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นายนภสินธุ์ เทวะเส

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สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
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SYNTHESIS AND CHARACTERIZATION OF ASYMMETRIC DIAMINE FOR TRANSPARENT POLYIMIDE FILM

Mr. Napasin Thevase

A Thesis Submitted in Partial Fulfillment of the Requirements
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By	Mr. Napasin Thevase
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor ML. Supakanok Thongyai, Ph.D.

Accepted by the Faculty of Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

………………………………….. Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

……………………………………………….. Chairman
(Professor Piyasan Praserthdham, Dr.Ing.)

……………………………………………….. Thesis Advisor
(Associate Professor M.L. Supakanok Thongyai, Ph.D.)

……………………………………………….. Examiner
(Assistant Professor Anongnat Somwangthanaroj, Ph.D.)

……………………………………………….. Examiner
(Assistant Professor Soorathep Kheawhom, Ph.D.)

……………………………………………….. External Examiner
(Assistant Professor Sirirat Wacharawichanant, D.Eng.)

นภสินธุ์ เทวะเส : การสังเคราะห์และวิเคราะห์ไดอะมีนอสมมาตรเพื่อใช้ในโพลิอีไมด์ฟิล์มแบบโปร่งใส (SYNTHESIS AND CHARACTERIZATION OF ASYMMETRIC DIAMINE FOR TRANSPARENT POLYIMIDE FILM) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. มล. ศุภกนก ทองใหญ่, 63 หน้า.

พอลิอิไมด์ถูกใช้อย่างกว้างขวางในงานอุตสาหกรรมไมโครอิเลคทรอนิกส์ เนื่องจากมีสมบัติที่เหมาะสมหลายด้าน ทั้งสมบัติเชิงกล สมบัติทางไฟฟ้า และสมบัติทางความร้อน อย่างไรก็ตาม พอลิอีไมด์ยังมีข้อจำกัด ในการนำไปใช้งาน ด้านแสง ซึ่งต้องการความใสของของวัสดุ เนื่องจากสีธรรมชาติของพอลิอีไมด์เป็นสีเหลืองอมน้ำตาลเข้ม ซึ่งเกิดจากผลของการส่งผ่านอิเล็กตรอนระหว่างกลุ่มอะมีนกับวงแหวนเบนซีนภายในโมเลกุลของพอลิอิไมด์ ในงานวิจัยนี้ได้ทำการสังเคราะห์ ไดอะมีนอะสมมาตรสำหรับใช้ในพอลิอีไมด์ เพื่อลดการเกิดการส่งผ่านอิเล็กตรอนในโมเลกุลดังกล่าว โดยประยุกต์ใช้ปฏิกิริยาการสังเคราะห์อีเธอของวิลเลียมสันและปฏิกิริยาไฮโดรจีเนชั่น สำหรับในการสังเคราะห์ไดอะมีนตัวที่ 1 เป็นการเปลี่ยน 2,2 Dinitrobiphenyl เป็น 2,2’ Diaminobiphenyl โดยใช้ปฏิกิริยาไฮโดรจิเนชั่นภายใต้บรรยากาศของไฮโดรเจนความดันสูง และในการสังเคราะห์ไดอะมีนตัวที่ 2 หรือ 2-(2-aminophenoxy)-5-(trifluoromethyl)aniline เป็นการทำปฏิกิริยาการสังเคราะห์ไดไนโตรอีเธอโดยใช้ 2-Nitrophenol และ 4-Chloro-3-nitrobenzotrifluoride จากนั้นจึงนำไปทำปฏิกิริยาไฮโดรจิเนชั่นภายใต้บรรยากาศของไฮโดรเจนความดันสูงเพื่อเปลี่ยนหมู่ไนโตรเป็นหมู่อะมีน และสามารถยืนยันโครงสร้างของสารที่สังเคราะห์ได้ด้วยเทคนิค Nuclear Magnetic Resonance (NMR) และ Fourier Transform Infrared (FTIR) spectrometers

พอลิอิไมด์ฟิล์มแบบโปรงใสสามารถสังเคราะห์ได้โดยใชปฏิกิริยาการสังเคราะห์พอลิเมอร์โดยการควบแน่น โดย PI-1 สังเคราะห์จากการทำพอลิเมอร์ร่วมระหว่าง ไดอะมีนตัวที่ 1: 6F-Diamin: 6FDA และ PI-2 ถูกสังเคราะห์จากการทำพอลิเมอร์ร่วมระหว่าง ไดอีมีนตัวที่ 2: 6FDiamine: 6FDA ฟิล์มทั้งสองสามารถยืนยันโครสร้างได้ ด้วยเทคนิค Fourier Transform Infrared (FTIR) spectrometers และทำการวิเคราะห์ด้วย Thermogravimetric analysis (TGA), Ultraviolet-Visible spectrophotometer (UV-vis) และการทดสอบการละลาย โดยงานวิจัยสามารถบรรลุเป้าหมายเพื่อลด ความยาวคลื่นคัทออฟให้ต่ำกว่า 350 nm. อย่างไรก็ตาม ฟิล์มที่สังเคราะห์ไม่สามารถลอกออกจากกระจกได้เนื่องจากตัวฟิล์มยังมีความเปราะ

ภาควิชา.........วิศวกรรมเคมี..... ลายมือชื่อ นิสิต..

สาขาวิชา.......วิศวกรรมเคมี.... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก...............................

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NAPASIN THEVASE : SYNTHESIS AND CHARACTERIZATION OF ASYMMETRIC DIAMINE FOR TRANSPARENT POLYIMIDE FILM

: ASSOC.PROF.M.L.SUPAKANOK THONGYAI, Ph.D., 63 pp.

Polyimide is widely used in microelectronic applications because there're good mechanical, electrical and thermal properties. However, most polyimides colour are yellow-orange that limiting to use in optical application. The colour in polyimide occurs from electron charge transfer between amine groups and benzene ring. To reduce it, the asymmetric diamine was induced to polymer backbone. In this study, aiming to synthesis new asymmetric diamines by apply the Williamson's ether synthesis and hydrogenation reaction. For 1st Diamine monomer, the sample from conversion of 2,2 Dinitrobiphenyl to 2,2' Diaminobiphenyl was successfully prepared by hydrogenation reaction in hydrogen atmosphere. For 2nd Diamine monomer, the reactant including 2-Nitrophenol and 4-Chloro-3-nitrobenzotrifluoride was reacted by Williamson's ether synthesis reaction to create asymmetric dinitro, then converse the dinitro to diamine as 2-(2-aminophenoxy)-5-(trifluoromethyl)aniline by hydrogenation reaction. Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FTIR) spectrometers then examined the product structure and they were confirmed.

The transparent film was made by thermal imidization, PI-1 and PI-2 were created from copolymer of 1st Diamine: 6F-Diamin: 6FDA and 2nd Diamine: 6FDiamine: 6FDA, respectively. The obtained films were characterized by Thermogravimetric analysis (TGA), Ultraviolet-Visible spectrophotometer (UV-vis) and solubility test. The target of cut off wavelength below 350 nm can be obtained. However, the synthesized film could not separate from glass substrate because of it's brittle.

Department : Chemical Engineering Student's Signature
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Finally, I would like to dedicate this thesis to my parents and my families, who generous supported and encouraged me through the year spent on this study.

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CHAPTER I

INTRODUCTION

Polyimide is a high performance polymer that has various applications in electronics industry for substrate, cover-layer, dielectric barrier etc. However, the simple polyimide such as Kapton possessed color of yellow to orange that limited the usage in the optical application such as transparent circuit, cover layer of LED and LCD display and substituting of glass cover layer in solar cell.

Recently, many methodologies to prepare transparent polyimide have been investigating and developing. The transparent or color property are obviously depends on Intermolecular interactions such as charge-transfer complex, electronic interaction, and intermolecular cohesive. There were many methods to reduce Intermolecular interactions by adding the intermolecular spacer such as adding of aryl-ether linkage in monomer for improvement, putting the unsymmetrical or twisty units into the polymer backbone and the last method was introducing the bulky, rigid units in the polymer main chain or in pendent groups. In 2010, Du Pont launched a new product of transparent colorless Kapton that utilized the asymmetric Dianhydride that contained the twisty rigid constrain of anhydride group in molecular structure and fluorinated diamine for colorless application. (Yang-Yen Yu, 2009) The polyimide films that include these improvements exhibited an excellent optical property while maintenance good mechanical and thermal property. In previous year, the research in developing of colorless polyimide in Chulalongkorn University was succeeded. The colorless polyimide has been produce. However the thermal property are still unacceptable.

In this work, the synthesis of diamine monomer by using the Williamson’s ether synthesis reaction and Hydrogenation on Pb/C is investigated. The diamines that we propose to prepare are including 2,2’-Diaminobiphenyl, 2-(2-aminophenoxy)-5-(trifluoromethyl)aniline and 6,6'-(1,2-phenylenebis(oxy))bis(3-(trifluoromethyl) aniline) which these amine structures will induce high twisty rigid constrain into the molecule of polyimide motivated by Du Pont succession in twisty rigid constrain Dianhydride, in order to apply in diamine and compare the effects from constrain in their molecule on the transparent properties of polyimide. Four types of Anhydrides, that were PMDA, 6FDA, BPDA, and ODPA, were chosen as ingredient to react with 3 synthetic Diamine monomers to synthesize polyimide films.

1.1 The Objective of This Thesis

1. To investigate and obtain knowhow to produce colorless transparent polyimide with acceptable color and thermal property.
2. To produce the films of colorless transparent polyimide with acceptable mechanical and thermal property.
3. To compare the effects from the rigidity and constrain in their molecular structures on the transparent properties of polyimide.

1.2 The Scope of This Thesis

1. To synthesize 3 diamine monomers including 2,2’-Diaminobiphenyl, 2-(2-aminophenoxy)-5-(trifluoromethyl)aniline and 6,6'-(1,2-phenylenebis(oxy))bis(3-(trifluoromethyl)aniline) via Williamson’s ether synthesis reaction and Hydrogenation on Pb/C.
2. To prepare polyimide film by use 3 diamine monomers react with four types of Anhydride including PMDA, 6FDA, BPDA, and ODPA.
3. To characterize polyimide film and compare with standard polyimide film that prepare from ODA and PMDA or Kapton.
4. To develop and modified the preparation method of transparent colorless polyimide film with acceptable color, mechanical and thermal property.

1.3 Benefits of The Research

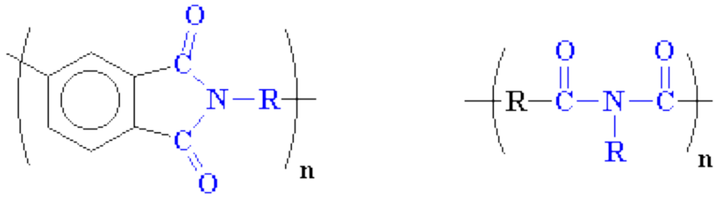
1. To obtain transparent polyimide sheet that can apply to use in optical application.
2. To investigate the application of Williamson’s ether synthesis and Hydrogenation to synthesize the new transparent polyimide diamine monomer.
3. To obtain freestanding colorless transparent polyimide film with acceptable mechanical and thermal property.
4. To obtain knowledge about the effect of constrain in diamine molecules on the transparent property of polyimide.

CHAPTER II

THEORY

2.1 Polyimide [1]

Polyimides are useful engineering polymers applied widely in electronic application since they exhibit exceptional thermal, thermo-oxidative, and chemical resistance, and good radiation resistance and dimensional stability, excellent in mechanical and electrical properties. The characteristic of polyimide main chain is the imide structure –CO–N–CO– as a linear or heterocyclic unit as showed in Figure 2.1.



aromatic heterocyclic polyimide

linear polyimide

Figure 2.1 Two type of polyimide [2]

In commercials, Aromatic polyimide films are widely used under the trade name UItem by General Electric and Kapton by Dupont. Normally, the Aromatic polyimide films are prepared by a two-step polymerization reaction of aromatic dianhydride with either aromatic diamine or aromatic diisocyanate in a suitable reaction medium.

By Another way, One-step polymerization can produce high molecular weight aromatic polyimides too. But this process is not practical in general case because the nature of polyimides is usually insoluble and intractable, but will be very useful for soluble polyimide.

2.2 Synthesis of polyimides

2.2.1 One-step method polymerization

One-step polymerization is a homogeneous solution polymerization at high temperature, so the organic solvents using in these process such as nitrobenzene, benzonitrile, α-chloronaphthalene, o-dichlorobenzene, trichlorobenzenes, and phenolic solvents such as m-cresol and chlorophenols in addition to dipolar aprotic amide solvents should withstand high temperature. Toluene is often used as a co-solvent to help removing water that occurred from reaction by azeotropic distillation. In general, the stoichiometric of monomers must exactly equal between amine and anhydride and the reaction was obtained at high boiling temperature about 140-250 ^{o}C up to boiling point of solvent. In the reaction, the imidization via amic acid intermediate still proceed. However, the quantity of amic acid groups at any time is very small, because it is not stable at high temperature and also can be imidized or reverted to amine and anhydride. Due to the water forming with imidizing in the reaction, some of the anhydride groups are rapidly hydrolyzed to o-dicarboxylic acid. At the beginning, when diamine and dianhydride are mixed and heated to 30-100 ^{o}C, the viscous solution of intermediate was formed as poly(amic acid). This stage usually observes the phase separation in nonpolar solvent. After the temperature rising to 120-160^{o}C, the reaction mixture will become homogeneous. The product occurred in this stage is a low molecular weight polyimide with o-dicarboxyl and amino end group. After that, the polycondensation between the end groups was generated slowly.

2.2.2 Two-step polymerization reaction [1-5]

The two-step polymerization through poly(amic acid) process is very important in polyimide synthesis procedure. In this process, the reaction between a dianhydride and a diamine will occur and produce poly(amic acid) at ambient conditions in a dipolar aprotic solvent (eg. DMAc, NMP). Then, poly(amic acid) will imidize into the final polyimide by thermal or chemical imidization process. Now days, this 2-step process is primary procedure for preparation of high performance aromatic polyimide films due to the infusible and insoluble properties of polyimide. Therefore, the film should be produce thought polyamic acid step which it can be soluble in solvent and the the imide ring will created by thermal or chemical imidization. The process also used in producing of the first significant commercial polyimide as Kapton that was the most extensively successfully developed with the great properties of mechanical, themal, and electrical. Kapton polyimide was synthesized from pyromellitic dianhydride (PMDA) and 4,4’-oxydianiline (ODA). The process and structure can be illustrated in Figure 2.2.

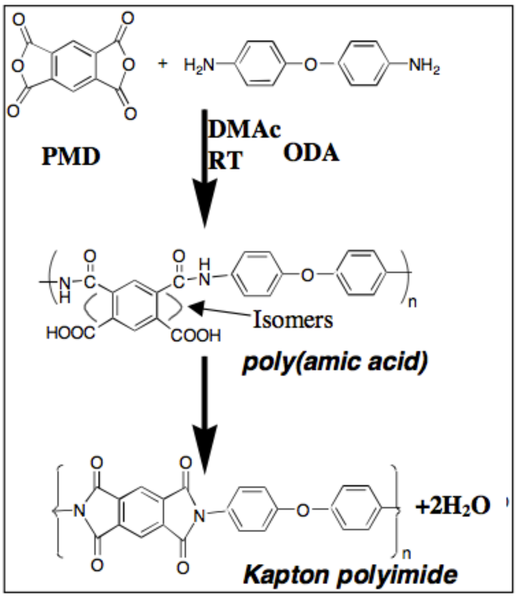


Figure 2.2 Reaction scheme for the preparation of Kapton [3]

The process from Figure 2.2 seems like a simple but there involved many steps of complex scheme [3]. The reaction was severely affected by many factors especially the reaction condition, mode of monomer addition, that can resulted the polyimide molecular weight [4-5]. The success of the overall reaction can yield high molecular weight polymers. Choice of monomers can be explaining individual case, the solvents, reaction conditions was also importance factor for control polymer properties. Explanation of every steps are followed paragraph.

- **Formation of poly(amicacids)[3,6-8]**

Poly(amic acid) is the intermediate component of polyimide synthesize rezation, it's occurred by dianhydride are mixed with diamine in a dipolar aprotic solvent such as DMAc or NMP at ambient temperatures. The amino group was a key role as a nucleophilic group for attacks on the carbonyl carbon of the anhydride group as show the steps of reaction in Figure 2.3. The reaction was start with opened the anhydride ring to form an amic acid group, this step cans revers with higher of forward rate constant [6]. By the way, the irreversible reaction will be offended in case of the most of pure reagents utilized. The high molecular weight formation is very affected firm this difference reaction rate constant. For the reverse reaction, the carboxyl proton will attacked the adjacent poly(amic acid) group [7]. Therefor, any reagent in this reaction can increase a chance of moving reaction equilibrium to the right hand side for more forward reaction.

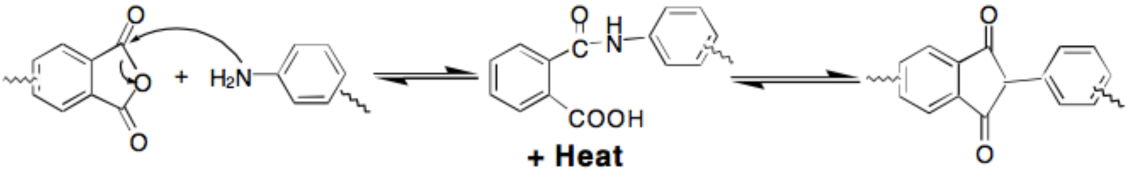


Figure 2.3 Generalized reaction mechanism of aromatic imide formation [3]

Strongly hydrogen bonded complexes formation in polar aprotic solvents with the free carboxyl groups can lead the equilibrium constants in excess of 10^5 l/mol at ambient conditions [6]. But if the reaction was occurred in ether or hydrocarbon solvents, the equilibrium constant differences are observed. Consideration of the difference is upon the amine's basicity and the dianhydrides electrophilicity [8].

Good of exothermic reaction by lower temperature is the one important characteristic of the poly(amic acid) formation, but it usually does not show any detectable effect on the reaction because the equilibrium is shifted so far to the right at ambient condition. In addition, the concentrations of monomers are also the one important key. As in the bimolecular forward reaction and the unimolecular reverse reaction, then if the monomer concentration increased, high molecular weight products will be produced. For the case of very dilute solutions, this feature is very important and produce an affect the decrease in molecular weight of the poly(amic acid).

