

ผลของโดแพนต์ต่อสมบัติไฟฟ้าและเคมีไฟฟ้าของพอลิเมอร์ที่มีหมู่ไตรฟีนิลเอมีน



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EFFECT OF DOPANTS ON ELECTRICAL AND ELECTROCHEMICAL PROPERTIES
OF POLYMERS CONTAINING TRIPHENYLAMINE MOIETY



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4-ทอลิลไดฟีนิลเอมีน (TDPA) และ เอ็น,เอ็นไดฟีนิล เอ็น,เอ็น-บิส(4-เมธิลฟีนิล)-1,1'-ไบฟีนิล-4,4'-ไดเอมีน (TPD) มอนอเมอร์ สังเคราะห์ได้ด้วยวิธีโตไซโซ พอลิเมอร์แบบเส้นตรงของมอนอเมอร์ทั้งสองชนิดและเบนซัลดีไฮด์ (BZA) สังเคราะห์ได้ด้วยกระบวนการพอลิเมอไรเซชันแบบควบแน่น โดยใช้คลอโรเบนซีนเป็นตัวทำละลายและกรดพาราทอลูอินซัลโฟนิกเป็นตัวเร่งปฏิกิริยา กระบวนการพอลิเมอไรเซชันของ TDPA และ BZA ทำโดยอาศัยการเปลี่ยนตัวแปร ผลที่ได้พบว่าเมื่อเพิ่มปริมาณตัวเร่งปฏิกิริยา, อัตราส่วนของมอนอเมอร์ และอุณหภูมิที่ใช้ในการทำปฏิกิริยา มีผลทำให้ได้พอลิเมอร์ที่มีน้ำหนักโมเลกุลสูงขึ้น

ในงานวิจัยนี้โดแพนต์สองชนิด ได้แก่ สารประกอบไอออนิก และตัวออกซิเดนต์ ถูกนำมาทดสอบการโด๊ปเบื้องต้นกับพอลิไวนิลคาร์บาไซล (PVK) ซึ่งเป็นพอลิเมอร์ทางการค้าที่ใช้กันโดยทั่วไปในด้านการนำไฟฟ้า ด้วยแสง สารประกอบไอออนิกทั้งสามชนิด ได้แก่ ลิเทียมเปอร์คลอเรต, เตตระเอทิลเปอร์คลอเรต และ เตตระบิวทิลเปอร์คลอเรตเกิดการรวมตัวและแยกตัวออกจาก PVK ในขณะที่ 2,3- ไดคลอโร-5,6-ไดไซยาโน-1,4-เบนโซควิโนน (DDQ) ให้ประสิทธิภาพผลมากที่สุด พอลิเมอร์ทั้งสองชนิดจึงถูกออกซิไดซ์ด้วย DDQ ด้วยปริมาณต่าง ๆ ที่อุณหภูมิห้อง และใช้เตตระไฮโดรพิวแรนเป็นตัวทำละลาย ผลจากโปรตอนเอ็นเอ็มอาร์ พบว่า สามารถออกซิไดซ์เมทายน์โปรตอนทั้งหมดของพอลิเมอร์ได้โดยใช้อัตราส่วนระหว่างหน่วยซ้ำ สองโมล ต่อ DDQ หนึ่งโมล และเวลาในการทำปฏิกิริยานานกว่า 24 ชั่วโมง

ระหว่างการออกซิเดชัน พบว่าไม่เกิดปฏิกิริยาการเชื่อมขวาง เนื่องจากน้ำหนักโมเลกุลเฉลี่ย และอุณหภูมิกลาสทรานซิชันของพอลิเมอร์หลังการทำปฏิกิริยาเพิ่มขึ้นเพียงเล็กน้อย FT-IR สเปกตรัมไม่ปรากฏสัญญาณของ DDQ และรีดิวซ์ฟอร์มของ DDQ ปนเปื้อนอยู่ในพอลิเมอร์ทั้งสองชนิดหลังการทำปฏิกิริยา แต่พบแถบการดูดกลืนรังสียูวี-วิสิเบิลใหม่ในช่วง 700 นาโนเมตร เนื่องจากคอนจูเกชันที่เพิ่มขึ้น และอนุมูลอิสระประจุบวกบนสายโซ่ของพอลิเมอร์ ซึ่งสามารถยืนยันอนุมูลอิสระดังกล่าวด้วยอิเล็กตรอนสปินเรโซแนนซ์สเปกโทรสโกปี พอลิเมอร์ทั้งสองชนิดหลังการทำปฏิกิริยา ให้ค่าศักย์ไฟฟ้าออกซิเดชันที่ผันกลับได้เท่ากับพอลิเมอร์ก่อนการทำปฏิกิริยา และความนำไฟฟ้าแบบกระแสตรงอยู่ในช่วง 10^{-11} S/cm ซึ่งมากกว่าพอลิเมอร์ก่อนการทำปฏิกิริยาสองเท่าขึ้นไป

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KEYWORD: TRIARYLAMINE CONTAINING POLYMERS/ 2,3-DICHLORO-5,6-DICYANO-1,4-BENZOQUINONE (DDQ)/ DOPING/ OXIDATION/ DC CONDUCTIVITY/ ESR

TIDARAT WANGWIJIT: EFFECT OF DOPANTS ON ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF POLYMERS CONTAINING TRIPHENYLAMINE MOIETY. THESIS ADVISOR: PROFESSOR SUPAWAN TANTAYANON, Ph.D. THESIS CO-ADVISOR: PROFESSOR HISAYA SATO, Ph.D. 104 pp. ISBN 974-346-668-1

4-Tolyldiphenylamine (TDPA) and *N,N'*-diphenyl-*N,N'*-bis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) monomers were synthesized via Tosoho method. The condensation polymerization of both monomers with benzaldehyde (BzA) was carried out to yield linear polymers using chlorobenzene as a solvent and *p*-toluenesulfonic acid as a catalyst. TDPA was polymerized with BzA at various conditions. It was found that the polymer with higher molecular weight (Mw) could be obtained when the amount of catalyst, the monomer ratio and the reaction temperature increased.

In this research, two types of dopant, i.e., ionic compounds and oxidants were preliminarily doped with poly(vinylcarbazole) (PVK), a commercially common polymer in photoconductive field. Three ionic compounds, i.e., lithium perchlorate, tetraethyl perchlorate and tetrabutyl perchlorate agglomerated and separated from PVK while 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) performed the most effective results. Both polymers were thus reacted with DDQ at various amount in tetrahydrofuran at room temperature. ¹H-NMR spectra indicated that all methine protons of the polymers could be completely oxidized at the mole ratio of repeating unit:DDQ of 2:1 with the reaction time longer than 24 hours.

Mw and glass transition temperature of the oxidized polymers were not significantly changed, which indicated that no crosslinking reaction occurred during the oxidation. FT-IR spectra indicated that neither residual DDQ nor its reduced form contaminated in the oxidized polymers. Both oxidized polymers performed the new UV-VIS absorbances around 700 nm due to the extended conjugation and radical cations on the polymer chains. ESR spectroscopy of both completely oxidized polymers clearly confirmed the existence of the radical on the polymer chains. Both completely oxidized polymers attained the same oxidation potentials as the starting polymers. DC conductivity of both completely oxidized polymers was in the range of 10⁻¹¹ S/cm, which was over 2 magnitudes higher than the starting polymers.

Department.....—..... Student's signature.....
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GLOSSARY OF ACRONYMS

AE	Auxiliary electrode
Bu ₄ NClO ₄	Tetrabutylammonium perchlorate
t-BuONa	Sodium tert-butylate
BzA	Benzaldehyde
CDCl ₃	Chloroform- <i>d</i>
CHCl ₃	Chloroform
CTM	Charge transporting material
CV	Cyclic voltammetry
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DNB	Dinitrobenzene
DSC	Differential Scanning Calorimeter
EL	Electroluminescence
EO	Electro-optic
ESR	Electron Spin Resonance
Et ₄ NClO ₄	Tetraethylammonium perchlorate
ETL	Electron transporting layer
ETM	Electron transporting material
FA	Paraformaldehyde
FT-IR	Fourier Transform - Infrared
GPC	Gel Permeation Chromatography
HTL	Hole transporting layer
HTM	Hole transporting material
ITO	Indium-tin-oxide

GLOSSARY OF ACRONYMS (continued)

LiClO ₄	Lithium perchlorate
NMR	Nuclear Magnetic Resonance
NOBF ₄	Nitrosonium tetrafluoroborate
NOSbF ₆	Nitrosyl hexafluoroantimonate
P-(t-Bu) ₃	Tri(tert-butylate) phosphine
Pd(OCOCH ₃) ₂	Palladium (II) acetate
PDA	<i>N,N'</i> -Diphenyl- <i>N,N'</i> -di(4-methylphenyl)-1,4-phenylenediamine
Ph ₃ CBF ₄	Triphenylmethyl tetrafluoroborate
Ph ₃ CClO ₄	Triphenylmethyl perchlorate
Ph ₃ CSbF ₆	Triphenylmethyl hexafluoroborate
PR	Photorefractive
PVK	Poly(vinylcarbazole)
RE	Reference electrode
TBAHA	tris-(<i>p</i> -Bromophenyl) aminium hexachloroantimonate (V)
TDPA	4-Tolyldiphenylamine
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Tetramethylsilane
TPA	Triphenylamine
TPD	<i>N,N'</i> -Diphenyl- <i>N,N'</i> -bis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine
WE	Working electrode

CHAPTER 1

INTRODUCTION

Numerous attempts have been made to produce polymers with electrical property such as conducting and charge transport properties. These electrical properties are believed to involve movement of electrons intramolecularly or intermolecularly. Many years ago, the idea of conducting polymer was purely a subject of theoretical debate. Polyacetylene, polypyrrole, polythiophene, polyaniline and organometallic polymers are some well-known conducting polymers. Charge transporting polymer plays an important role in many electrical and optical applications such as electrochromic, electroluminescence and electrophotography applications. The charge transport polymeric materials has been developed within this decade to overcome many problems of the old type charge transporting material (CTM) made from organic compounds, which shows poor mechanical and thermal properties and they would be difficult to maintain long-term morphological stability. As a consequence, the devices using low molecular weight compounds will have short lifetime and low durability. Additionally, the polymeric materials may have many advantages, such as ability against morphological changes, good processability, the possibility of various chemical modifications and the possibility of enhancing the device durability due to the increased morphological stability.

It is well-known that aromatic amine derivatives such as triphenylamine (TPA) derivatives have been widely used as CTMs, which are divided into two groups. The first type is hole transporting material (HTM), which easily donates

electrons to other molecules and possesses positive charge. The second type is electron transporting material (ETM), which tends to receive electrons from other molecules and possesses negative charge. HTM is exclusively used as CTM because of a higher charge mobility.

One method to develop the electrical property of organic compounds or polymers is doping, the term applied to the process of changing the state of oxidation or reduction of conjugated polymers with a concomitant change in the electronic properties of the material, e.g., to increase their conductivity. Therefore, doping process also means to physically mixing or chemical reaction that can change the electronic properties of the material. There are many kinds of dopants in the electrical field, for example; ionic compounds and oxidants.

In this research, the effects of dopants on electrical and electrochemical properties of synthesized polymers containing TPA moiety were investigated by preliminarily doping with two types of dopants, i.e., ionic compound and oxidant to poly(vinylcarbazole) (PVK) which has been widely used as a commercial polymer in photoconductive device. The polymers were prepared from condensation reaction of either 4-tolyldiphenylamine (TDPA) or *N, N'*-Diphenyl-*N, N'*-bis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and benzaldehyde (BzA).

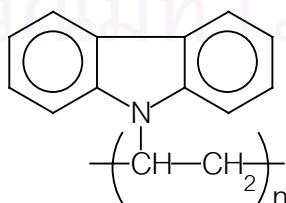


Figure 1.1: Poly (vinylcarbazole).

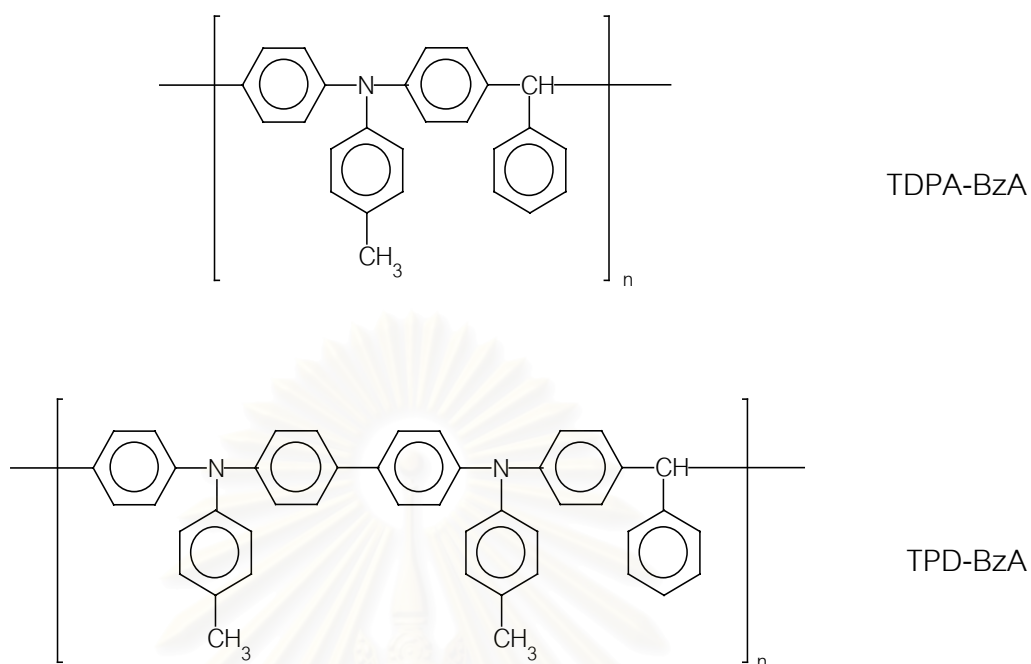


Figure 1.2: Polymers containing triphenylamine moiety.

1.1 OBJECTIVES

1. To synthesize polymers containing TPA moiety.
2. To study the effect of dopants on electrical and electrochemical properties of synthesized polymers.

1.2 SCOPE OF THE RESEARCH

For the preparation of polymers, 4-tolyldiphenylamine (TDPA) and *N,N'*-diphenyl-*N,N'*-bis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) monomers were synthesized from Tosho method (1) and the appropriate condensation polymerization conditions were studied. PVK was preliminarily investigated for doping with ionic compound or oxidant. After that the synthesized polymers with acceptable properties were doped with the effective dopant and then

characterization of the structure of doped polymers. The effect of dopants on electrical and electrochemical properties was investigated.

1. Literature survey and in-depth study of this research.
2. Synthesis of TDPA and TPD monomers by Tosoho method.
3. Polymerization of TDPA and TPD with BzA in chlorobenzene using *p*-toluenesulfonic acid as a catalyst.
4. Several parameters of these polymerization were varied, i.e., the monomer ratio, the amount of catalyst, the reaction temperature and the reaction time.
5. Characterization of synthesized polymers.
6. The polymers with the acceptable properties were doped with the effective dopant, which could be obtained from the feasibility doping with PVK at different amount.
7. Characterization of doped polymers in comparison with undoped polymers.
8. Measurement of the electrical and electrochemical properties of doped polymers such as redox potential and conductivity.
9. Discussion and conclusion.

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CHAPTER 2

BACKGROUND AND THEORY

Polymers are normally used in electrical applications as insulators, where advantages of their high resistivities and good dielectric performances are taken. Typical examples of this type of application include cable sheathing, capacitor films, printed circuit substrates and various encapsulants and conformal protective coatings. However, polymers are also widely exploited because of their other advantages including mechanical strength, flexibility, stability, low cost and ease of processing and it is the promise of combining these properties with electrical conductivity that has prompted the now great interest in conductive polymers.

Many researches have shown that organic polymers can have the property of possessing high electrical conductivity and can exhibit a range of properties from semiconducting to near-metallic behavior. Therefore, conductive polymers have found increasing use in all walks of life, both industrial and consumer. Some conductive polymers offer many advantages over their metal analogue such as lightweight, rustproof property, ease of molding and recycling.

2.1 ELECTRONIC AND ELECTRICAL PROPERTIES OF POLYMER

Most polymers are good insulators; however, many polymers can have high conductivity because of their electronic and electrical properties that is believed to involve the movement of electron intramolecularly or intermolecularly.

2.1.1) CHARGE TRANSPORT PROPERTY

Charge transport can be viewed as a one-electron oxidation-reduction process. For hole transport, some groups are initially positively charged resulting a formation of cation radicals (so-called polarons) under an applied field. Neutral molecules will transfer electrons to the cation radicals. In order to occur this oxidation process, which causes the motion of positive charge, the groups must be electron donor in their neutral state. Similarly for electron transport, electrons are displaced from anion radicals to the neutral molecules, which must be electron acceptor in their neutral state.

Once injected, the charges (not the molecules) migrate through the transport medium to reach the opposite electrode. It is now commonly accepted that migrations of charge carriers, electrons or holes or both involve hopping, i.e. a sequence of transfers of charges among localized. These localized sites are associated with individual molecules or functional groups or with segments of the polymer chain.

The prevalent feature of polymers having charge transport property is that they all either

1. have an extended π -electron or conjugated system in the backbone or in groups pendant to the chain.
2. are σ -conjugated, as in the case of silicon backbone polymers (polysilylenes).
3. have a suitable morphology. Configurational and conformational factors, influence charge transport. For example, conductivity of polyacetylene film in the direction of molecular alignment is increased by stretching.

These features guarantee delocalization and therefore stabilization of transiting charges.

2.1.2) NATURE OF CHARGE TRANSPORT IN CONJUGATED POLYMER

Both theoretical and experimental evidence suggest that the precise nature of the charge carriers in conjugated polymer systems varies from material to material and it is still a subject of debate in many cases. A discussion of the various theoretical modes for the electronic structure of conjugated polymers is given below in Figure 2.1, using polyacetylene and poly(paraphenylene) as examples.



(e) a soliton defect at a phase boundary between the two trans phases of polyacetylene, where sections A and B are mirror images

Figure 2.1: Possible structures for polyacetylene chains.

A number of structures are possible for polyacetylene with this periodic bond alternation, two trans-forms, and two cis-forms as shown in Figure 2.1. It should be noted that the two trans-forms are essentially equivalent and are both stable. The trans-material gives rise to the possibility of structural defects in chains, where there is a bond alternation (Figure 2.1e).

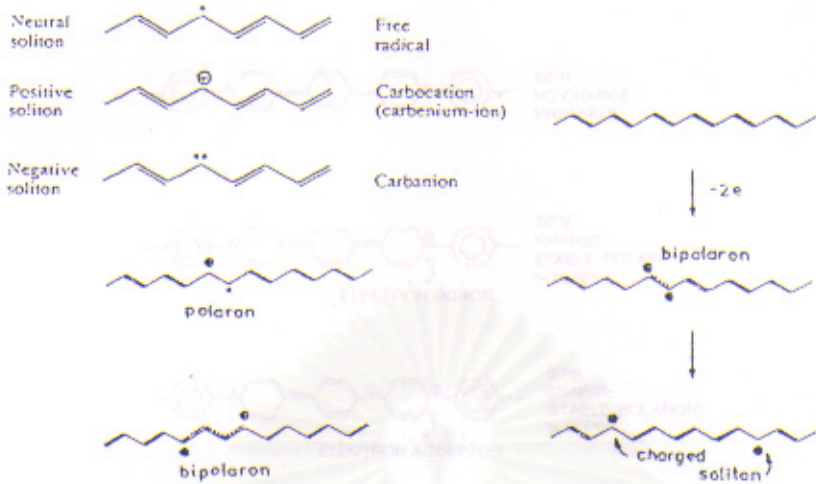


Figure 2.2: Structures of various excited states of polyacetylene.

Two neutral solitons on the same chain will tend to recombine but two charged solitons and a charged one can however achieve a minimum energy configuration by pairing (when they occur on the same chain) to give a polaron and this polaron defect gives rise to two states in the band gap (a bonding and an antibonding orbital), symmetrically placed about the mid-gap energy.

This can be illustrated with reference to poly(paraphenylene), which can be drawn with either a benzenoid or quinoid structure

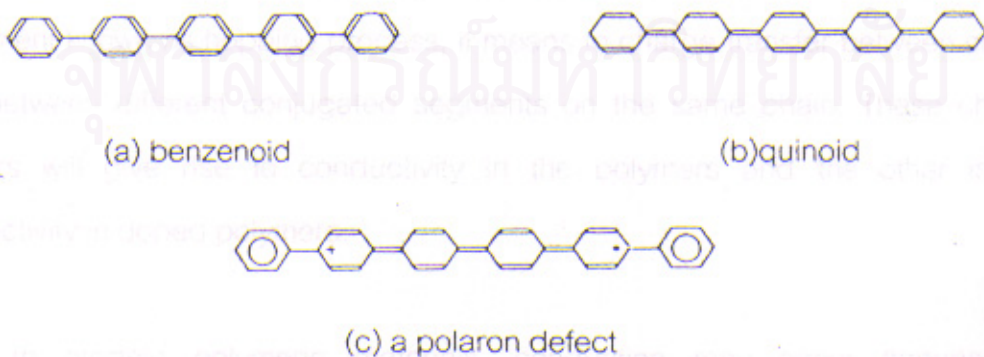


Figure 2.3: Structural diagram for poly(paraphenylene).

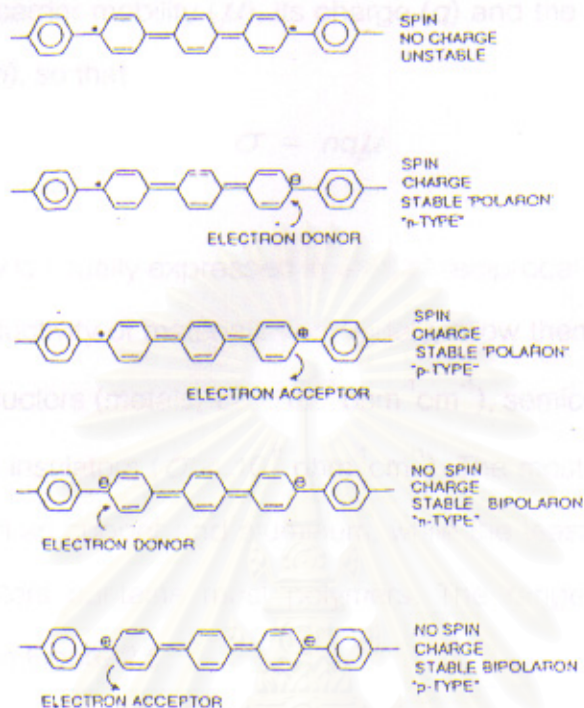


Figure 2.4: Structures of various excited states of poly(paraphenylene).

2.1.3) CONDUCTION

Conduction is believed to involve movement of electrons intramolecularly and intermolecularly via the positive or negative solitons. For intermolecularly movement known as hopping process, it means to charge transfer between chains and between different conjugated segments on the same chain. These charge carriers will give rise to conductivity in the polymers and the other is the conductivity in doped polymers.

