Synthesis of Polyimide: Polymerization via Nucleophilic Substitution Reaction

by

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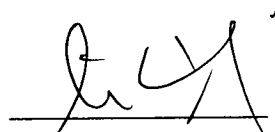Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Polymerization via Nucleophilic Substitution Reaction

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A project dissertation submitted to the

Chemical Engineering Programme

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(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr. Oh Pei Ching)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, and the original work is produced on my own except as specified in the references and acknowledgement, and it has not been undertaken or done by unspecified sources or person.

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(Mohamad Faez Bin Azam Mohar)

ABSTRACT

Polyimide is a type of polymer with high end characteristics. These high end characteristics has made polyimide important in the industries as the application of usage of polyimide has broaden and highly specific. Common industrial application of polyimide is for gas separation. This project highly focuses on synthesizing polyimide from dianhydride and diamine monomers via the classic two step method. Variation in synthesize condition is done so as to be able to determine the optimum condition for the polyimide to exhibit specific characteristics. These characteristics then characterized through the Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Problem statement of the project is that polyimide is not widely used in the industry compared to other polymer, especially in gas membrane. The project aims to be able to widen the perspective of polyimide in the industry in Malaysia. Characterization of the polyimide is done to provide information on the characteristics and behaviors of the polyimide to the industry so that the application of polyimide can be broaden. The study involve the synthesis of polyimide from PMDA and ODA in DMAc and DMF solvent via the two step method. The two step method is the formation of poly (amic acid) and thermal imidization. The synthesis is varied in term of the condition to obtain difference in the characteristics. The polyimide then characterize using the said equipment. FTIR band occurring at approximately 1780-, 1730-, 1375- and 720 cm-1 confirms the presence of imide functional group in polyimide oligomers (Dunson, 2000).

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CHAPTER 1

INTRODUCTION

This chapter will describe the overview of the project that covers the following topics.

- Background of Study
- Problem Statement
- Purpose of Study
- Objective
- Significance and Feasibility of Study

1. BACKGROUND STUDY

The usage of polymer has grown largely in today's lifestyle and also in various industries. Reason is due to the variety of characteristics of polymer that makes them suitable for specific usage. With growing economics and technologies, demand for certain polymer with certain characteristics has also increased. Polyimides is a type of polymer that has very high mechanical characteristics and high thermal stability, which makes it demandable in specific industries usage. Demand also increase due to the characteristics of polyimides, which makes them difficult to synthesize. Polyimides can be synthesize by nucleophilic substitution. One method is called the two-step method in which poly (amic acid) is first synthesize and then undergo thermal imidization to produce polyimides. Via this two-step method, the poly (amic acid) produce as intermediate makes it possible to process the polyimides for certain industries use. The poly (amic acid) then undergo thermal imidization to degrade into polyimides.

1.1 Polymer

The word polymer is derived from Greek words, *poly* and *meros* which mean many and parts respectively (Carraher, 2010). Polymers existed everywhere in our daily life. There are naturally existing polymers such as protein and also synthesized polymers such as polyethylene. Since ancient times, human has incorporated the use of polymers in everyday life. For example, the Aztecs of early South American civilization, used natural rubber for making elastic articles and for waterproofing fabrics.

Even with many polymers in the surrounding, in the 18th century the science of polymers were not of great focus. Thanks to Charles Goodyear, who started experimenting natural rubber with anything he could find to produce rubber with better characteristics. This marked the first step of the development and detail research in polymerization and soon a variety of polymers were produced.

Polymers is everyday life, from animal and plant to human, they all consist of polymers. Everyday materials that makes present day living simpler and easier are also made up of different kind of polymers. Examples include plastic bags and plastic bottles.

There are different types of polymers being synthesized and produced commercially into household items and other necessary products. Some of the polymers are polystyrene, polyvinyl chloride, polyethylene, polyamide, polyimide and etc.

1.2 Polyimide

Polyimide is obtained from dianhydride and diamine. Polyimide is a group of polymer than are thermally stable and possess high mechanical properties. These characteristics are due to the stiff aromatic backbones of the polyimide itself.

Polyimide study is wide as many synthesizing methods are available and its characteristics can be altered by minor variation in the structure. The different synthesizing method are accounted to produce different molecular weight polyimide and to allow polyimide to be commercially available. Due to its characteristics, processing polyimide into usable products comes with its limitation. In addition, the structure of the polyimide are also being studied and altered to produce a friendlier polyimide in terms of producing it commercially and also to achieve specific characteristics.

For this study, polyimide is synthesized as it is thermally stable, thus can withstand high temperature without degradation or decomposition. Some of the polyimide being synthesized can undergo continuous exposure to temperature up to 480 °C.

Mechanical properties of polyimide are generally good at ambient and high temperature (Biron, 2004). Special grade polyimide are also being developed to give low coefficient of friction and low wear rate. Polyimide also possess low or moderate thermal expansion coefficient.