- **Thermal imidization of a poly(amic acid)**

After poly(amic acid) are produced, the converted to the final polyimide by the thermal imidization route are useful when the final product is desired as a film or a coating form. Films are firstly cast on a substrate such as a glass plate and then undertaken through a thermal cycle with temperatures ranging from 100°C to 350°C. There has been considerable debate in the literature regarding the exact thermal cycle to be utilized for achieving close to 100% imidization of the poly(amic acids). There are two main different types of thermal cycles utilized that can be shown as follows,

1) Heating gradually to 250°C-350°C, depending on the stability and Tg of the polyimide [7,9].
2) Heating the poly(amic acid) mixture to 100°C and holding for one hour, heating from 100°C to 200°C and holding for one hour, heating from 200°C

to 300°C and holding for one hour and slow cooling to room temperature from 300°C [9-11].

There are very complicated factors involved in thermal imidization process that determine the degree of imidization of the polyimide film. The imidization can be occurring in very concentrated viscous solution. Then, the residual solvents from initial and intermediate state (polyamic acid formation) play a very important role in effect to the film property. In this regard, the imidization proceeds faster in the presence of dipolar amide solvents due to several reasons, some of which are;

1) Specific solvation allows the favorable conformation of the amic acid group to cyclize [12].

2) Plasticizing effect of the solvent to increase the mobility of the reacting functional groups [9].

3) The basicity of the amide solvent allows it to accept protons and may be responsible for the specific effect [7].

A simple kinetic expression for the imidization reaction cannot be explained in overall process details because it involves several interrelated elementary reactions and dynamically changing physical properties such as diffusion rate, chain mobility, solvation and acidity. The initial stages will be faster due to the presence of solvent and shorter chain sizes, resulted in an increased chain mobility. In the later stages, the rate tapers off due to it's loss of residual solvent that occurs due to the extended heating [13]. There also have a relation between T_g of the polymer and degree of imidization reaction. If T_g of the polymer increases, the degree of imidization reaction proceeds and as the T_g approaches the reaction temperature, the imidization rate is slower down markedly due to the decreased in chain mobility.

2.3 Effect of molecule structure on film property

Glass transition temperature (T_g) - structure relationships [1]

The exact nature of relationship for glass transition temperature of linear aromatic polyimides and their structures is complex due to several factors involved in determining the T_g. The chain stiffness is certainly the most important aspect, and other substantial factors like chain-chain interactions affect the T_g. The factors that effect to T_g also include isomeric attachments of the flexible/rigid groups and presence of bulky side groups, which affect both the chain stiffness and the chain-to-chain interactions too. Other factors such as crystallinity and molecular weight can also contribute to influencing of the T_g.

Polyimide chain-chain interactions

The charge transfer complex (CTC) formation between the dianhydride and diamine groups in polypyromellitic diimides using UV spectroscopy to describe the color changes in the materials by a cut-off wave length of optical wavelengths was first proposed by Kotov et al. [14] in. A cut-off of optical wavelengths found that it was inversely correlated with the ionization potential of the diamines. After that, in **1984 Fryd** [15] applied the same reason as Kotov by CTC formation between dianhydride and diamine groups in polyimides hypothesis that were important reason for polyimides with high T_g. the high interchain interaction is strongly affected for polyimide T_g which can also proposed that the presence of any bridging group in the dianhydride had a strong influence on the glass transition as it changed its electron affinity and hence promoted the possibility of CTC formation.

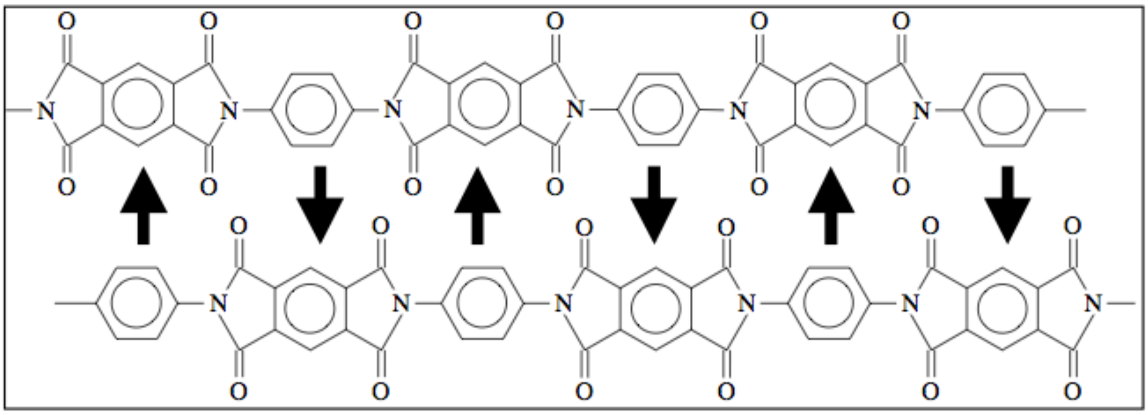


Figure 2.4 interactions between the dianhydride and diamine groups [3]

Figure 2.4 was illustrated of an interaction between the dianhydride and diamine groups. Nevertheless, the alignment of repeating units will not occur over more than a few repeating units. The values of E_a cannot be used directly to measure or estimate the interaction in quantitative, but in this case, PMDA that have more electron deficient was certainly had a much larger affinity than ODPA for the electron rich amine-derived center. This type of interaction can also be looked as a Lewis acid-base kind [16]. For now, many researchers show a very strong electronic interaction in polyimides that can affect to the polyimide film color [17]. They also studied and investigated to reduce this electronic interaction in order to develop the transparent colorless polyimides, to increase solubility and lower the dielectric constant [18-20]. Therefore, the *qualitative* nature of the relationship between the T_g of the polyimides and the E_a of the dianhydrides for several polyimides can successfully explained by the CTC model, but the T_g seemed to become insensitive to E_a of the dianhydride especially in case of the bridging group in the dianhydride becomes longer [16].

For another type to inlustrated the chain-to-chain interaction in polyimide molecule such as the preferred layer packing arrangement where the dianhydride and the diamine sections of the one chain were correspondingly packed alongside the dianhydride and diamine sections of another chain [3]. This type of chain-to-chain interaction that will occur in the crystalline state can be shown in Figure 2.5.

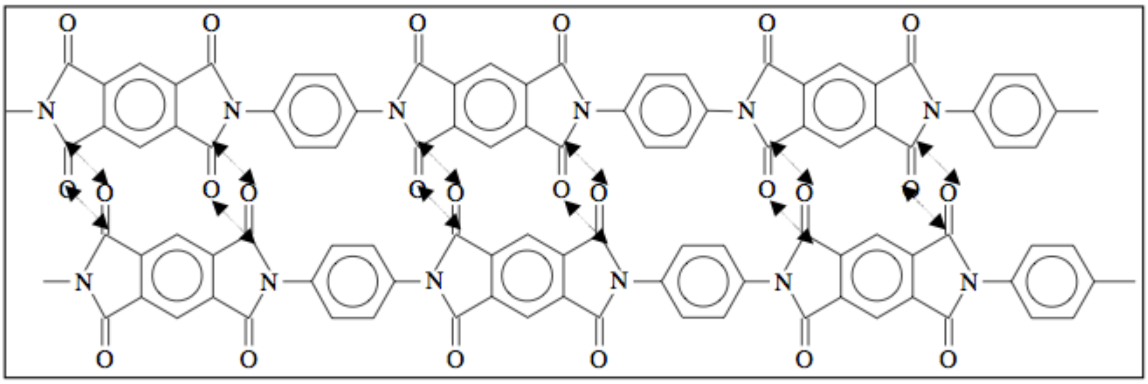


Figure 2.5 Idealized polymer chain-chain interaction in the crystalline state [3].

Such chain packing models had also been utilized to qualitatively explain the predominating effects of any bridging groups present in the dianhydride, which then may disrupt the packing arrangement by inhibiting the carbonyl-carbonyl dipolar attractions. Inducing of bridging or bulky groups in the diamine had been proposed to only reduce the packing density which it directly factor that effect to final T_g [3]. While such explanations provided some degree of qualitative explanation of T_g behavior, they cannot be utilized for any convenient quantification to predict the Tg. Although such ideal chain-to-chain interactions had been hypothesized, the structural arrangements within any polyimide should be governed by minimum energy conformations.

Dielectric properties [17]

Once polyimide had been considered as viable candidates for use in electronic, an microelectronic device, it had become important to address reliability issues before and after exposing the devices to environmental stresses. The main incentives for introducing polyimide as dielectric layers in multilevel interconnect system are their good planarizing properties, excellent thermal resistant at 400-450 °C, and low dielectric constant.

The two type of capacitors that have been use to determine the dielectric properties of the commercial polymers can be represented as in **Figure 2.6.**

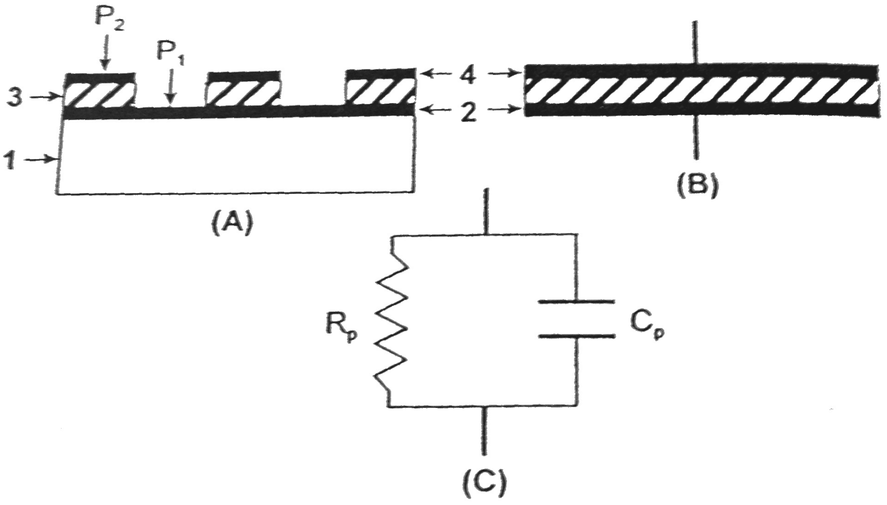


Figure 2.6 The two type of capacitors that have been use to determine the dielectric properties [17]

Design 2.6(A) shows the cross-section of capacitors made by conventional semiconductor technologies using silicon wafers covered with a thin layer of aluminium or gold. IP305PI$_2$Q or IP200PPQ solutions are then spin coated over the metallized substrate to obtain 0.5-5.0 micrometer thick dielectric films after curing at 400-450 °C. Top metallization was deposited by evaporation or sputtering, and patterned by photolithography to form 3 x 3 mm^2 test devices. Electrical contacts for measuring capacitance are taken in P$_1$ and P$_2$. Figure 2.6 (B) represent the cross-section of capacitors fabricate by casting thick layer of polyimide over Al foil. Subsequent metallization provides the top conductor film, the assembly being then cut into 33 mm diameter circular disks. This process, had been used for evaluation of the permittivity and dissipation factor of 10-30 micrometer thick IP620 and IP625 polyimide

Polyimide dielectric properties were determined by connecting a sinusoidal voltage source (AC-current) to the capacitor electrodes. Polymer responses depended on its polarizability as that arises form electronic, atomic and molecular reorientation in the electric field. As molecular dipoles absorbed energy from the electric field to align themselves with the alternating applied current, a resistive component, R_p, was added in parallel to the capacitor, C_p as shown in Figure 2.6(C). The dissipation factor was thus defined as the ratio between the resistive current and the capacitive current. The complex permittivity, **ε,** which accounts for the loss factor, is expressed as **ε= ε'-i ε'',** where **ε'** and **ε''** are the permittivity and dielectric loss factor, respectively.

One theoretical approach for calculating polymer permittivity consider that the **ε** value is related to van der Waals' parameters by the following relation:

$$\varepsilon = 0.303[\frac{\sum_1^i \Delta E_i^*}{N_A \sum_1^i W_i}]$$

Where ΔE_i^* is the sum of apparent cohesive energy of the additive increments characterizing the effect on the dielectric constant of each atom and each type of intermolecular interaction. Two terms are thus appearing in the expression of ΔE_i^*, the later taking into account the presence of polar groups:

$$\Delta E_i^* = \Delta E_i^d + \Delta E_i^p$$

Whose formalization allowed the establish of the general equation:

$$\varepsilon = 0.303\left[\frac{\sum_1^i \Delta E_i^*}{N_A \sum_1^i W_i}\right] + [\frac{\sum_1^i \Delta E_i^*}{N_A \sum_1^i W_i}]^{0.5} + 0.304$$

When applied to a series of conventional polyimide, this formula shows a very good correlation (2-5%) between calculated value and its experimental measurement.

2.4 The visible light spectrum

The visible light spectrum or know as the optical spectrum of light is the electromagnetic radiation spectrum section that can visible on human eye. It just ranges in wavelength from approximately 400 nm (4×10^{-7} m) to 700 nm (7×10^{-7} m). The color that occur on human eye related by the wavelength of light which it relate by energy and frequency that listed in the table below.

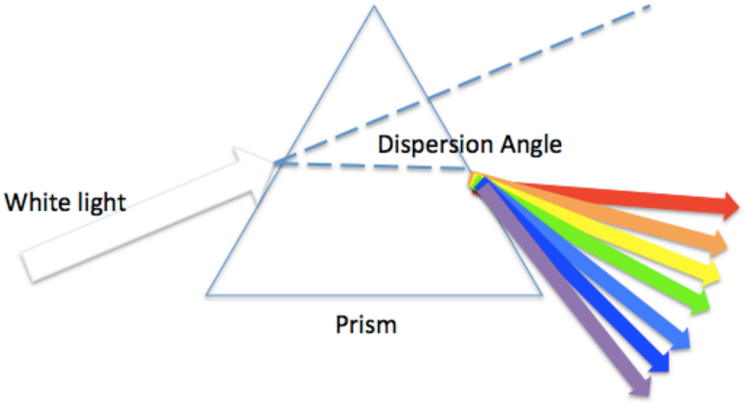


Figure 2.7 spectra of visible light

White light is the light that contains all of light in range of visible light that most interact to our eye. If the white light radiate through prism, the light will be separated into many colors due to the difference of optical refraction of each color of light (relate with wavelength) in prism. The order of wavelengths (as shown to the right) is in order of wavelength, which can be remembered by the mneumonic "Roy G. Biv" for Red, Orange, Yellow, Green, Blue, Indigo (the blue/violet border), and Violet. You'll notice that in the image and table Cyan is also appears fairly distinctly, between green & blue.

Reflection and transmission of light waves can be occuring from the cause of not match frequencies of the light waves to the objects natural vibration frequencies. When light waves of these frequencies strike an object, the electrons in the atoms of the object will vibrate. The vibrating will not occour in resonance at a large amplitude, but the electrons vibrate just for brief periods of time with small amplitudes of vibration. After that, the energy is reemitted in term of electronic wave in rang of the visible light wavelenght. In case of the transparent object, the vibrations of the electrons can passed from surface atoms to next atoms through the bulk in the material and reemitted on the opposite side of the object, this behavior of frequencies of light waves are “transmitted”. In case of opaque object, the electrons vibrations are not passed from surface atoms to next atoms through the bulk of the material. By the way, material's surface atommic electrons will exhebits short periods of time vibration. After that, energy will reemite as a reflected light wave. this behavior of frequencies of light waves are “reflected”. These two propose can explain the obsevation color of the object, due to the way those objects interact with light and ultimately reflect or transmit it to our eyes. We can said that the seeing color of an object is not actually came from the object itself. In other words, the color is in the light that shines from it and is ultimately reflected or transmitted to our eyes. We know that the visible light spectrum consists of a range of frequencies, each of which corresponds to a specific color. As the explanation in previous, when visible light strikes an object, some of specific frequency will be absorbed by object and the light in that frequency never make it to our eyes. Any visible light that strikes the object and becomes reflected or transmitted to our eyes will contribute to the color appearance of that object.

Table 2.1 The Visible Light Spectrum

Color	**Wavelength (nm)**
Red	**625 - 740**
Orange	**590 - 625**
Yellow	**565 - 590**
Green	**520 - 565**
Cyan	**500 - 520**
Blue	**435 - 500**
Violet	**380 - 435**

2.5 Transparent Polyimide

Transparent polyimide has been developed for use in optical electronic application such as cover layer of solar cell, LCD or LED display, and transparent circuit. From literature review, the transparent or color property were obviously depended on Intermolecular interactions such as charge-transfer complex, electronic interaction, and intermolecular cohesive.

There are many methods to reduce Intermolecular interactions by add the intermolecular space such as,

-Aryl-ether linkage in monomer improved

-Unsymmetrical or twisty units into the polymer backbone

-Introduction of bulky, rigid units in the polymer main chain or as pendent groups

-Hybrid with inorganic material

In 2009, **Yang-Yen Yu**[18] prepared the transparent PI-silica hybrid thin films (Figure 2.8) from soluble fluorine-containing polyimide and 12 nm monodispersed colloidal silica. In the result, UV-vis spectra showed that the cutoff wavelength of all prepared hybrid films was less than 272 nm and could be tunable through the silica content. Morever, The analysis showed that the refractive index (n) of PS hybrid films was in the range of 1.575–1.479, which depended on the silica content. The extinction coefficients (k) were almost zero in the 300–900 nm wavelength range, indicating that the prepared hybrid films had an excellent optical transparency in both the UV and visible regions. There for, the results demonstrated the potential of the prepared polyimide–silica hybrid thin films for optical applications.