In organic polymeric materials, conduction may occur through the movement of either electrons or ions. In each case, the conductivity (σ) is equal to

the product of the carrier mobility (μ), its charge (q) and the number of carriers or the concentration (n), so that

$$\sigma = nq\mu$$

Conductivity is usually expressed in units of reciprocal ohms per centimeter. The electrical conductivity of materials vary widely, allow them to be classified into groups called conductors (metals, $\sigma > 10^{12} \text{ ohm}^{-1}\text{cm}^{-1}$), semiconductors ($\sigma = 10^{-7} - 10^1 \text{ ohm}^{-1}\text{cm}^{-1}$) and insulators ($\sigma < 10^{-8} \text{ ohm}^{-1}\text{cm}^{-1}$). The most conductive materials are the metals such as copper and aluminum, while the least conductive group of materials or insulators contains most polymers. The range of conductivities of materials is shown in Figure 2.5.

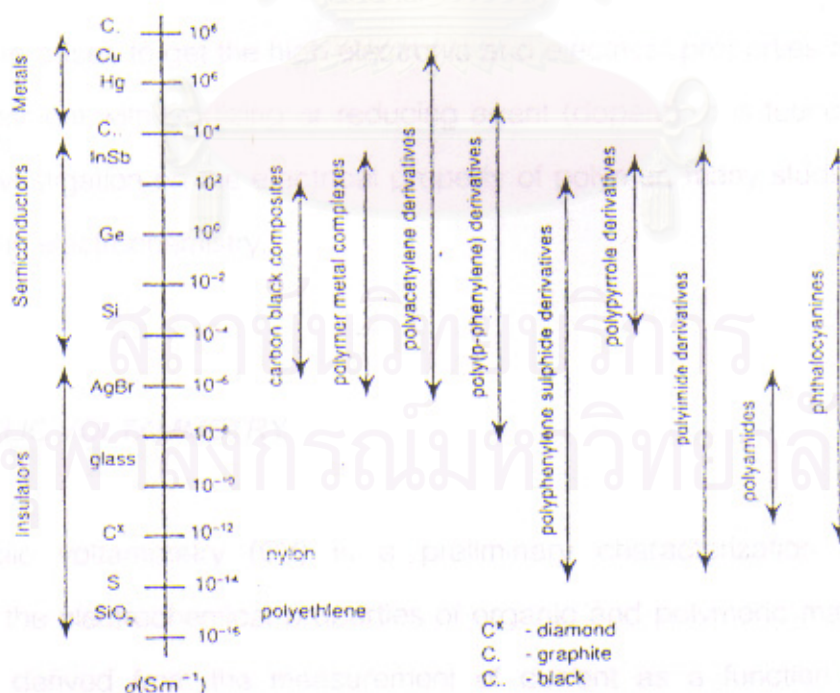


Figure 2.5: Conductivities of various elements, compounds and polymers.

2.2.2) CYCLIC VOLTAMMETRIC EXPERIMENT



Figure 2.6: Band structure for insulator, semiconductor and conductor.

2.2 ELECTROCHEMICAL PROPERTY OF POLYMER

Some cases to get the high electronic and electrical properties of polymers rely on treatment with oxidizing or reducing agent (dopant). It is found that apart from the investigation on the electrical property of polymer, many studies are also concerned in electrochemistry.

2.2.1) CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) is a preliminary characterization method to determine the electrochemical properties of organic and polymeric materials. The analyte is derived from the measurement of current as a function of applied potential obtained in an electrochemical cell. CV is an important tool for the study of mechanisms and rates of oxidation-reduction processes, particularly in organic and metal-organic systems.

2.2.2) CYCLIC VOLTAMMETRIC EXPERIMENT

A typical cell design for a cyclic voltammetric experiment is shown in Figure 2.7. The simplest approach is merely to have the three electrodes immersed in the solution. Cyclic voltammetric experiment typically used three electrodes, i.e., auxiliary electrode (AE), working electrode (WE) and reference electrode (RE).

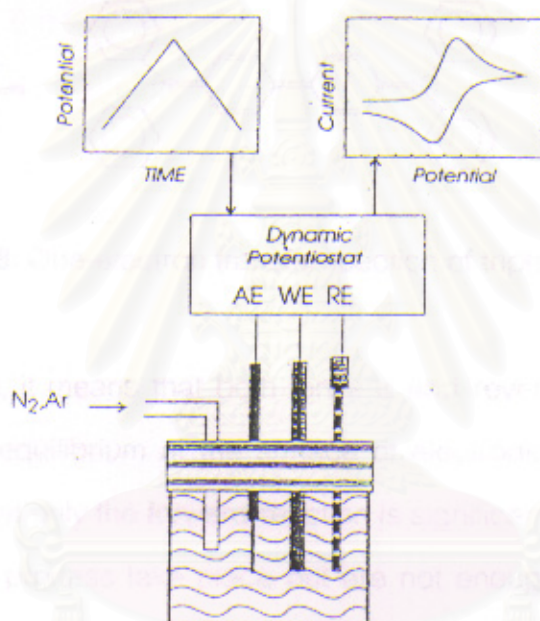


Figure 2.7: Overall view of CV experiment.

2.2.3) ELECTROCHEMICAL MECHANISM

The electrochemical mechanism in cyclic voltammetric experiment is generally used as a tool to examine the CV response. Figure 2.8 gives an example for electrochemical mechanism of one-electron transfer reaction of triphenylamine. In this case, forward process is an oxidation reaction and reverse process is a reduction reaction.

Figure 2.9: Typical shapes of cyclic voltammogram.

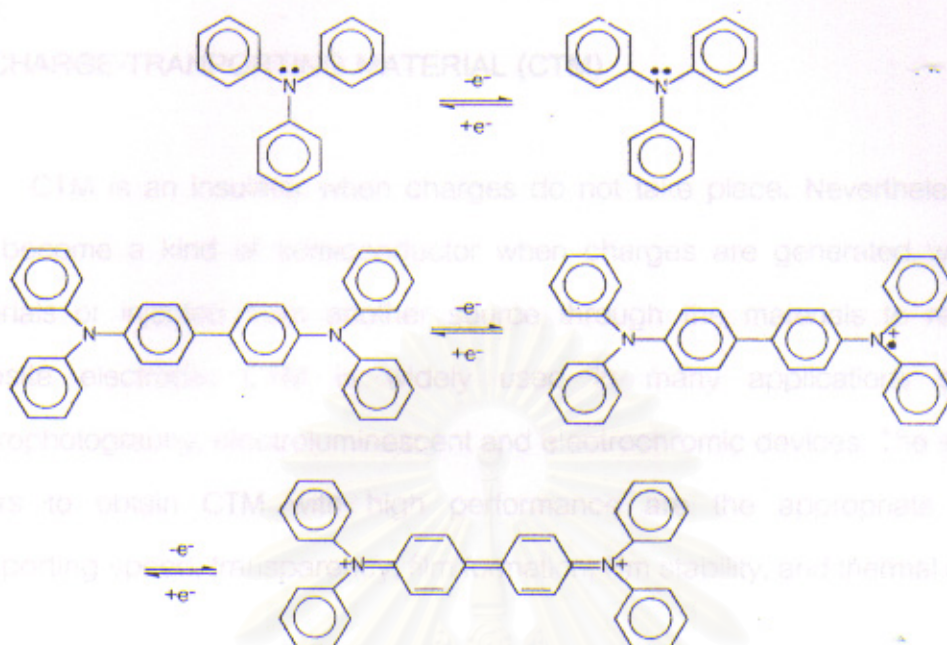


Figure 2.8: One-electron transfer reaction of triphenylamine.

For reversible, it means that both forward and reverse processes are fast enough to maintain equilibrium at the surface of electrode. On the other hands, irreversible means that only the forward reaction is significant. In the case that both forward and reverse process take place but are not enough to be considered at equilibrium. This system is so called quasi-reversible. Figure 2.9 shows typical cyclic voltammometric curves for three analytes.

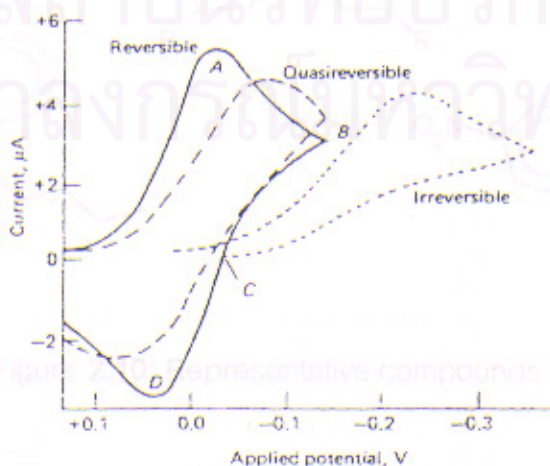


Figure 2.9: Typical shapes of cyclic voltammogram.

2.3 CHARGE-TRANSPORTING MATERIAL (CTM)

CTM is an insulator when charges do not take place. Nevertheless, CTM can become a kind of semiconductor when charges are generated within the materials or injected from another source through the materials to reach the opposite electrode. CTM is widely used in many applications such as electrophotography, electroluminescent and electrochromic devices. The important factors to obtain CTM with high performance are the appropriate charge-transporting speed, transparency, film formation, film stability, and thermal stability.

2.3.1) ELECTRON-TRANSPORTING MATERIAL (ETM)

ETM must be electron acceptors expected potentially to have electron-transporting ability. The chromophore having very strong electron affinity such as trinitrofluorenone, anthraquinone and tetracyanoethylene are well known as ETMs.

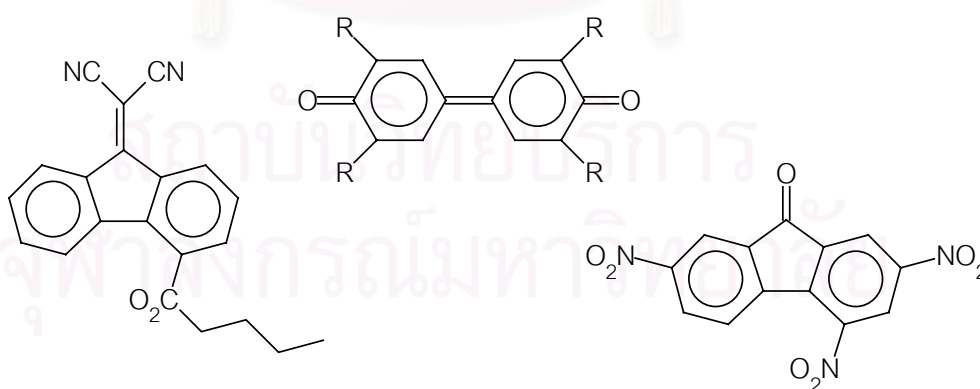


Figure 2.10: Representative compounds of ETM.

2.3.2) HOLE-TRANSPORTING MATERIAL (HTM)

HTMs are electron donors that contain groups with large π -electron clouds such as strongly donating groups; aromatic amines, pyrazoline and hydrazone derivatives. Figure 2.11 gives some representative well-known compounds of HTM. Unlike ETM, HTM has been widely utilized in practical use for many applications such as xerographic, photoreceptor and electroluminescent application because of its higher drift mobility than ETM.

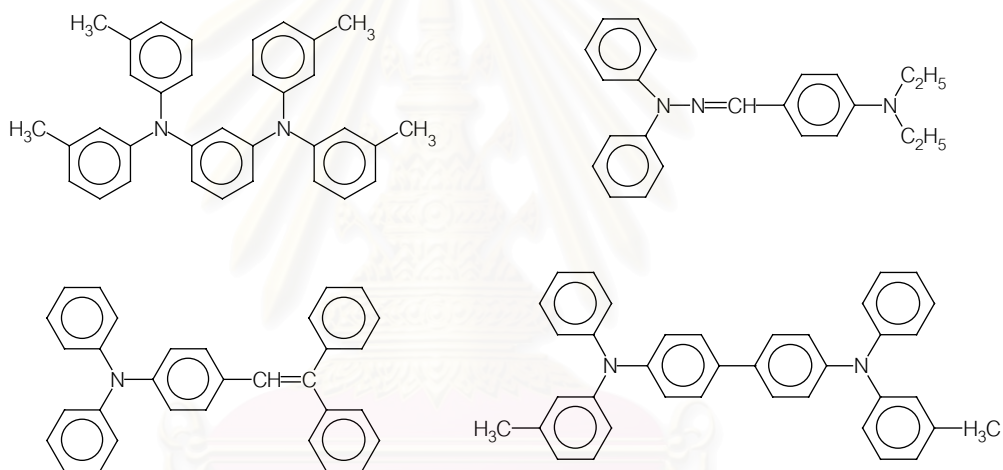


Figure 2.11: Representative compounds of HTM.

2.4 CONDUCTING POLYMER

Polymers can be made electrically conducting via their own structures in three ways; doping, pyrolysis and producing an inherently conductive polymer structure such as via the incorporation of a transition metal atom into the polymer backbone or via doping.

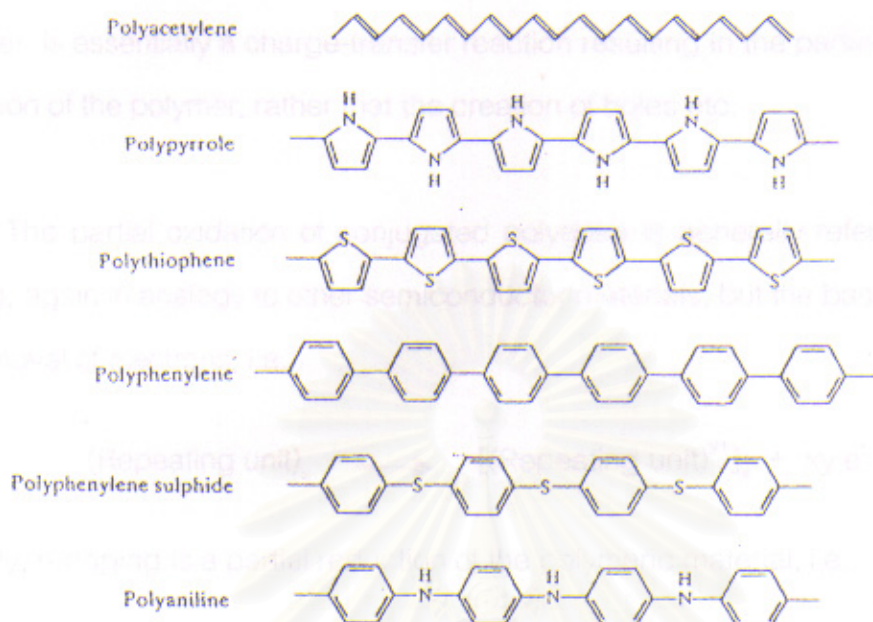


Figure 2.12: The chemical structures of some conducting polymers.

2.5 DOPING

Doping is the term applied to the process of changing the state of oxidation or reduction of conjugated polymers with a concomitant change in the electronic properties of the material (e.g., to increase their conductivity), and arises from the initial interest in these materials from semiconductor physicists. In other words, doping is the addition of a donor or acceptor molecule to the polymer. The doping of polymer involves the formation of a polymer salt and this can be effected either by mixing or immersing the polymer in a solution of the reagent, which will be doped into the polymer (so-called dopant) or by electrochemical methods.

Although the term doping as applied to these processes is strictly correct, in that small quantities of the dopant give rise to disproportionately large changes in the properties of the doped material. The doping reaction in conjugated polymers

Table 2.1: Dopants in conductive polymers and their conductivities.

Polymer	Dopant	Conductivities ($\text{ohm}^{-1}\text{cm}^{-1}$)
Polyacetylene	AsF_5	1.5×10^5
Poly(sulfur nitride)	Br_2	3.8×10^4
Poly(p-phenylene)	AsF_5	500
Polypyrrole	I_2	100
Polyphthalocyaninesiloxane	I_2	1.4
Poly(phenylene sulfide)	AsF_5	1

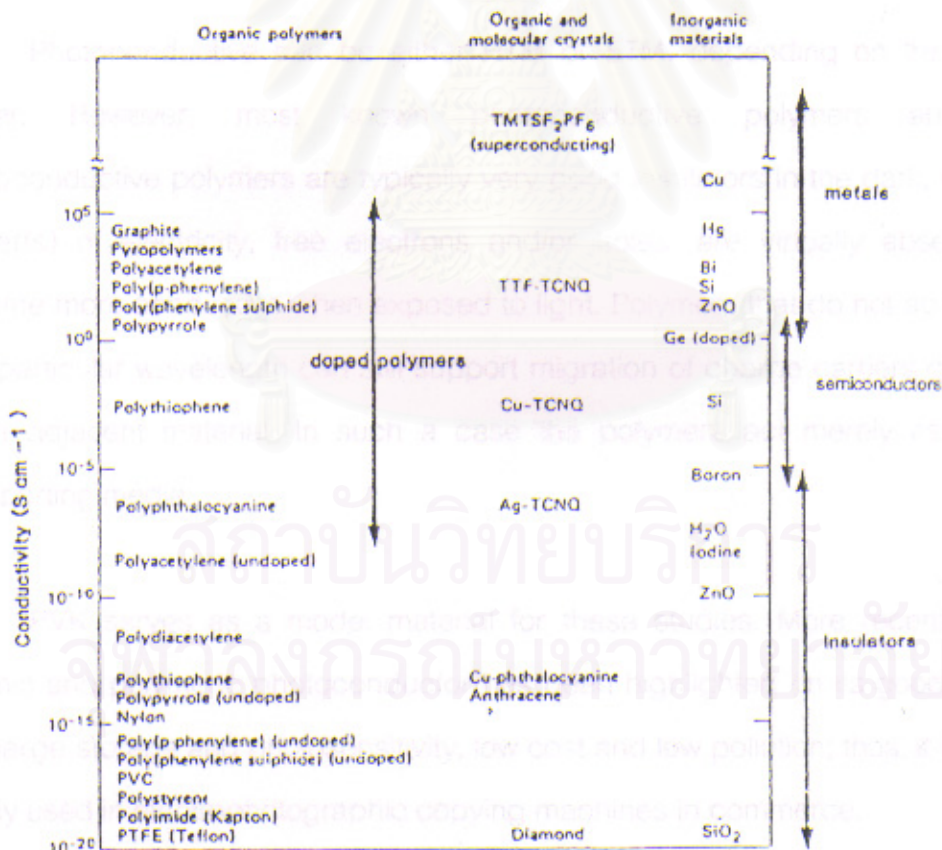


Figure 2.13: Conductivity ranges for doped and undoped polymers, inorganic, materials and molecular crystals.

2.6 APPLICATIONS

CTM is widely used in many applications such as electrophotography, electroluminescent and electrochromic devices. CTM and conductive polymer applications include xerographic, plastic batteries, sensors, photo- and electrochromic displays. One of the principal attractions is the possibility of using in fabrication of microelectrodes.

2.6.1) PHOTOCONDUCTIVE DEVICE

Photoconductive can be either HTM or ETM, depending on the majority carrier. However, most known photoconductive polymers are HTM. Photoconductive polymers are typically very good insulators in the dark, when the carrier(s) of electricity, free electrons and/or holes, are virtually absent. They become more conductive when exposed to light. Polymers that do not absorb light of a particular wavelength can still support migration of charge carriers generated in an adjacent material. In such a case the polymers act merely as charge-transporting media.

PVK serves as a model material for these studies. More recently years, organic and polymeric photoconductor has been highlighted on its good features of charge storage and photosensitivity, low cost and low pollution; thus, it has been widely used in electrophotographic copying machines in commerce.

2.6.2) PHOTOREFRACTIVE DEVICE

CTMs also play an important role in photorefractive (PR) materials, which combine photoconductivity and an electro-optic (EO) response to manifest a photorefractive effect. Many PR polymers have been reported since the required functionalities are easily provided by the addition of specific molecules into polymeric systems, and they can be classified into two groups: (1) host-guest systems that consist of photoconducting polymers doped with EO active chromophore or EO polymers doped with charge transporting agents and (2) fully functionalized polymers that possess all the components required chemically linked to the polymer chain.

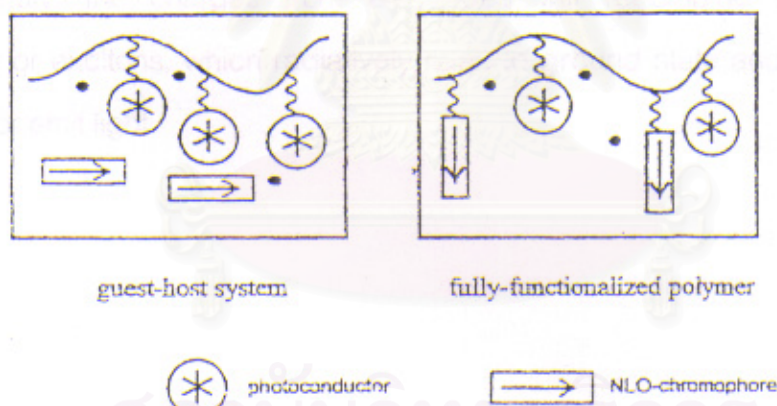


Figure 2.14: Two groups of photorefractive device.

2.6.3) ELECTROLUMINESCENT DEVICE

Electroluminescence (EL) is the phenomenon wherein positive and negative charges are injected from electrodes into a luminescent material, recombining to emit light. The typical EL device consists of an indium-tin-oxide (ITO) anode coated

with tertiary amine hole transport layer, an aluminium coordination complex electron transport layer and a cathode.

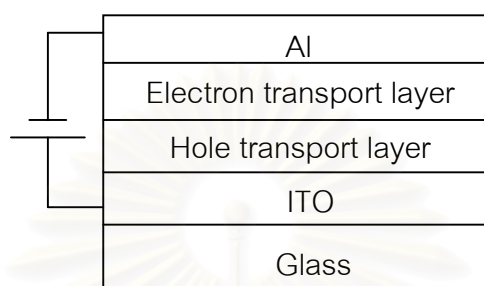


Figure 2.15: Typical configuration of EL device.

Ideally, the charges from electrodes will recombine to give excited molecules or excitons, which radiatively relax to ground state and perform the EL emission or emit light.

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CHAPTER 3

LITERATURE REVIEW

Most of conducting materials has been constructed from inorganic or organic or low molecular weight compounds, which have many problems about mechanical properties, short lifetime and low durability. However, the first report of polymeric materials with semiconducting properties was obtained in 1970s. Many attempts have been made to produce polymers with a high level of electronic conduction. Polyacetylene is still the archetype of organic conducting material and has been studied of all the conducting polymer systems. Much effort has been directed towards the synthesis of polyacetylene because it can be formed in two possible isomeric structures, i.e. cis and trans isomers. Films of polyacetylene will usually contain a mixture of the two isomeric forms. Heating of the films can produce isomerization of the less-conducting cis form into the more highly conducting trans form.

There are many researches about polymers with electric properties including donors or acceptors or dopants to develop the high charge transport ability or conductivity in order to get the suitable polymeric materials for electrical and many applications. Some researchers found that type and amount of dopants affect charge transport property and conductivity of the doped polymer. Hermann and Rembaum found the mechanism of semiconductance and photoconductance occurring in PVK-based materials (2). In most cases, hole migration was dominant, although with iodine as additive and electron mobility was also presented.