Other good characteristics of polyimide are resistance against high-energy radiation, resistance to wide variety of chemicals, fire resistant and also possesses good insulating properties.

1.3 Polymerization

Polymerization is a process of reacting a monomer to form chains of monomer or polymer or a network of polymer. As discussed, polymer is an important aspect in everyday life. Polymer exist almost in every part of everyday life, but how is polymer being made?

Polymer is made from a step called polymerization. In polymerization, a monomer is being reacted with another monomer and so on to form chains of repeated monomers. The chain length can be of any length depending on the purpose of the polymer or the usage of the polymer. Polymer that needs to be flexible and clear is of shorter chain, while longer chain will produce polymer with more rigid structure and opaque. The science of polymerization has improved over the years and instead of polymer with straight chains, polymer with network structure can be produce. The network structure of polymer results in the polymer being characteristically higher than straight chain polymer.

Polymerization can be divided into two, namely step-growth polymerization and chain-growth polymerization. In step-growth polymerization, the monomer involve usually end up with different structure in the chain as some functional group leave the monomer as the monomer react with another monomer. Step-growth polymerization are usually slow and takes a lot of time to achieve high molecular weight. As for chain-growth polymerization, the monomer usually contain one or more internal bond that can be break to form bond with another polymer. This polymerization need an initiator to start the reaction. Once the bond of one monomer is broken, it will attack another monomer and break the bond and so on, forming like a chain reaction. The polymerization is much faster and achieve high molecular weight in short time.

1.4 Nucleophilic Substitution Reaction

Nucleophilic substitution reaction is a reaction where it involve a nucleophile. A nucleophile is a molecule or ion which is attracted to a region of positive charge. Nucleophile can be a fully negative ion or molecule which have negative dipole charge somewhere in the molecule. Commonly, nucleophile contain lone pair of electrons. This lone pair of electron resulted in the dipole negative charge of the molecule. Example of nucleophile are hydroxide ion, water and ammonia.

Nucleophilic substitution reaction can be divided into two reaction, which is S_n2 and S_n1. In S_n2 reaction, the molecule to be attacked by nucleophile will have an induced charge due to its structure. The nucleophile, which is attracted to the positive charge, will come from the backside of the molecule and begin to create bond, while the negative part of the molecule will moves away and begin to lose its bond. This will create an intermediate. The nucleophile will move closer and then form bond the molecule and at the same time the negative part of the molecule will lose its bond and move out of the molecule.
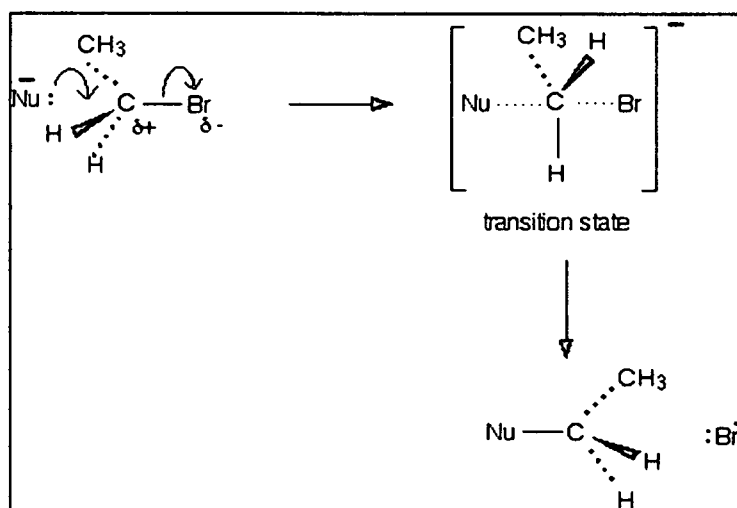
Figure 1 : Example of Sn2 reaction

As for S_n1 reaction mechanism, the nucleophile still attack the positive part of the molecule, but it is hindered by the molecular structure of the molecule. In other words, the nucleophile cannot approach the backside of the molecule. In this condition, the negative part of the molecule loses its bond first and then the nucleophile comes from the front and create bond with the molecule at the same place as the negative part.

Figure 2 : Example of Sn I reaction – slow

Figure 3 : Example of Sn1 reaction – fast

2. PROBLEM STATEMENT

Polymer products play a major role in everyday live, from daily usage to many industrial usage. As to cater for the different condition or specifications required by the industries, high performing polymer is needed, namely the polyimide. With the use of polyimide, industries can be further developed to achieve higher production and better technologies that are cost effective and with better outcomes.
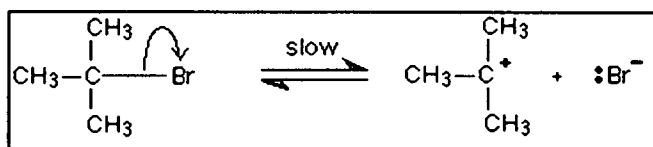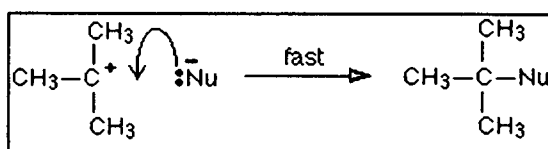
The use of polyimide is of great importance in industries. For example in certain processes that requires high performance material. Polyimide can cater the needs due to its high characteristics such as being thermally stable and high mechanical properties. Polyimide is also use in gas separation processes as membrane.