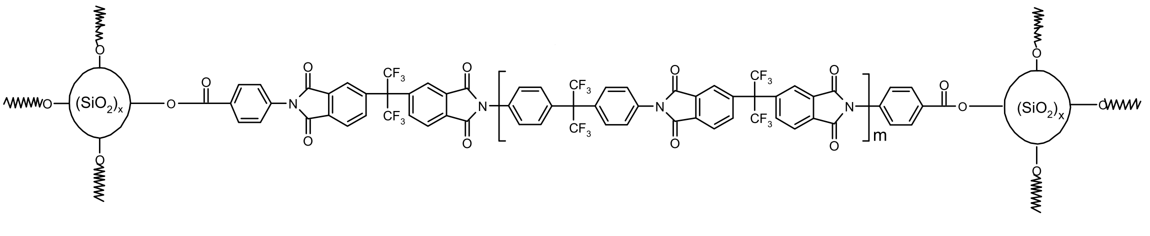


Figure 2.8 Transparent PI-silica hybrid thin films structure [18]

In 2010 **Du Pont** launched a new product of transparent colorless Kapton that utilized the asymmetric dianhydride and fluorinated diamine for colorless application. Then many researchers have been interested and investigated this concept of producing asymmetric and fluorinated monomer to prepare the transparent polyimide while kept good thermal and mechanical property. [19]

In 2010 **Sheng-Huei Hsiao** [20] applied the new synthetic diamine PI monomer that added the Aryl-ether linkage and CF_3 bulky unit (Figure 2.9). The film cast by this diamine monomer with various conventional dianhydride has three improvements as follows,

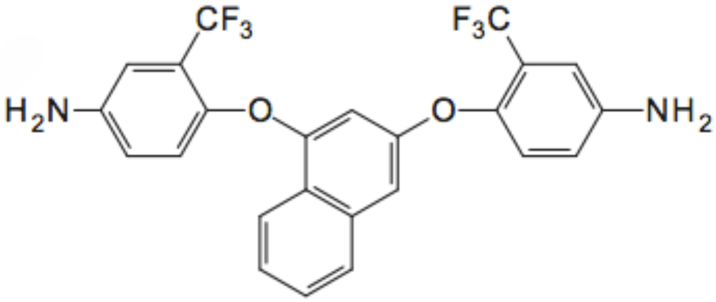


Figure 2.9 Synthetic diamine PI monomer [20]

-Unsymmetrical or twisty units into the polymer backbone

-Aryl-ether linkage in monomer improved for

Better solubility

Melt processing characteristics

Improved toughness

- Introduction of bulky, rigid units in the polymer main chain or as pendent groups

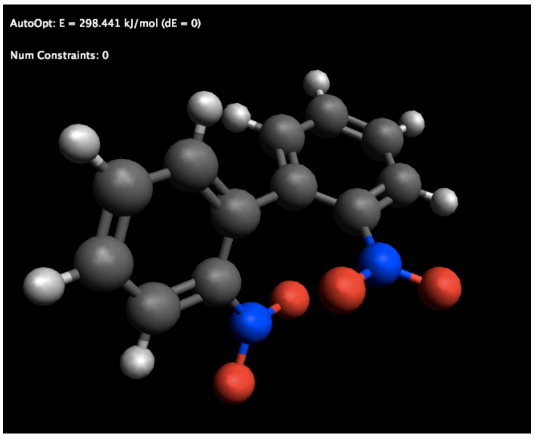
Increase in T_gs (restricting the segmental mobility)

Enhanced solubility (decreased packing density and crystallinity)

As a result, transparent property, water resistant and process ability of polyimide film were increased. The almost colorless should be the effect from the reduction of intermolecular and intramolecular charge-transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. Also, CF_3 groups in their diamine moieties could be explained by that the hexafluoroisopropylidene moiety could separate the chromophoric groups and reduced electronic interaction. The light colors of the polyimides with the CF_3 groups in their diamine moieties also could be explained from the decreased intermolecular interactions. The bulky and electron-withdrawing CF_3 group in diamine was effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). Another positive effect of the CF_3 groups on the film transparency was the weakened intermolecular cohesive force due to lower polarizability of the C–F bond. The decrease in intermolecular CTC formation was reasonable also from the significant solubility of the polyimides prepared from CF_3-diamine.

Due to the optical transparency and coloration of polyimide films are strongly depended on their molecular structure. In order to get a comprehensive understanding of the relationship between optical properties and polymer structure, the investigated of the three-dimensional molecular structures of the model compounds for polyimide was necessary [21]. The structure geometries could be optimized basically base on calculations using Universal Force Field theory (UFF). The molecular orbital energies of these model compounds were determined by molecular orbital (MO) calculation. The molecular orbital energy could be shown the effect to transparent property of polyimide.

The Universal force field (UFF), was described wherein the force field parameters were estimated using general rules based only on the element, its hybridization, and its connectivity [22]. The parameters used for the generation of Universal force field included a set of hybridization dependent atomic bond radii, a set of hybridization angles, van der Waals parameters, torsional and inversion barriers, and a set of effective nuclear charges. The UFF theory was widely use to simulated the three dimensions molecular structure because of lower error and common usage with any molecule. In present, the tree-dimension molecular structure model could be simulated based on UFF by computer program such as Avogadro as show in Figure 2.10.



```
AutoOpt: E = 298.441 kJ/mol (dE = 0)
Num Constraints: 0
```

Figure 2.10 the 3D molecular structure created by Avogadro, optimized molecule by UFF; Carbon, Hydrogen, Nitrogen and oxygen was describe in grey, white, blue and red, respectively.

2.6 Reaction to prepare diamine

2.6.1 Williamson’s ether synthesis [23]

The Williamson’s ether synthesis reaction is widely used in both of laboratory and industrial. In the case of asymmetrical ethers, there are two possibilities for the choice of reactants. One is usually preferable either on the basis of availability or reactivity. Another profit from Williamson’s ether synthesis reaction is applied to preparation of ether indirectly from two alcohols.

For the alkoxide (or aroxide) may be primary, secondary or tertiary. The alkylating agent, on the other hand is most preferably primary. The reaction also occurs in secondary alkylating agents, but in the last tertiary ones are usually too obtain to side reactions that it used in practical. Halide or a sulfonate is the most using as the leaving group in ester prparation for the purposed reaction. Due to the reaction condition is quite strong forcing. Then, the protecting groups are usually applied to use in reaction to pacify other parts of the reacting molecules (e.g. other alcohols, amines, etc.).

The alkoxide ions are usually prepared immediately prior to the reaction due to their highly reactivity. The carbonate base or potassium hydroxide are widely use in laboratory scale in chemistry academic while in industrial syntheses phase transfer catalysis is very common. The reaction can accomplish by many polar aprotic solvent. Nevertheless, in apolar solvent and protic solvent, the reaction is trend to slow as a result of lowering the availability of the free nucleophile. For this reason, acetonitrile and N,N-dimethylformamide are particularly commonly used in this reaction.

In General, the Williamson’s ether synthesis reaction can occur in the range of temperature from 50–100 °C and will complete in 1–8 hours. In the laboratory, the reaction can be complete around 50-60% yield due to the most of side reaction that can be occurs while reaction, as same behavior in commercial industry, the same number of %yield will occur.

This reaction can obtain with no need for catalysis in the lab scale. Nevertheles, for unreactive alkylating agent (e.g. an alkyl chloride) need to improve the rate of reaction by the addition of a catalytic quantity of a soluble iodide salt (which undergoes halide exchange with the chloride to yield a much more reactive iodide, a variant of the Finkelstein reaction). In some extreme case, silver salts may be added to catalyze the reaction, for example silver oxide (Figure 2.11)[23].

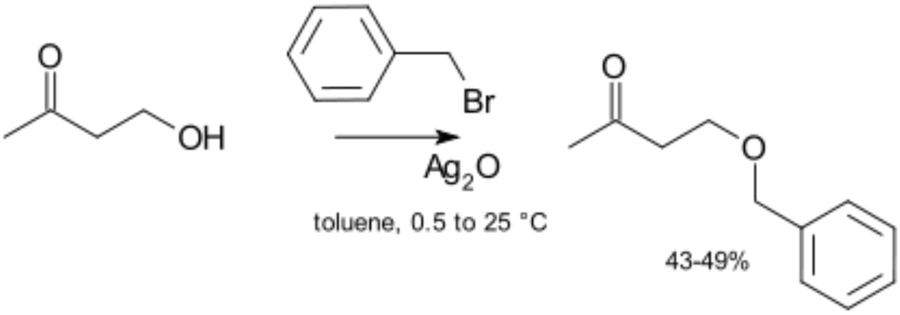


Figure 2.11 Winlliamson's ether synthesis [23]

The silver ions that add in to the reaction will coordinate with halide group to separate it from the molecule of reactant, the reaction to substitute hydroxyl group can be easy obtain. In some case, the phase transfer catalysts also can be used (e.g. tetrabutylammonium bromide or 18-crown-6) in order to increase the solubility of the alkoxide by which it contributes a softer counter-ion.

In general, The Williamson's reaction is completes by the base catalyzed elimination of alkylating agent and the suitable condition as temperature and the type of solvent using in the reaction. In addition, the natures of the leaving group are also strongly effect to the reaction such as some structure of alkylating agent can be particularly prone to elimination.

If the nucleophile is an aroxide ion, the Williamson's ether synthesis reaction will obtained with alkylation on the ring since the aroxide is an ambient nucleophile.

2.6.2 Hydrogenation on Pd/C[24]

Hydrogenation reaction is a one form of chemical reduction, is a chemical reaction which it occur between molecular hydrogen (H_2) and another compound or element. The reactions are usually in the presence of a catalyst. The advantage of hydrogenation process is commonly used to saturate the hydrocarbon or the unsaturated compound. In general, the hydrogenation process are propose to substitute hydrogen atom into double bond or triple bond, but in some process the hydrogenation can applied to the reduction reaction for molecule with high oxidation group such as NO_2.. The reaction can be succeed in high temperature condition or obtain in lower condition with catalysis process.[24]

The reaction that relate with hydrogenation is widely develop such now a day due to the benefits from hydrogen. Basically, the process can be done by hydrogenation in gas phase of hydrogen (H_2). Nevertheless, the hydrogen atom can be obtain from another source in some process which these processes are called transfer hydrogenations. The reaction of hydrogenation can be reverse by removal of hydrogen atom which it called “dehydrogenation”. The position of the bonds that broken when hydrogen adding is called “hydrogenolysis”, a reaction that may occur to carbon-carbon and carbon-heteroatom (oxygen, nitrogen or halogen) bonds.

An obviously seen of example of a hydrogenation reaction is the insertion of hydrogen atom into maleic acid to form succinic acid.[25] At present, the reaction is include many important applications of this petrochemical such it found in pharmaceutical and food industries. For example, the hydrogenation of unsaturated fats produced more saturated fats and, in some cases, trans fats.

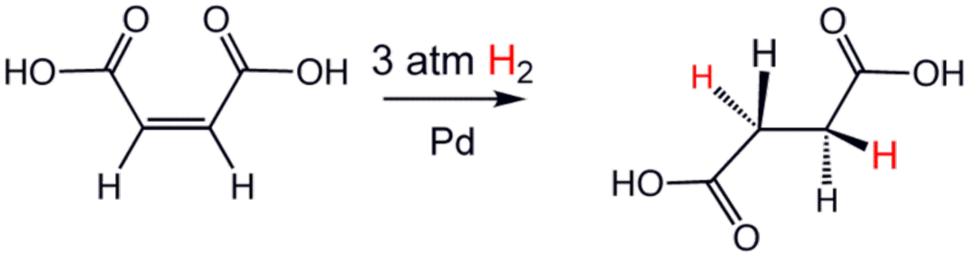


Figure 2.12 Hydrogenation of unsaturated fats produces saturated trans fats [24]

The hydrogenation reaction on Pd/C was use in preparation of amine functional group from nitro group, eg. In 2009, **S. Dehghanpour and F. Rominger** [26] used hydrogenation on Pd/C to prepare 2,2'-diaminobiphenyl from 2,2'-dinitrobiphenyl.

2.7 Solvent [27]

A solvent was defined that the solid, liquid or gas which dissolved another solid, liquid or gas. In the solution system, a solvent was define that the one of the most compound. Common usages for organic solvents were in dry cleaning (e.g. tetrachloroethylene), as paint thinners (e.g. toluene, turpentine), as nail polish removers and glue solvents (acetone, methyl acetate, ethyl acetate), in spot removers (e.g. hexane, petrol ether), in detergents (citrus terpenes), in perfumes (ethanol), and in chemical synthesis. The use of inorganic solvents (other than water) was typically limited to research chemistry and some technological processes.

Protic solvent

Protic solvent is a polar solvent that has a hydrogen atom bound to an oxygen as in a hydroxyl group or a nitrogen as in an amine group. Including any molecular solvent that contains dissociable H^+ such as hydrogen fluoride. The molecules of such solvents can donate an H^+ (proton). Conversely, aprotic solvents cannot donate hydrogen.

- **Polar protic solvents** are solvents that share ion-dissolving power with aprotic solvents but have acidic hydrogen. These solvents generally have low dielectric constants and low polarity such as water, methanol, ethanol, formic acid, hydrogen fluoride and ammonia. Common characteristics of protic solvents are as follows,

- Solvents display hydrogen bonding
- Solvents have an acidic hydrogen (although they may be very weak acids)
- Solvents are able to stabilize ions
    - cations by unshared free electron pairs
    - anions by hydrogen bonding

- **Polar aprotic solvents** are solvents that share ion-dissolving power with protic solvents but lack acidic hydrogen. These solvents generally have high dielectric constants and high polarity such as dimethyl sulfoxide, dimethylformamide, dioxane and hexamethyl phosphorotriamide, tetrahydrofuran. Common characteristics of aprotic solvents are as follows,

- Solvents do not display hydrogen bonding
- Solvents do not have an acidic hydrogen
- Solvents are able to stabilize ions

Apart from solvent effects, polar aprotic solvents may be essential for reactions that use strong bases, such as reactions involving Grignard reagents or *n*-butyllithium. If a protic solvent were to be used, the reagent would be consumed by a side reaction with the solvent.

The solvents are grouped into non-polar, polar aprotic, and polar protic solvents and ordered by increasing polarity. The polarity is given as the dielectric constant. The properties of solvents that exceed those of water are bolded.

Table 2.2 Properties of Non-Polar Solvents

Solvent	Chemical Formula	Boiling point (^oC)	Dielectric constant	Density (g/ml)	Dipole moment
Hexane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_3	69	2.0	0.655	0.00
Benzene	C_6H_6	80	2.3	0.879	0.00
Toluene	C_6H_5-CH_3	111	2.4	0.867	0.36
1,4-Dioxane	/-CH_2-CH_2-O-CH_2-CH_2-O-\	101	2.3	1.033	0.45
Chloroform	$CHCl_3$	61	4.8	1.498	1.04
Diethyl ether	CH_3CH_2-O-CH_2-CH_3	35	4.3	0.713	1.15

Table 2.3 Properties of Polar Aprotic Solvents

Solvent	Chemical Formula	Boiling point (°C)	Dielectric constant	Density (g/ml)	Dipole moment
Dichloromethane (DCM)	CH_2Cl_2	40	9.1	1.327	1.60
Tetrahydrofuran (THF)	/-CH_2-CH_2-O-CH_2-CH_2-\	66	7.5	0.886	1.75
Ethyl acetate	CH_3-C(=O)-O-CH_2-CH_3	77	6.0	0.894	1.78
Acetone	CH_3-C(=O)-CH_3	56	21.0	0.786	2.88
Dimethylformamide (DMF)	H-C(=O)N$(CH_3)_2$	153	38.0	0.944	3.82
Acetonitrile (MeCN)	CH_3-C≡N	82	37.0	0.786	3.92
Dimethyl sulfoxide (DMSO)	CH_3-S(=O)-CH_3	189	47.0	1.092	3.96

Table 2.4 Properties of Polar Protic Solvents

Solvent	Chemical Formula	Boiling point (°C)	Dielectric constant	Density (g/ml)	Dipole moment
Formic acid	H-C(=O)OH	101	58.0	1.210	1.41
n-Butanol	CH_3-CH_2-CH_2-CH_2-OH	118	18.0	0.810	1.63
Isopropanol (IPA)	CH_3-CH(-OH)-CH_3	82	18.0	0.785	1.66
n-Propanol	CH_3-CH_2-CH_2-OH	97	20.0	0.803	1.68
Ethanol	CH_3-CH_2-OH	79	30.0	0.789	1.69
Methanol	CH_3-OH	65	33.0	0.791	1.70
Acetic acid	CH_3-C(=O)OH	118	6.2	1.049	1.74
Water	H-O-H	100	80.0	1.000	1.85

CHAPTER III

EXPERIMENT

The experimental procedures in this study are divided into five parts as below;

(i) Materials and chemicals
(ii) Equipment
(iii) Preparation of Diamine
(iv) Preparation of the polyimide films
(v) Characterization Instruments

3.1 Materials and Chemicals

1. 2,2'-Bis-(3,4-Dicarboxyphenyl)hexafluoropropanedianhydride (6FDA) purchased from Aldrich chemical Company, Inc.
2. 4,4'-(Hexafluoroisopropylidene)dianiline (6F-Diamine) purchased from Tokyo Chemical Industry Co., Ltd. (TCI)
3. Hydrazine monohydrate purchased from Tokyo Chemical Industry Co., Ltd. (TCI)
4. 2,2 Dinitrobiphenyl purchased from Tokyo Chemical Industry Co., Ltd. (TCI)
5. 4-Nitro-3-chlorobenzotrifluoride purchased from Tokyo Chemical Industry Co., Ltd. (TCI)
6. 2-Nitrophenol purchased from Tokyo Chemical Industry Co., Ltd. (TCI)
7. Catechol purchased from Tokyo Chemical Industry Co., Ltd. (TCI)
8. Potassium carbonate (K_2CO_3) purchased from Merck KGaA Germany.
9. N-Methyl-2-pyrrolidinone (NMP) purchased from Merck KGaA Germany.
10. N,N-Dimethylformamide (DMF) purchased from Aldrich chemical Company, Inc.
11. Dimethyl sulfoxide (DMSO) purchased from Aldrich chemical Company, Inc.
12. Chloroform deuterate ($CDCL_3$-d) purchased from Aldrich chemical Company, Inc.

13. Argon gas (Ultra high purity grade, 99.999 %) was purchased from Thai Industrial Gas Co.,Ltd.(TIG) and further purified by passing through columns packed with copper catalyst, NaOH, P_2O_5 and molecular sieve 4A to remove traces of oxygen and moisture.