Some investigations showed that in both their semiconductance and photoconductance behaviors, charge migration in PVK-based materials was controlled by a hopping mechanism between traps and that such migration was field and thermally stimulated (3-7). These various studies suggested that undoped and doped PVK provided matrix for a hole and/or electron migration, which was very efficient and more efficient than many other readily accessible polymers.

In 1977, Block et al. reported on conductivities of PVK containing cation radicals (8). It was found that partial oxidation of crosslinked PVK containing dimeric carbazylum cation radicals provided a significant semiconductivity up to $\sim 10^{-5}$ S/cm at 293 K. The partial oxidative PVK was prepared from introducing unpaired electrons by the formation of free radicals in PVK using tris-(*p*-bromophenyl) aminium hexachloroantimonate (V) (TBAHA) as an oxidant.

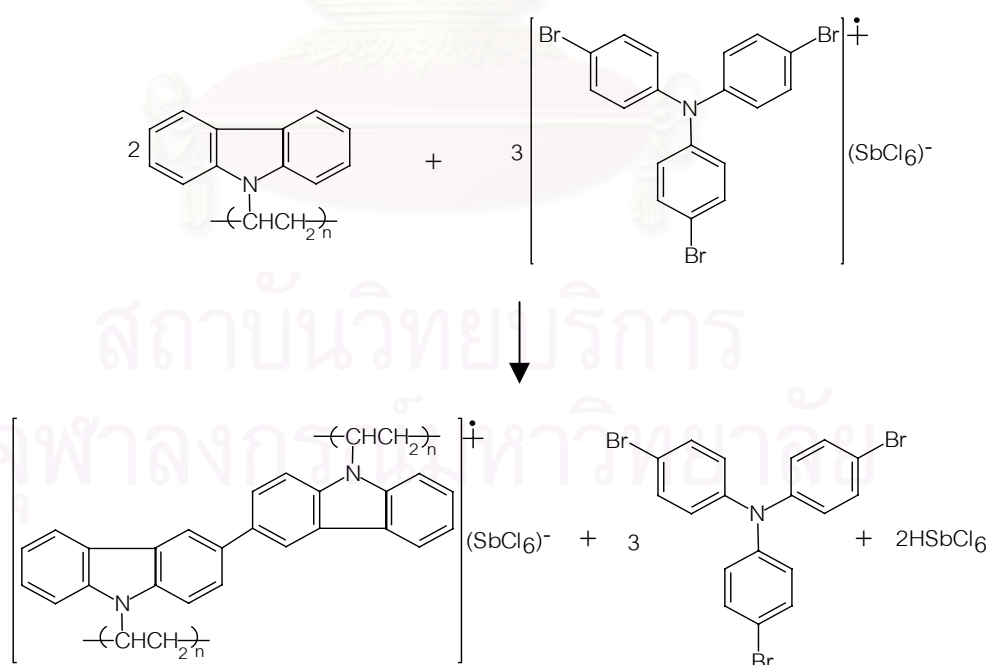


Figure 3.1: Synthetic route of partial oxidative crosslinked PVK.

After that, the effect of dopants on electrical and electrochemical properties polymers was studied by many researchers. In 1985, Samson et al. reported on electrically conducting complexes of poly(3,6-*N*-methylcarbazolyl methylene) (9). It was found that poly(3,6-*N*-methylcarbazolyl methylene) prepared by acid-catalysed condensation polymerization of *N*-methylcarbazole with formaldehyde exhibits p-type semiconducting properties when doped with electron acceptors such as triphenylmethyl tetrafluoroborate, hexafluoroborate and perchlorate (Ph_3CBF_4 , Ph_3CSbF_6 and Ph_3CClO_4), nitrosonium tetrafluoroborate and nitrosyl hexafluoroantimonate (NOBF_4 and NOSbF_6). The polymer complexes with dopant anions (I_3^- , Br_3^- , BF_4^-) to polymer repeating unit ratio of 0.67-0.95 performed a direct current conductivity of 10^{-3} to 10^{-1} S/cm.

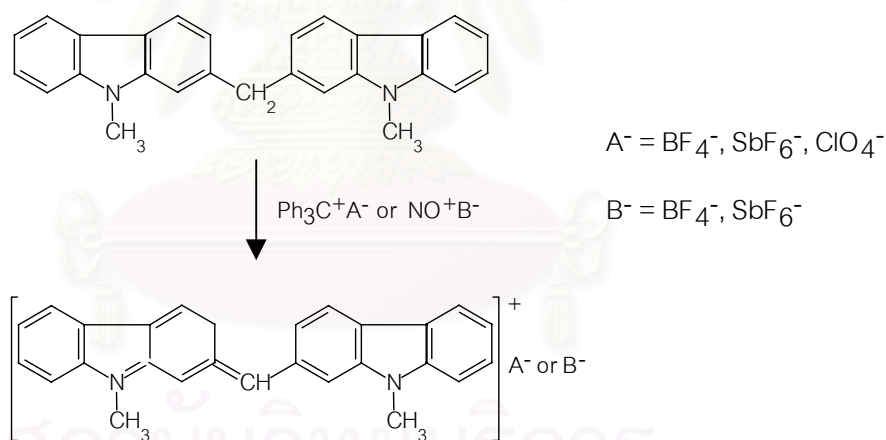


Figure 3.2: Undoped and doped poly(3,6-*N*-methylcarbazolyl methylene).

In 1987, poly(3-methylthiophene) was synthesized as thin films in acetonitrile using PF_6^- , ClO_4^- , BF_4^- and CF_3SO_3^- as the doping anion and Li^+ , Bu_4N^+ as the counter-cation by Marque et al. (10) The results led to propose that nature of anion plays a determining role on the structure of polymer during its synthesis and nature of cation essentially affects the behavior of the polymer film during the

charge-discharge process. The amount of charge reversibly changed during the redox cycle decreased steadily in the following anion sequence: $\text{PF}_6^- < \text{ClO}_4^- < \text{BF}_4^- < \text{CF}_3\text{SO}_3^-$. The electrochemical characteristic of the polymer was enhanced as the size of anion. The oxidation process of the polymer was not only governed by anion transport but was also affected by the nature of the cation. Lithium ion seemed to assist the redox reaction of the polymer by lowering the oxidation potential and the higher mobility of lithium ion leaving the polymer.

Several studies on oxidative polymerization catalysts have emphasized on an electron acceptor; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (11-13). L. Tolbert et. al. found that spin-cast films of poly(3-alkyl-2,2'-bithiophene) could be doped with solutions of DDQ to produce a highly conducting material up to 0.45 S/cm (14). Alkyl-substituted poly(1,4-naphthylenevinylenes) oxidized by DDQ could attain the conductivities of 15 S/cm by Pu et al. (15).

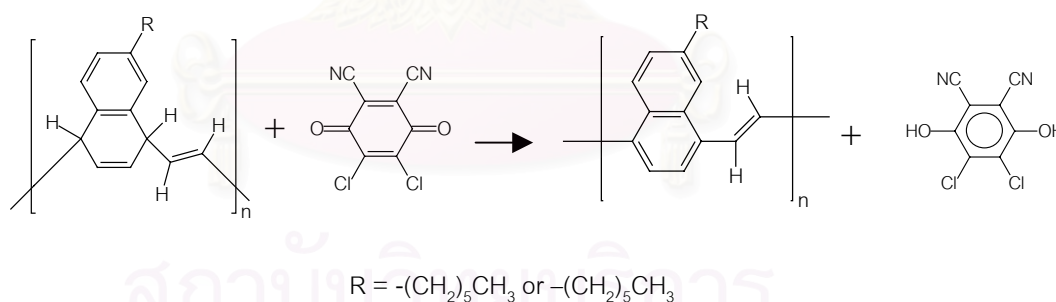


Figure 3.3: Oxidation of alkyl-substituted poly(1,4-naphthylenevinylenes).

Vannikov et al. performed model experiments in which polar o- and m-dinitrobenzenes (DNBs) were added to polystyrene molecularly doped with TPA in 1989 (16). The authors found that the orientation and hole mobility of polystyrene were affected by DNB and TPA used as dopants. In 1991, Oshita et al. found that

organosilicon polymer treated with antimony pentafluoride vapor as a dopant gave conducting thin films with conductivities in the range 1-10 S/cm (17).

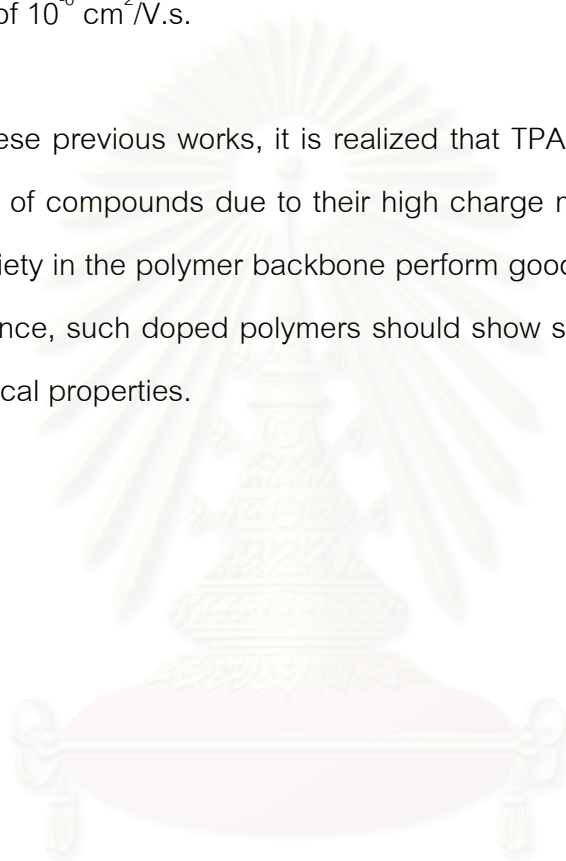
As a consequence, some reports showed that polymers doped with TPA derivatives provided good electrical and electrochemical properties (18-20). The hole mobility in PVK, which has been exclusively used as a photoconducting polymer, was $5 \times 10^{-7} \text{ cm}^2/\text{V}\cdot\text{s}$ at an electric field of $2 \times 10^5 \text{ V/cm}$ and it was lower than that of the materials molecularly doped with TPA derivatives.

Thereafter, during 1995 to 1997, many researchers investigated on the preparation of TPA derivative monomers and their polymers to introduce TPA unit into the polymer backbone (21-26). Son et al. reported on synthesis of polymer for HTM and ETM in organic electroluminescent devices in 1997 (27). Synthetic route of TPD-Styrene or TPD-ST monomer and its polymer is shown in Figure 3.5. This polymer film showed good stability and sufficient morphological stability. Electroluminescent device used this polymer as hole transporting layer (HTL) provided current density higher than 100 mA/cm^2 and emitted luminescence about 10 cd/m^2 when oxadiazole-styrene polymer was used as electron transporting layer (ETL).

Another attempt was the preparation of HTMs by condensation reaction of TPA with carbonyl compounds and paraformaldehyde (FA) in the presence of acid catalyst by Son et al. (28-29) It was found that TPA was reacted with carbonyl compounds such as formaldehyde, butyraldehyde, benzaldehyde and acetone using *p*-toluenesulfonic acid as an acidic catalyst. TPA condensation provided high molecular weight polymers. For the condensation of TPA derivatives such as TDPA and *N,N'*-diphenyl-*N,N'*-di(4-methylphenyl)-1,4-phenylenediamine (PDA) with paraformaldehyde (FA) under the same catalyst, it was found that TDPA and PDA

units were linked not only by methylene linkages but also methylene ether linkages. Additionally, the number of methylene ether linkage was increased with the increasing of concentration of FA. These polymers showed sufficient morphological stability after the film formation and the hole drift mobility of PDA-FA was found in the magnitude of $10^{-6} \text{ cm}^2/\text{V.s}$.

From these previous works, it is realized that TPA derivatives constitute an important class of compounds due to their high charge mobility and the polymers having TPA moiety in the polymer backbone perform good charge transport ability. As a consequence, such doped polymers should show some interesting electrical or electrochemical properties.



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CHAPTER 4

EXPERIMENTAL

4.1 CHEMICALS

Diphenylamine	<i>p</i> -Toluenesulfonic acid
N,N-diphenylbenzidine	Liquid nitrogen
4-Bromotoluene	Xylene
Sodium tert-butylate (t-BuONa)	Hexane
Tri(tert-butylate) phosphine (P-(t-Bu) ₃)	Toluene
Palladium (II) acetate (Pd(OCOCH ₃) ₂)	Chloroform
Benzaldehyde (BzA)	Acetone
Lithium perchlorate (LiClO ₄)	Chlorobenzene
Tetraethylammonium perchlorate (Et ₄ NClO ₄)	Tetrahydrofuran
Tetrabutylammonium perchlorate (Bu ₄ NClO ₄)	Methanol
Nitrosonium tetrafluoroborate (NOBF ₄)	Chloroform- <i>d</i> / TMS
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)	

4.2 LABORATORY GLASSWARE

2-neck flask	Column	Condenser	Slide glass
Pair-shape flask	Adapter	Glass ampoule	Glass bar
Volumetric flask	Funnel	Volumetric flask	Beaker
Separating funnel	Beaker	Suction flask	Thermometer
Perpendicular disk			

4.3 APPARATUS AND INSTRUMENT

NMR: JEOL α -500 spectrometer operating at 500 MHz

IR: Jasco FT/IR-5300

GPC: Jasco 880-PU pump

Column packed with styrene-divinylbenzene gel beads

Jasco UV-970 detector.

DSC: Rigaku Thermo plus DSC 8230

ESR: JEOL JES-FA series

UV: Jasco-Ubest-30 UV-VIS spectrometer

CV: One-compartment cell with a polarization unit (Toho PS-06)

Platinum electrode

Platinum spiral electrode

Ag/AgCl electrode

Conductivity: Cell

Oscilloscope

Palletizer

4.4 SYNTHESIS OF MONOMER

The triphenylamine derivative monomers, i.e., 4-tolyldiphenylamine (TDPA) and *N, N'*-diphenyl-*N, N'*-bis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) were prepared from Tosoho method (1).

4.4.1) TDPA MONOMER

A 300-ml two-neck flask fitted with a mechanical stirrer and a condenser was charged with 30.46 g (180 mmole) of diphenylamine, 30.79 g (180 mmole) of 4-bromotoluene, 51.90 g (540 mmole) of sodium tert-butyrate, 0.04 g (0.18 mmole) of palladium (II) acetate, 4.5 ml (0.45 mmole) of 0.1 M tri-tert-butylphosphine. The reaction mixture was stirred and heated at 120 °C for 4 hours using 130 ml of xylene as a solvent and then cooled down. After cooling, 120 ml of water was added into the reaction mixture then well stirred for 20 minutes. To remove unreacted reactants, the reaction mixture was poured into a separating funnel and the organic layer was collected. Then, the organic layer was evaporated to remove the solvent. After that thin layer chromatography (TLC) was obtained to observe all components include TDPA in the crude product. Consequently, the crude product was purified by column chromatography using silica gel as a packing material and toluene:hexane in the ratio of 1:3 as an eluent. The eluate containing TDPA was evaporated, thereafter, and 100 ml of ethanol was added for precipitation. Then the precipitate was purified by reprecipitation from ethanol, followed by drying in vacuum for 24 hours.

4.4.2) TPD MONOMER

In the same manner, TPD was prepared from *N, N'*-diphenyl-1,4-diphenylenediamine instead of diphenylamine as describe in section 4.4.1.

A 500-ml two-neck flask fitted with a mechanical stirrer and a condenser was charged with 60.56 g (180 mmole) of *N, N'*-diphenyl-1,4-diphenylenediamine, 67.74 g (396 mmole) of 4-bromotoluene, 51.90 g (540 mmole) of sodium tert-butylate, 0.04 g (0.18 mmole) of palladium (II) acetate, 7.2 ml (0.72 mmole) of 0.1 M tri-tert-butylphosphine. The reaction mixture was stirred and heated at 120 °C for 4 hours using 200 ml of xylene as a solvent and then cooled down. After cooling, 180 ml of water was added into the reaction mixture then well stirred for 20 minutes. To remove unreacted reactants, the reaction mixture was poured into a separating funnel and the organic layer was collected. Then, the organic layer was evaporated to remove the solvent. After that TLC was obtained to observe all components include TPD in the crude product.

The crude product was purified by column chromatography using silica gel as a packing material and toluene:hexane in the ratio of 1:1 as an eluent. The eluate containing TPD was evaporated, thereafter, and 100 ml of ethanol was added for precipitation. Then the precipitate was purified by reprecipitation from ethanol, followed by drying in vacuum for 24 hours.

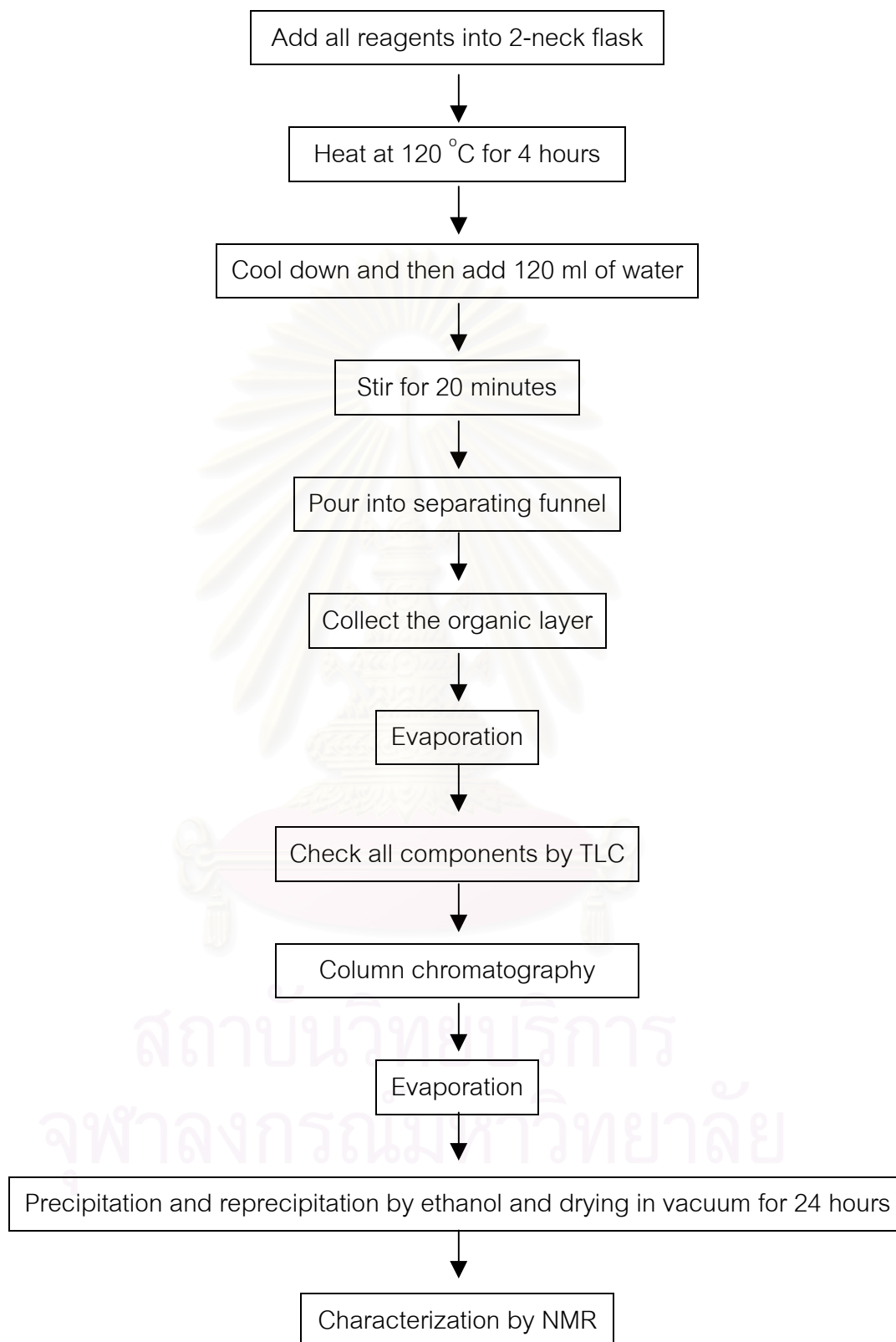


Figure 4.1: Diagram for synthesis of the monomers.

4.5 SYNTHESIS OF POLYMER

TDPA or TPD monomer was polymerized with benzaldehyde (BzA) in chlorobenzene in the presence of *p*-toluenesulfonic acid.

4.5.1) TDPA-BzA POLYMER

0.6484 g (2.50 mmole) of TDPA and 0.3184 g (3.00 mmole) of BzA were added into a glass ampoule, then vacuumed and purged nitrogen gas for three times. After that, 1.50 ml of chlorobenzene and 0.0190 g (0.11 mmole) of *p*-toluenesulfonic acid were added into a glass ampoule, respectively. Then, the glass ampoule was suddenly sealed with a flame and heated at 110 °C for 480 minutes. The polymer was recovered by pouring the reaction mixture into the large amount of acetone and adding 2 drops of ammonia solution. The mixture was stirred for one hour then filtered and purified by reprecipitating the polymer solution in chloroform from acetone, followed by drying in vacuum for 24 hours. After that, TDPA-BzA polymerizations were followed as shown the conditions in Table 4.1.

4.5.2) TPD-BzA POLYMER

In the same way, TPD was polymerized with BzA in the mole ratio of 1:1.2 using 4 mole% of total monomers of *p*-toluenesulfonic acid. The polymerization mixture was heated at 120 °C for 90 minutes.

Table 4.1: The reaction conditions for synthesis of TDPA-BzA polymer.