This project will mainly focuses on the following problem statement:

- o Increase and expand the market of polyimide as high characteristic polymer via the two step reaction especially in the gas separation technology in Malaysia

- o Characterize the synthesize polyimide to provide information to the industries so as to widen the scope of polyimide manufacturing.

3. PURPOSE OF STUDY

The purpose of this study or project is to be able to synthesize polyimide from two step reaction and to be able to characterize the produced polyimide based on its reaction conditions.

4. OBJECTIVE

The objectives of this study are:
1. To synthesize polyimide from dianhydride and diamine via the two step reaction method.
2. To determine the optimum conditions for two step reaction for polyimide synthesis with desirable characteristics.
3. To characterize the synthesized polyimide via Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM)

5. SIGNIFICANCE AND FEASIBILITY OF STUDY

Conducive research is conducted in order to synthesize polyimide via nucleophilic substitution reaction. The substitution reaction involve the two step reaction. Through the project, the polyimide synthesized will be characterized to determine its characteristics. The reaction condition will be varied so as to determine which condition can produce polyimide with specific characteristics. In the industries, polyimide with different characteristics have different use or purpose. The time frame for the project is two semesters. For the first semester, emphasis will be place on extensive research, analysis, planning, designing and early deducting. The second semester will focus on carrying out the project.

Table 1 : Duration

No	Step	Duration
1	Experimental set-up and preparation	1 hour
2	Preparation of poly (amic acid) solution	4 hours
3	Imidization	24 hours
Total		29 hours

CHAPTER 2

LITERATURE REVIEW

1. INTRODUCTION

Growth in the modern technology has imposed an impact in materials that can perform well or has better characteristics than the readily available materials. The use of polymer can cater to the needs for materials that can perform under harsh conditions such as at high temperature. This later introduced the term polyimide in the society. Polyimide then became one of the major part in the polymer science.

The earliest scouting research took place in the exploratory laboratory of DuPont's Film Department (Ghosh & Mittal, 2000). Early investigations reveals that polyimides have an array of characteristic superior to other polymer such as high thermal stability, chemical resistance, radiation resistance, low dielectric constant, selective permeability to gases, film toughness under various conditions and retention of high mechanical strength over wide range of temperatures (Dunson, 2000).

These versatile characteristics of polyimides have stimulated the growing of polyimides application in different areas such as in aerospace and automotive.

2. POLYIMIDE

Polyimide is a polymer consisting of imide monomers. Figure 4 shows the general structure of an imide monomer. Polyimide can be classified into three types, namely aliphatic polyimide, semi-aromatic polyimide and aromatic polyimide. Aliphatic polyimides are polyimides with straight chain, while semi-aromatic polyimides are a mixture of aliphatic and aromatic polyimides. Aromatic polyimides are polyimides consisting of aromatic rings. The R_2 and R_3 of the imide in Figure 4 is a part of an aromatic ring. R_1 comes from a diamine monomer and R_2 and R_3 form a dianhydride.
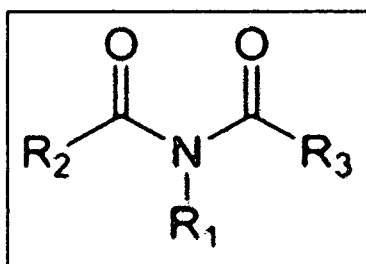
Figure 4 : General structure of imide monomer

The type of polyimide is mainly being determined by the monomers used to produce the polyimide. Most common monomers used are aromatic dianhydride and aromatic diamine to produce aromatic polyimide. Aromatic dianhydride is when two dianhydride come together and R_1 and R_2 of both anhydride forms an aromatic ring as in Figure 5. The A_1 part can be a ring or two rings being connected by a bridge.
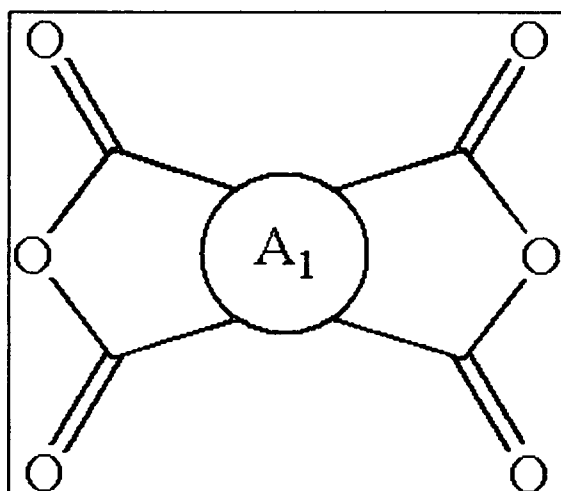
Figure 5 : General structure of aromatic dianhydride

