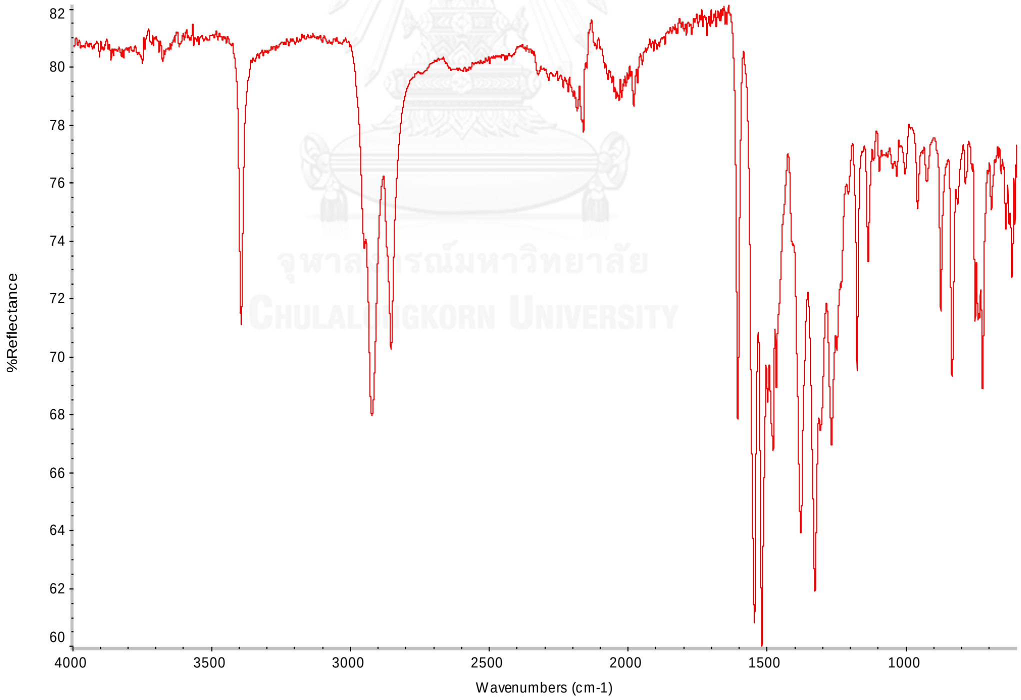

Figure A.57 IR spectrum of compound **16**

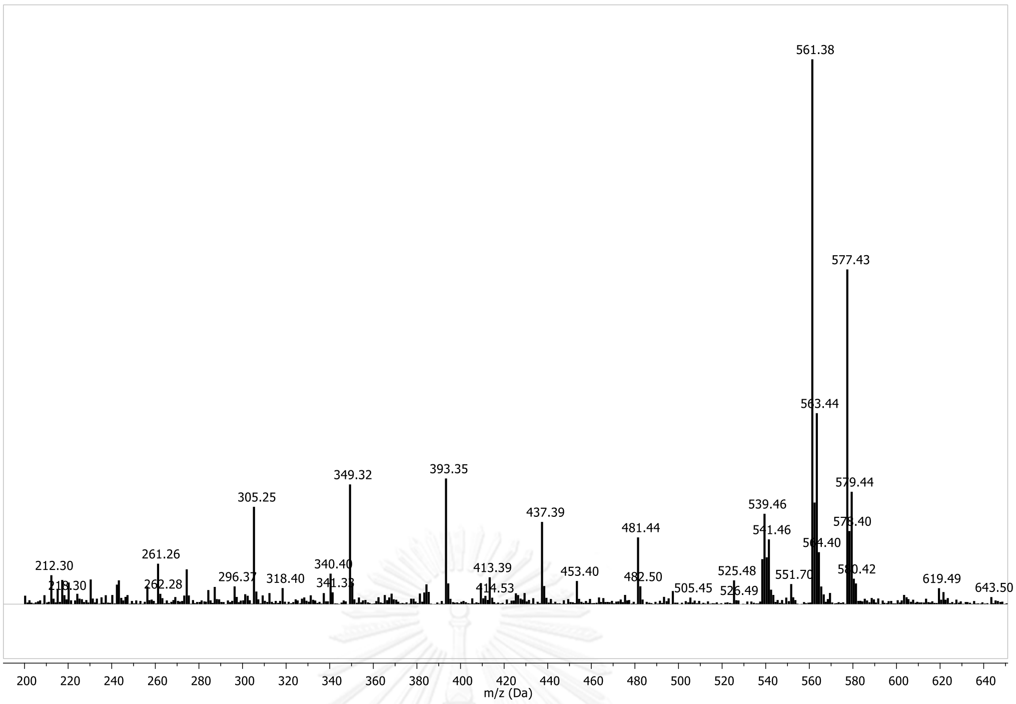

Figure A.58 Mass spectrum of compound **16**