No.	TDPA:BzA (mole ratio)	TDPA (mmole)	BzA (mmole)	Total monomers (mmole)	p-toluenesulfonic acid		Reaction temp. (°C)	Reaction time (min)
					mole% of total monomers	mmole		
1.	1:1.2	2.50	3.00	5.50	2	0.11	110	480
2.	1:1.2	2.50	3.00	5.50	4	0.22	110	480
3.	1:1.2	2.50	3.00	5.50	4	0.22	110	90
4.	1:1.5	2.50	3.75	6.25	4	0.25	110	90
5.	1:1.5	2.50	3.75	6.25	4	0.25	110	50
6.	1:1.2	2.50	3.00	5.50	4	0.22	120	90
7.	1:1.2	2.50	3.00	5.50	4	0.22	120	60

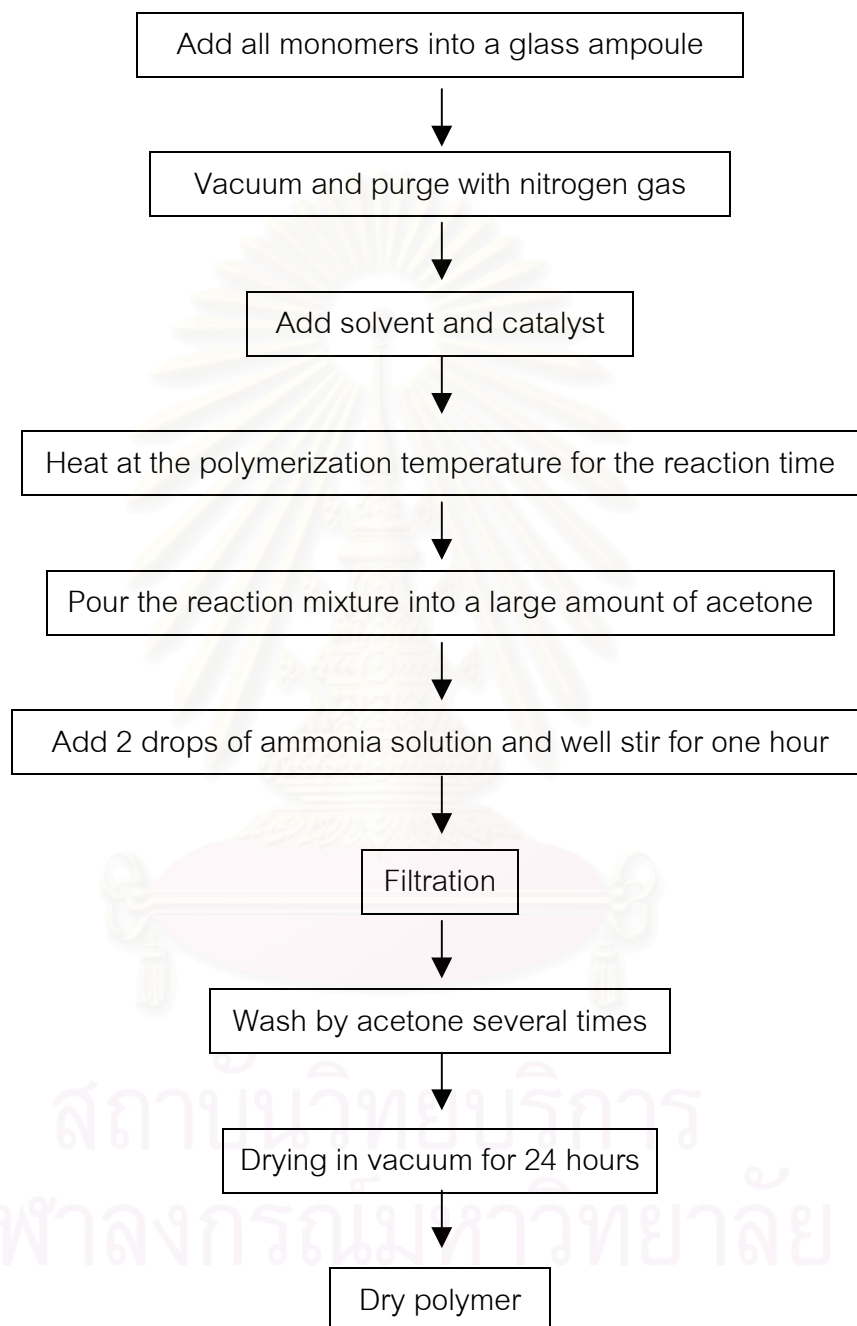


Figure 4.2: Diagram for synthesis of the polymers.

4.6 DOPING

4.6.1) DOPING OF POLY(VINYLCARBAZOLE)

4.6.1.1) IONIC COMPOUNDS

5 mg/0.3 ml of lithium perchlorate (LiClO_4) in tetrahydrofuran (THF) was added into the chlorobenzene solution of poly(vinylcarbazole) (PVK) with the concentration of 95 mg/0.7 ml. The mixture solution was well stirred in a sample container with a cap at room temperature for an hour. The doped PVK film was prepared by using a glass bar and coated on a slide glass.

In similar manner, tetraethylammonium perchlorate (Et_4NClO_4) and tetrabutylammonium perchlorate (Bu_4NClO_4) were doped into PVK by 5-10 %wt.

4.6.1.2) OXIDANTS

0.0556 g of nitrosonium tetrafluoroborate (NOBF_4) was added into the THF solution of PVK in the concentration of 0.5000 g/5 ml. The reaction mixture was well stirred in a sample container with a cap at room temperature for 24 hours. The polymer was recovered by pouring the mixture into a large amount of methanol then well stirring for one hour, followed by filtrating, washing with a large amount of methanol several times and drying in vacuum for 24 hours.

PVK was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at the mole ratio of PVK:DDQ of 2:0.19 and 2:1.2 by the same way.

4.6.2) OXIDATION OF THE POLYMERS

0.0556 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added into the THF solution of TDPA-BzA polymer in the concentration of 0.5000 g/5 ml. The reaction mixture was well stirred in a sample container with a cap at room temperature for 24 hours. The polymer was recovered by pouring the mixture into a large amount of methanol then well stirring for one hour, followed by filtrating. The polymer was washed with a large amount of methanol several times or until the colorless of the solution from washing could be observed, after that the resulting polymer was dried in vacuum for 24 hours.

In the same way, TDPA-BzA and TPD-BzA polymers were oxidized with DDQ at various conditions as shown in Table 4.2.

Table 4.2: The conditions for oxidation of the polymers with DDQ.

Polymer	Reaction time (hrs)	Amount of DDQ (%wt)	Polymer:DDQ (mole ratio)
TDPA-BzA	24 or 36	0	2:0.00
		10	2:0.34
		20	2:0.77
		30	2:1.31
		40	2:2.04
TPD-BzA	36	0	2:0.00
		10	2:0.59
		15	2:0.94
		20	2:1.33
		30	2:2.28

4.7 CHARACTERIZATION

4.7.1) STRUCTURE OF SYNTHESIZED COMPOUNDS

To determine the structures of all synthesized compounds, $^1\text{H-NMR}$ spectra were recorded using a JEOL α -500 spectrometer operating at $50\text{ }^\circ\text{C}$. Samples were dissolved in chloroform-*d* (CDCl_3) containing a small amount of tetramethylsilane (TMS) as an internal standard.

4.7.2) DETERMINATION OF MOLECULAR WEIGHT

The molecular weight of polymer was determined by gel permeation chromatography (GPC) using a JASCO 880-PU pump, a column packed with styrene-divinylbenzene gel beads and a JASCO UV-970 detector. The measurement was carried out using 0.01 g/ml of polymer in chloroform, which was used as an eluent also and the molecular weight was calibrated using polystyrene standards (Shodex).

4.7.3) DETERMINATION OF GLASS TRANSITION TEMPERATURE

Glass transition temperature (T_g) was measured by differential scanning calorimeter (DSC) technique on a Rigaku Thermo plus DSC 8230 at the temperature-increasing rate of 10 K/min.

4.8 MEASUREMENT

4.8.1) IR SPECTROSCOPY

FT-IR spectra were obtained from a Jasco FT/IR 5300 spectrometer. The chloroform solution of sample in the concentration of 0.25 mg/ml was used to prepare a film on NaCl disk.

4.8.2) UV-VISIBLE SPECTROSCOPY

UV-vis spectra were obtained by a Jasco-Ubest-30 UV-VIS spectrometer using the chloroform solutions of polymers with the concentration of 0.0125 mg/ml.

4.8.3) ELECTRON SPIN RESONANCE

Electron spin resonance (ESR) spectra were carried out on a JEOL JES-FA series using the chloroform solution of the completely oxidized polymers in the concentration of 10 mg/ml. ESR measurement was operated at the frequency of 9.43 GHz under nitrogen atmosphere.

4.8.4) ELECTROCHEMICAL PROPERTY

The oxidation potential was calculated from cyclic voltamogram. CV carried out on a one-compartment cell with a polarization unit (TOHO PS-60) using 0.1 M of tetrabutylammonium perchlorate (Bu_4NClO_4) in dry acetonitrile as an electrolyte under nitrogen atmosphere using 20 mg/ml of the polymer in chloroform. The sample solution was casted on a platinum-working electrode. Platinum spiral was used as a counter electrode and Ag/AgCl as a reference electrode.

4.8.5) ELECTRICAL PROPERTY

Conductivity was measured by direct current method using the polymer pellet with the diameter of 1 cm. The sample was applied voltage in the range of 200-1000 volt. The signal was observed on an oscilloscope and transferred to a personal computer to calculate the output value. Figure 4.3 shows the schematic diagram for conductivity measurement in the research.

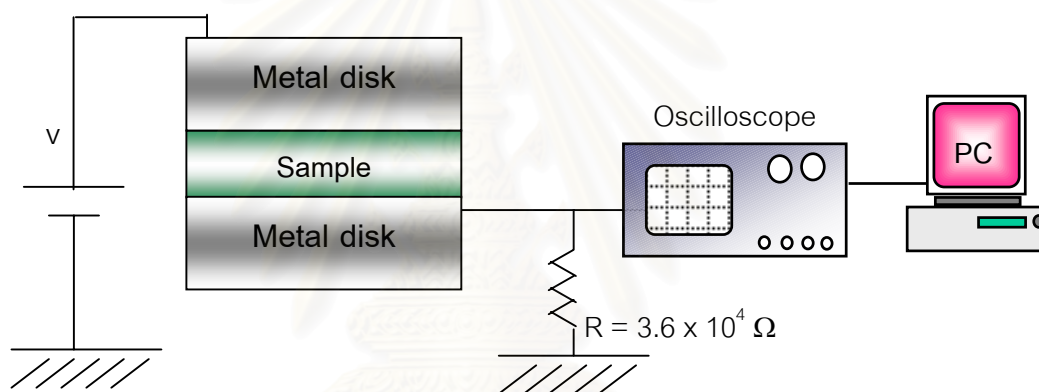


Figure 4.3: A schematic diagram for measurement of conductivity.

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CHAPTER 5

RESULTS AND DISCUSSION

5.1 SYNTHESIS AND CHARACTERIZATION OF MONOMERS

In some other previous works, 4-tolyldiphenylamine (TDPA) and *N,N'*-diphenyl-*N,N'*-bis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) were prepared from Ullmann reaction starting from diphenylamine and *N,N'*-diphenylbenzidine, respectively by reacting with 4-iodotoluene, anhydrous potassium carbonate, copper (I) iodide and 18-crown-6 as a phase transfer catalyst (23, 27, 29-30, 31).

However, Ullmann reaction needed a long sequence of reaction steps and consequently gave low yield. In this work, the synthesis of both monomers was followed Tosho method, which was found that it required the shorter procedures and gave the higher yield.

5.1.1 TDPA MONOMER

TDPA monomer was prepared from diphenylamine and 4-bromotoluene in xylene by Tosho method as shown in Figure 5.1 (1). The reaction was stirred at 120 °C for 4 hours or until diphenylamine completely reacted as verified by TLC, the R_f value of diphenylamine of 0.54 using toluene:hexane in the ratio of 1:3 as an eluent while TDPA appeared R_f value at 0.71.

After purification by column chromatography and reprecipitation, TDPA could be obtained in white solid with 75% yield. It was soluble in conventional organic solvents such as chloroform, and chlorobenzene.

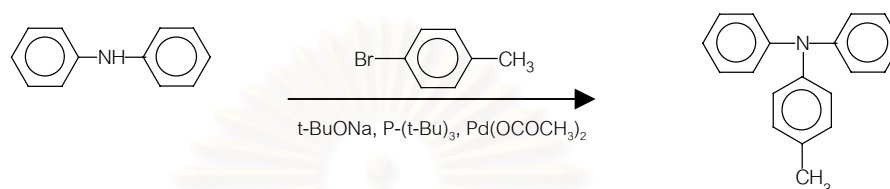


Figure 5.1: Synthesis of TDPA monomer via Tosho method.

$^1\text{H-NMR}$ spectroscopic technique was used to characterize the structure of the monomers in chloroform-d (CDCl_3). Its $^1\text{H-NMR}$ spectrum (Figure 5.2) showed the signal at δ 2.3 ppm (s, 3H), which was assigned to protons in $-\text{CH}_3$ group. The signal at δ 6.9-7.3 ppm (m, 14H) indicated the presence of the aromatic protons.

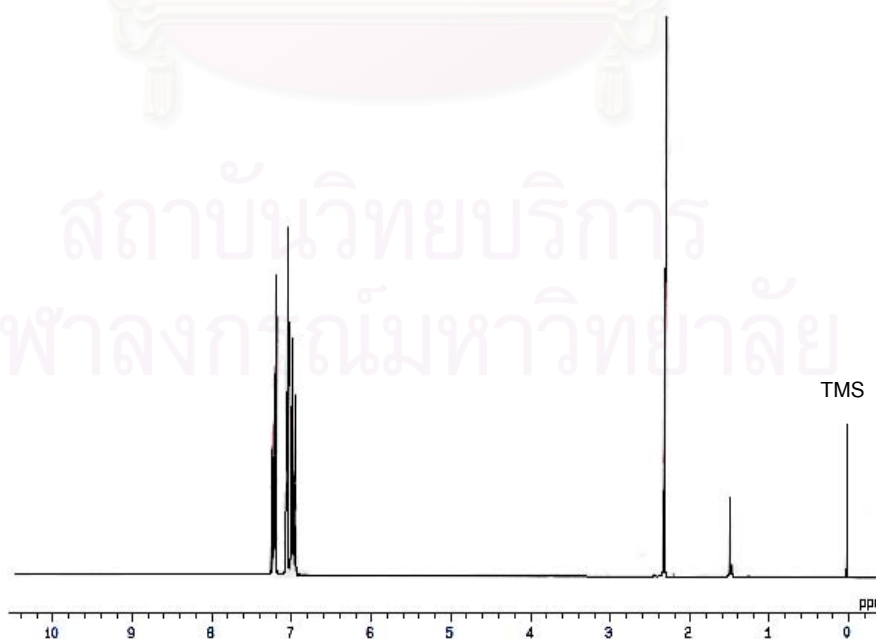


Figure 5.2: $^1\text{H-NMR}$ spectrum of TDPA monomer (CDCl_3/TMS).

5.1.2 TPD MONOMER

In the same manner, TPD monomer was prepared from *N,N'*-diphenylbenzidine and 4-bromotoluene in the ratio of 1:2 in xylene as in Figure 5.3.

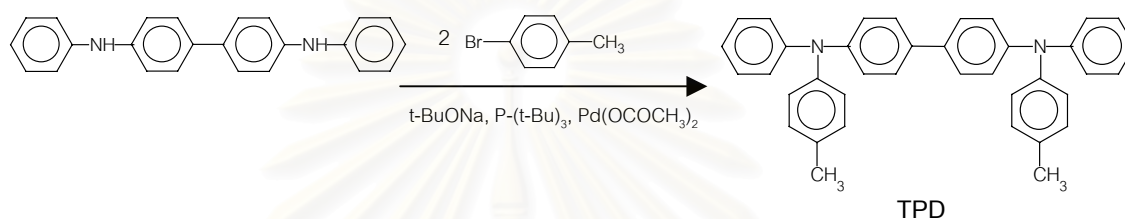


Figure 5.3: Synthesis of TPD monomer via Tosho method.

The reaction was stirred at 120 °C for 4 hours or till the absence of *N,N'*-diphenylbenzidine as verified by TLC, which showed the R_f of *N,N'*-diphenylbenzidine of 0.45 using toluene:hexane in the ratio of 1:2 as an eluent while TPD gave R_f of 0.75. After purification by column chromatography and reprecipitation, TPD could be obtained in white solid with 90% yield. It was soluble in conventional organic solvents such as chloroform, and chlorobenzene.

$^1\text{H-NMR}$ spectroscopic technique was used to confirm the structure of TPD monomer in the same condition for the measurement of TDPA monomer. Its $^1\text{H-NMR}$ spectrum (Figure 5.4) exhibited the signals at δ 2.3 ppm (s, 6H) and δ 6.9-7.45 ppm (m, 26H), which were assigned to the protons in $-\text{CH}_3$ group and aromatic protons, respectively.

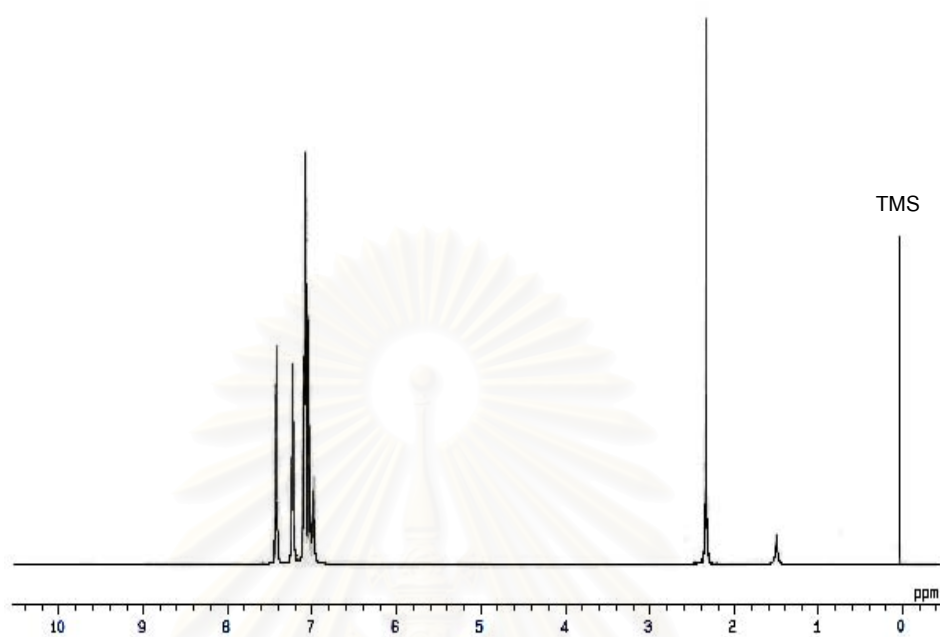


Figure 5.4: ^1H -NMR spectrum of TPD monomer (CDCl_3/TMS).

5.2 SYNTHESIS OF POLYMERS

In other work by Son et al., TPD was successfully polymerized with benzaldehyde (BzA) to obtain the linear polymer at the best condition (30). TPD-BzA polymer could reach the high molecular weight (Mw) of 3.22×10^5 .

In this work, the polymerization of TDPA with BzA was investigated. Then, the properties of TDPA-BzA polymer was compared with TPD-BzA prepared in this research work.

5.2.1) TDPA-BzA POLYMER

TDPA was polymerized with BzA in chlorobenzene in the presence of *p*-toluenesulfonic acid as a catalyst. The polymerization is shown in Figure 5.5. The optimum polymerization condition was determined by varying the monomer ratio, the amount of catalyst, the reaction temperature and the reaction time.

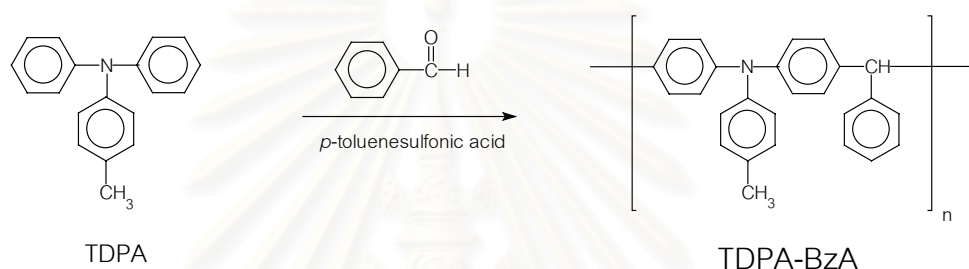


Figure 5.5: Polymerization of TDPA-BzA polymer.

The monomer ratio was varied in the range of 1:1.2 to 1:1.5 and the amount of catalyst was used at 2 and 4 mole% of total mole of monomers. The polymerization was carried out at 110 and 120 °C in the range of 50 to 480 hours for the reaction time. Table 5.1 shows all the conditions of TDPA-BzA polymerization.

The polymerization mixture of TDPA-BzA became dark green when heated, which indicated that TDPA was protonated. The color vanished after a few drops of ammonia solution was added into the reaction mixture. TDPA-BzA polymer was obtained as white powder and could be soluble in conventional organic solvents such as chloroform and tetrahydrofuran (THF). Table 5.1 shows yield, Mw and other characteristics of polymers obtained at various conditions.

Table 5.1: Polymerization conditions and molecular weights of TDPA-BzA polymer.

No.	TDPA:BzA	Catalyst (mole%)	Reaction Temp. (°C)	Reaction Time (min)	Yield (%)	Mn ^a (x10 ⁻³)	Mw ^a (x10 ⁻³)	PDI ^a
1.	1:1.2	2	110	480	85	10	203	20
2.	1:1.2	4	110	480	92(18) ^b	14	305	22
3.	1:1.2	4	110	90	75	5.5	64	8
4.	1:1.5	4	110	90	(99)	-	-	-
5.	1:1.5	4	110	50	70	4.3	48	11
6.	1:1.2	4	120	90	(99)	-	-	-
7.	1:1.2	4	120	60	91	15	311	21

^a Estimated values by GPC using chloroform as an eluent (polystyrene standards).

^b Value in the parenthesis indicates the gel portion.

5.2.1.1) EFFECT OF AMOUNT OF CATALYST

TDPA was polymerized with BzA in the monomer ratio of TDPA:BzA of 1:1.2 at 110 °C for 480 minutes at the two amounts of catalyst; 2 mole% and 4 mole% (batch No. 1 and No. 2). It was found that the polymerization at 4 mole% of catalyst gave the higher Mw than at 2 mole%. Consequently, the polymer at 4 mole% of catalyst could be recovered with the higher yield than at 2 mole% because of its higher weight, which is more quantitatively collected when filtration.

However, the high Mw of polymer from batch No. 2 gave a portion of insoluble gel about 18% due to the entanglement of some segments of the polymer chain, which supported an increasing in the viscosity of the polymer mixture, which consequently formed the insoluble polymer (so-called gel). However, the gel could be eliminated by reducing of the reaction time as shown in batch No.3 that gave low Mw because of too short reaction time.

5.2.1.2) EFFECT OF MONOMER RATIO

The polymerization at 4 mole% of catalyst showed the more better results than at 2 mole%, therefore, the monomer ratio of TDPA:BzA was increased from 1:1.2 to 1:1.5 in order to study the effect of the monomer ratio. The polymerization was investigated at 110 °C for 90 minutes in batch No. 4.

It was found that the polymerization mixture totally became gel due to the over optimum reaction time, at which the viscosity of mixture was greatly increased by the entanglement of the polymer chain. However, low Mw was obtained form batch No.5 that was reduced the reaction time from 90 to 50 minutes in order to

control the formation of gel. It is known that the condensation polymerization with the greatly difference from stoichiometric equivalence of monomers led the increasing of oligomer formation, which performed the low-Mw polymer and low yield, consequently.

5.2.1.3) EFFECT OF REACTION TEMPERATURE

In any case, the polymer with low Mw and yield still was obtained, though, the monomer ratio was already varied. Therefore, the reaction temperature became an important factor to increase the Mw of polymer. The polymerization with the monomer ratio of TDPA:BzA of 1:1.2 at 4 mole% of catalyst for 90 minutes was carried out with increasing in the reaction temperature from 110°C to 120°C (batch no.3 and no.6). It was found that all polymerization mixture became gel due to the over optimum reaction time.

However, the TDPA-BzA polymer with high Mw and yield could be obtained from the batch No. 7 using the monomer ratio of TDPA:BzA of 1:1.2 and 4 mole% of catalyst at 120 °C for 60 minutes.

5.2.1.4) EFFECT OF REACTION TIME

It is known that long reaction time was essential for obtaining high Mw from condensation polymerization in order to increase the chance of polymerization of oligomer to produce high Mw. However, too long reaction time led to the gel formation. This was observed in batch No. 2, 4 and 5. On the other hand, at too short reaction time, it gave the polymer with low Mw and yield.