Aromatic diamine is when two primary amine being connected by an aromatic group or a pair of aromatic rings connected by a bridge. Figure 6 shows the general structure of an aromatic diamine, with two primary amine being connected by a cyclic structure.
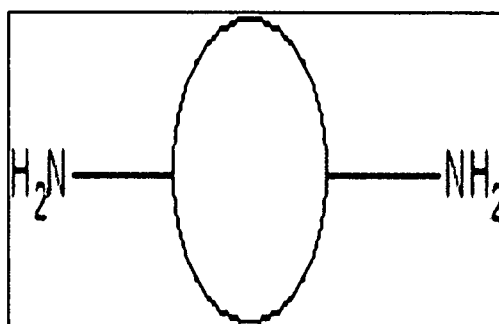

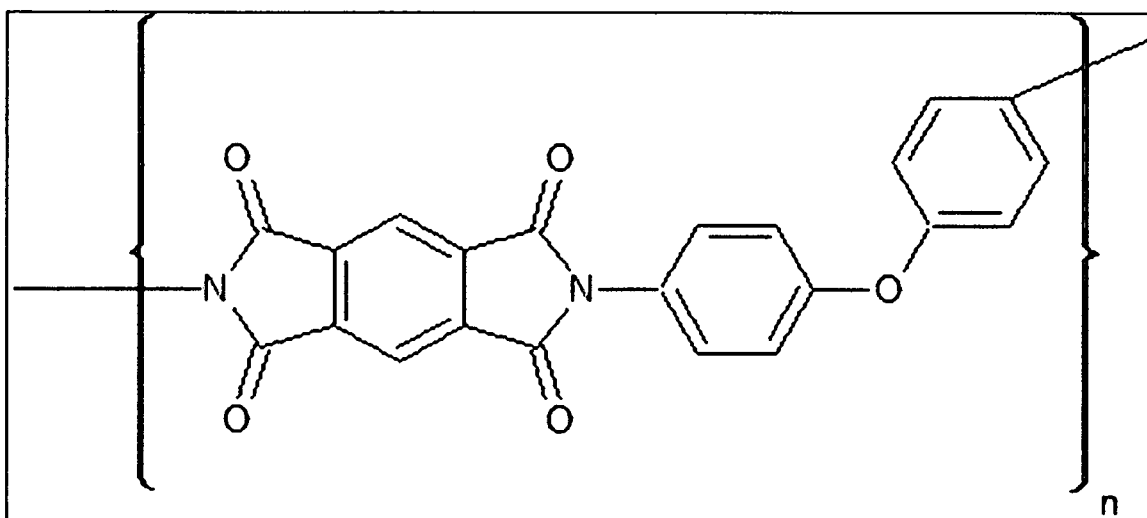Figure 6 : General structure of aromatic diamine

Figure 7 : Structure of PMDA and ODA polyimide (industrially known as Kapton)

3. SYNTHESIS OF POLYIMIDE

In general, polyimides comprised of five membered heterocyclic imide units and aromatic rings as shown in Figure 7. The cyclic chain structure of polyimides are the reason why polyimides are insoluble or intractable (Dunson, 2000). Due to these properties, polyimides are not synthesizable by the traditional melt poly-condensation reactions. Early attempt to synthesize polyimides from the melt poly-condensation made by DuPont in 1950 resulted in precipitation of intractable low molecular weight polyimides (Dunson, 2000). In 1956, Dr. A. Endrey successfully obtained polyimide through a soluble or processable intermediate, which is poly (amic acid) (Dunson, 2000); (Ghosh & Mittal, 2000).

3.3'-4.4'-biphenyltetracarboxylic dianhydride (BPDA)   2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)

2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA)

benzophenonetetracarboxylic dianhydride (BTDA)   pyromellitic dianhydride (PMDA)

m-phenylene diamine (m-PDA)   4,4'-diaminophenyl sulfone (4,4'-DDS)   p-phenylene diamine (p-PDA)