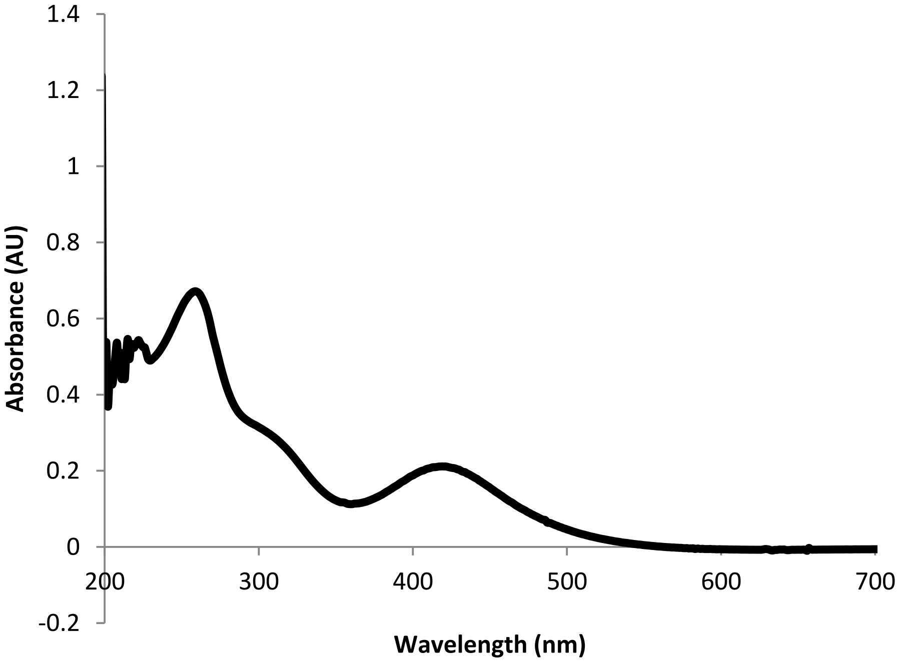

Figure A.59 Solution UV-Vis absorption spectrum of compound **16**

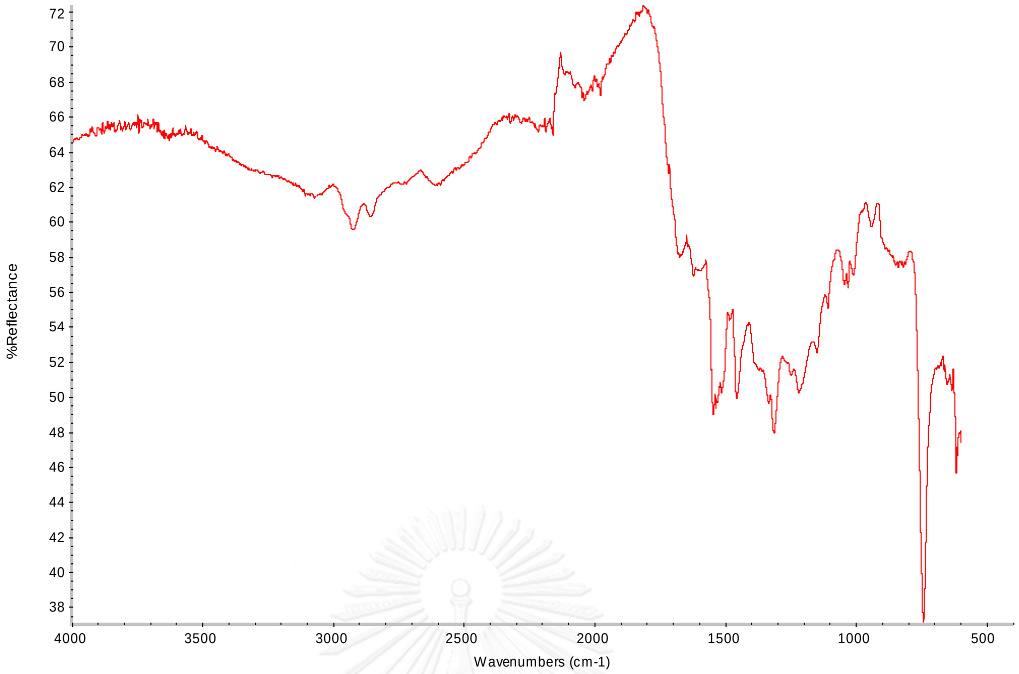

Figure A.60 IR spectrum of polymer **18**