Others important chemical and chemical structure was showed in table 3.1

Table 3.1 Chemical structure of materials used in this research

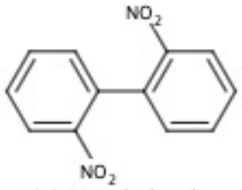
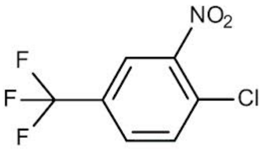
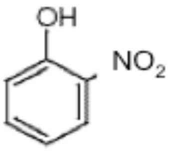
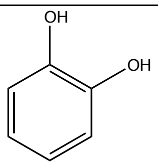
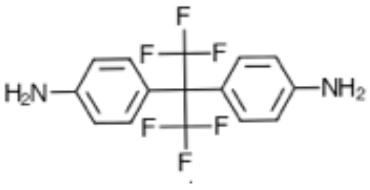
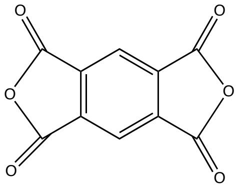
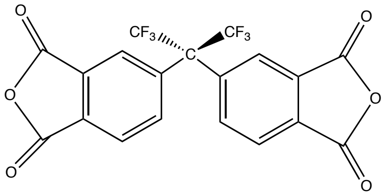
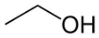
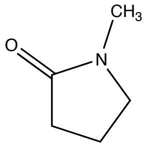
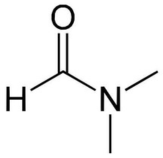
Materials	**Structure**
Diamine Preparing Substance	
2,2-Dinitrobiphynyl	
Hydrazine Monohydrate	$H_2NNH_2 \cdot H_2O$
3-Nitro-4-Chlorobenzotrifluoride	
2-nitrophenol	
Catechol	
Diamine for PI Synthesis	
6F-Diamine	

Table 3.1 (Continue) Chemical structure of materials used in this research

Materials	**Structure**
Dianhydride for PI Synthesis	
PMDA	
6FDA	
Catalyst	
Paladium 5% on Carbon	N/A
Sodium Hydride	N/A
Solvent	
Ethanol	
NMP	
Hexane	
DMF	

3.2 Equipment

3.2.1 Asymmetric Diamines synthesis part

In this part, the most of chemical that it uses as a reactant are sensitively with moisture and oxygen. Some chemical are also the health hazardous. Therefore, to handling with them including to storing, loading, and using, the special technique and advance equipment from hereinafter lists must be applied.

- **Glove box** is the equipment that used to storing the chemical that sensitive with air. The atmospheres in the box was control the moisture and oxygen which it both generally below 0.1 ppm. In the box were always recirculating by inert gas such as Argon. Every sensitive chemical was storing and loading in this equipment. The Glove box was shown in Figure 3.1.

Figure 3.1 Glove box

- **Schlenk line** with the inert gas line that used for purging the reactor to make inert atmosphere. The Schlenk line also included the vacuum line that were used for the application to make the system staying in vacuum such as the vacuum filtration. The Schlenk line was shown in Figure 3.2.

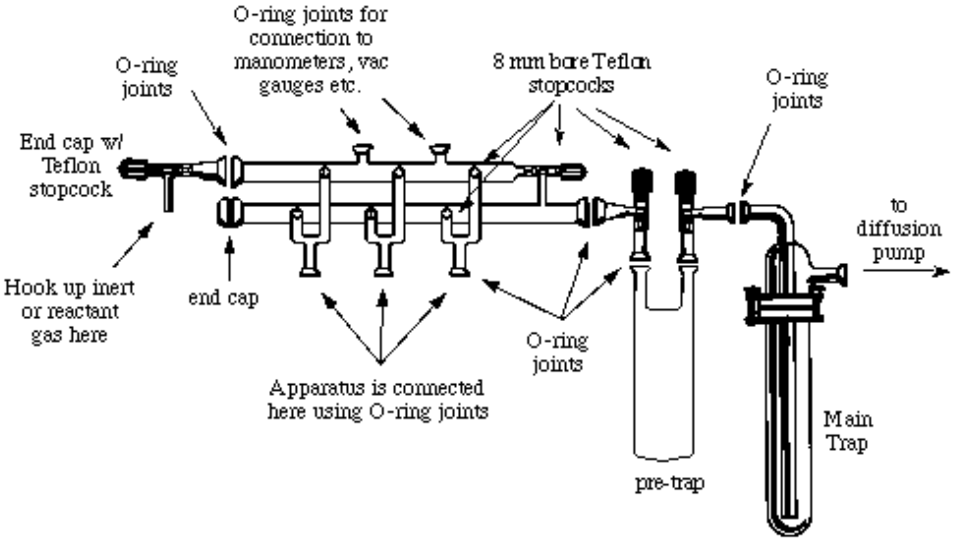


Figure 3.2 Schlenk line [28]

- **Vacuums pump** that used for supplying the low pressure about 10^{-1} to 10^{-3} mmHg to the vacuum line of the Schlenk line. The pump model is 195 from Labconco Coporation as shown in Figure 3.3.

Figure 3.3 Vacuums pump

- **Inert gas system** (Argon) was design by considering for the most purify Ar gas feeding to system, the Ar from cylinder was feeding passed BASF catalyst, R3-11G column to traped O_2 and the molecular sieve column as the moisture trap. The high purity Ar from the system was used for supplying the Schlenk line and purge to the reactor that contained innert atmosphere, needed for special reaction.
- **Parr Bomb reactor** with hydrogen gas feed system was used in Hydrogenation reaction. The reactor was designed to handle with high temperature and pressure system with 20 ml of liquid volume. The Parr Bomb reactor can be shown in Figure 3.4

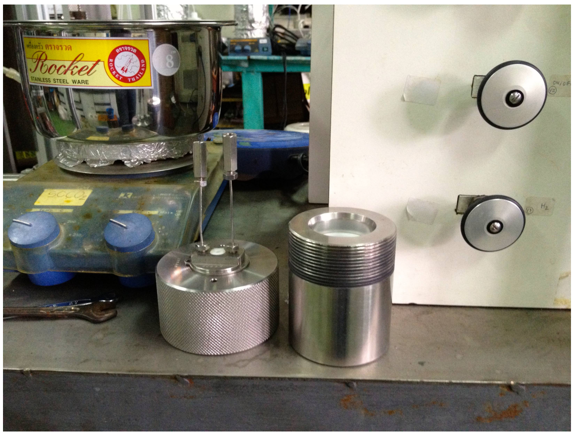


Figure 3.4 Parr Bomb reactor

- **Magnetic stirrer and Hot plate** The magnetic stirrer and hot plate model RCT basic from IKA Labortechnik were used.

- **Syringe and Needle** that used in these experiments had a volume of 20 ml, 10 ml, 3 ml and 1 ml with the needle No. 13g, 17 and 18 were cooperated.

3.2.2 Film preparation part

- **Three necks reactor, Dean stark and cooling tube** was used to the preparation of polyimide with one-step method polymerization. The equipment was assembled as shown in Figure 3.5.

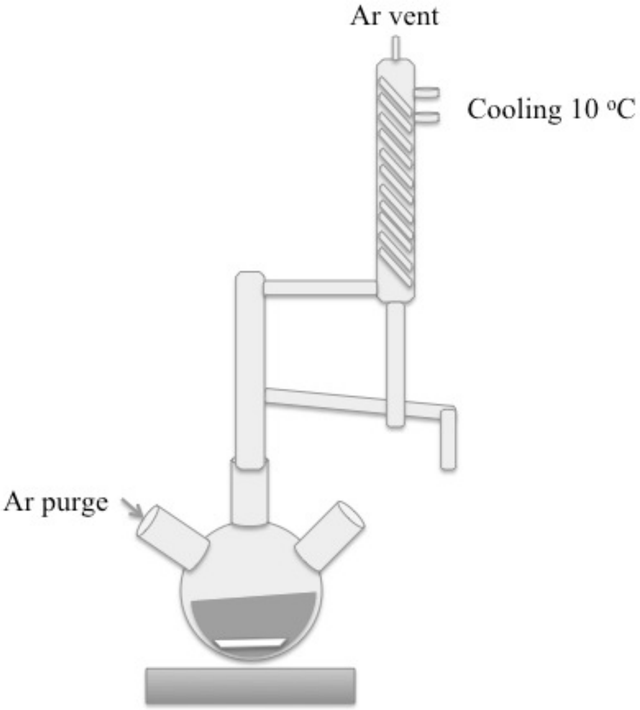


Figure 3.5 Three necks reactor, Dean stark and cooling tube

- **Vacuum Oven** as shown in Figure 3.6 was used for removing the solvent form polymer and also use to cure polymer in two-step method polymerization of Polyimide. Digital panel could monitor working conditions such as pressure and temperature which it could rise the maximum temperature up to 400°C

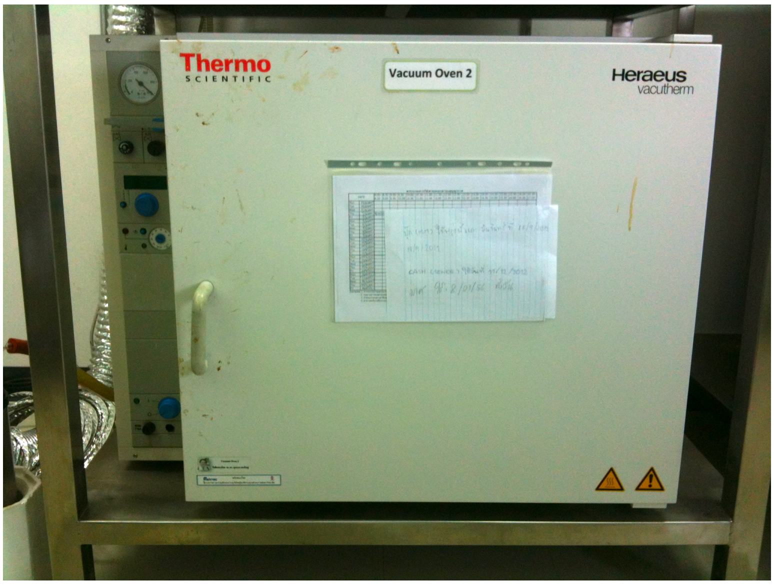


Figure 3.6 Vacuum Oven

3.3 Preparation of Asymmetric Diamines Monomer

This research was studied to synthesize three Diamines monomer including the 1st Diamine monomer as 2,2' Diaminobiphenyl, the 2nd Diamine monomer as 2-(2-aminophenoxy)-5-(trifluoromethyl)aniline and the 3rd Diamine monomer as. The preparation of these three Diamines would explain separately.

1st Diamine preparation

3.3.1 Preparation of 2,2' Diaminobiphenyl (1)

2,2-Dinitrobiphenyl was dissolved in ethanol in Parr Bomb reactor then 5% Pd/C and $NH_2NH_2.H_2O$ were added. The mixture was stirred at and heat in high pressure of H_2 atmosphere for 4 h as can be shown in Figure 3.7, and then filtered. The filtrate was poured in to 100 ml water, the precipitated was collected and purified by recrystallized in water/hexane. The structure of **(1)** was characterized by FTIR and ^{1}H-NMR with $CDCL_3$ solvent.

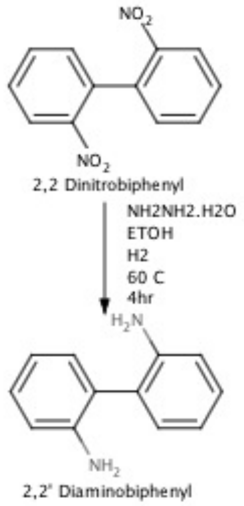


Figure 3.7 Synthesis of 2,2' Diaminobiphenyl **(1)**

2nd Diamine preparation

2nd Diamine had pretty more complicate structure than 1st (1). Therefor, the reactions to prepare 2nd were more complicated too. The reaction started by combining of reactants that both contain nitro group via Williamson's ether synthesis. The product from Williamson's ether synthesis reaction would be a Dinitro compound, which it reacted by Hydrogenation reaction to prepare Diamine. Details of both reactions would explain in 3.3.2 and 3.3.3 respectively.

3.3.2 Preparation of 2-(2-nitrophenoxy)-5-(trifluoromethyl)benzene (2a)

2-Nitrophenol and K_2CO_3 was added into DMF solvent in Ar atmosphere, stir for a while. Then, 4-Chloro-3-nitrobenzotrifluoride was added into the solution. The reactant mixture was stirred and heated to ~100 °C for 24 hour as shown in Figure 3.8. After that, cooled down by leaving in room condition till cooled down and poured the mixture into Diethylether. Then, the solution was extracted with water in separator funnel to separate the product from K_2CO_3 which it can be well dissolved in water. the diethylether phase was collected and remove all solvent by rotary evaporator. the solid product was collected. Washing the product repeatedly by water and purifing by recrystallization in hexane/water. The final purified product was characterized their structures by FTIR and NMR to assure the correctness.

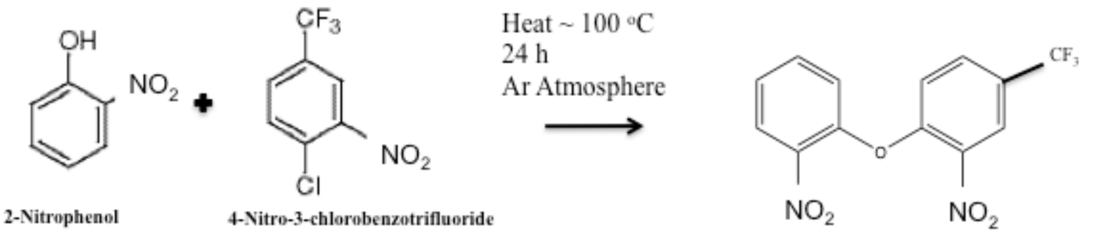


Figure 3.8 Preparation of **2-(2-nitrophenoxy)-5-(trifluoromethyl)benzene (2a)**

3.3.3 Preparation of 2-(2-aminophenoxy)-5-(trifluoromethyl)aniline (2)

2-(2-nitrophenoxy)-5-(trifluoromethyl)benzene (2a) was dissolved in 10 ml of ethanol in Parr Bomb reactor then 5% Pd/C and $NH_2NH_2.H_2O$ were added. The mixture was stirred and heat in high pressure H_2 atmosphere for 8 h as can be shown in Figure 3.9, and then filtered to remove the catalyst. The filtrate was removes all solvent by rotary evaporator. The structure of **(2)** was characterized by FTIR and ^{1}H-NMR with $CDCL_3$ solvent.

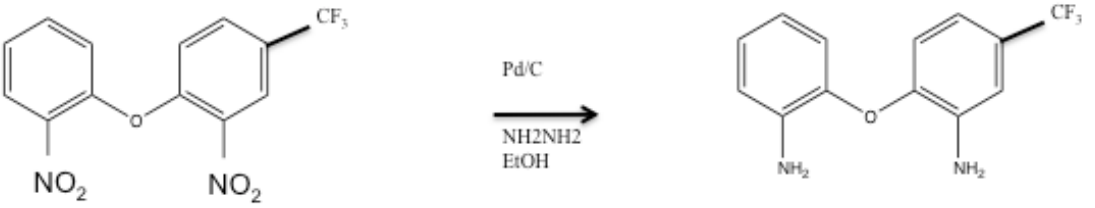


Figure 3.9 Preparation of 2-(2-aminophenoxy)-5-(trifluoromethyl)aniline (2)

3rd Diamine preparation

The steps of reaction to synthesize of the 3rd Diamine preparation were the same as the 2nd Diamine preparation. The reaction would started with dinitro synthesize via the Williamson's ether synthesis. The reaction was aiming to combine two reactants including by created the aryl ether linkage. After reaction, the Dinitro compound was reduced to change NO_2 group by Hydrogenation reaction to prepare 3rd Diamine.

3.3.4 Preparation of 6,6'-(1,2-phenylenebis(oxy))bis(1-nitro-3-(trifluoromethyl) benzine) (3a)

Catechol and K_2CO_3 were dissolved in DMF solvent in Ar atmosphere. Then, 4-Chloro-3-nitrobenzotrifluoride was added into the solution. The reactant mixture was stirred and heated for 48 hour as shown in Figure 3.10. After that, extracted with diethyl ether/water to separate the product from K_2CO_3. the diethylether phase was collected and remove all solvent by rotary evaporator. the solid product was collected. recrystallization in water/methanol. The final purified product was characterized their structures by FTIR and NMR to assure the correctness.

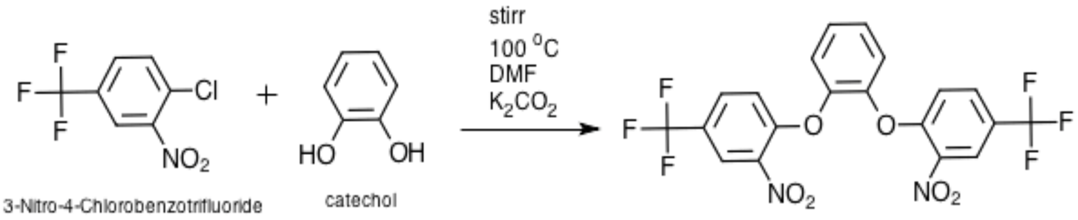


Figure 3.10 Preparation of 6,6'-(1,2-phenylenebis(oxy))bis(1-nitro-3-(trifluoro-methyl) benzine) **(3a)**

3.4 Preparation of the polyimide films

3.4.1 Preparation of the polyimide films from 1st Diamine (PI-1)

The dried Diamine monomer **(1)** was collaborated with 6F-Diamine to react with commercially available aromatic Dianhydride, 6FDA to give the polyimides as shown in Figure 3.11. The mole ratio and solid content of **(1)**:6F-Diamine:6FDA was 1:1:2 and 18 wt% respectively. 6F-Diamine and **(1)** was dissolved in NMP and then 6FDA was added. The solution was stirred at room temperature for 1 hour to forming the poly(amic acid)(PAA) in NMP as a viscous solution Then it was poured into 10 x 20 cm glass plate which some of solvent was removed in Vacuum Oven at 90 °C for 2 hours and 150 °C for 1 hour. Then, the haft-dried PAA was continued to cure at 250 °C in Oven for 1 hour, forming polyimide film.