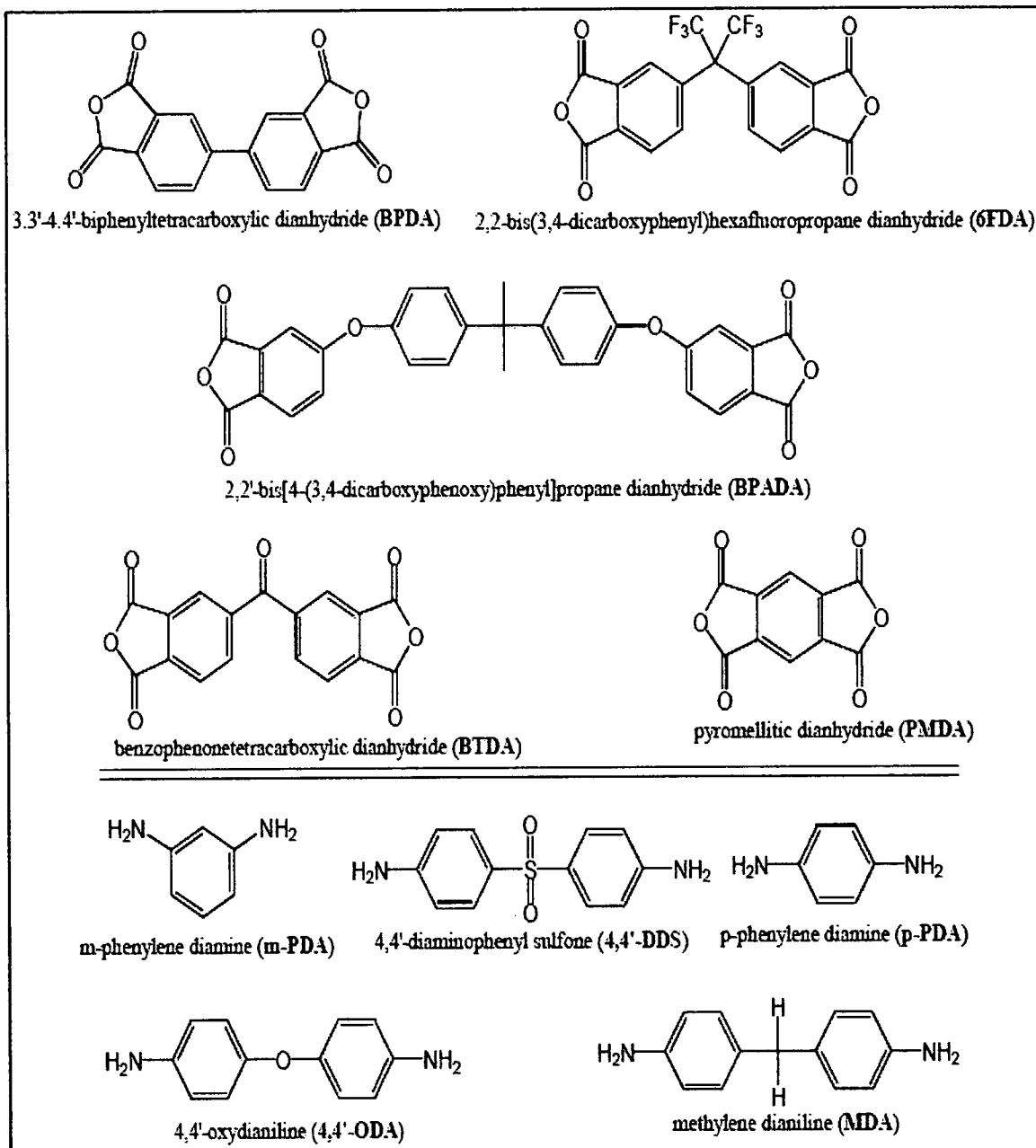4,4'-oxydianiline (4,4'-ODA)   methylene dianiline (MDA)

Figure 8 : Common Aromatic Dianhydride and Diamine

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3.1 Two Step Method

In the two step method, the first step is to prepare a solution of aromatic diamine in a polar aprotic solvent such as N,N-dimethylformamide (DMF) (Dunson, 2000). Aromatic dianhydride is then added to the solution. The aromatic diamine and aromatic dianhydride react to form poly (amic acid) at ambient temperature and the reaction is complete after 24 hours depending on the monomer's reactivity. The poly (amic acid) produced is of high molecular weight and are soluble in the solution. In other words, it can be processed to cater for the needs of the industries. The solution of the poly (amic acid) can be cast onto a film and then proceed with the next step to form polyimides. The poly (amic acid) undergo thermal imidization or cyclodehydration by heating the film at elevated temperature. Other than thermal imidization, the polyimides can also be produced through chemical imidization.