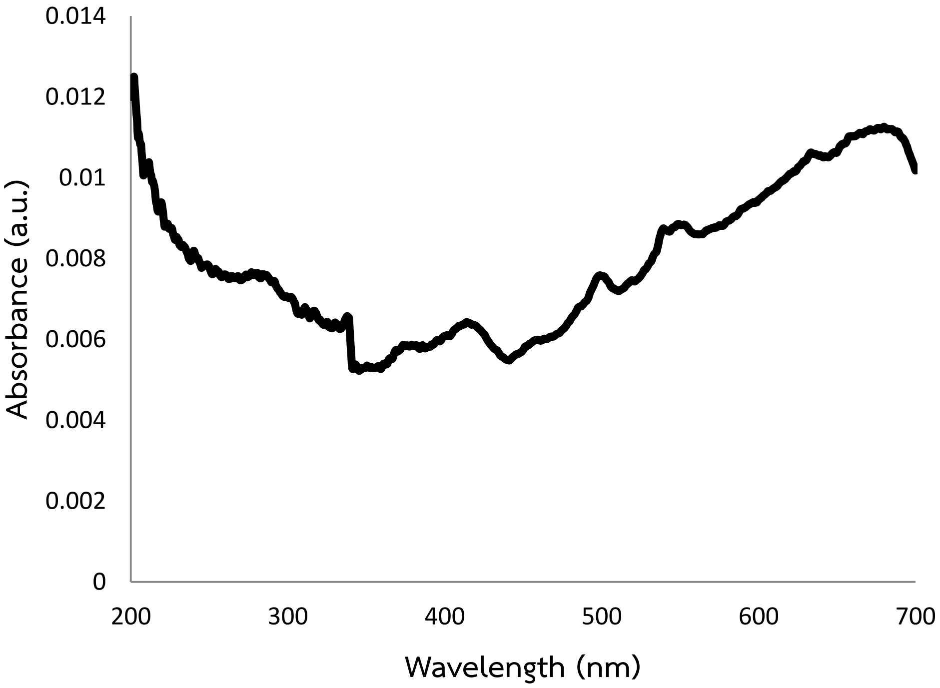

Figure A.61 Solid UV-Vis absorption spectrum of polymer **18**

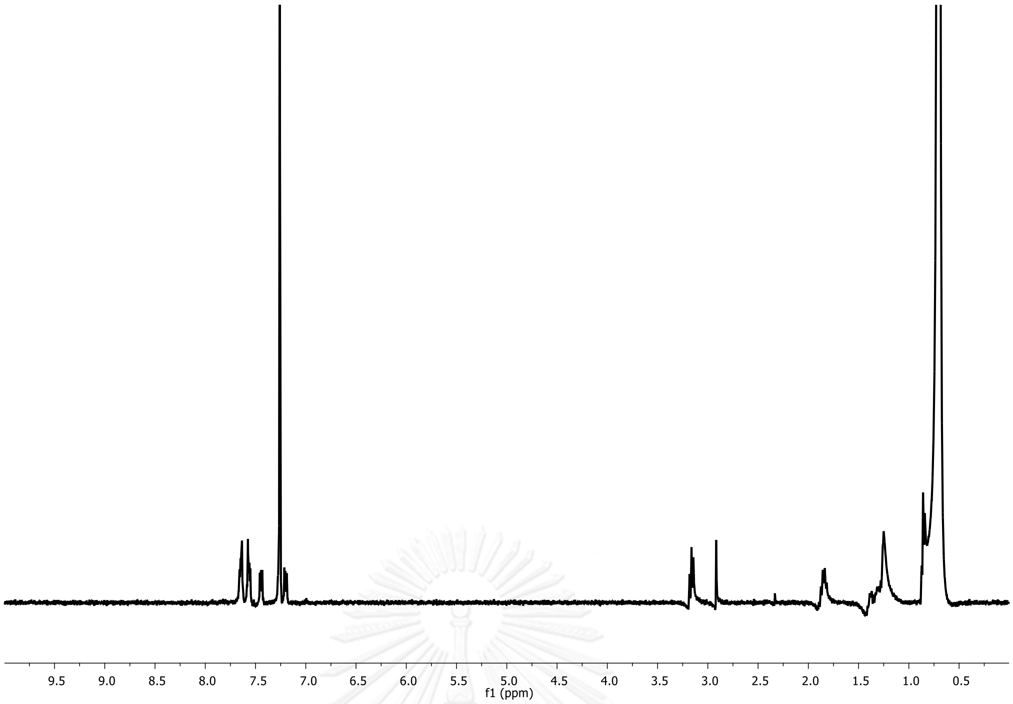

Figure A.62 ^{1}NMR (CDCl$_3$) spectrum of compound **19**