5.2.2 TPD-BzA POLYMER

In the same manner, TPD-BzA polymer could be prepared in chlorobenzene using *p*-toluenesulfonic acid as a catalyst. The polymerization was performed at the same condition as for reported by Son et al. (30).

TPD was reacted with BzA at the mole ratio of TPD to BzA of 1:1.2. The polymerization was carried out at 120 °C using catalyst 4 mole% of total monomers for 90 minutes.

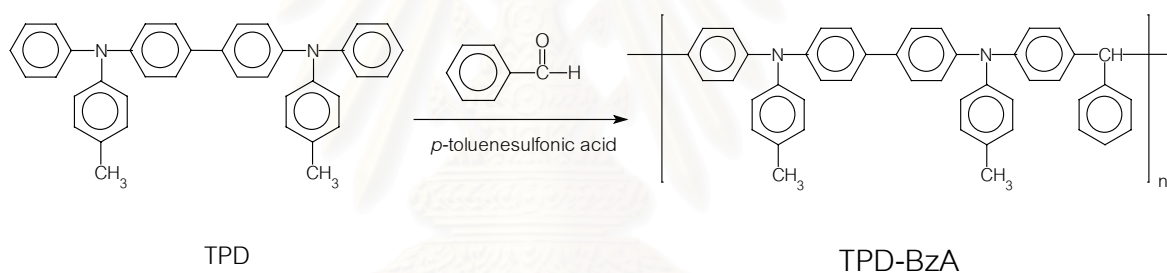


Figure 5.6: Polymerization of TPD-BzA polymer.

TPD-BzA polymer was obtained as pale green powder with 98% yield. It had Mw of 3.20×10^5 and could be soluble in general organic solvents such as chloroform, toluene and THF.

5.3 CHARACTERIZATION OF POLYMERS

$^1\text{H-NMR}$ spectroscopic technique was used to confirm the structure of the polymers, whose spectra were recorded at $50\text{ }^\circ\text{C}$.

5.3.1 TDPA-BzA POLYMER

Since TDPA-BzA polymer has three types of protons in the repeating unit, therefore, its $^1\text{H-NMR}$ spectrum exhibited the signals in three regions. The signal at δ 2.24 ppm (3H), which was assigned to protons in methyl ($-\text{CH}_3$) group and the signal at δ 5.35 ppm (1H) of methine ($-\text{CH}$) proton due to benzaldehyde part. The signal in the range of δ 6.90-7.30 ppm (18H) indicated the aromatic protons.

Accordingly, Figure 5.7 shows the $^1\text{H-NMR}$ spectrum of TDPA-BzA polymer.

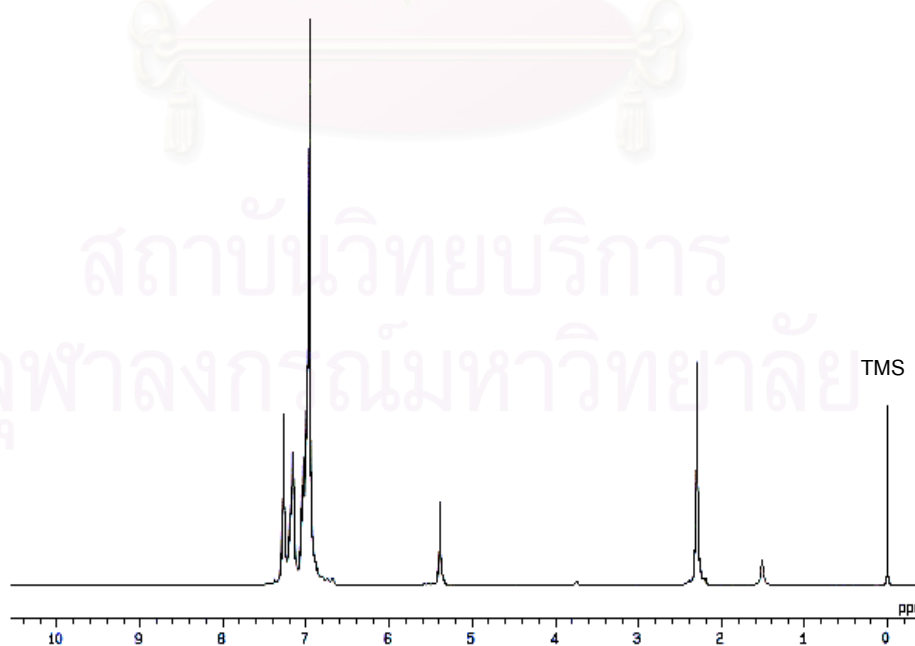


Figure 5.7: $^1\text{H-NMR}$ spectrum of TDPA-BzA polymer (CDCl_3/TMS).

5.3.2 TPD-BzA POLYMER

The repeating unit of TPD-BzA polymer is similar to TDPA-BzA polymer. Therefore, TPD-BzA polymer also exhibited the $^1\text{H-NMR}$ signals as shown in Figure 5.8 in the same three regions as TDPA-BzA polymer.

The signal at δ 2.24 ppm (6H) was assigned to protons in methyl group and the signal of methine proton was observed at δ 5.40 ppm (1H). The signal in the range of δ 6.90-7.45 ppm (29H) was interpreted for the aromatic protons. Accordingly, $^1\text{H-NMR}$ spectroscopy confirmed the structure of TPD-BzA polymer.

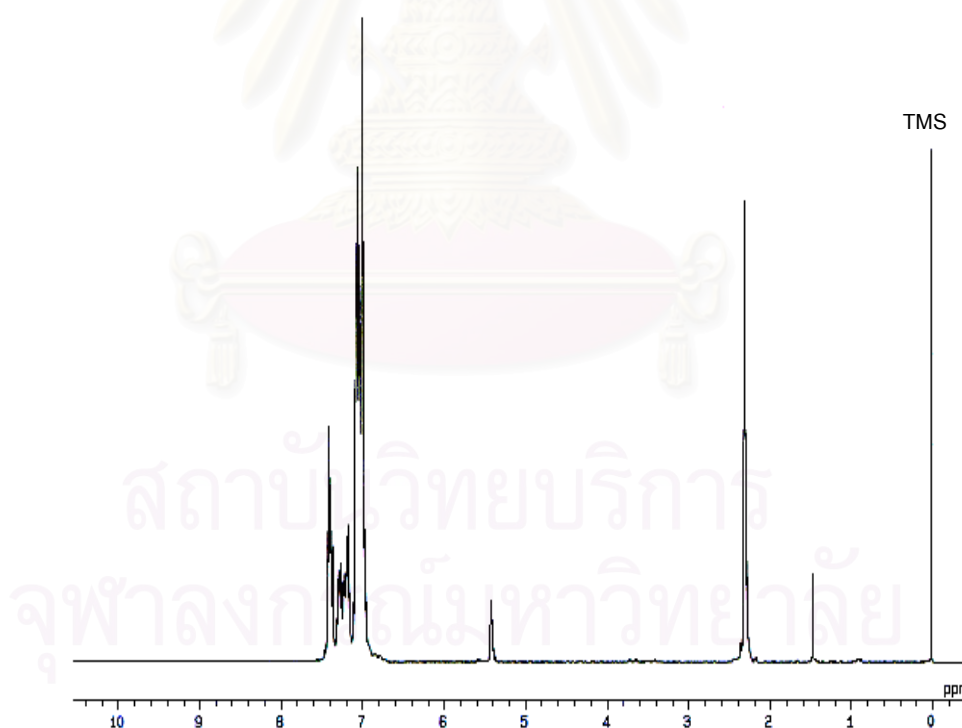


Figure 5.8: $^1\text{H-NMR}$ spectrum of TPD-BzA polymer (CDCl_3/TMS).

5.4 DOPING OF POLY(VINYLCARBAZOLE)

It is known that PVK has been widely used as a commercial polymer in photoconductive application. In some previous works, the performance of their devices was illustrated in comparison with PVK (18-20, 23).

Therefore, in this study, PVK was used as a polymer model to preliminarily investigate for the effective dopant, which would then be introduced to incorporate in TDPA-BzA and TPD-BzA later.

PVK was doped with two types of dopants, i.e., ionic compound and oxidant. All dopants in this research are commercially available and were used without further purification.

5.4.1) IONIC COMPOUNDS

Ionic compound has been normally used to enhance the electrochemical characteristics of polymer (10, 31-33). Bobacka et al. found that poly (3-octylthiophene) doped with LiClO_4 , LiBF_4 and LiPF_6 exhibited the higher conductivity than undoped poly (3-octylthiophene) around 2 orders of the magnitude (32).

In this work, the electrochemical property would be revealed by cyclic voltammetry (CV), which required the film of sample on the working electrode. Therefore, it was necessary to mix the dopant into polymer solution and the solvent had to be removed completely after film formation on a slide glass.

PVK was doped with the following ionic compounds; lithium perchlorate (LiClO_4), tetraethylammonium perchlorate (Et_4NClO_4), tetrabutylammonium perchlorate (Bu_4NClO_4). All ionic compounds were mixed into PVK by 5-10 %wt as shown in Table 5.2.

Table 5.2: PVK doped with ionic compounds.

Doping Level (%wt)	PVK ^(a) (mg)	Ionic Compound ^(b) (mg)	Film Appearance
10	90	10	Rough
5	95	5	Rough

(a) Soluble in chlorobenzene 0.7 ml

(b) Soluble in THF 0.3 ml

After well stirring at room temperature for an hour, the mixture solution was casted on a slide glass using a glass bar.

After drying at room temperature for an hour, it was found that all the doped polymers gave film with rough surface. It was found that the ionic compounds agglomerated and separated from the polymer matrix and cracked into pieces.

Therefore, this type of dopant was not suitable to dope into PVK.

5.4.2) OXIDANTS

Oxidant is also the one type of dopants. It showed an important role in the electrochemical and especially in electrical property of polymers, e.g., conductivity (13-15, 33-35). However, the oxidant in some previous works was used for the oxidative polymerization and the polymers showed good electrical property (9, 11-13).

In this work, PVK was reacted with two types of oxidant, i.e., nitrosonium tetrafluoroborate (NOBF_4) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as shown in Table 5.3. The reaction was carried out in a sample container with a cap at room temperature for 24 hours using THF as a solvent.

After adding NOBF_4 or DDQ to the PVK solution, the colorless solution suddenly became green due to partial oxidation and then dark green when the oxidation was completed as excess amount of DDQ was added. The resulting PVK was recovered by pouring the reaction mixture into a large amount of methanol.

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Table 5.3: Oxidation conditions of PVK.

Oxidation level	Polymer:Dopant (mole ratio) ^(a)	Solution color	Precipitation	Polmer in solution	Polymer color	Solubility
Partially Oxidation	PVK:NOBF ₄ ^(b) = 1:0.01	Green	72%	-	Green	Slight soluble in CHCl ₃
	PVK:DDQ ^(c) = 2:0.19	Green	-	89%	Pale green	CHCl ₃ , THF
Completely Oxidation	PVK:DDQ = 2:1.2	Dark Green	-	93%	Light green	CHCl ₃ , THF

(a) mole of repeating unit of PVK : mole of dopant

(b) Theoretical mole ratio; 1:1

(c) Theoretical mole ratio; 2:1

In the case of NOBF_4 , the precipitate was collected by centrifugation, then pouring the residue solution into a large amount of methanol, in which no precipitation could be observed. Partial oxidation with NOBF_4 gave precipitate having very poor solubility while the oxidation with DDQ gave the soluble PVK though using the excess amount of DDQ. PVK after doping has changed from white to green solid.

In any case, the color change might come from two cases; chemical reaction and complex formation between polymer and dopant. In the first case, chemical reaction, after washing the doped polymer with methanol, color of solid still remains. For the latter, color of solid was disappeared by washing by methanol. The precipitation during doping in the case of partially oxidation of NOBF_4 might refer to the gel bonding between polymer and dopant in two cases. One is chemical bonding (primary bonding) between the functional group of polymer and the dopant. This bond will give the strong gel, which can not dissolve in general solvent such as chloroform or THF. The other case is the weak gel or physical complex, which takes place from the secondary bonding between a part of polymer chain and dopant.

These results indicated that the reaction of PVK with both oxidants was proceeded. However, the oxidation of NOBF_4 gave the insoluble precipitate, from which the film could not be prepared so that its electrochemical and electrical properties could not be investigated. Therefore, DDQ was an effective dopant and suitable for oxidizing TDPA-BzA and TPD-BzA polymers.

5.5 OXIDATION OF THE POLYMERS WITH DDQ

Polymer could be developed the structure of repeating unit to improve its property, e.g., electrochemical and electrical properties. In some other previous works, the conductivity of polymers was increased 2 orders of magnitude higher than the starting polymers by oxidation with DDQ (14-15).

It is believed that polymers with the structure allowing long electron delocalization on the main chain would show the good electrochemical and electrical properties. In this research, the oxidation of the polymers with DDQ might perform the effect on the structure of the repeating unit and their properties consequently. $^1\text{H-NMR}$ spectroscopic technique was used to verify the oxidation of the polymers with DDQ. $^1\text{H-NMR}$ measurement was operating at 50°C in CDCl_3 .

5.5.1) TDPA-BzA POLYMER

TDPA-BzA polymer with the acceptable properties from the polymerization in batch No. 7 was oxidized with DDQ.

5.5.1.1) PRELIMINARILY OXIDATION

In this experiment, TDPA-BzA was preliminary investigated for its reaction with DDQ. The reaction shown in Figure 5.9 indicates that one mole of DDQ is able to react with two repeating units of TDPA-BzA polymer. Partial oxidation of TDPA-BzA polymer with DDQ was carried out in a sample container with a cap using THF as a solvent at room temperature for 24 hours using 10 %wt of DDQ that equals to the mole ratio of TDPA:DDQ of 2:0.34.

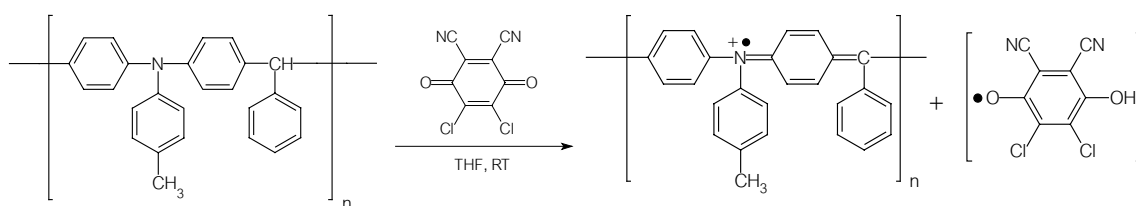
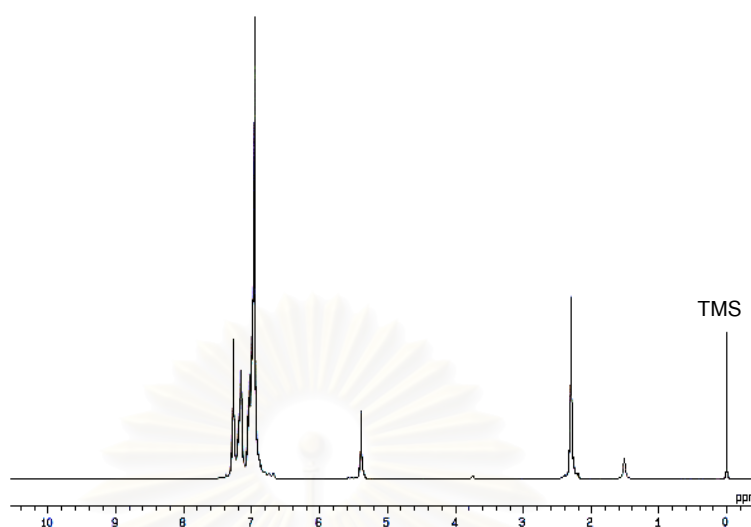


Figure 5.9: The oxidation of TDPA-BzA polymer with DDQ.

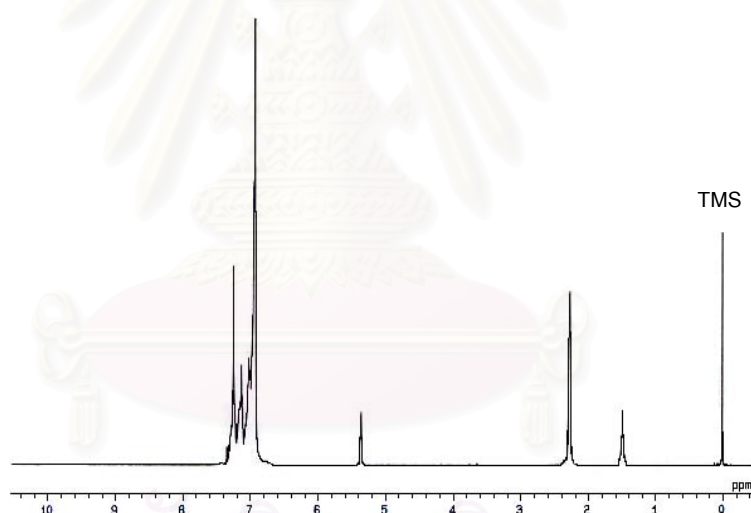
After adding DDQ to the polymer solution, the light yellow solution suddenly became dark green solution. The polymer was also soluble in the reaction mixture and no precipitation was observed. The resulting polymer was recovered by pouring the reaction mixture into a large amount of methanol as dark green solid with 88 %yield and could be soluble in chloroform, THF and slightly soluble in toluene and benzene.

The reaction was confirmed by $^1\text{H-NMR}$ spectrum of TDPA-BzA polymer before and after oxidation. The methine proton signal of TDPA-BzA polymer before oxidation was observed at δ 5.35 ppm. Therefore, the abstraction of methine proton could be verified by the decrease in the intensity of the signal at δ 5.35 ppm and measured from the intensity of the signal of methine proton at δ 5.35 ppm relative to the signal of methyl protons at δ 2.24 ppm.

Figure 5.10 (b) shows the $^1\text{H-NMR}$ spectrum of the partially oxidized TDPA-BzA polymer. The signal at δ 2.24 ppm and the signal in the range of δ 6.90-7.31 ppm were interpreted to the methyl and aromatic protons, respectively. The integration of the signal at δ 5.35 of such methine proton was decreased to 0.6790, which indicated that the methine proton of TDPA-BzA polymer was abstracted by oxidation with DDQ.



(a) Before oxidation



(b) After oxidation

Figure 5.10: ¹H-NMR spectrum of TDPA-BzA polymer (a) before and (b) after oxidation with 10%wt. of DDQ. (CDCl₃/TMS)

These results confirmed that DDQ was effective with TDPA-BzA polymer and DDQ would be effective with TPD-BzA polymer also because of its similar repeating unit.

5.5.1.2) THE INFLUENCE OF THE AMOUNT OF DDQ

As discussed above, the methine proton in the polymer chain was abstracted by oxidation with DDQ. It is expected that the amount of methine proton would be decreased by increasing the amount of DDQ and disappeared when oxidation with the excess amount of DDQ and that the protonation could generate the extended electron delocalized on the polymer chain.

Therefore, the polymer was reacted at various amounts of DDQ from partially to completely oxidation. TDPA-BzA polymer was oxidized with various amounts of DDQ from 10-40 %wt. in a sample container with a cap in THF at room temperature for 24 hours as the reaction time. Table 5.4 shows the oxidation conditions.

After adding DDQ to the polymer solution, the light yellow solution suddenly became dark green solution for partial oxidation and dark blue-green solution for completely oxidation. All the polymers were also soluble in the reaction mixture and no precipitation was observed. The resulting polymers were recovered almost quantitatively by pouring the reaction mixture into a large amount of methanol and could be soluble in chloroform, THF and slightly soluble in toluene and benzene.

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Table 5.4: The CH- proton remaining in TDPA-BzA polymers before and after oxidation at 24 hours of the reaction time.

Amount of DDQ (%wt)	Polymer:DDQ (mole ratio)	Polymer Color	Yield (%)	CH- proton remaining from $^1\text{H-NMR}$	
				Theoretical	Experimental
0	2:0.00	white	91	1.0000	1.0721
10	2:0.34	Dark green	88	0.6600	0.6796
20	2:0.77	Dark green	90	0.2300	0.2803
30	2:1.31	Dark green	89	0.0000	0.0920
40	2:2.04	Dark blue	91	0.0000	0.0913

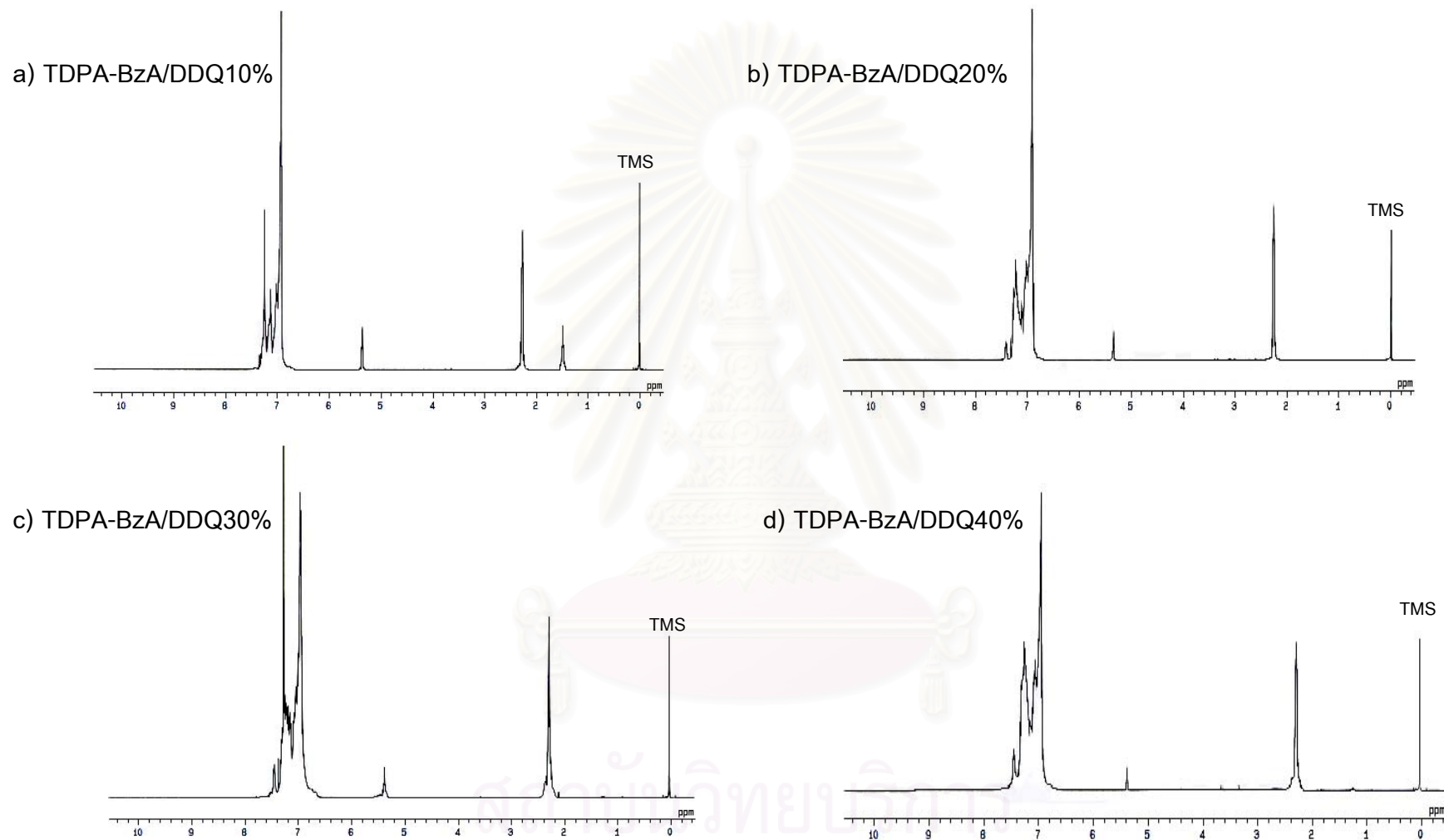


Figure 5.11: $^1\text{H-NMR}$ spectra of the oxidized TDPA-BzA polymer at 24 hrs of the reaction time (CDCl_3/TMS).