Figure 9 shows the reaction of the two step method. The reactants are aromatic dianhydride and aromatic diamine. The two reactants react to produce the intermediate poly (amic acid). The poly (amic acid) is in form of solution and can be easily processed. After that, the poly (amic acid) will undergo thermal imidization to give polyimide polymer.
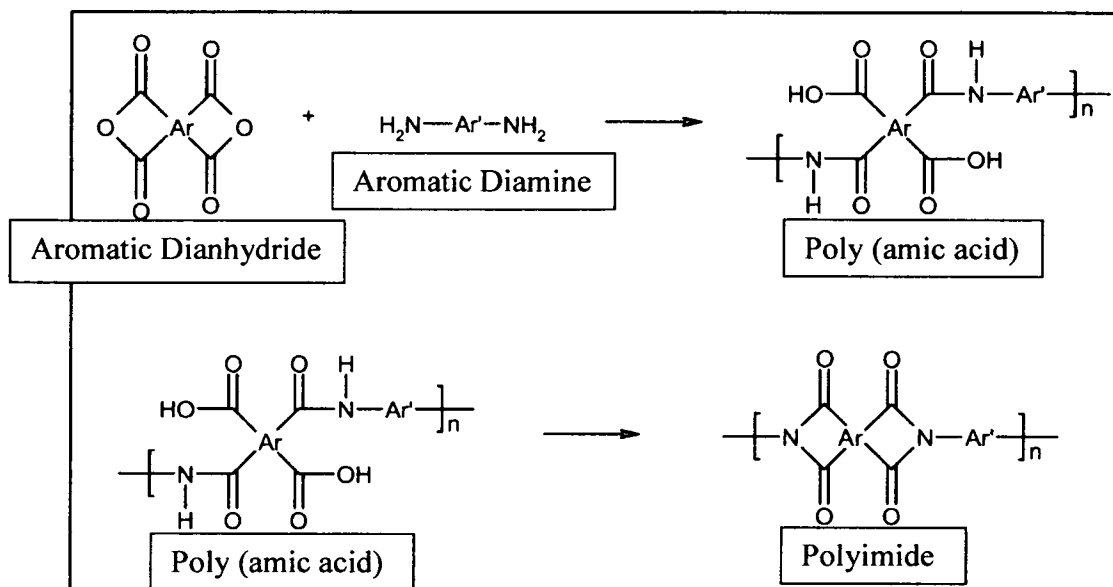
Figure 9 : Two step method of polyimides synthesis

3.1.1 Reaction Mechanism

The nucleophilic acyl substitution occurs at one of the carbonyl carbons of dianhydride (Dunson, 2000), as shown in Figure 10. The attacking nucleophile is the nitrogen from the aromatic diamine group. This is because the nitrogen consist of a lone pair of electrons. The lone pair of electrons make the nitrogen become more negative.

The nitrogen bonded with the carbonyl carbon and formed a cyclic intermediate. The intermediate are short-lived as the negative charge is shifted back to form the carbonyl double bond and at the same time caused the breaking of the ring.

The bond that need to be broken is the bond of the central oxygen atom. On the other hand, if the bond between the nitrogen to the carbonyl carbon is broken, this would reverse the reaction and produces free dianhydride and diamine monomer. The reaction is a reversible reaction. The forward reaction rate need to be of higher magnitude to obtain high molecular weight polyimides (Ghosh & Mittal, 2000).

It is important to identify the driving forces of the reaction that favors the forward reaction over the reverse reaction (Ghosh & Mittal, 2000). By identifying these forces, the characteristics of the polyimides can be controlled. Some of the driving forces for the forward reaction are high monomer concentrations and basicity of the solvent.
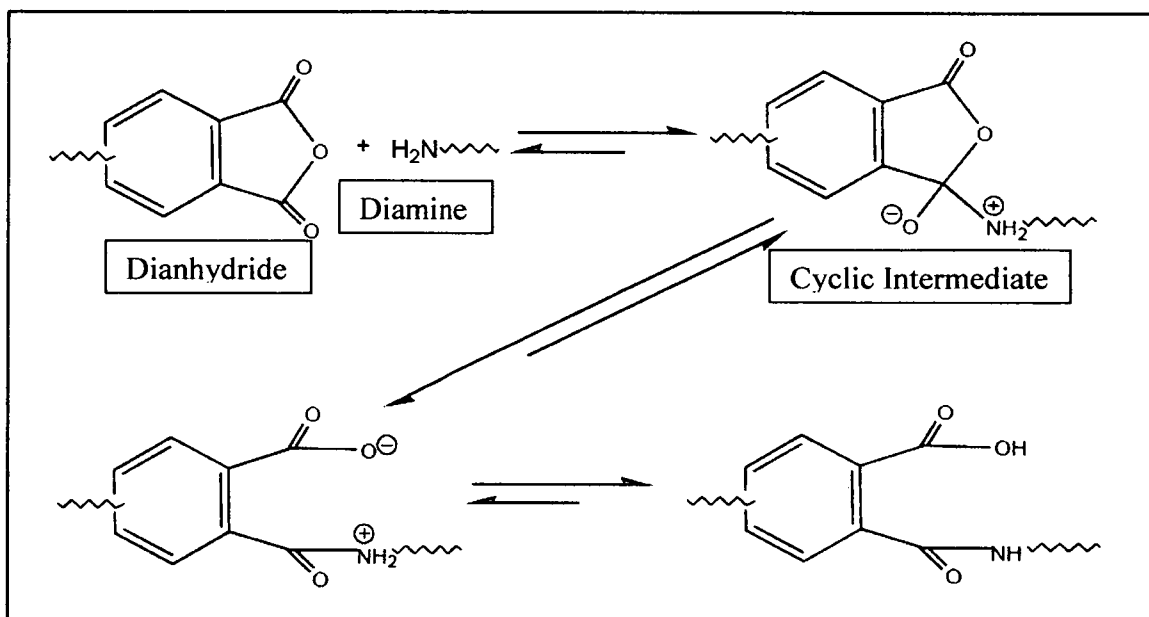