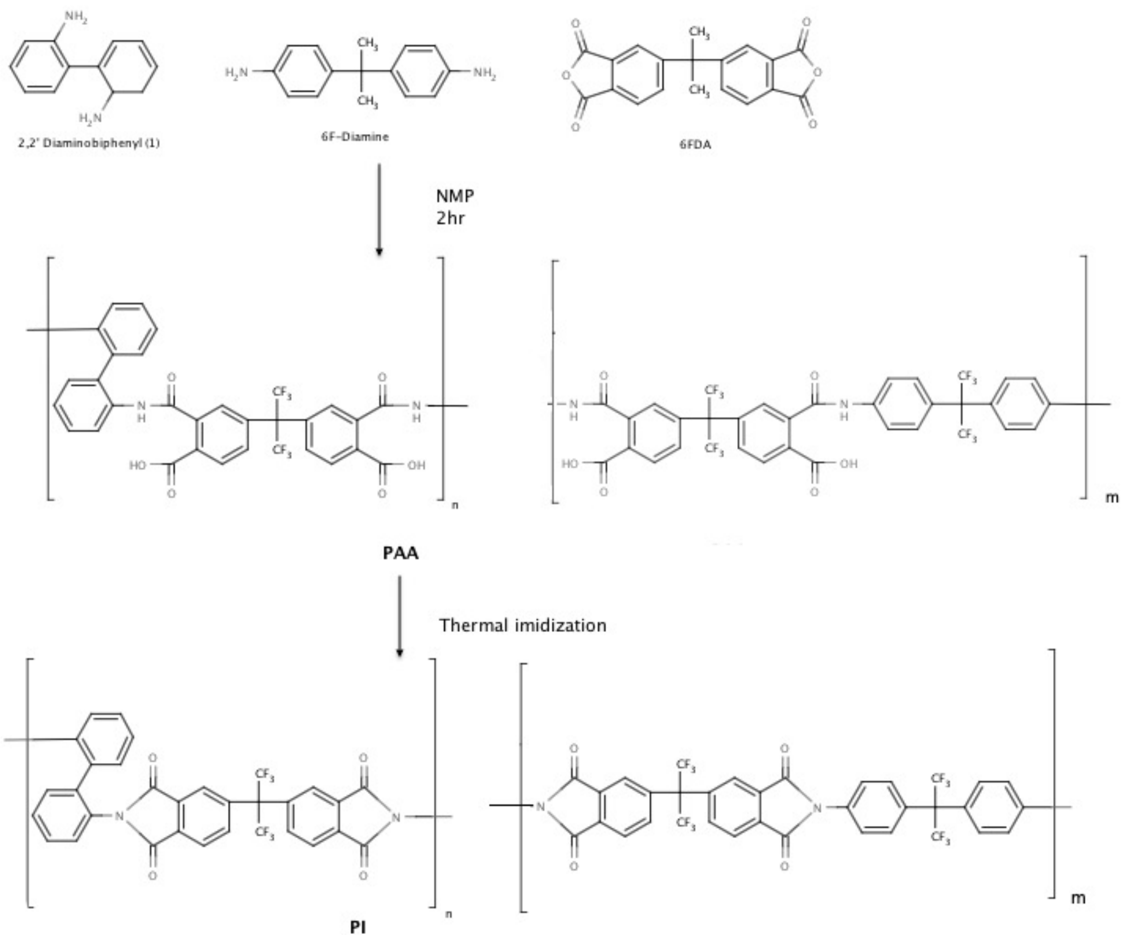


Figure 3.11 Preparation of the polyimide films from 1st Diamine **(PI-1)**

3.4.2 Preparation of the polyimide films from 2nd Diamine (PI-2)

In case of (2), The Diamine was not able to 100% purify. Therefore, the one-step condensation polymerization was applied. The Diamine monomer **(2)** was collaborated with 6F-Diamine to react with commercially available aromatic Dianhydride, 6FDA to give the polyimides as shown in Figure 3.12. The mole ratio and solid content of **(2)**: 6F-Diamine: 6FDA is 1:1:2 respectively. Dissolving 6F-Diamine in NMP, called as solution A. Dissolving 6FDA in NMP, called as solution B. Dissolving Diamine monomer **(2)** in NMP, called as solution C. Prepare NMP for washing (Total NMP in system equal to 20 ml per 3 gram solid in usage) Pour A and C to in 3-neck reactor that connected with Dean-stark and cooling column and purging with Argon gas, the mixture was stirred for 10 minute. After that, solution B was added and followed by 10 ml of toluene into reactor. The solution was stirred while heated for 8 h.

After 8 h of heating, to solution was continued stirred while leaving it to cool down in room condition. After that, the solution was poured into the water through the syringe to precipitate the polymer, and then separated by vacuum filtration technique. The solid polymer collected and dried in vacuum oven at 60 °C for 4 h.

The dried polymer 1.5 g was dissolved in 10 ml of NMP and stirred until all solid disappeared. Then, the polymer solution was poured into 10 x 20 cm glass plate to cast the PI film. The glass plate with polymer with the solvent was removed the solvent out in vacuum oven at 60 °C, 80 °C, 100 °C and 150 °C for 3, 1, 1, 1 h respectively.

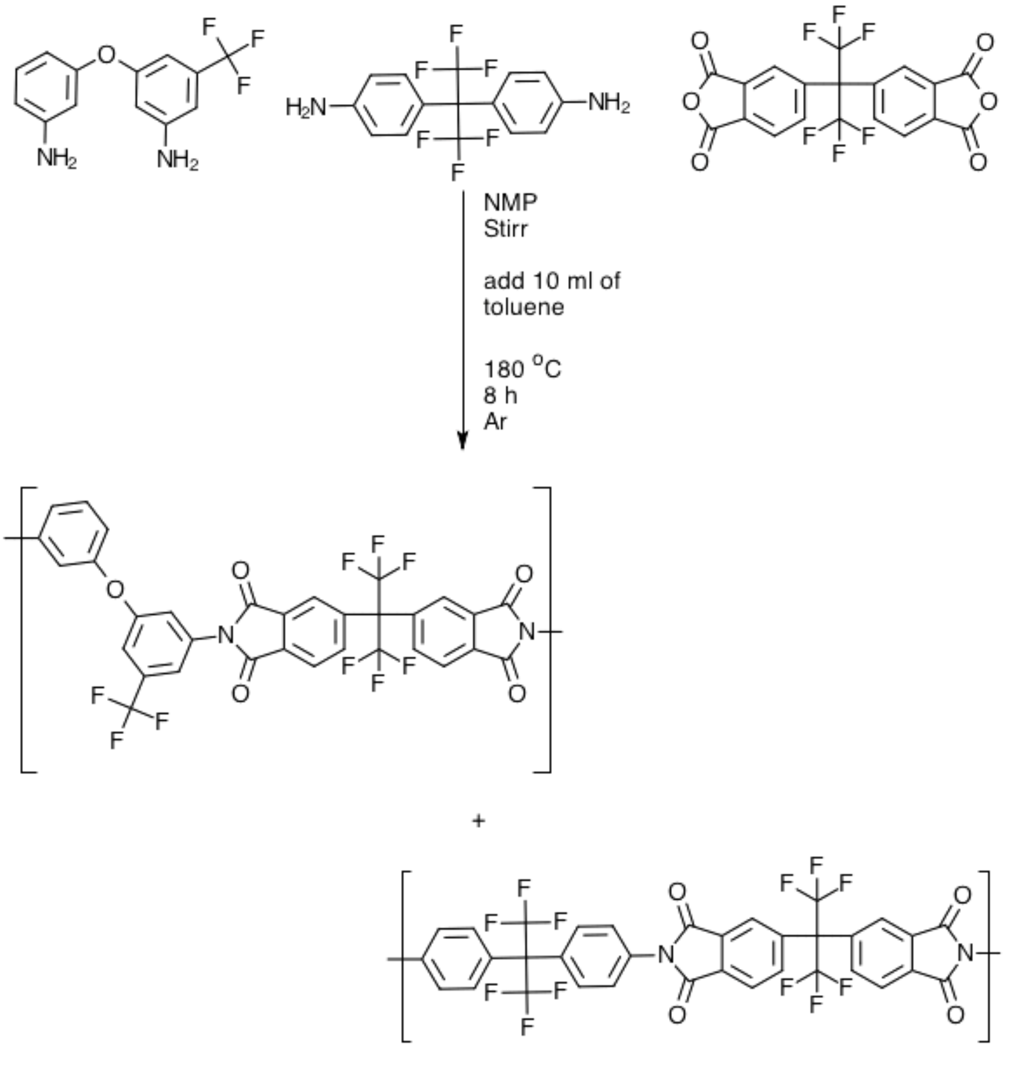


Figure 3.12 Preparation of the polyimide films from 2nd Diamine **(PI-2)**

3.5 Characterization

3.5.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^{1}H-NMR spectra were recorded with Bruker 400 Ultra Shield ^{1}H NMR spectrometer. Scaning conditions as TD and Number of Scan were seted at 64 Hz and 500 at room temperature respectively. The Chloroform deuterate ($CDCL_3$-d) was used as a NMR solution.

Figure 3.13 Nuclear Magnetic Resonance (NMR) Equipment

3.5.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was recorded with Nicolet 6700 FTIR spectrometer. The scanning ranged from 400 to 4000 cm^{-1} with 64 scanned time per sample. The functional groups of the composite films were identified.

Figure 3.14 Fourier transform infrared spectroscopy (FTIR) Equipment

3.5.3 Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) thermograms were performed using a Diamond TG/DTA Thermo gravimetric/Differential Thermal Analyzer, 3-10 mg weights of sample was used. The temperature range was 50 to 800°C at a heating rate of 10°C/min with nitrogen purge flow rate of 100 ml/min.

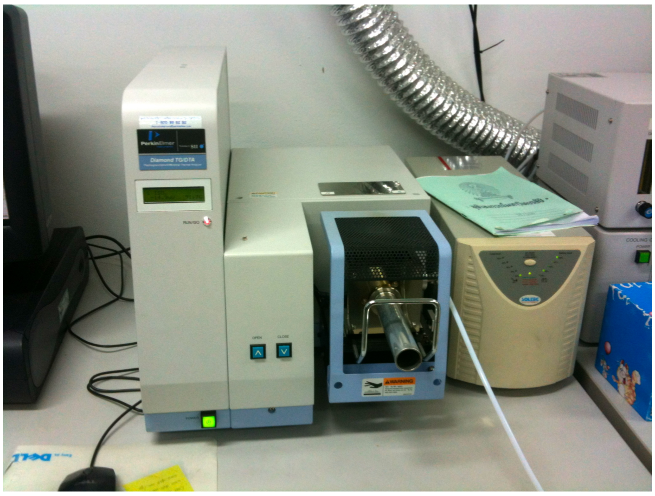


Figure 3.15 Thermo gravimetric analysis (TGA) Equipment

3.5.4 Ultraviolet-visible spectroscopy (UV-vis)

The optical properties of the polyimide films were measured by Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) at room temperature. The sample was a film that casted on slide glass, which also used as a blank too. The %transmitant was measured from 300 to 800 nm.

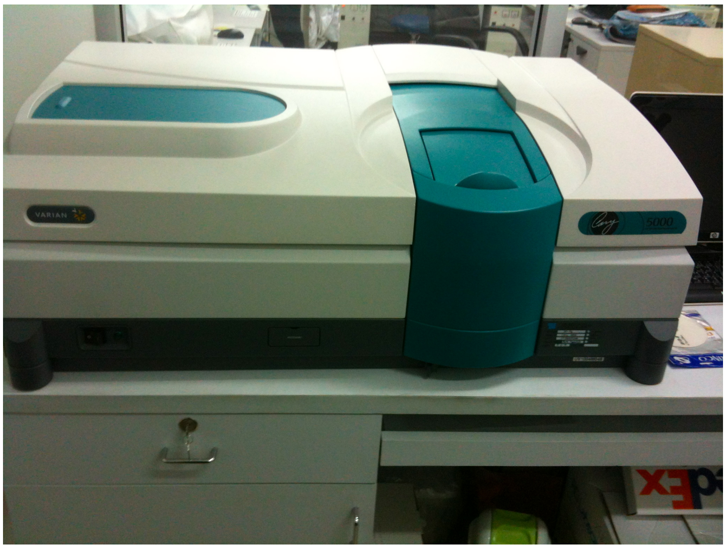


Figure 3.16 Ultraviolet-visible spectroscopy (UV-vis) Equipment

3.6 Research Methodology

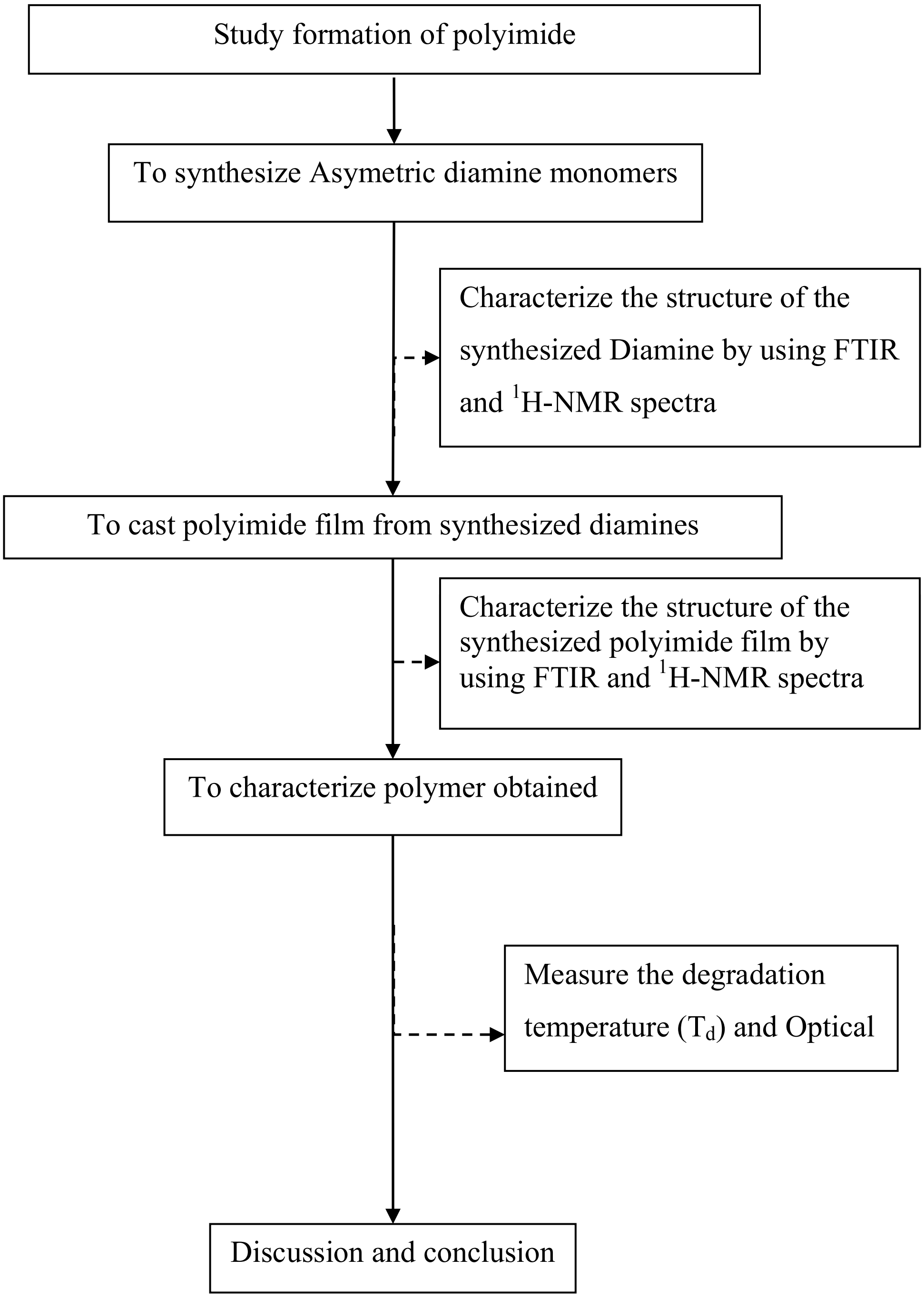


Figure 3.18 Flow diagram of research methodology.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results from experiments in chapter III, that included the information about the synthesis of two asymetric diamine and preparation of transparent polyimide flim, were discused. Both of two synthetics asymetric diamine monomers were used for the preparation of transparent polyimide flims by collaborated with 6F-Diamine and polymerized with 6FDA. The effects from the constrain in their molecules on the transparent properties, thermal properties and mechanical properties of polyimide were investigated.

4.1 Synthesis of Asymmetric Diamine monomer

Due to the objective of this reseach, sinthesis of two asymetric diamine using two chemical reaction included Williamson's ether synthesis and Hydrogenation reaction were studied. The structures of 1st and 2nd asymmetric diamines were assured by FTIR and NMR that were discussed in subtopic number 4.1.1 and 4.1.2 respectively.

1st Diamine preparation

4.1.1 Synthesis of 2,2' Diaminobiphenyl (1)

- Hydrogenation of 2,2 dinitrobiphenyl by refluxing method

From the literature reviews, there were 2 methods that can be used to synthesized 2,2' Diaminobiphenyl by reducing 2,2 Dinitrobiphenyl. The first one that was introduced in this research was reaction in the atmospheric pressure with Ar purging, and the reaction was prepared in the reflux temperature of ethanol that was using as a solvent. The Pd/C was used in reaction as a catalyst and Hydrazine monohydrate as a reducing agent. The lab was set in 5 batches by varied of time to reaction from 2, 4, 6,8 and 24 h as shown in table 4.1

Table 4.1 2,2' Diaminophenyl synthesized conditions

Condiotions	Sampl1B1	Sample1B2	Sample1B3	Sample1B4	Sample1B5
2,2 Dinitrobiphenyl (g)	0.9999	1.0000	0.9999	0.3000	4.0000
5% Pd/C (g)	0.0436	0.0412	0.0436	0.02	0.2
Adding of Hydrazine	YES	YES	YES	YES	YES
EtOH (ml)	15	15	15	15	60
Heated	YES	YES	YES	YES	YES
Time (h)	2	4	6	8	24

The obtained product of Sample1B1 was very small amount about 0.1720 g, and it was characterized by ^{1}H-NMR as shown in Figure 4.2. Four spectra occurred in a range of 7.5 ppm to 8.3 ppm was determining 4 proton of aromatic rings in the twist structure. Nevertheless, the spectra wasn't show the significantly difference from the 2,2 dinitrobiphenyl (the reactant) which it shown in Figure 4.1, and Importantly, there was occurred a lot of impurity spectra in range of 1 ppm to 4 ppm which it could hide the spectra of proton from Diamine group as same as sample1B2, sample1B3 and sample1B4.