Figure 5.11 shows the $^1\text{H-NMR}$ spectra of the oxidized TDPA-BzA polymers at 24 hours of reaction time. Methyl protons of the oxidized polymers showed the same chemical shift of 2.24 ppm as the non-oxidized polymer but the signal of methyl protons became broader for the oxidation with excess amount of DDQ. Aromatic proton signals in the range of δ 6.90-7.30 ppm also became broader and shifted to low field by 0.07 to 0.17 ppm for the completely oxidized TDPA-BzA polymer.

The signal at δ 5.35 ppm of methine protons was gradually decreased while increasing the amount of DDQ as shown the remaining $-\text{CH}$ proton in Table 5.4. However, it should be noted that the signal of methine protons still could be observed and indicated the small amount of remaining methine protons about 9% though the polymer was reacted with the excess amount of DDQ.

It can be explained that DDQ hardly abstracted the methine protons of high-Mw polymer having the complicated entanglement due to single bond along the polymer chain. As a consequence, the polymer at the edge of its coil was firstly oxidized by DDQ and formed double bond that stretched up its chain while the oxidation was proceeding. This allowed DDQ could reach the polymer chain and reacted more easily.

However, the stretching of the polymer chain required long time, which 24 hours of the reaction time was not enough to completely oxidize such methine protons. Therefore, the longer reaction time than 24 hours was an important factor to remove the methine protons completely.

5.5.1.3) THE INFLUENCE OF THE REACTION TIME

In this experiment, TDPA-BzA polymer was oxidized with DDQ at 36 hours of the reaction time with various amount of DDQ from 10-40% as shown in Table 5.5. The reaction was proceeded as same as at 24 hours and the polymer was recovered with the characteristics as shown in Table 5.5.

Figure 5.12 shows the $^1\text{H-NMR}$ spectra of the oxidized TDPA-BzA polymers at 36 hours of reaction time. Methyl protons of the oxidized polymers showed the same chemical shift of 2.24 ppm as the non-oxidized polymer but the signal of methyl protons became broader for the oxidation with excess amount of DDQ. Aromatic proton signals in the range of δ 6.90-7.30 ppm became broader and shifted to low field by 0.07 to 0.17 ppm for the completely oxidized TDPA-BzA polymer.

The signal at δ 5.35 ppm of methine protons was gradually decreased while increasing the amount of DDQ as shown the remaining $-\text{CH}$ proton in Table 5.5. However, it should be noted that the signal of methine protons was completely disappeared when the polymer was reacted with the excess amount of DDQ for 36 hours. Therefore, 36 hours of the reaction time was long enough for proton abstraction by DDQ and the longer reaction time than 24 hours could remove the methine protons completely.

Table 5.5: The CH- proton remaining in TDPA-BzA polymers before and after oxidation at 36 hours of the reaction time.

Amount of DDQ (%wt)	Polymer:DDQ (mole ratio)	Polymer Color	Yield (%)	CH- proton remaining from $^1\text{H-NMR}$	
				Theoretical	Experimental
0	2:0.00	white	91	1.0000	1.0721
10	2:0.34	Dark green	84	0.6600	0.6611
20	2:0.77	Dark green	86	0.2300	0.2326
30	2:1.31	Dark green	91	0.0000	0.0184
40	2:2.04	Dark blue	92	0.0000	0.0000

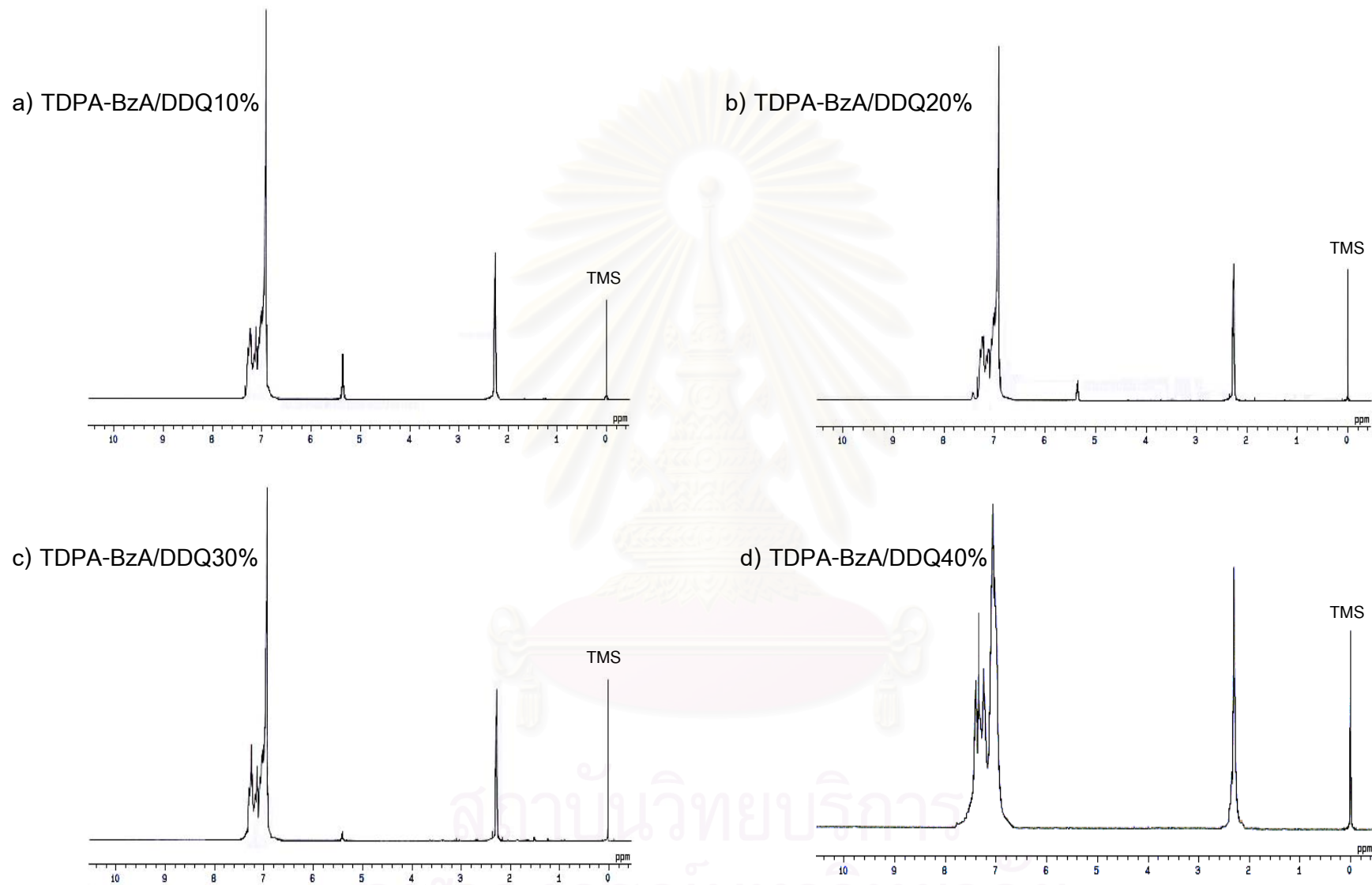


Figure 5.12: $^1\text{H-NMR}$ spectra of the oxidized TDPA-BzA polymer at 36 hrs of the reaction time (CDCl_3/TMS).

In any case, the amount of remaining methine protons from the oxidation of TDPA-BzA polymers at 24 and 36 hours of the reaction time as shown in Table 5.4 and 5.5, respectively was plotted against the mole ratio of DDQ to the polymer as shown in Figure 5.13 that illustrates the oxidation tendency of TDPA-BzA polymer at both of 24 and 36 hours of the reaction time.

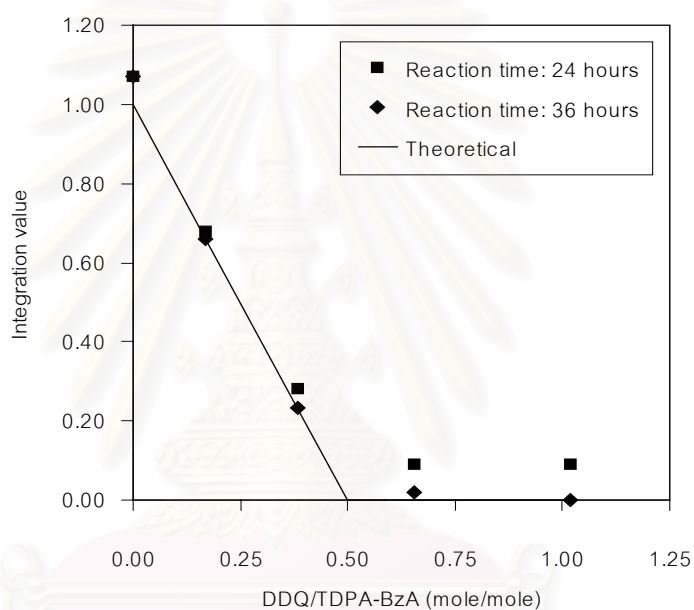


Figure 5.13: The influence of the oxidation of TDPA-BzA polymer with DDQ.

The solid line shows the tendency of theoretical amount. The intensity of methine proton signal or the number of methine protons was decreased when increasing of DDQ amount. It was so obviously that the remaining methine protons were almost the same as the expected values and this indicated that the oxidation of TPD-BzA polymers was proceeded theoretically.

5.5.2) TPD-BzA POLYMER

As TDPA-BzA polymer, in this experiment, TPD-BzA polymer was oxidized with DDQ using 36 hours of the reaction time. The reaction shown in Figure 5.14 indicated that one mole of DDQ is able to react with two repeating units of TPD-BzA polymer. TPD-BzA polymer was oxidized with various amounts of DDQ from 10-30 %wt. The oxidation was carried out in a sample container with a cap using THF as a solvent at room temperature.

After adding DDQ to the TPD-BzA polymer solution, the light yellow solution suddenly became dark green solution for partial oxidation and dark blue-green solution for completely oxidation. All polymers were also soluble in the reaction mixture and no precipitation was observed. The resulting polymers were recovered almost quantitatively and were soluble in chloroform, THF and slightly soluble in toluene and benzene. Table 5.6 shows yield and other characteristics of TPD-BzA polymers for each oxidation condition.

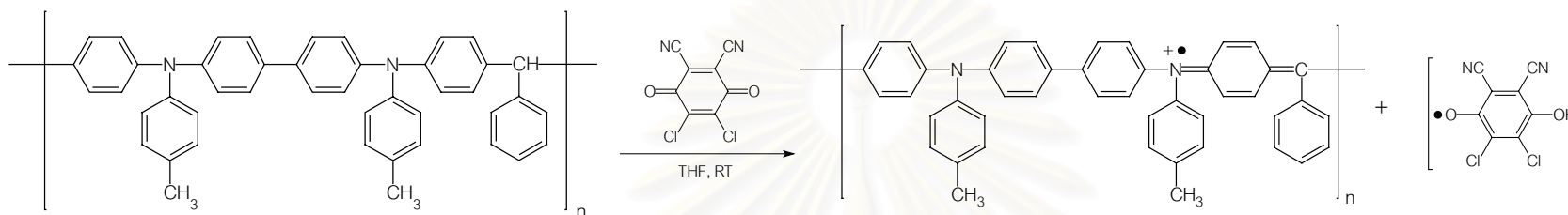


Figure 5.14: The oxidation of TPD-BzA polymer with DDQ.

Table 5.6: The CH- proton remaining in TPD-BzA polymers before and after oxidation at 36 hours of the reaction time.

Amount of DDQ (%wt)	Polymer:DDQ (mole ratio)	Polymer Color	Yield (%)	CH- proton remaining from $^1\text{H-NMR}$	
				Theoretical	Experimental
0	2:0.00	Pale green	98	1.0000	1.0027
10	2:0.59	Dark green	96	0.4100	0.4656
15	2:0.94	Dark green	92	0.0600	0.0656
20	2:1.33	Dark green	92	0.0000	0.0000
30	2:2.28	Dark blue	92	0.0000	0.0000

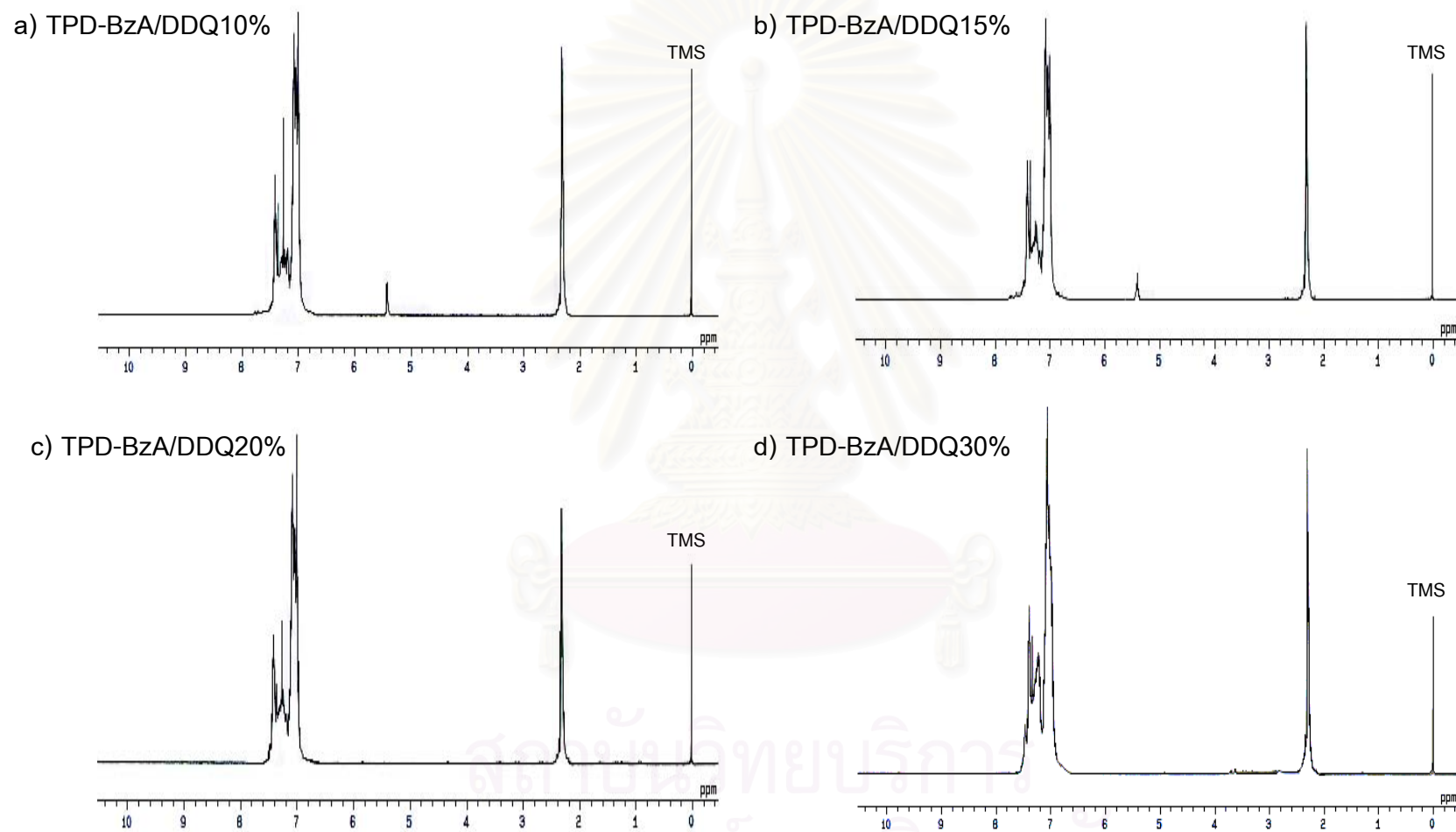


Figure 5.15: $^1\text{H-NMR}$ spectra of the oxidized TPD-BzA polymer at 36 hrs of the reaction time (CDCl_3/TMS).

Figure 5.15 shows $^1\text{H-NMR}$ spectra of the oxidized TPD-BzA polymers at 36 hours of reaction time. The repeating unit of TPD-BzA polymer is similar to TDPA-BzA, thus its $^1\text{H-NMR}$ spectrum showed the signals in three regions as TDPA-BzA.

The methyl proton of the oxidized TPD-BzA polymers showed the same chemical shift of 2.24 ppm as the non-oxidized polymer but its signal became slightly broader. The signals at δ 5.40 ppm of methine protons were gradually reduced while increasing the amount of DDQ and were completely disappeared when oxidation with the excess amount of DDQ. Aromatic proton signals in the range of δ 6.9-7.45 ppm shifted to low field by 0.01 to 0.07 ppm for the completely oxidized TPD-BzA polymer.

However, it was obviously that the both of completely oxidized TDPA-BzA and TPD-BzA polymers performed the chemical shift change and the peak broadening, which might come from the effect of the absence of the methine protons in the polymer chain. The oxidized TDPA-BzA polymer showed the larger effect than the oxidized TPD-BzA polymer which can be explained by the smaller repeating unit of TDPA-BzA polymer and that only one proton was abstracted from one repeating unit.

The amount of remaining methine protons from the oxidation of TPD-BzA polymers shown in Table 5.6 was plotted against the mole ratio of DDQ to the polymer as shown in Figure 5.16. The solid line shows the tendency of theoretical amount.

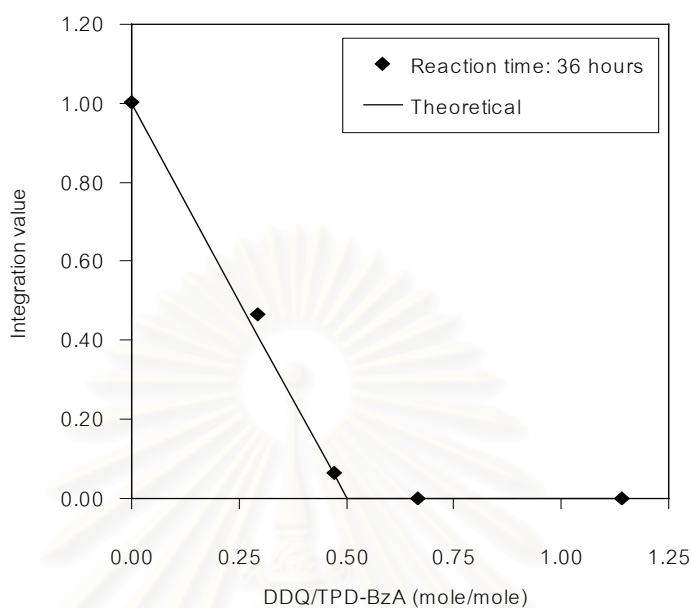


Figure 5.16: The influence of the oxidation of TPD-BzA polymer with DDQ.

In the same manner as TDPA-BzA polymer, the intensity of methine proton signal or the number of methine proton of TPD-BzA polymer was decreased when increasing of DDQ amount and the remaining methine protons were almost the same as the expected values. This indicated that the oxidation of TPD-BzA polymers was proceeded theoretically.

Table 5.7 : The non-oxidized and oxidized polymers for 36 hours reaction time.

Polymer	Amount of DDQ (%wt)	Polymer:DDQ (mole ratio)	Mw ($\times 10^{-3}$)	Tg ^a (°C)	Polymer Color	UV absorption (nm)
TDPA-BzA	0	2:0.00	311	215	white	314.00
	10	2:0.34	-	-	Dark green	-
	20	2:0.77	-	-	Dark green	314.00, 697.00
	30	2:1.31	-	-	Dark green	-
	40	2:2.04	322	225	Dark blue	316.00, 697.00
TPD-BzA	0	2:0.00	320	230	Pale green	318.50, 358.00
	10	2:0.59	-	-	Dark green	-
	15	2:0.94	-	-	Dark green	321.50, 359.00, 722.50
	20	2:1.33	-	-	Dark green	-
	30	2:2.28	334	250	Dark blue	326.50, 359.00, 722.50

^aMeasured values by DSC (temperature incremental rate of 10 K/min)

5.5.3) MOLECULAR WEIGHT AND GLASS TRANSITION TEMPERATURE OF THE OXIDIZED POLYMERS

During the oxidation, other side reactions, for example, crosslinking reaction between the polymer chains, may be occurred. Such reaction can be verified by investigation of Mw and glass transition temperature (T_g) of the oxidized polymer.

In this work, Mw of polymers was determined by gel permeation chromatography (GPC) using a column packed with styrene-divinylbenzene gel beads. The measurement was carried out using 0.01 g/ml of polymer in chloroform, which was used as an eluent also. It was found that Mw of both oxidized polymers showed no significant change as shown in Table 5.7. These results indicated that no crosslinking reaction occurred.

T_g of the polymers was measured by DSC operating at starting temperature of 50 °C with increasing temperature of 10 K/min till the final temperature was reached at 280 °C.

The completely oxidized TDPA-BzA polymer had T_g of 230 °C slightly higher than the corresponding non-oxidized polymer, which had T_g of 215 °C. Similarly, the completely oxidized TPD-BzA polymer had T_g of 250 °C while the non-oxidized polymer had T_g of 215 °C.

Therefore, it clearly confirmed that no crosslinking reaction occurred during the oxidation with DDQ.

5.5.4) CHARACTERIZATION OF THE OXIDIZED POLYMERS

5.5.4.1) IR SPECTROSCOPY

After precipitating and washing the precipitate by methanol several times, the oxidized polymers were examined for the presence of DDQ, which could be contaminated from the reaction mixture. This was performed by FT-IR spectroscopic technique. Figure 5.17 and 5.18 shows IR spectra of the polymers before and after oxidation for TDPA-BzA and TPD-BzA polymers, respectively.

Obviously, the absence of the absorption band of -CN group around 2850-2910 nm, the absorption band of -C=O group around 1700 nm and the broad peak of -OH group around 3600-3700 nm indicated that neither residual DDQ nor its reduced form contaminated in the oxidized polymers (13).