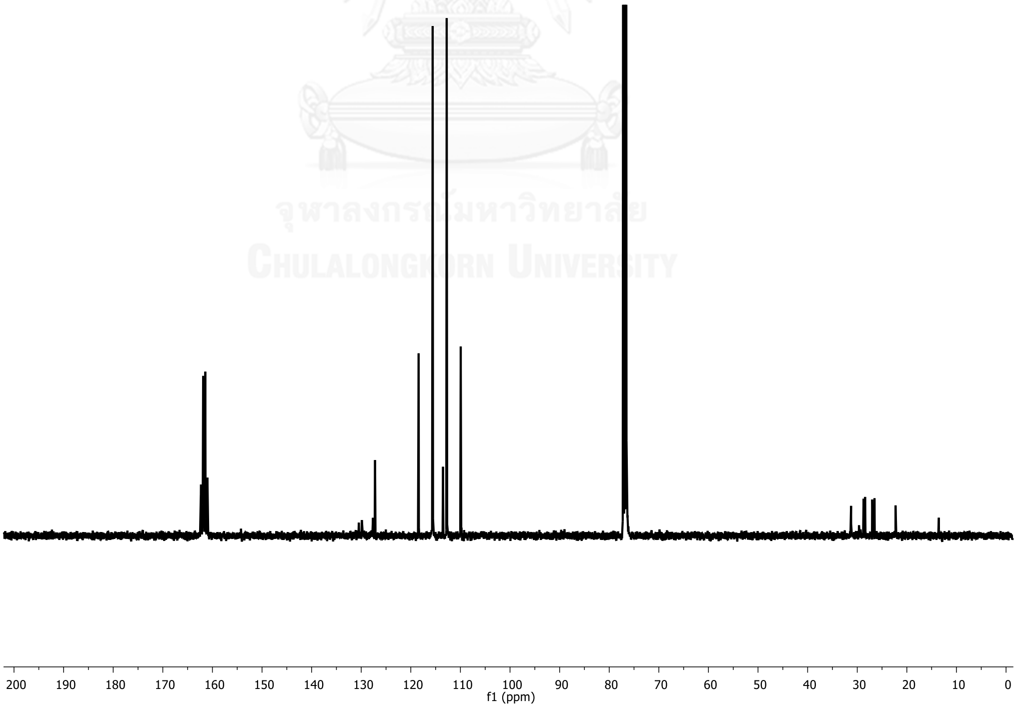

Figure A.63 ^{13}C NMR (CDCl$_3$) spectrum of compound **19**

VITA

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