Figure 10 : Reaction mechanism of poly (amic acid)

3.1.2 Reactivity of Monomers

Higher molecular weight polyimides are more desirable than low molecular weight polyimides. In order to obtain high molecular weight of the polyimides, the poly (amic acid) must also be of high molecular weight. Reactivity of the monomers plays an important part in determining the molecular weight.

The reaction is primarily governed by the electrophilicity of the carbonyl groups of dianhydride and the nucleophilicity of the amino nitrogen atom of the diamine. The electrophilicity of dianhydride can be measured in terms of electron affinity, E_a, tendency to accept electron of a molecule. The higher the eletron affinity, the better the tendency to accept electron. Table 2 shows the electron affinity of some dianhydride.

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As for diamine, the ability of diamine to donate electron does not correlate with the reaction rate. Instead, the reactivity of diamine instead correlates well with its basicity, pK_a. The more basic the diamine is, the higher the reactivity of the diamine. Table 3 shows pK_a value of some diamine towards PMDA.

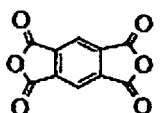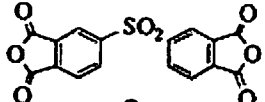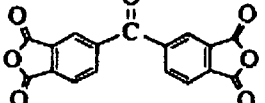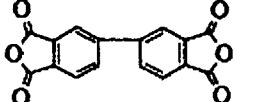Table 2 : Electron Affinity of Aromatic Dianhydride
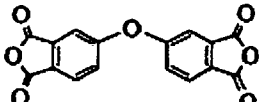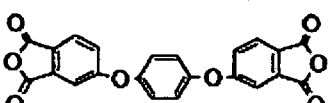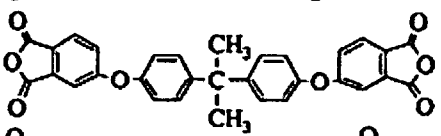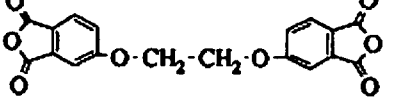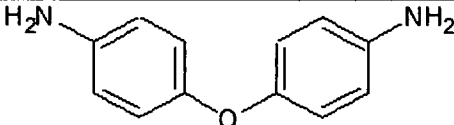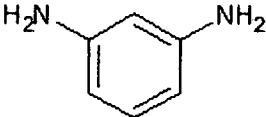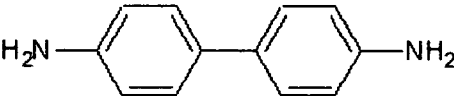
Dianhydrides		E_a (eV)
	(PMDA)	1.90
	(DSDA)	1.57
	(BTDA)	1.55
	(BPDA)	1.38
	(ODPA)	1.30
	(HQDA)	1.19
	(BPADA)	1.12
	(EDA)	1.10

Table 3 : Basicity of Diamines and Reactivity Toward PMDA

Diamine		pK$_a$	log K
H$_2$N—⟨benzene⟩—NH$_2$	PPD	6.08	2.12
H$_2$N—⟨benzene⟩—O—⟨benzene⟩—NH$_2$	ODA	5.20	0.78
H$_2$N—⟨benzene⟩—NH$_2$	MPD	4.80	0
H$_2$N—⟨benzene⟩—⟨benzene⟩—NH$_2$	Benzidine	4.60	0.37

3.1.3 Effect of Solvents

A solvent must be used in the process of synthesizing polyimide to obtain the poly (amic acid) intermediate. Direct polymerization of polyimide is not possible as low molecular weight polyimide is obtain. This is due to the characteristics of the polyimide. Using solvent, allow the dianhydride and diamine to react to form long chain poly (amic acid) which is the imidize to give polyimide.

Most commonly used solvents are dipolar aprotic amide solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methylpyrrolidinone (NMP), Tetramethylurea (TMU) (Ghosh & Mittal, 2000).

The important properties of the solvents is the basicity in Lewis' Base. However, the starting reagent are weakly basic aromatic and nonprotic anhydride or in simple word is basic. The product from the reaction is a strong protic acid. Notice that the starting mixture is basic and the product is acid. The strong acid-base interaction between the amic acid and the amide solvent is a major source of exothermicity of the reaction and one of the most important driving forces (Ghosh & Mittal, 2000). The rate of poly (amic-acid) formation is expected to be faster in basic and polar solvents such as N,N-dimethylacetamide (DMAc).