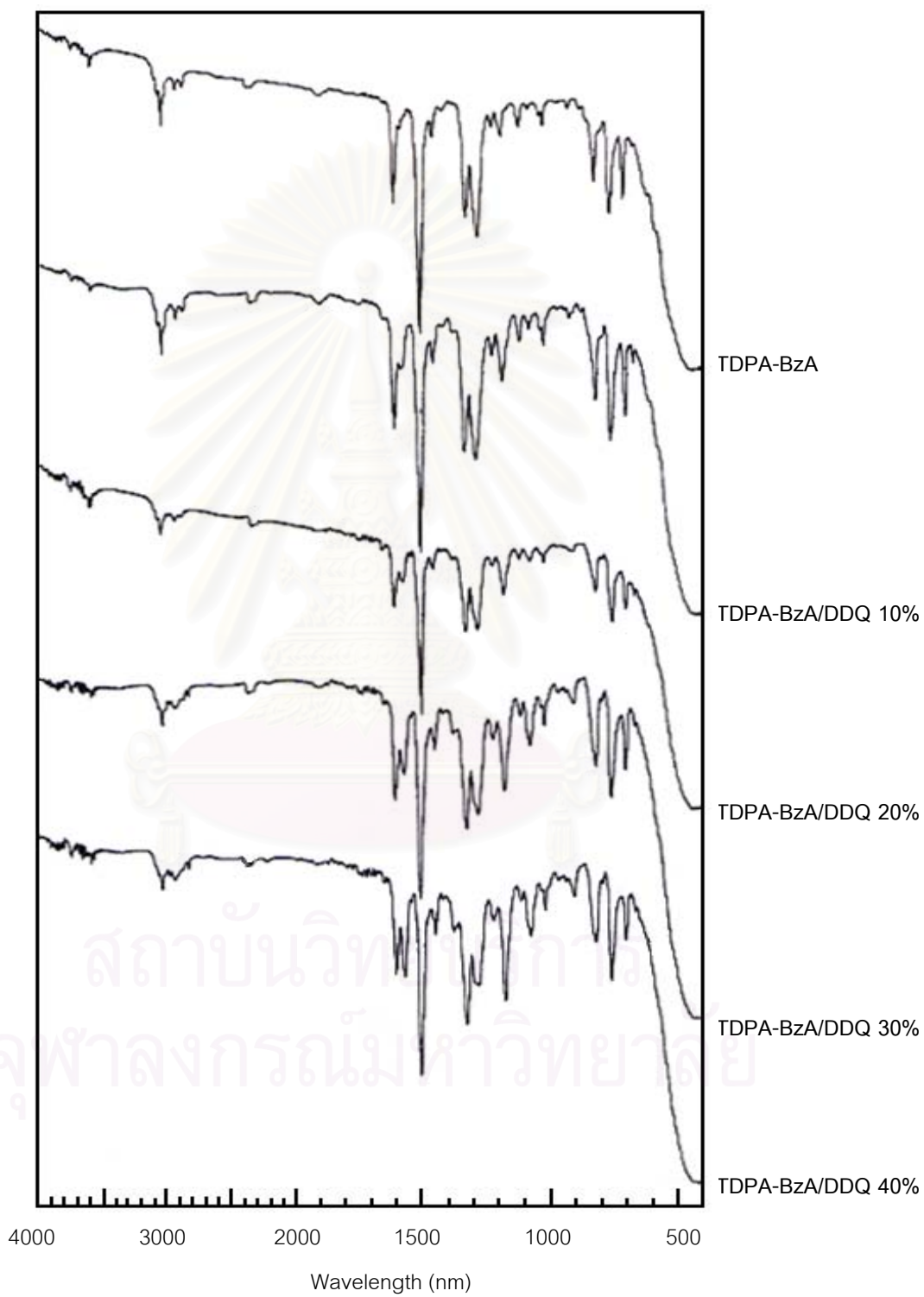


Figure 5.17: IR spectra of the non-oxidized and oxidized TDPA-BzA polymers.

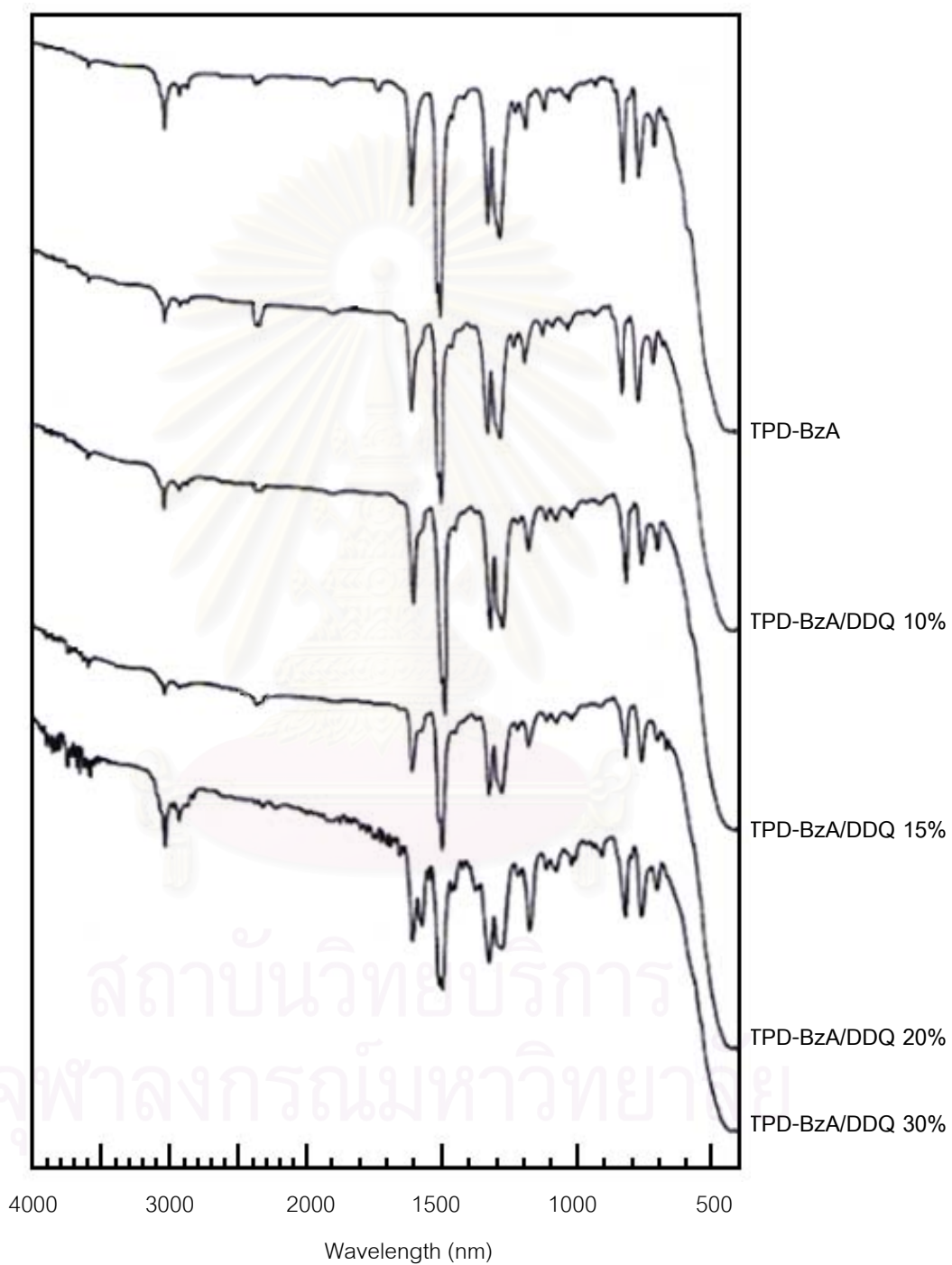


Figure 5.18: IR spectra of the non-oxidized and oxidized TPD-BzA polymers.

5.5.4.2) UV-VISIBLE SPECTROSCOPY

The oxidized polymers showed dark green and dark blue green color for the completely oxidized polymers. The dark color of material and polycyclic aromatic chromophore with the long-chain conjugated system usually absorbed visible light and indicated the electronic transition and the alternation of electron π -conjugation in the polymer chain.

Figure 5.19 shows UV-VIS spectra of TDPA-BzA polymer before and after oxidation. The non-oxidized TDPA-BzA polymer white solid had only one absorbance at 314 nm due to the aromatic ring chromophore. The oxidized TDPA-BzA polymers performed bathochromic shift (red shift), which was observed the new absorbance at 697 nm (36).

Figure 5.20 shows UV-VIS spectra of TPD-BzA polymer before and after oxidation. The non-oxidized TPD-BzA polymer pale green solid had two absorbances at 318 and 358 nm due to the aromatic ring chromophore and its auxochrome, respectively (36). Similarly, the oxidized TPD-BzA polymers exhibited bathochromic shift, which was observed the new absorbances at 722.50 nm.

These new absorbances of both polymers were assigned as polaron or radical cation as shown in Figure 2.3 on the polymer chain (37) and confirmed the formation of the extended electron π -conjugation in the polymer chain (15). However, the oxidized TDPA-BzA polymers showed the stronger absorption band, around 700 nm, than the oxidized TPD-BzA polymers, which can be explained by the smaller repeating unit of TDPA-BzA polymer and that only one proton was abstracted from one repeating unit.

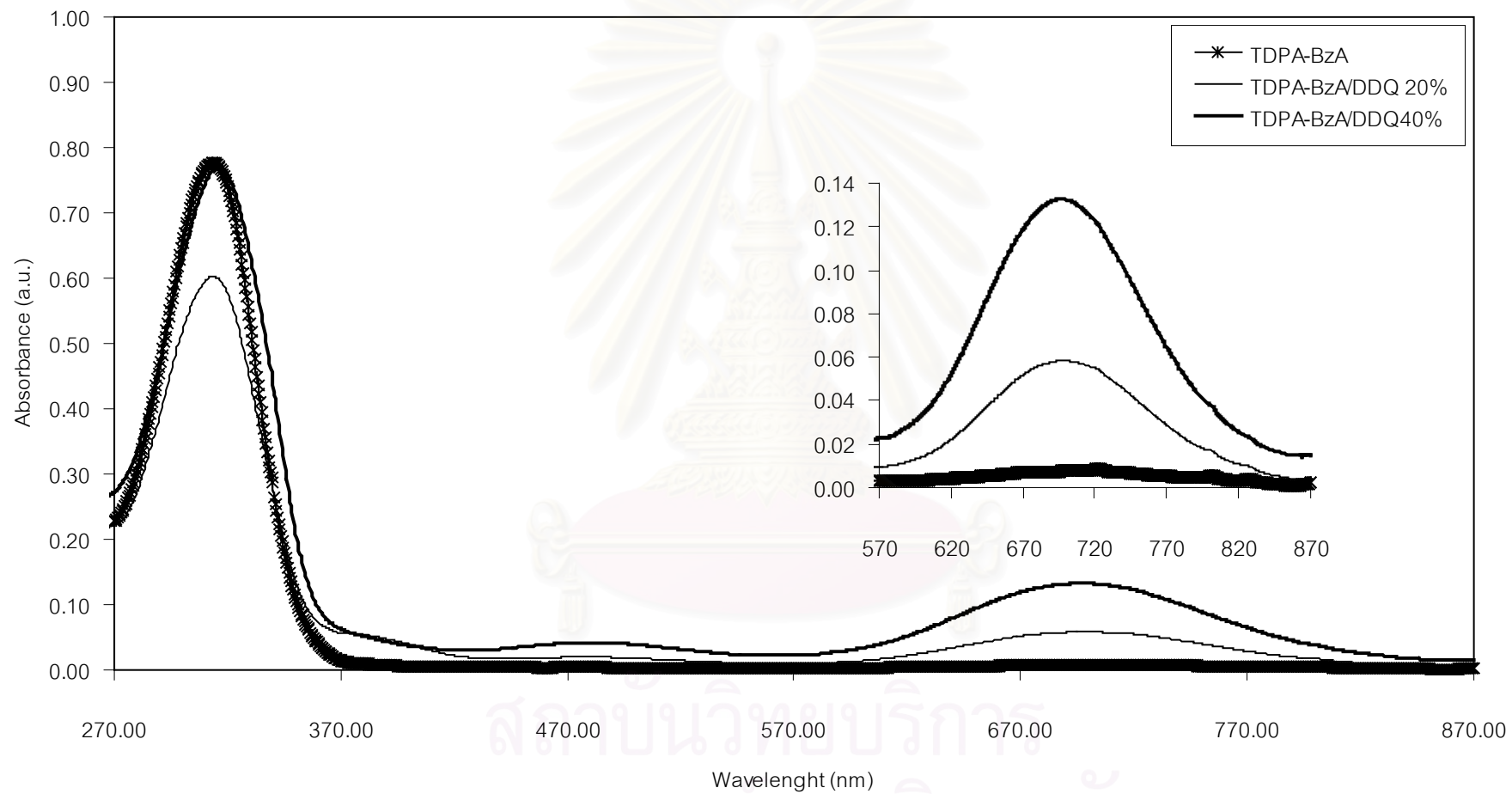


Figure 5.19: UV-vis spectra of the non-oxidized and oxidized TDPA-BzA polymers.

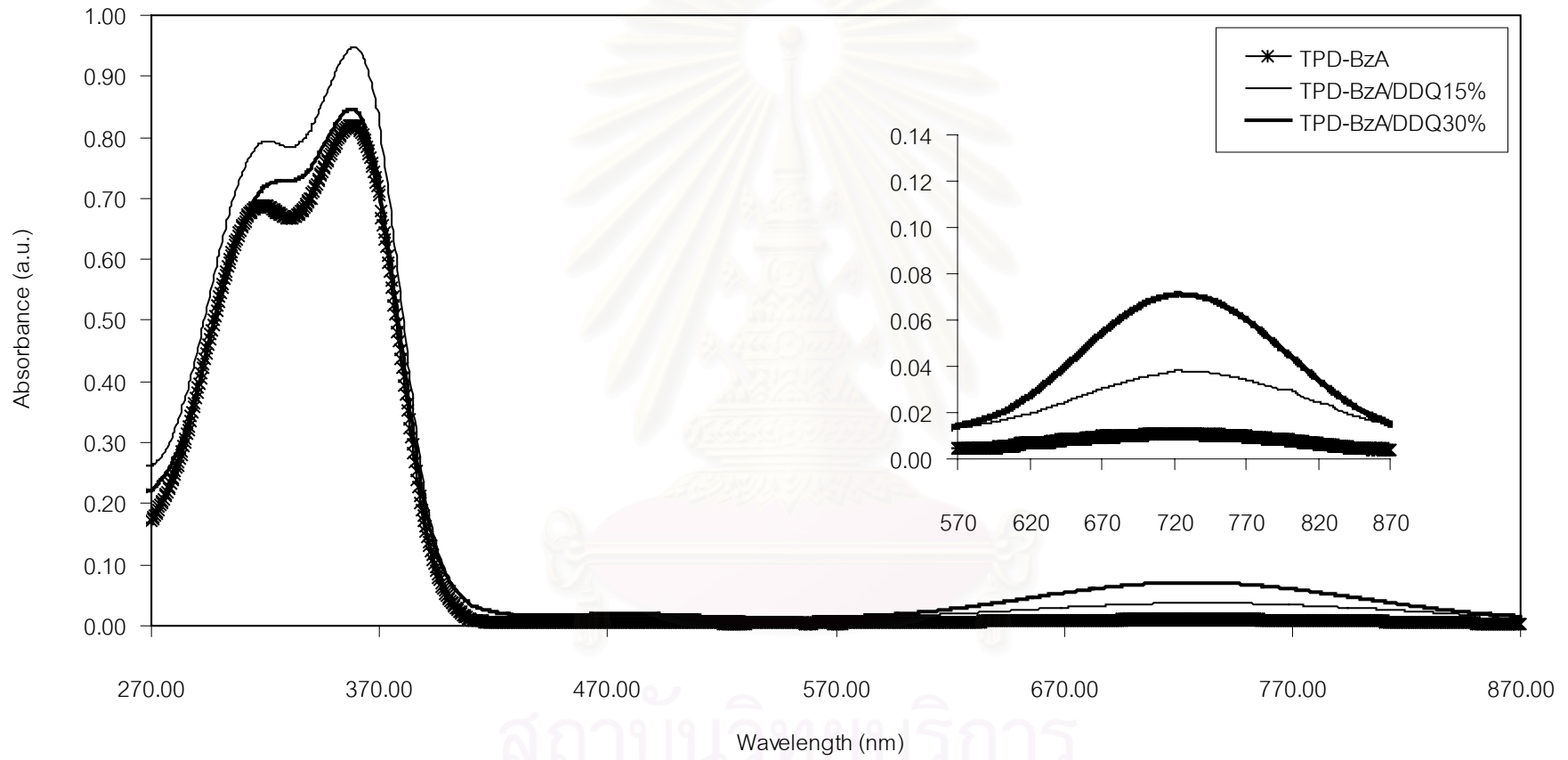


Figure 5.20: UV-vis spectra of the non-oxidized and oxidized TPD-BzA polymers.

5.5.4.3) ESR SPECTROSCOPY

In some other works, generally, the radical on polymer was studied by electron spin resonance (ESR) (37-42). According to the new UV-VIS absorbances of both oxidized polymers due to the polaron or radical cation, in this research, ESR spectroscopic technique was also used to investigate the presence of the radical on the polymer chain after oxidation. The ESR measurement was operated under nitrogen atmosphere with the frequency of 9.43 GHz, using chloroform to dissolve the completely oxidized polymers with the concentration of 10 mg/ml.

The ESR spectra of the completely oxidized TDPA-BzA and TPD-BzA polymers are shown in Figure 5.21 and 5.22, respectively. The ESR spectrum exhibited penta splitting with g-values of 2.0056 and 2.0063 for the completely oxidized TDPA-BzA and TPD-BzA polymers, respectively, with the same intensity ratio of 1:2:3:2:1. The ESR spectra showed an asymmetric signal, which indicated the formation of radical cations, which can generate polaron (Figure 2.3) in the polymer chain, by the protonation (38).

Therefore, ESR spectroscopy of both polymers clearly confirmed that the radical exists on both polymer chains.

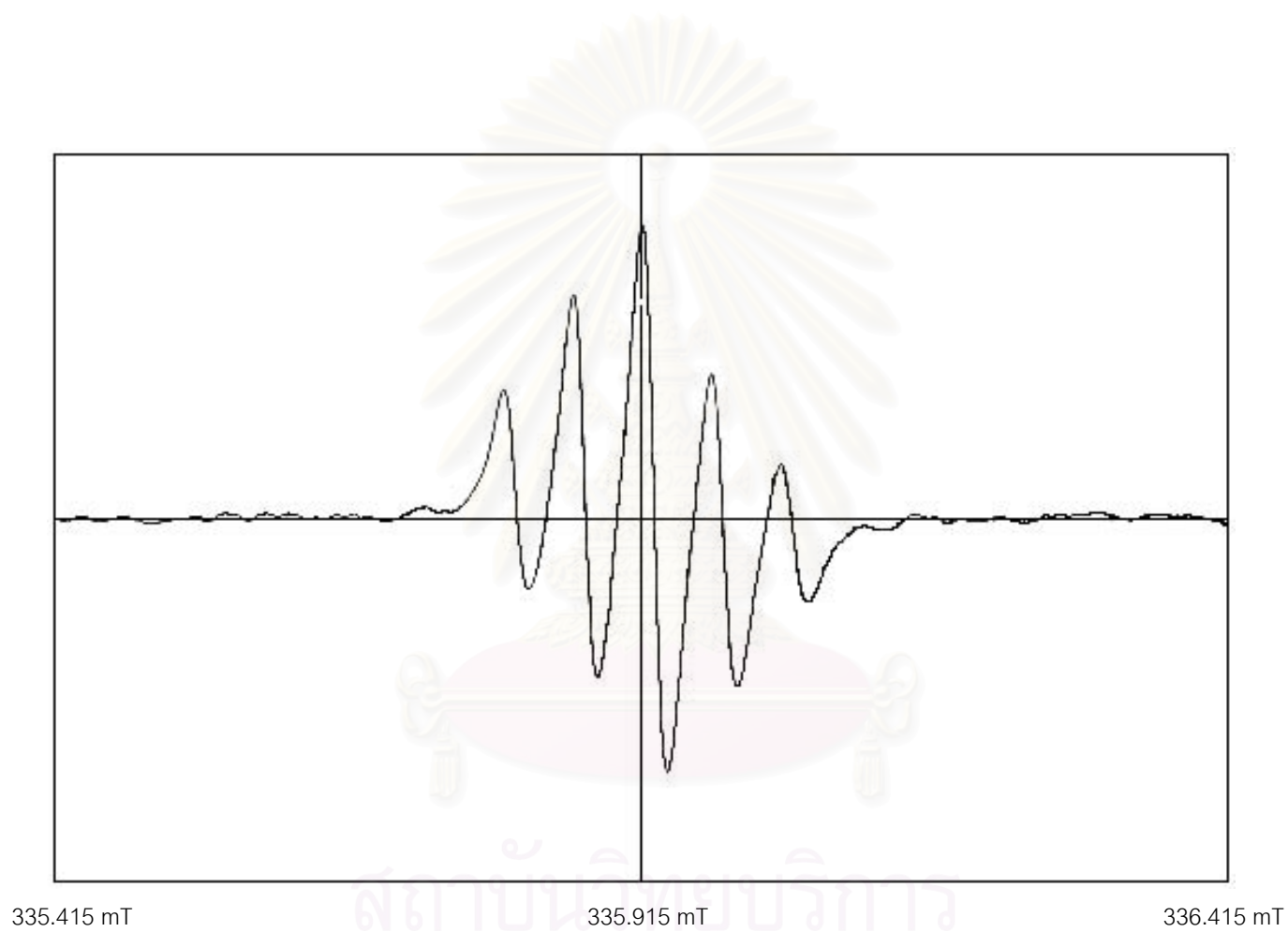


Figure 5.21: ESR spectra of the completely oxidized TDPA-BzA polymers.