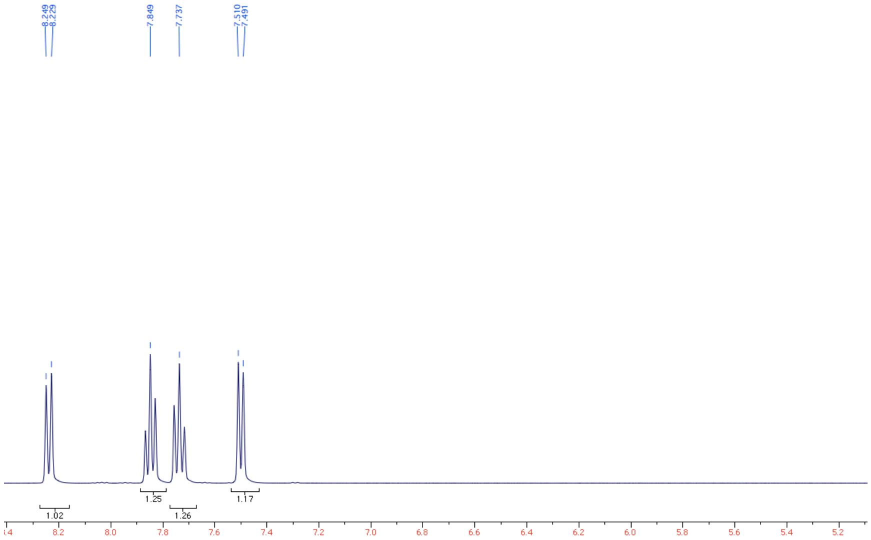


Figure 4.1 ^{1}H NMR Spectra of 2,2 Dinitrobiphenyl

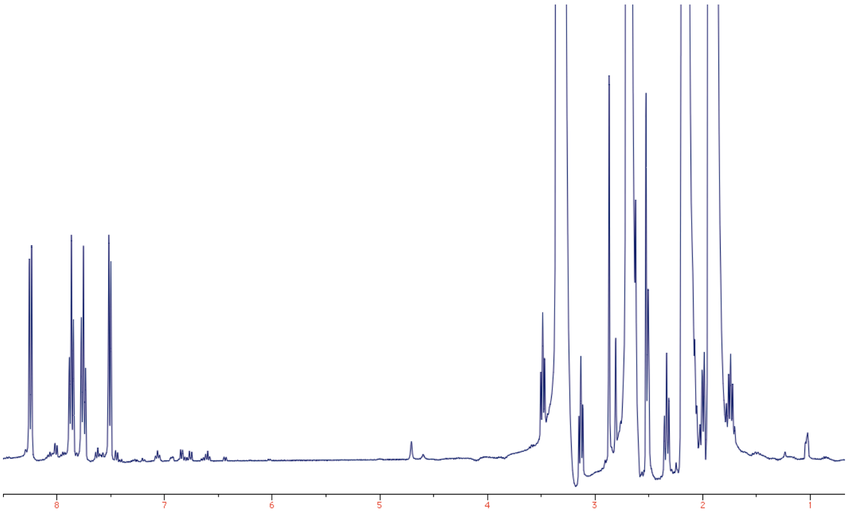


Figure 4.2 ^{1}H NMR Spectra of Sample1B1

The best-obtained result of this method was collected from the sample1B6 that it synthesized by 24 h of reaction time. The product also could be purified by recrystallized in water and collected amount of product was 0.6026 g (%yields = 11.33%). The solid crystalline was characterized by ^{1}H NMR spectra as shown in Figure 4.3. The spectra showed that the group of aromatic proton spectra was shifted to above of 8 ppm and the amine spectra was observed at 3.5 ppm. But the result was denied by integrated ratio confliction, which it should be 1: 1: 2: 2 from left to right respectively. Therefore, the first method wasn't recommend due to the low of productivity, impurity and long reaction time.

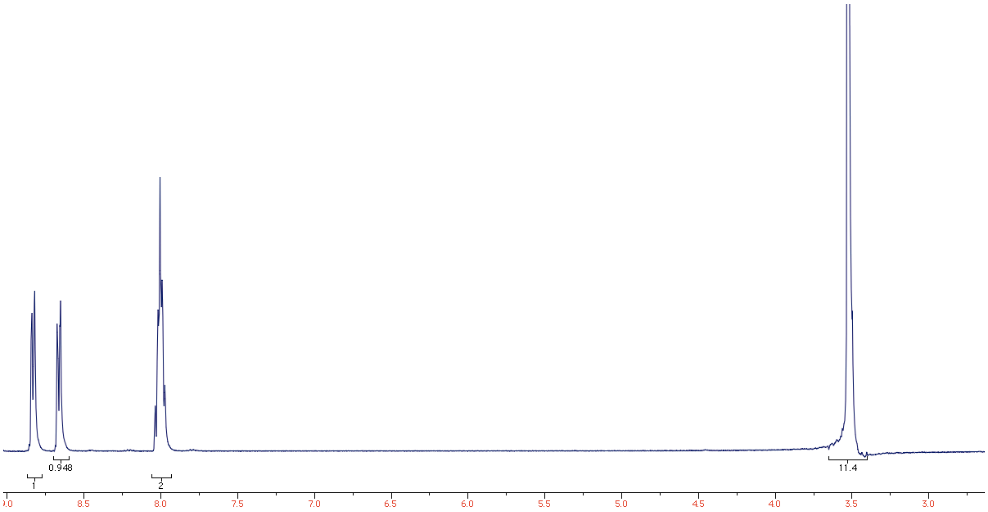


Figure 4.3 ^{1}H NMR Spectra of Sample1B5

- <u>Hydrogenation of 2,2 dinitrobiphenyl by High H_2 pressure</u>

The 1st Diamine was a 2, 2’ Diaminobiphenyl that can be synthesized by reduction of NO_2 group of 2,2 Dinitrobiphenyl by Hydrogen gas and using Pd/C as catalyst as can be shown in Figure 3.9. The reaction of reducing NO_2 to NH_2 was investigated and reported by many researchers. The reaction could be occurred in high-pressure H_2 (2~8 bar gauge) at moderate temperature at 50~70 °C for 2-8 h. to applied the high pressure of hydrogen into the reaction, the hydrogenation vessel called “Parr Bomb reactor” was use. For this method, varies of reaction conditions were shown in Table 4.2.

Table 4.2 2,2’ Diaminophenyl synthesized conditions by Parr Bomb reactor

Condiotions	Sampl1B7	Sample1B8	Sample1B9	Sample1B10	Sample1B11
2,2 Dinitrobiphenyl (g)	1.0021	1.0102	1.0043	1.0001	4.0000
5% Pd/C (g)	0.2042	0.2022	0.2003	0.2057	0.8186
Adding of Hydrazine	NO	YES	NO	YES	YES
EtOH (ml)	-	-	-	10	15
EtOAc (ml)	10	10	10	-	-
Heated	NO	NO	YES	YES	YES
Time (h)	4	4	4	4	4
H_2 Pressure (bar)	3	3	4	4	4
Product	*	*	*		
Weight (g)	-	-	-	0.3352	1.7695
%Yields (%)	-	-	-	44.47%	58.80

*: The product wasn’t precipitated in water/hexane

The differences of all these conditions were about solvent, temperature, pressure and reducing agent addition as hydrazine. The H-NMR spectra analysis spectra were shown in appendix. For Sample1B7 the reaction was prepare at room temperature, no reducing agent and using ethyl acetate as a solvent as the reference paper. Sample1B8 was the same condition to Sample 1B7 but adding hydrazine into the reaction. The last one of the sample with ethyl acetate solvent was a Sample1B9 with it was heated to 60 °C but no hydrazine addition. The last product form these 3 batches weren't precipitated in the water as it should be. NMR result had shown that Sample1B8 had spectra of amine group at 3.55 ppm. Nevertheless, the intergraded ratio of proton of amine group was too less while comparing to protons of aromatic ring in range of 7.3 ppm to 8.3 ppm. The NMR result of Sample1B9 also shown the same behavior to Sample1B8, which it's mean the higher temperature and the addition of reducing agent was helping to the reaction.

The result of all 3 first batches was introduced the way to changed the solvent to ethanol as show in Sample1B10. The NMR spectra of sample1B10 can confirm that the structure of 2,2' Diaminobiphenyl was created. However, the spectra also showed the impurity in product. Then, the conditions of Sample1B10 were repeated in Sample 1B11 by higher condensation, the product also purified by very slow recrystallized in water/acetone in at 5:1 ratio. After recrystallized, the yellow-white crystal of product was obtained.

The structure of Asymmetric Diamine (1) from Sample1B11 was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy as shown in Figure 4.4 and 4.5 respectively. Signals in the range of 6.80-7.25 ppm were ascribed to the protons of the aromatic ring. The signal of protons from amine groups was appeared at 3.664 ppm. The intergraded peaks ratio was matched with a ratio of hydrogen molecules in the structure.

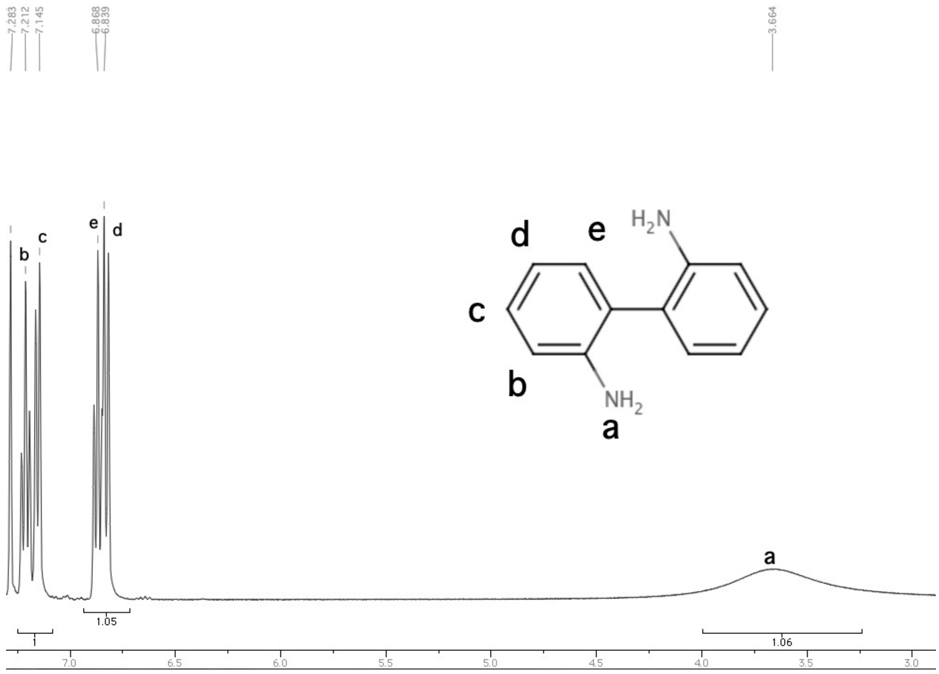


Figure 4.4 ^{1}H NMR spectra of diamine monomer **(1)**, (400 MHz, $CDCL_3$-d)

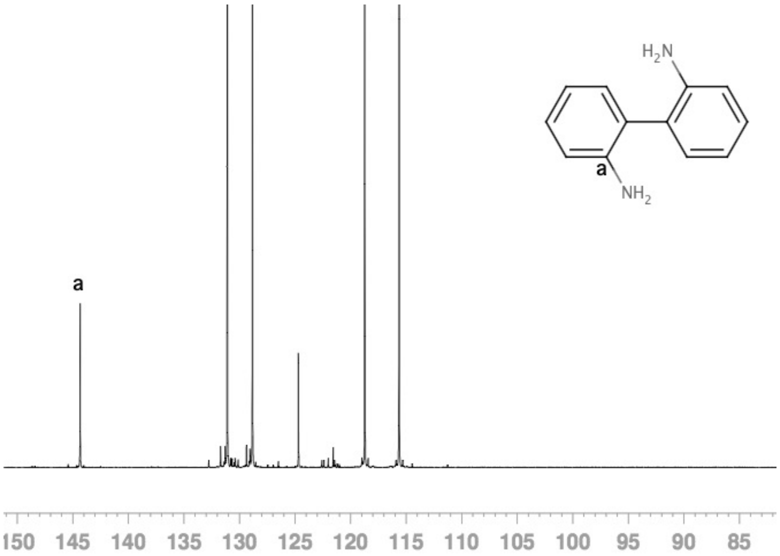


Figure 4.5 ^{13}C NMR spectra of diamine monomer **(1)**, (400 MHz, $CDCL_3$-d)

In the 13C NMR spectra, the signal of carbon which it contained the amine group was occurred at 144 ppm and 5 peaks in range of 115 to 133 were represented the peak of other 5 carbon in aromatic ring. With both ^{1}H NMR and ^{13}C NMR confirmed the Asymmetric Diamine structure of the product as 2,2' Diaminobiphenyl.

2nd Diamine preparation

4.1.2 Synthesis of 2-(2-nitrophenoxy)-5-(trifluoromethyl)benzene (2a)

2nd Diamine was designed to add the Aryl ether linkage and CF_3 group into the structure. The Aryl ether linkages were created by very simple reaction like the Williamson's ether synthesis. In general, the nucleophilic substitution reaction could be occurred between OH and Halogen group in base solution at high temperature around 100-120 °C for 24 h up to the solvent. 3-Nitro-4-Chlorobenzotrifluoride was chosen as the first reactant that containing Cl group due to the reason of cost and reactivity and then, 2-Nitrophenol was chosen with the same reason.

Table 4.3 was shown all varied condition of the Williamson's ether synthesis. The difference between two batches was proposed to compare about the reactivity between the using of NaH and K_2CO_3 as a nucleophile. The result was shown as %yields of product after recrystallized. Sample2B2 with K_2CO_3 was shown very impressive of productivity with 98.66% (1.1981 g) while the Sample2B1 with NaH was shown very low productivity as 12.54% (0.1523 g). Therefore, the condition from Sample2B2 was repeated and characterized.

Table 4.3 Synthesis of 2-(2-nitrophenoxy)-5-(trifluoromethyl)benzene (2a) synthesize conditions

Condiotions	Sampl2B1 (dinitro)	Sample2B2 (dinitro)
2-nitrophenol (g)	0.5706	0.5606
4-nitro-3-chlorobenzotrifluoride (ml)	0.56	0.56
Adding of NaH (g)	YES	NO
Adding of K_2CO_3 (g)	NO	YES
DMF (ml)	10	10
Heated	YES	YES
Time (h)	24	24
Product		
Weight (g)	0.1523	1.1981
%yields (%)	12.54	98.66

After 24 h of reaction, the dinitro compound **(2a)** from the repeated of Sample 2B2 was obtained and the structure of the product were confirmed by FTIR and ^{1}H NMR. Figure 4.6 showned FTIR spectra of dinitro compound **(2a).** As shown by spectrums, there was no characteristic peak of OH group appeared in the range around 3300 cm^{-1} - 3400 cm^{-1} and the spectrums showed the characteristic peak of ether at 1260 cm^{-1}. These results conformed the ether synthesis reaction, which explained as the OH groups were substituted to form ether group, so the OH disappeared and the ether bond would exist instead.