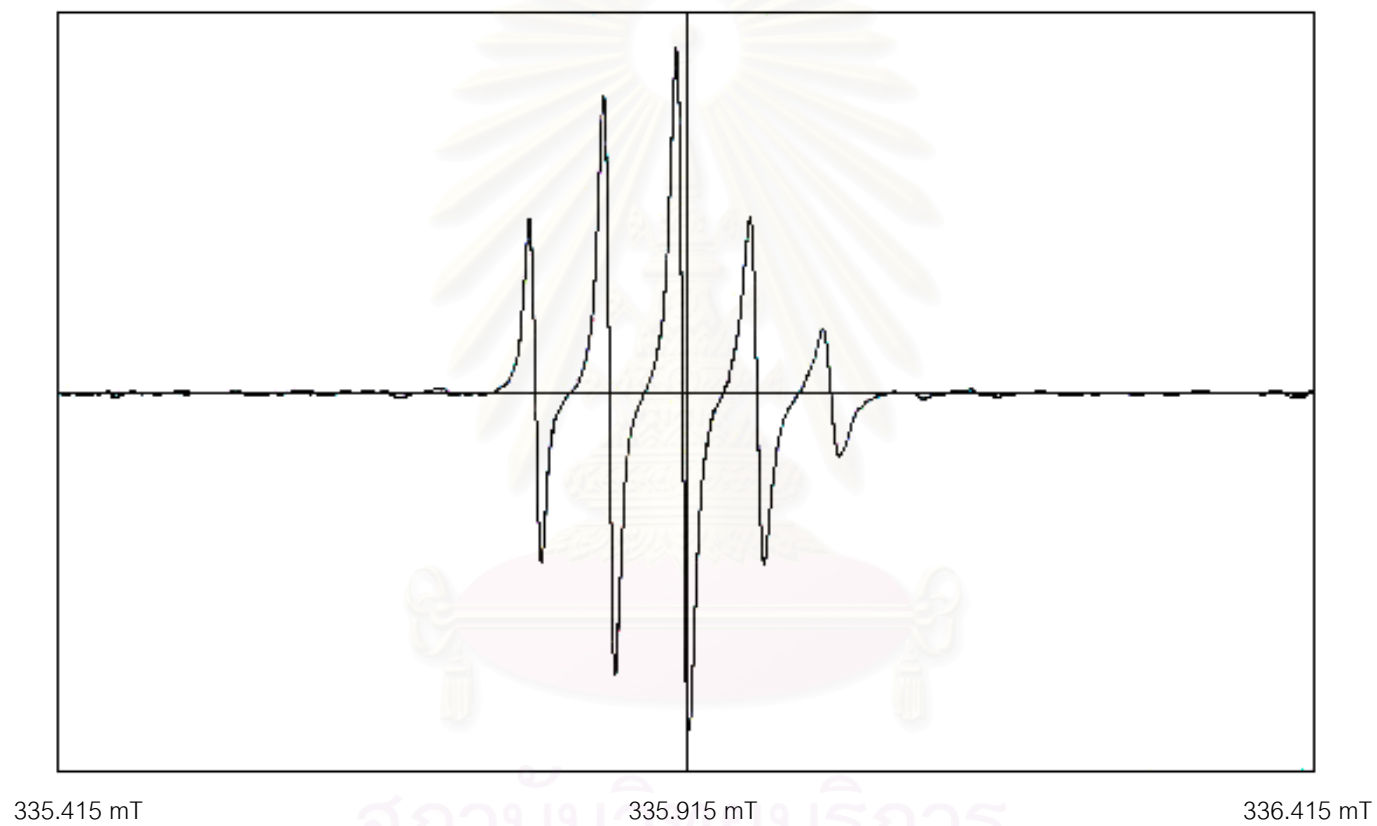


Figure 5.22: ESR spectra of the completely oxidized TPD-BzA polymers.

5.6 ELECTROCHEMICAL AND ELECTRICAL MEASUREMENT

The electrochemical and electrical properties of the completely oxidized polymers were investigated in comparison with the non-oxidized polymers.

5.6.1) *ELECTROCHEMICAL PROPERTY*

Cyclic voltammetry (CV) is a preliminary characterization method to determine the redox property of organic and polymeric materials. In this work, CV measurement of the polymers was investigated under nitrogen atmosphere using 0.1 M of Bu_4NClO_4 in dry acetonitrile as an electrolyte.

The redox potential of material indicated the required potential to change its electronic state. Cyclic voltammograms of TDPA-BzA and TPD-BzA polymers are shown in Figure 5.23 and 5.24, respectively.

The Oxidation potentials of the oxidized polymers from the second cycle were almost equal to those of the non-oxidized polymers as shown in Table 5.8 while the cyclic voltammograms of the first cycle was greatly changed. TDPA-BzA polymers before and after oxidation had the same oxidation potential of 0.994 volt. In the same manner, the non-oxidized and completely oxidized TPD-BzA polymers exhibited 1.021 volt of oxidation potential slightly higher than TDPA-BzA polymers, which indicated that TPD-BzA polymer needed the higher potential to change the electronic state due to its bigger repeating unit and more complicated polymer chain than TDPA-BzA polymer. However, all polymers showed hole transport ability (23, 27-30).

a) TDPA-BzA

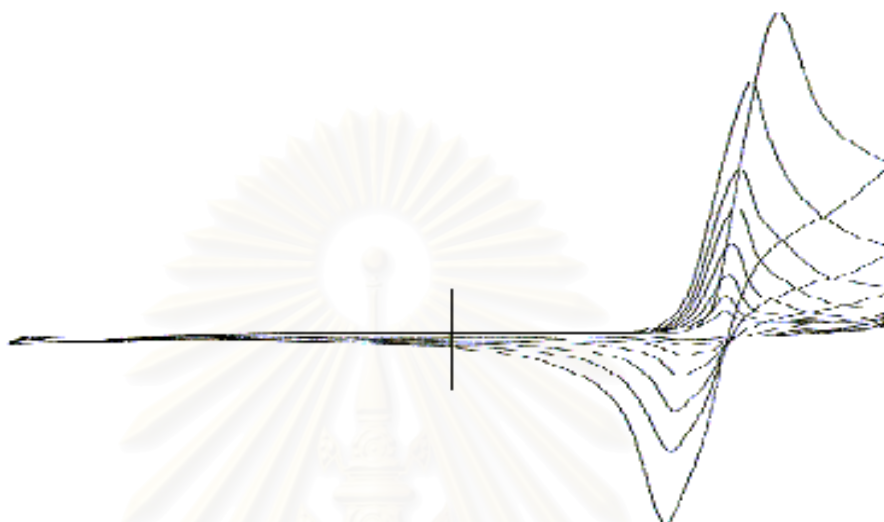


b) TDPA-BzA/DDQ40%



Figure 5.23: Cyclic voltammograms of the non-oxidized and completely oxidized TDPA-BzA polymers.

a) TPD-BzA



b) TPD-BzA/DDQ30%

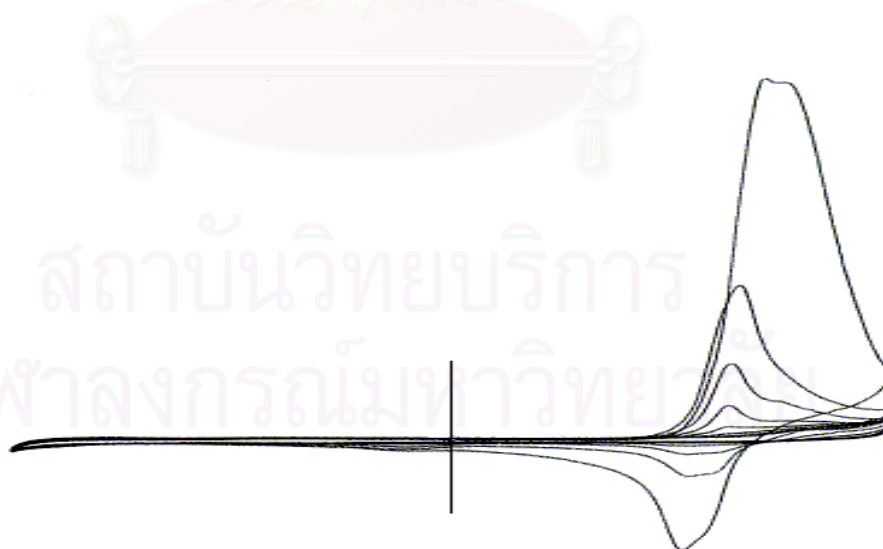


Figure 5.24: Cyclic voltammograms of the non-oxidized and completely oxidized TPD-BzA polymers.

Table 5.8: Electrochemical and electrical properties of the non-oxidized and completely oxidized polymers.

Measurement	TDPA-BzA		TPD-BzA	
	Non-Oxidized	Oxidized	Non-Oxidized	Oxidized
Oxidation potential (V)	0.994	0.994	1.021	1.021
DC conductivity (S/cm)	$< 10^{-13}$	2.01×10^{-11}	$< 10^{-13}$	1.25×10^{-11}

5.6.2) ELECTRICAL PROPERTY

Actually, DC conductivity can be determined from the polymer film on the aluminum vapor deposited on a slide glass. Unfortunately, the non-oxidized and completely oxidized TDPA-BzA polymers showed very poor film formation. Therefore, in this work, DC conductivity of both polymers was measured from their pellets with 1 cm of diameter. The sample was mounted between two metal disks with the same diameter. Then the voltage in the range of 200-1000 volt was applied.

DC conductivities of the polymers are shown in Table 5.8. The completely oxidized polymers show low conductivities in the magnitude of 10^{-11} S/cm. However, the completely oxidized TDPA-BzA and TPD-BzA polymers showed no significant difference of conductivity and both non-oxidized polymers had the conductivities lower than 10^{-13} S/cm. Therefore, the oxidation with DDQ enhanced the conductivity of the polymers over 100 times of the starting polymers.

CHAPTER 6

CONCLUSION

In this work, 4-Tolyldiphenylamine (TDPA) and *N,N'*-diphenyl-*N,N'*-bis(4-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) monomers could be obtained from Tosho method with higher yield than the Ullmann reaction, which has been used before. The condensation polymerization of TDPA and benzaldehyde (BzA) was successfully proceeded in chlorobenzene using *p*-toluenesulfonic acid as a catalyst and the polymer with high Mw and yield could be obtained.

Poly(vinylcarbazole) (PVK), which has been widely used for photoconductive application, was used as a polymer. It was found that three ionic compounds agglomerated themselves out from the polymer matrix. This indicated that ionic compounds were not appropriately doped into the polymers. Therefore, the influence on their electrochemical and electrical properties could not be investigated. However, the oxidation of PVK with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) demonstrated the reliable results.

Both polymers were oxidized in tetrahydrofuran with various amount of DDQ at room temperature. As the amount of DDQ increased, more polymers were oxidized as revealed by the decrease in intensity of methine proton signal in their ¹H-NMR spectra. When the amount of DDQ higher than the theoretical one (1 mole to 2 mole of repeating unit) was applied for 24 hours, the methine proton signal was almost completely disappeared. When the reaction was carried out longer, for 36 hours, such methine proton signal was completely disappeared. These results

indicated that the methine protons of the polymers were abstracted by DDQ and that the longer reaction time than 24 hours was necessary to completely oxidize the methine protons of the polymers since the complicated entanglement of their polymer chains. Eventhough, the rest of the proton signals, i.e, methyl and aromatic proton signals, was similar to the starting polymers but their chemical shifts were slightly shifted and the signals became broader. This could be due to the influence of the generated radical on the oxidized polymers.

The resulting polymers were recovered almost quantitatively as dark green and dark blue solid for partial and completely oxidation, respectively. All polymers were soluble in chloroform, THF and slightly soluble in toluene and benzene. The average molecular weight and glass transition temperature of the reacted polymer were not significantly changed. Therefore, no side reaction such as crosslinking could occur during the oxidation.

The absence of the absorption band of -CN group around 2130-2190 nm and the broad peak of -OH group around 3600-3700 nm indicated that neither residual DDQ nor its reduced form contaminated in the oxidized polymers. UV-vis spectra of the oxidized polymers performed the bathochromic shift due to the new absorbance observed at 697.00 nm and 722.50 nm for TDPA-BzA and TPD-BzA polymers, respectively. This could be due to the extended electron π -conjugation and the polaron or radical cations in the polymer chains. ESR spectroscopy of the completely oxidized polymers demonstrated an asymmetric signal with penta splitting, which clearly confirmed the existence of the radical by the proton abstraction along the polymer chains.

Both polymers after the oxidation still maintained their electrochemical properties as revealed by cyclic voltammetry. The reversible oxidation potentials of the completely oxidized polymers were equal to those of non-oxidized polymers.

TDPA-BzA and TPD-BzA polymers had 0.994 and 1.021 volt of oxidation potentials, respectively. However, all polymers performed hole transport ability. Particularly, the electrical properties of both polymers were greatly improved after the oxidation. Both completely oxidized polymers attained DC conductivity in the magnitude of 10^{-11} S/cm, which was over 2 orders higher than the starting polymers.

Therefore, this work demonstrated that the oxidant, which is the one type of dopant exhibited the most effective results on the polymers containing triphenylamine derivative moiety, TDPA-BzA and TPD-BzA polymers. The chemical structure of the repeating unit was approved to generate the extended π -conjugation electron delocalized and radical cations along the polymer chain since the proton abstraction by DDQ. Consequently, the electrical property presented as DC conductivity of the polymers after oxidation was greatly increased over hundred times higher than the starting polymers and the electrochemical property still could be maintained in the acceptable level.

SUGGESTIONS FOR FUTURE WORK

The substituent group on polymer backbone is one of important factors for a possibility of good film formation. In order to improve the film formation of this kind of polymer, The substituent should be more polar group. Some possibility groups to develop the polymer having more polarity are as followed; --CN, --OCH₂CH₂CH₂CH₃, --NO₂, and --OH groups.

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APPENDICES

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APPENDIX A

Calculation of Polymer:Dopant mole ratio

- *In the case of oxidation of the polymer with DDQ*

For **example**: The oxidation of TDPA-BzA polymer with 10% wt DDQ

TDPA-BzA: Mer weight = 347.4586

DDQ: Molecular weight = 227.01

Doping level: 10% wt

TDPA-BzA	90	mg	=	2.59×10^{-4}	mol
DDQ	10	mg	=	4.40×10^{-5}	mol

Therefore;

Theoretical mol ratio of TDPA-BzA : DDQ = 2 : 0.34

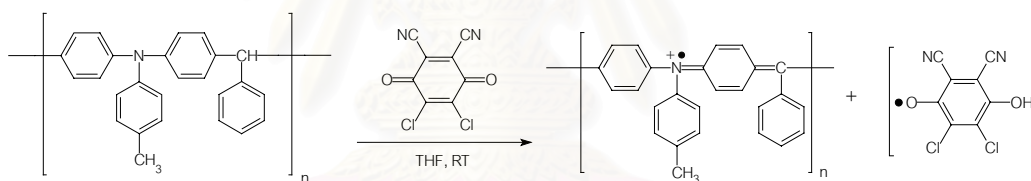
APPENDIX B

Calculation of Theoretical –CH Remaining

- In the case of oxidation of the polymer with DDQ

For example: The oxidation of TDPA-BzA polymer with 10% wt DDQ

Reaction equation:



$$\text{Theoretical TDPA-BzA : DDQ} = 2 : 1$$

According to Appendix A (Doping level 0% wt):

$$\text{Theoretical TDPA-BzA : DDQ} = 2 : 0.34$$

Therefore;

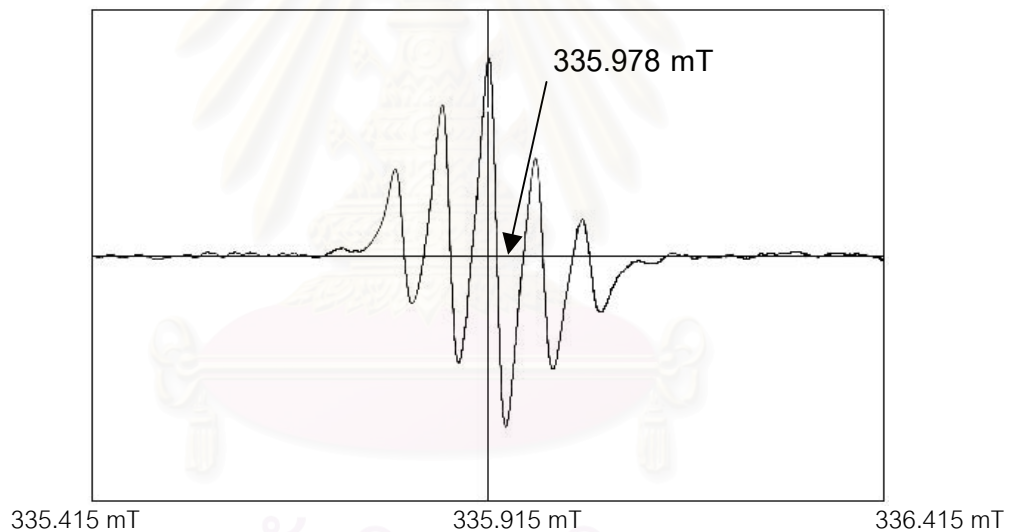
$$\text{Theoretical –CH Remaining} = 1 - 0.34 = 0.66 \text{ mol}$$

APPENDIX C

Calculation of g-Value

- *In the case of oxidation of the polymer with DDQ*

For example: The ESR spectrum of TDPA-BzA/DDQ40%



Equation:

$$h\nu = g\beta H$$

Where:

- h = Plank Constant; 6.626196×10^{-27} erg.s
- ν = Operated Frequency; 9.43 GHz.
- g = Free Electron
- β = Constant; 9.273×10^{-21} erg.gauss⁻¹
- H = Applied Magnetic Field; 335.978 mT

Therefore;

$$g = \frac{h\nu}{\beta H}$$
$$= \frac{(6.626196 \times 10^{-27} \text{ erg.s}) (9.43 \times 10^9 \text{ Hz})}{(9.273 \times 10^{-21} \text{ erg.gauss}^{-1}) (335.978 \text{ mT} \times 10 \text{ gauss.mT}^{-1})}$$
$$g = 2.0056 \quad (\text{no unit})$$

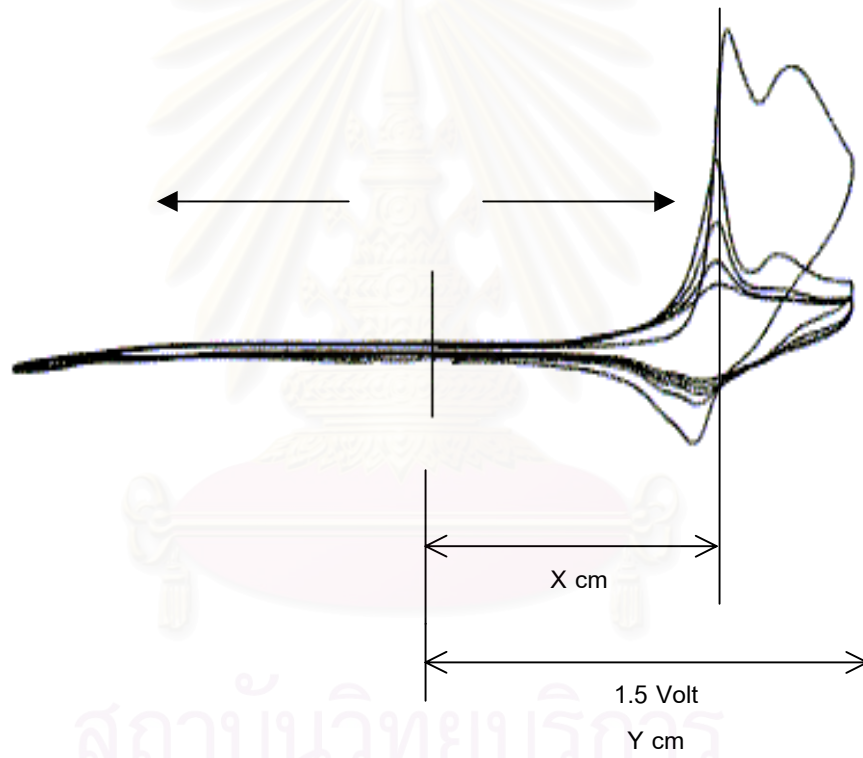


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APPENDIX D

Calculation of oxidation potential

For example: The Cyclic Voltammogram of TDPA-BzA/DDQ40%

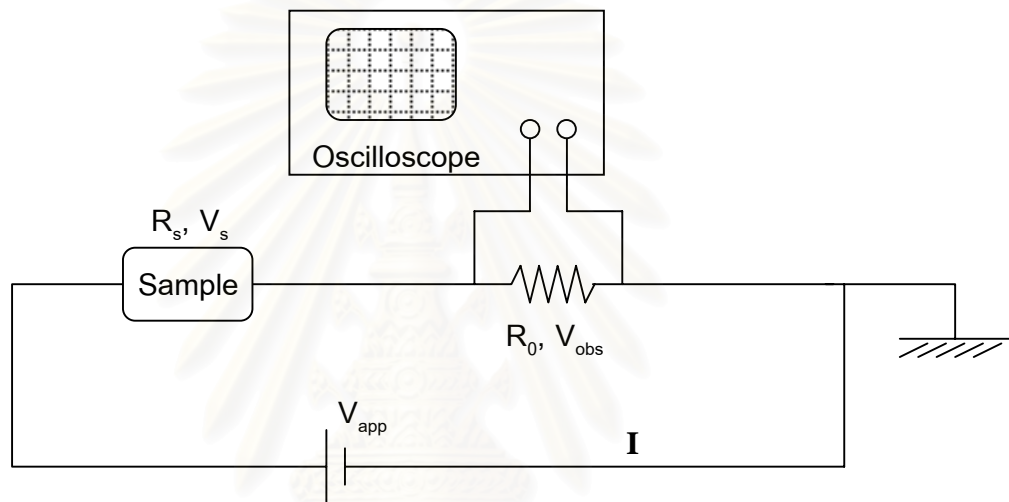


The peak indicated oxidation potential.

$$\text{Oxidation potential} = \frac{1.5X}{Y} \text{ Volt}$$

APPENDIX E

Calculation of DC conductivity



$$R_s = V_s / I$$

$$V_{app} = V_s + V_{obs}$$

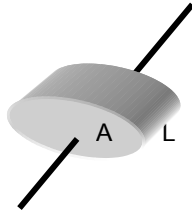
V_{obs} is very small when compare to V_{app} , Therefore;

$$V_s = V_{app}$$

$$I = V_{obs} / R_0$$

Therefore;

$$R_s = V_{app} R_0 / V_{obs}$$



$$\frac{\rho L}{A} = \frac{V_{\text{app}} R_0}{V_{\text{obs}}}$$

$$\frac{1}{\rho} = \sigma = \frac{L V_{\text{obs}}}{V_{\text{app}} R_0 A}$$

Therefore;

$$\sigma = \frac{L V_{\text{obs}}}{V_{\text{app}} R_0 (\pi r^2)}$$

Where;

ρ = Resistivity ($\Omega \cdot \text{cm}$)

A = Disk Area (cm^2)

σ = Conductivity ($\Omega^{-1} \cdot \text{cm}^{-1}$ or $\text{S} \cdot \text{cm}^{-1}$)

L = Sample Thickness (cm)

V_{obs} = Observed Voltage (Volt)

V_{app} = Applied Voltage (Volt)

R_0 = Resistance = 3.6×10^4 (Ω)

r = Disk Radius = 0.5 (cm)

- *TDPA-BzA/DDQ40% and TPD-BzA/DDQ30%*

Polymer	L (cm)	V _{app} (V)	V _{obs} (mV)	σ (S.cm ⁻¹)
TDPA-BzA/ DDQ40%	0.0510	0	0.00	0.00
		200	3.13	2.82 x 10 ⁻¹¹
		400	6.25	2.82 x 10 ⁻¹¹
		600	6.25	1.88 x 10 ⁻¹¹
		800	6.25	1.41 x 10 ⁻¹¹
		1000	6.25	1.13 x 10 ⁻¹¹
	Average			2.01 x 10 ⁻¹¹
TPD-BzA/ DDQ30%	0.0199	0	0.00	0.00
		200	3.13	1.10 x 10 ⁻¹¹
		400	6.25	1.10 x 10 ⁻¹¹
		600	9.57	1.12 x 10 ⁻¹¹
		800	15.70	1.38 x 10 ⁻¹¹
		1000	21.90	1.54 x 10 ⁻¹¹
	Average			1.25 x 10 ⁻¹¹

Therefore;

$$\text{Conductivity of TDPA-BzA/DDQ40\%} = 2.01 \times 10^{-11} \text{ S/cm}$$

$$\text{Conductivity of TPD-BzA/DDQ30\%} = 1.25 \times 10^{-11} \text{ S/cm}$$

VITA

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