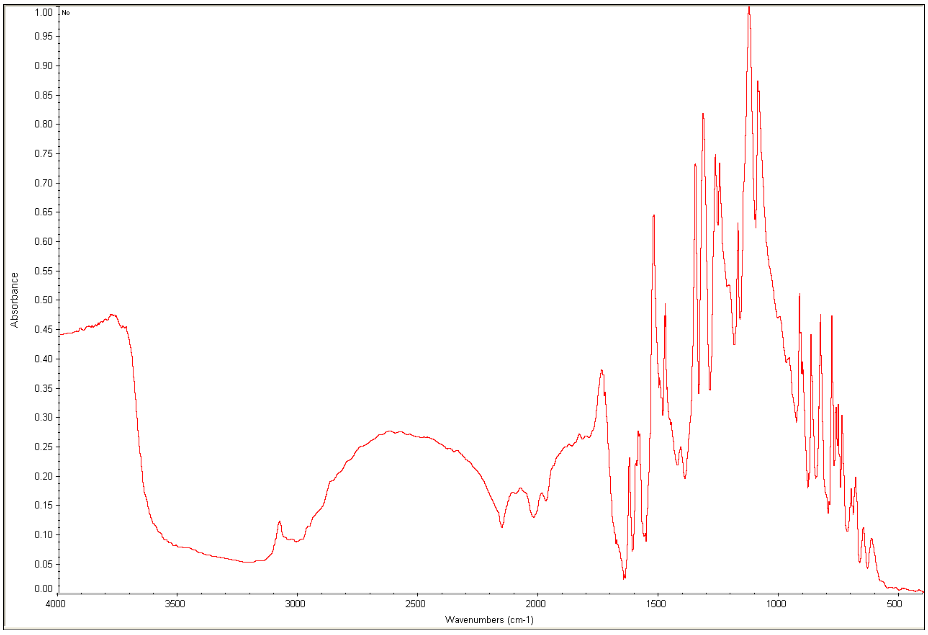


Figure 4.6 FTIR spectra of dinitro compound **(2a)**

The structure of dinitro compound **(2a)** was also confirmed by ^{1}H NMR spectra that shown in Figure 4.7. The spetrum showed peak of 7 protron in range of 7.0 to 8.4 ppm that similar to the NMR theory prediction. The integrated ratio of peaks were also conformed with ratio of hydrogen in the structure, represented dinitro compound **(2a).**

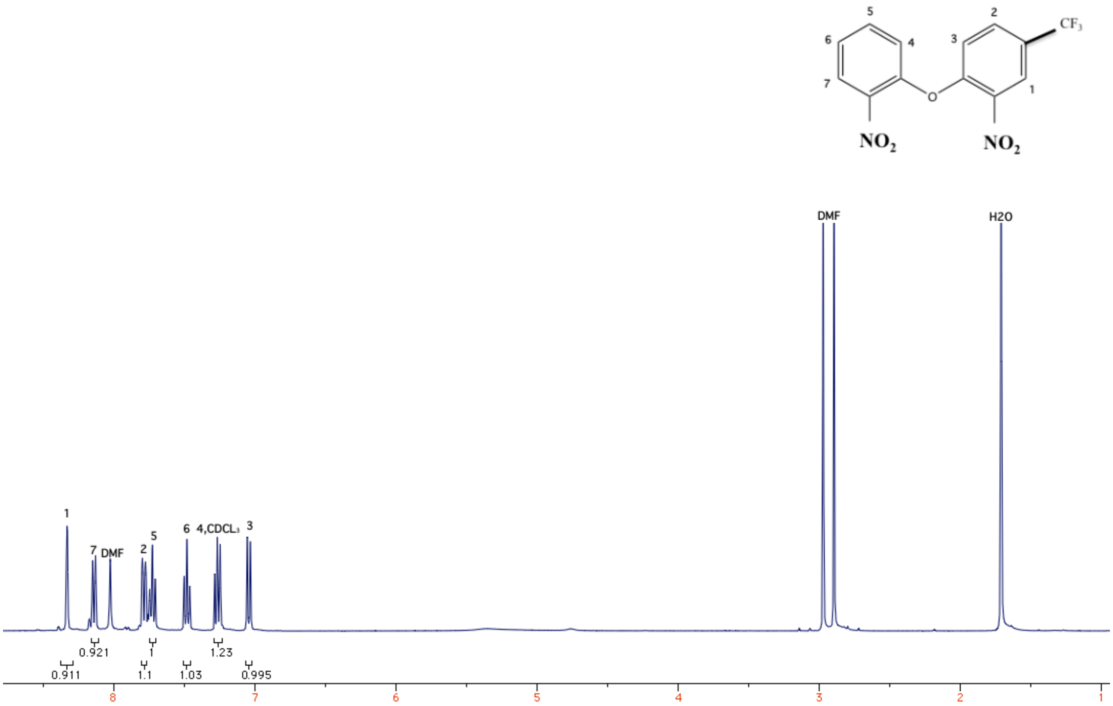


Figure 4.7 ^{1}H NMR spectra of dinitro compound **(2a)**

4.1.3 Synthesis of 2-(2-aminophenoxy)-5-(trifluoromethyl)aniline (2)

Dinitro compound **(2a)** was reduced to NH_2 group by hydrogen gas with Pd/C catalyst as same as reaction of **(1)** with different condition. The stearic effect from CF_3 groups and – O – groups in the structure that can be retarded the reaction. Therefor, to increase the productivity, time of reaction, temperature and pressure were adjusted to longer and higher as showed in Figure 3.11.

Figure 4.8 shown the FTIR spectra of 2nd Diamine monomer (2), which showed the arise of NH_2 characteristic peak (3360 cm^{-1}). Comparing Figure 4.3 against Figure 4.2, which shown the decreased of NO_2 characteristic peak (1350 cm^{-1}). These results confirmed the reaction of replacement of the NO_2 to NH_2, so that the amine peaks were occurred and nitro peaks were disappeared.

Figure 4.9 showed the ^{1}H NMR spectra of 2nd Diamine monomer (2). The spetrum showed the spetra of 4 protron from NH_2 group at 3.9 ppm and spectra of 7 protrons of the aromatic ring in the range of 6.7 to 7.1 ppm conformed the prediction by theory. The integrated ratio of peaks also confirmed with ratio of hydrogen in the structure, which confirmed the structure of the product was 2nd Diamine monomer (2).

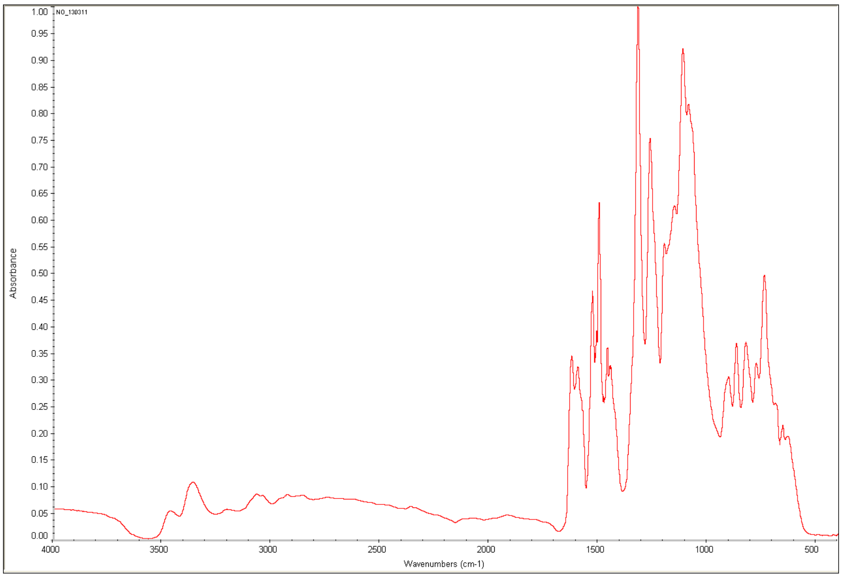


Figure 4.8 FTIR spectra of 2nd Diamine monomer **(2)**

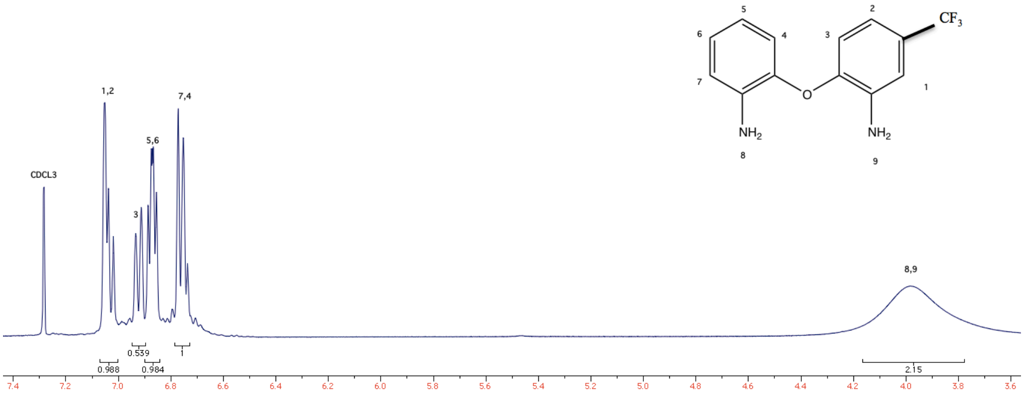


Figure 4.9 ^{1}H NMR spectra of 2nd Diamine monomer **(2)**

3rd Diamine preparation

The attempt to synthesized the third diamine was terminated due to the failure of reaction, represented by NMR result, which did not have the peaks of the desired structure. In other words, the designed reaction condition was not approppreate to synthesized the desired structure.

4.2 Preparation of the polyimide films

Polyimide films were synthesized from 1st **(1)** and 2nd **(2)** asymmtric diamine. For **(1)**, the purpose of using these Diamine for polyimide films synthesis in this research were related to their very rigid constrain structure of location of NH_2 groups. The very rigid constrain structures would make the molecular structure of polyimide more complex that can be reduced the molecular packing ability, increased the inter-molecular spaces that was resulted in a more transparent properties, predicted by a basically theory of the preparation of the transparent film. For diamine **(2)**, the monomer structure was designed to contained rigid constrain of NH_2 but more flexible than diamine **(1)** because of ether linkage in the middle of the structure**.** The structure of diamine **(2)** contained the aryl ether linkage, which provided more flexible of molecule and CF_3 bulky unit, which could produce more effect of higher intermolecular spaces.

PI film that was synthesized from diamine **(1)** and **(2)** called PI-1 and PI-2 respectively. Both PI films were synthesized by collaboration of the 6F-Diamine and polymerized with 6FDA in 1:1:2 mole ratios to improve the transparent of film. Figure 4.10 and 4.11 showed the FTIR spectra that confirmed the synthesized structures of PI-1 and PI-2 respectively. The spectra showed characteristic imide group absorptions peak around 1780 and 1725 cm^{-1} (C=O asymmetrical and symmetrical stretch), 1380 (C–N stretch), respectively.

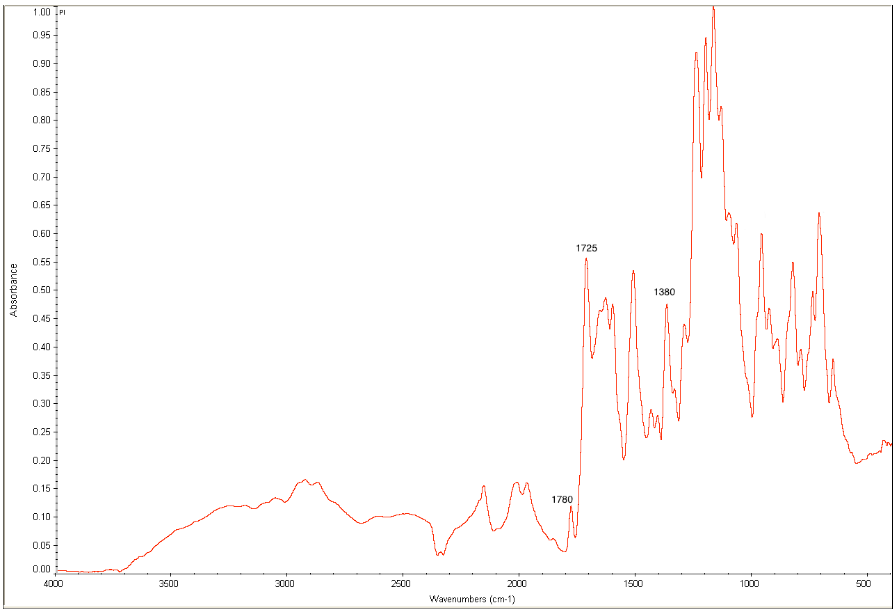


Figure 4.10 FTIR spectra of PI-1

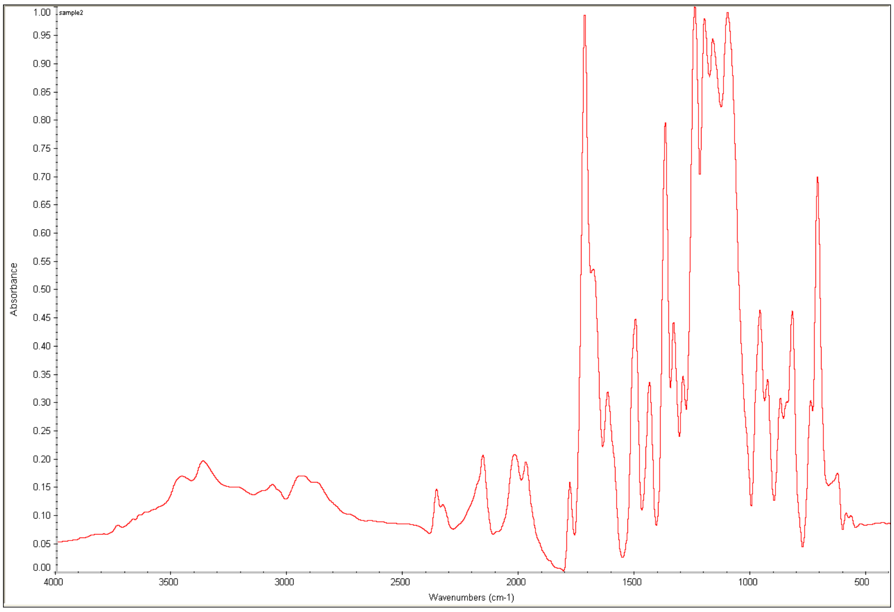


Figure 4.11 FTIR spectra of PI-2

4.3 Optical properties

Optical property of the synthesized polyimide flim was evaluated by the physical appearance and UV-vis spectra. Figure 4.8 showed the physical appearance color of three polyimide films; standard commercial polyimide as Figure 4.12 (a), PI-1 as (b) and PI-2 as (c). The UV photographies occurred showed more colorless of two transparent films of the synthesis PI films from the asymmetric diamine monomers than the standard PI film at the film thickness about 11~14 micrometer.

(a) (b) (c)

Figure 4.12 Physical appearance color polyimide (a) reference-PI (ODA/PMDA) (b) PI-1 and (c) PI-2

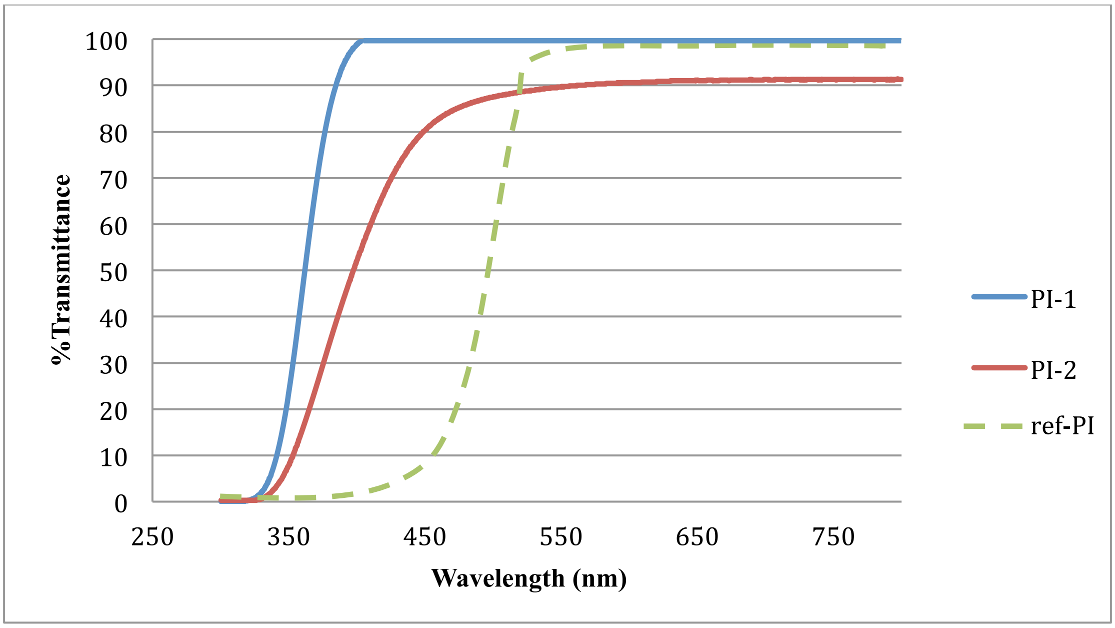


Figure 4.13 UV-vis spectra of PI

By the comparison between PI-1 and PI-2, which have significant difference of their color that can be confirm by UV-vis spectra as showed in Figure 4.13.

Due to the both of PI films could not be separated from a glass because of poor mechanical property. Therefore, method to analyze by UV-vis spectra was modified. The polyimide was dissolve in NMP at 15%wt and re-casting on the slide glass. To measure the transmittance of PI only, the blank slide glass was used as the standard calibration sample.

The cutoff wavelengths of both two asymmetric polyimides were significantly shifted from standard PI cutoff wavelength to the left that it was lower than 350 nm, which that meant all of spectra in the visible light range could better transmitted through asymmetric PI than standard PI. As expected, PI-1 was more colorless than PI-2 due to the very rigid constrain of the twisty unit in PI-1 structure than the PI-2. The significant effect of the twisty was about molecular arrangement. Structure of PI-1 was very chaotic which that meant the polymer chain would not tightly packed that brought about more intermolecular spaces. The intermolecular spaces were the one key factor that will determine many properties in polyimide. In this case, the intermolecular space of PI-1 was decreased the charged transfer complex (CTC) between polymer chains that affected the reduction of PI-1 color.

In PI-2, the molecular structure was contained both of aryl ether linkage and CF_3 bulky unit and polymer chains were also slightly twisty but less effect than PI-1 because of the more flexibility of ether linkage. In addition, asymmetric PI films also affected by the CF_3 bulky group from 6FDA and 6F-Diamine which that was proposed to increase the mechanical property while preserving the optical property of films. The optical transparency gained from the UV-vis spectra, including cutoff wavelength and %transmittance for different wavelengths were summarized in Table 4.1.

Table 4.4 Optical transparency of polyimide film

PI	Thickness (micrometer)	Cutoff wavelength	T_{400} (%)	T_{450} (%)	T_{500} (%)
PI-1	14	336	98	100	100
PI-2	11	344	52	80	87
PI-ref	13	444	0	2	58

Note: T_{400}, T_{450}, T_{500}: %transmittance at 400, 450 and 500 nm respectively

PI-ref: standard PI film derived from PMDA and ODA (Kapton films).

4.4 Solubility

To mesured of solubility, PI was dissolved in difference commercial organic solvent with PI:sovent ratio as 0.02 g : 1 ml. Both of asymmetric PI could be easy dissolved in polar solvents such as N-methyl-2-pyrrolidinone (NMP), N,N-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), Acetone and Chloroform deuterate ($CDCL_3$-d) at room temperature. The good polar sovents solubility of PI was related with the polymer backbone which it contained a much of fluorine from 6FDA and 6F-Diamine (in case of PI-2, PI backbone also gived fluorine from 2nd diamine too). On the other hand, asymmetric PI has poorer solubility in non-polar solvents due to the high polarity of fluorine in PI backbone.

The solubility of synthetic asymmetric polyimide films can be shown in Table 4.5.

Table 4.5 Solubility of synthesized asymmetric polyimide

PI	Solvents							
	Polar solvents						Non-polar solvents	
	NMP	DMF	DMSO	Acetone	$CDCL_3$	MeOH	Toluene	hexane
PI-1	+	+	+	+	+	-	+Δ	-
PI-2	+	+	+	+	+	-	+Δ	-

Note: measured by 0.02 g/ml^{-1} PI conc; **(+)** soluble at room temp; (+Δ) soluble by heated to 70 ^{O}C; (-) insoluble.

4.5 Thermal property

Thermal properties of asymmetric polyimide films were evaluated by Thermo gravimetric analysis (TGA). With the measured condition of 10^{o}C/min heating rate from 50 ^{o}C to 800 ^{o}C under nitrogen atmosphere, the result was showed in Figure 4.14. The thermal decomposition of PI-1 and PI-2 was started at 170 -180 and 155-165 ^{o}C, respectively. Decomposition behavior was observed as two-step degradition which started by decomposition of the bulky aromatic group in the polymer backbone, the second step followed by the decomposition of the imide structures in the polymer main chains. The graphycial showed that PI-1 was slightly better thermal stability than PI-2 because of more aromatic structure of PI-1

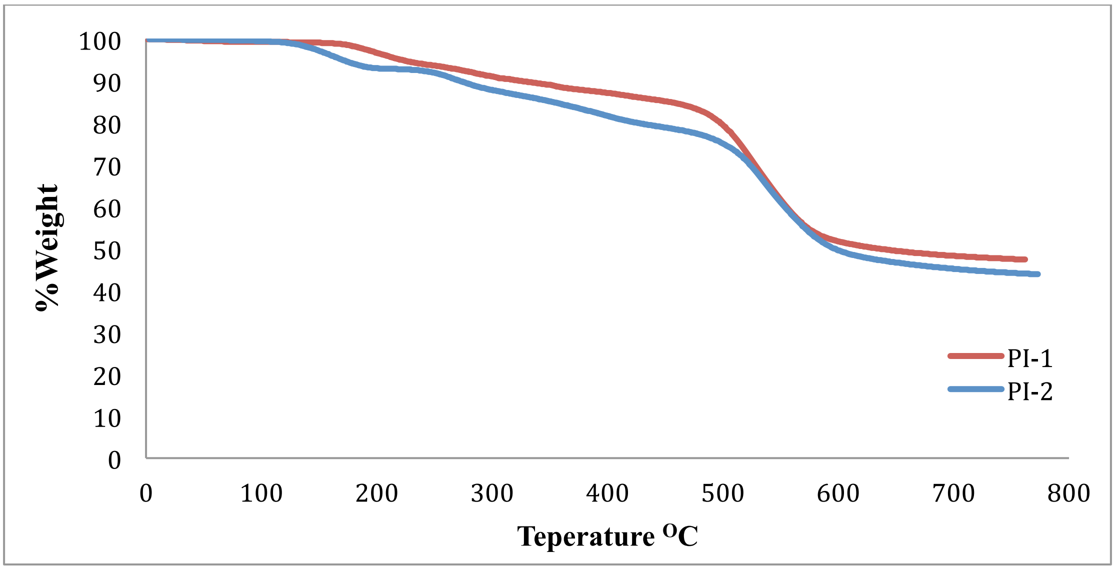


Figure 4.14 TGA of asymmetric polyimide

Table 4.6 showed decomposition temperature at 5% weight loss of PI-1 at 223 ^{o}C and PI-2 at 171 ^{o}C, while decomposition temperature of 10% weight loss of PI-1 and PI-2 were 325 ^{o}C and 271 ^{o}C, respectively. The table also showed the residual weight retention (R_w) at 700 ^{o}C in nitrogen which that both asymmetric PI-1 and PI-2 was about 49.29% and 45.19%, respectively because the higher contribution of more aromatic part in PI-1 than PI-2.

Table 4.6 Thermal property of synthesized asymmetric polyimide

PI	$T_{d5\%}$	$T_{d10\%}$	R_w (%)
PI-1	223	325	48.29
PI-2	171	271	45.19

Note: $T_{d5\%}$, $T_{d10\%}$: the decomposition temperatures at 5% and 10% weight loss, respectively; R_w: residual weight retention at 700 ^{o}C in nitrogen

4.6 Molecular structures

The investigation of three-dimension molecular structure model for asymmetric PI molecular structure was studied in this research. With the three-dimension molecular structure model, PI properties such as transparency and mechanical can be explained. The model structure geometry was created by Avogadro program that base calculation on the Universal Force Field theory (UFF).[22]

Figure 4.15 show the molecular model of asymmetric PI. For PI-1 that not contained the ether linkage in Diamine monomer. The dihedral angle between imide ring and phenyl ring was observed at 38.8^{o}, and also 143.8^{o} dihedral between the biphenyl that it twisted. Comparing to the PI -2, which it had C-O-C bond with 154.8^{o} dihedral and angle between imide ring and phenyl ring was 40.2^{o}. The twisted angle of –C-O-C- in PI-2 are slightly too much than the biphenyl bond in PI-1 that make PI-2 with better solubility [21]. Due to the otho-point of amines was attracting on phenyl molecule, the effected of steric inherences of amine was restricted of the spin in amine structure. In three-dimension model, PI-2 had more twisted than PI-1 because of the nature of ether with otho-amine that will made the molecule structure more strained if it twisted small more than 154.8^{o}, so the PI-1 showed higher transparency than PI-2[21]. By the way, the molecular structure model of both asymmetric PI was show that the polyimide main chained would be very chaotic comparing with the PI-ref that bring about molecular packing in asymmetric PI would not be tightly, that can prevent the CTC between molecule and made the molecule more transparency but poor mechanical property comparing to the PI-ref films.

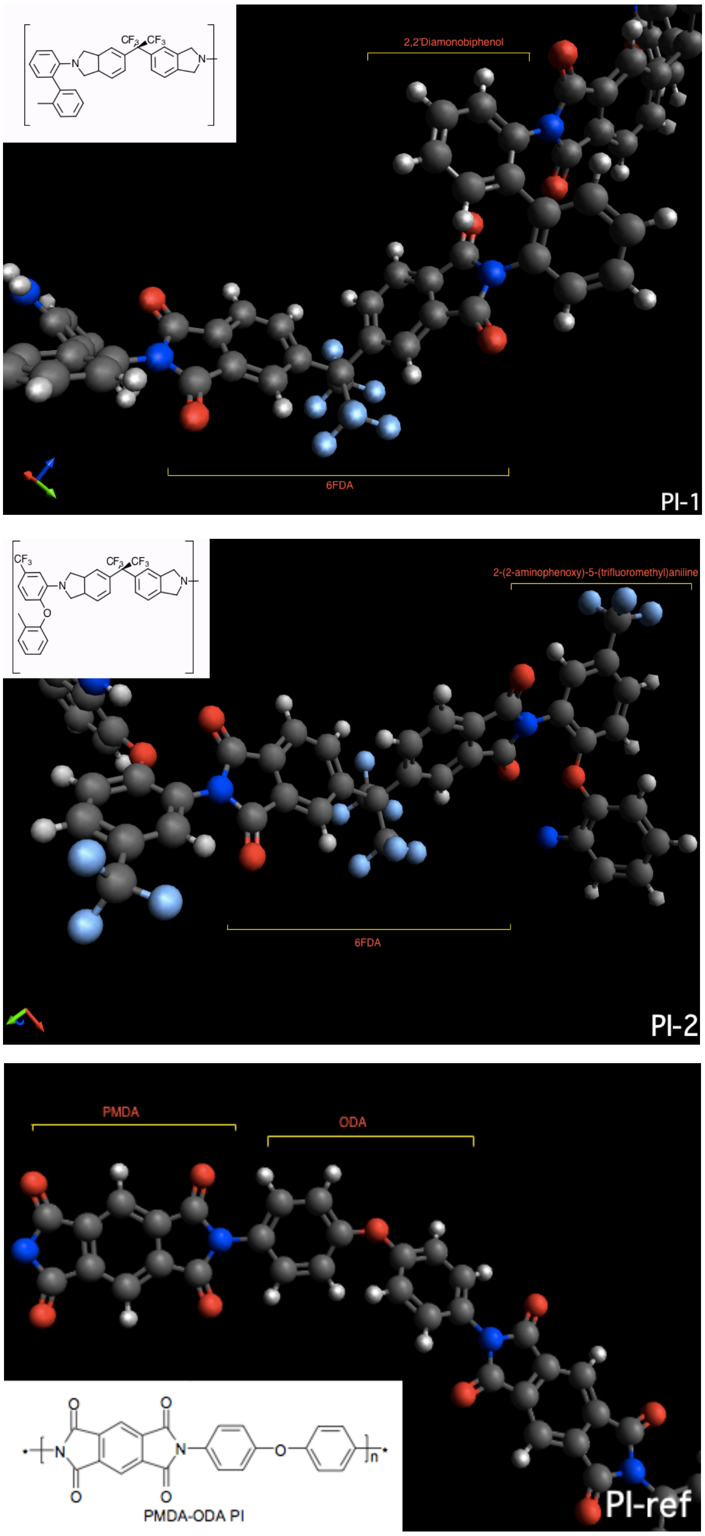


Figure 4.15 Three-dimension molecular structure model for asymmetric PI The model structure geometry was calculated by the Universal Force Field theory (UFF); grey, white, red, blue and cyan of each molecular structure display C, H, O, N, and F respectively.

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The synthesis of two new asymmetric diamine monomers for transparent colorless polyimide was investigated in this research. The Williamson's ether synthesis reactions including Hydrogenation reaction were used for the synthesis. The transparency, solubility, thermal properties, and mechanical properties of the polyimides, synthesized from asymmetric diamine were investigated.

5.1.1 Synthesis of Asymmetric Diamine

Asymmetric diamine was synthesized by Hydrogenation reaction and Williamson's ether synthesis. The result from characterized by ^{1}H NMR and FTIR could confirm that both of synthesized diamine had a desired structures.

5.1.2 Preparation of the polyimide films

The result of this research can be summarized as follows,

- The polyimides that synthesized from asymmetric diamine blend, in this research, used Fourier-transform infrared spectroscopy (FT-IR) to confirm the imide structure and completeness of imidization.
- All polyimide, including PI-1 and PI-2, was exhibited cut-off wavelengths lower than 400 nm and appearance as the colorless transparent in physical because of the effect of very rigid constrain of amine group in asymmetric diamine.
- When comparing between PI-1 and PI-2, the PI-1 was more colorless than PI-2 because of the structure of 1st diamine monomer can slightly free to spin than 2nd diamine monomer. Therefore, the PI-1 polymer chain are more random twisted that resulted in reducing the molecular packing and reducing charge transfer complex (CTC), the cause of color in polyimide.
- All asymmetric polyimide films in this research were brittle and had poor mechanical properties regardless of the 6F-Diamine blending. The film could

not separate from glass substrate and all shattered. The poor mechanical property resulted from the rigid constrain of asymmetric polyimide structure that made polymer chain a random twisted and could not pack their molecule tightly.

- Thermal stability of asymmetric polyimide in this research was declined from Kapton film property and $T_{d5\%}$ and $T_{d10\%}$ of PI-1 were slightly higher than PI-2 because PI-1 did not have less ether bond in its structure.
- The solubility of both PI-1 and PI-2 asymmetric polyimide films was excellent in many of commercial polar solvent because of high free volume resulted from less packing of molecules.
- The 3D molecular structure model of PI-1 and PI-2 showed that the polymer backbone were very chaotic, because of dihedral twist angle bonding between imide ring and phenyl ring (~40^{o}) and also dihedral twist angle bonding between aromatic ring in diamine monomer (~140^{o}-150^{o}). Due to the dihedral of polymer backbone and twisty rigid constrains of amine group that could cause the molecular unsightly packing which reducing CTC, cause less color.

5.2 Recommendations

- From this research, the molecular structure of synthesize were not easy to synthesize due to the otho-position of activation groups would retarded the reaction by much more steric effects from near groups. However, the Williamson's ether synthesis in 3rd diamine monomer wasn't succeeded which it could be caused by the otho-group steric effect. To trying to synthesize this structure, the reaction should be changed to stronger polar halogen group than Chlorine, such as Bromine or Iodine, which it's very effective in ether synthesis reaction.
- To clearly explanation about relation between the molecular structure of polyimide film and film properties. There should be much more knowledge about the quantum molecule theory such as molecular orbital energy, High-occupied molecular orbital energy and Low unoccupied molecular orbital energy (HOMO-LUMO calculation). These theories can explain and predict property of film by just calculating from the model of molecular structure.

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APPENDICES

APPENDIX A

^{1}H NMR CHARACTERIZATIONS OF DIAMINE MONOMER

A-1 ^{1}H NMR spectra of Diamine monomer

1st Diamine monomer

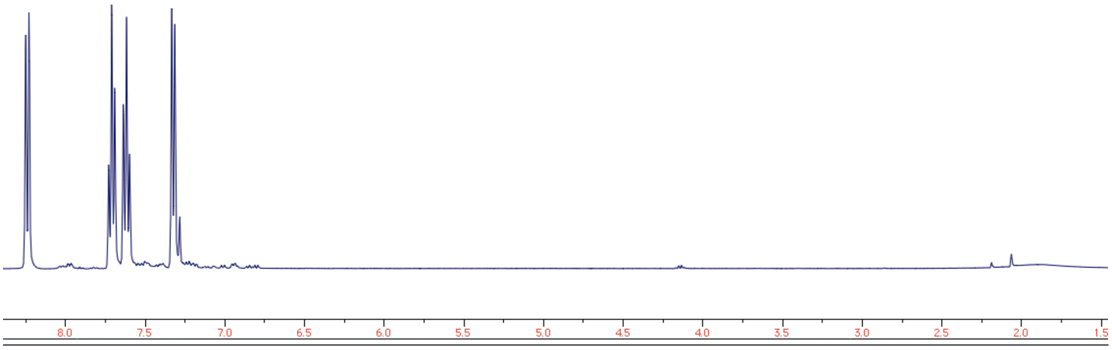

Figure A-1 H NMR Spectra of Sample1B7

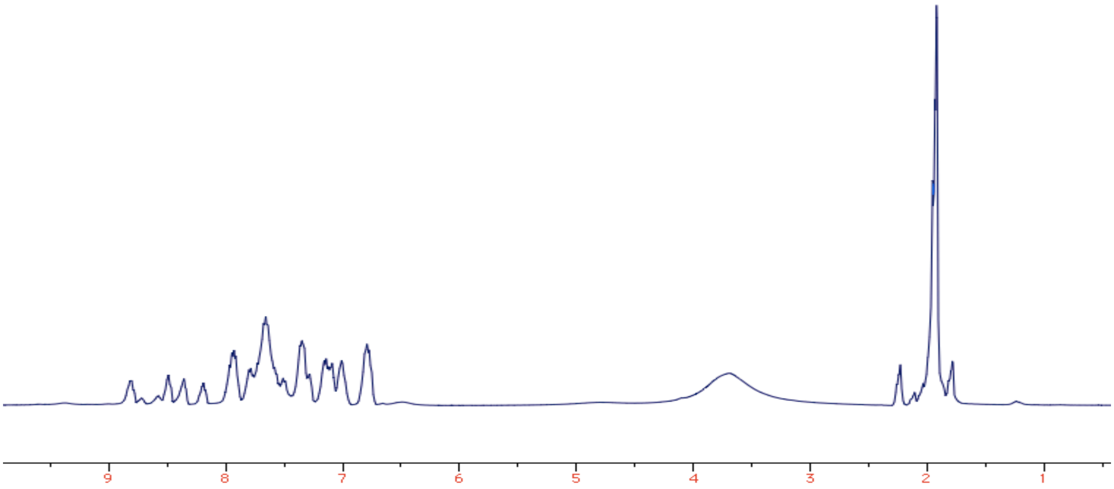

Figure A-2 H NMR Spectra of Sample1B8

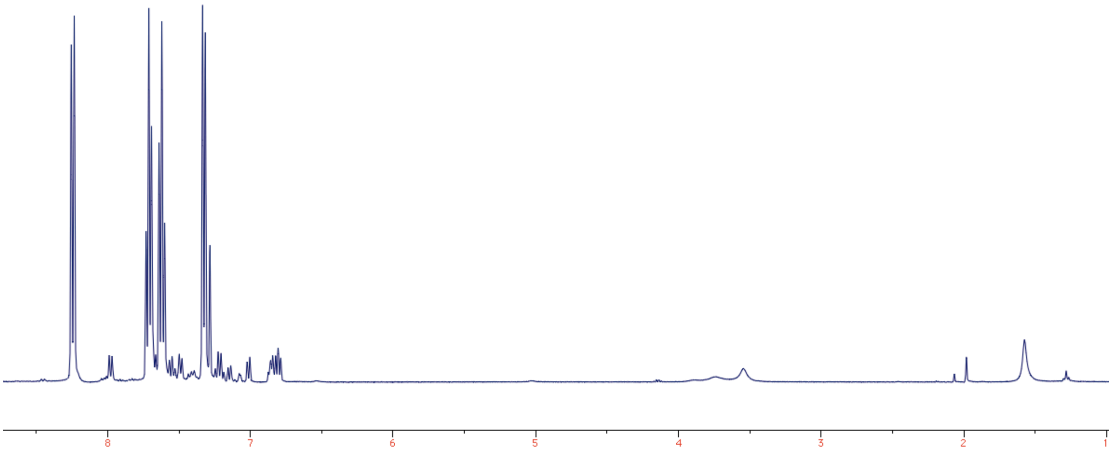

Figure A-3 H NMR Spectra of Sample1B9

Figure A-4 H NMR Spectra of Sample1B10

APPENDIX B

THE PROCEEDING PUBLICATION

Faculty of Science

PACCON
PURE AND APPLIED CHEMISTRY INTERNATIONAL CONFERENCE 2013

March 13, 2013

Faculty of Science, Burapha University
Bangsaen, Chonburi, 20131, Thailand

Acceptance Letter for PACCON 2013 Proceeding

On behalf of PACCON 2013, I am glad to inform you that the submitted article entitled **"SYNTHESIS AND CHARACTERIZATION OF ASYMMETRIC DIAMINE FOR TRANSPARENT POLYIMIDE FILM"** authored by NAPASIN THEVASE has been accepted for publication in the book of proceeding of Pure and Applied Chemistry International Conference 2013 which was held in January 23-25, 2013 at The Tide Resort, Chonburi, Thailand.

Thank you for your participation in the conference.

Sincerely yours,

T. Usavadee

Usavadee Tantiwaranurak
Dean, Faculty of Science, Burapha University, Chonburi, Thailand

VITA

Mr. Napasin Thevase was born June 24, 1988 in Mahasarakarm, Thailand. He received the Bachelor's Degree in Chemical Engineering from Department of Chemical Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang in March 2011, He entered the Master of Engineering in Chemical Engineering at Chulalongkorn University in May, 2011.