It is also found that the rate is much faster in acidic solvents such as m-cresol, showing that the reaction is catalyzed by acid (Ghosh & Mittal, 2000). As the reaction produce an acid, it can be said that the reaction is autocatalyzed by its product.

3.1.4 Side Reactions

In the reaction of poly (amic acid), there are side reaction. Usually the side reaction is not significant to the overall reaction. Nevertheless, under certain condition, the side reaction can become significant.

At ambient temperature, poly (amic acid) are known to undergo hydrolytic degradation (Ghosh & Mittal, 2000). The reaction of poly (amic acid) is a reversible reaction and therefore a small amount of dianhydride will always be present. The hydrolytic degradation of poly (amic acid) produces water into the solution. The nucleophilicity of water is enhanced in dipolar aprotic solvent and by strong acid-base interaction of the product with the dipolar solvent. Water as nucleophile will attack the small amount of dianhydride to form dicarboxylic group. Figure 11 shows the main reaction and side reaction of dianhydride.

The side reaction is cause by the presence of water, which normally exist in the solvent and monomers. By using pure solvent and monomers, the effect of side reaction can be reduced. The side reaction cannot be avoid as small amount of water if formed during thermal imidization of poly (amic acid). In order to maintain the properties of the poly (amic acid), it is necessary to keep the poly (amic acid) refrigerated (Ghosh & Mittal, 2000).
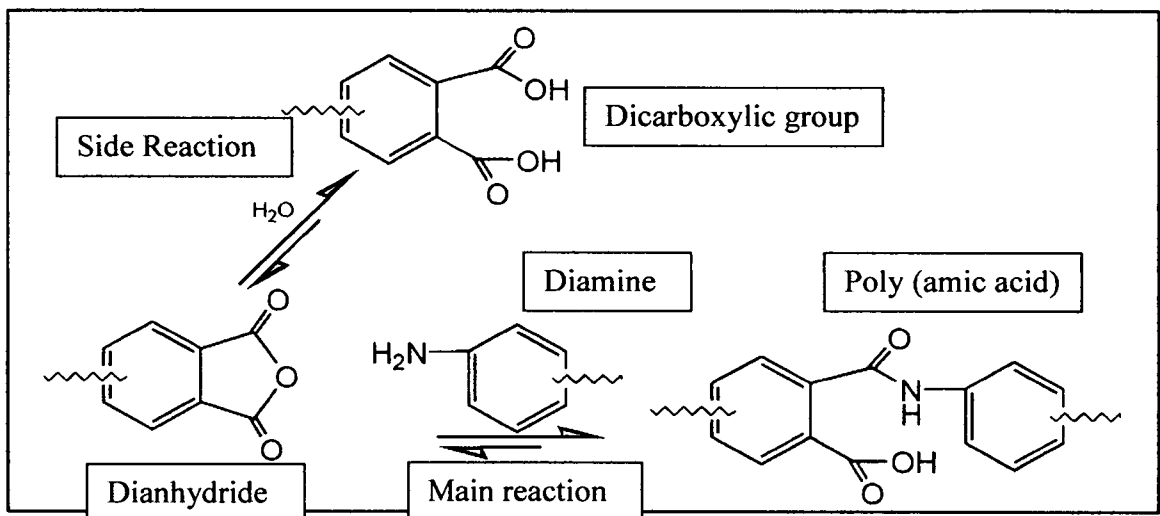

Figure 11 : Anhydride Reactions

3.1.5 Imidization

Poly (amic acid) can be converted to the corresponding polyimides thermally in solid state. The method is suitable for preparation of films, coatings, fibers and powders in order to allow diffusion of by-product and solvent without forming bristles and voids (Ghosh & Mittal, 2000). Poly (amic acid) is gradually heated to effect solvent removal and the cyclodehydration reaction to form polyimides (Dunson, 2000). Heating is performed as in following:

1. Two hours at 60 °C
2. One hour at 80 °C
3. One hour at 100 °C
4. Three hour at 200 °C

During the cyclodehydration, a rigid imide structure is formed and this increases the T_g dramatically and can rise above the reaction temperature (Dunson, 2000). The formation of rigid structure reduces the chain mobility. Reduction in chain mobility hinders the attainment of intramolecular conformation which favors the cyclodehydration.

Initially the rate of imidization is rapid as the amic acid is not converted to rigid structure of polyimides yet. This allows mobility of the poly (amic acid) to orient to the favorable conformation. In the later stage, slower rate of imidization is attributed to the unfavorable conformation, which need to orient to the favorable conformation. This orientation is much hindered by the rigid structure of the formed polyimides. Figure 12 shows the favorable and unfavorable conformations of the poly (amic acid).
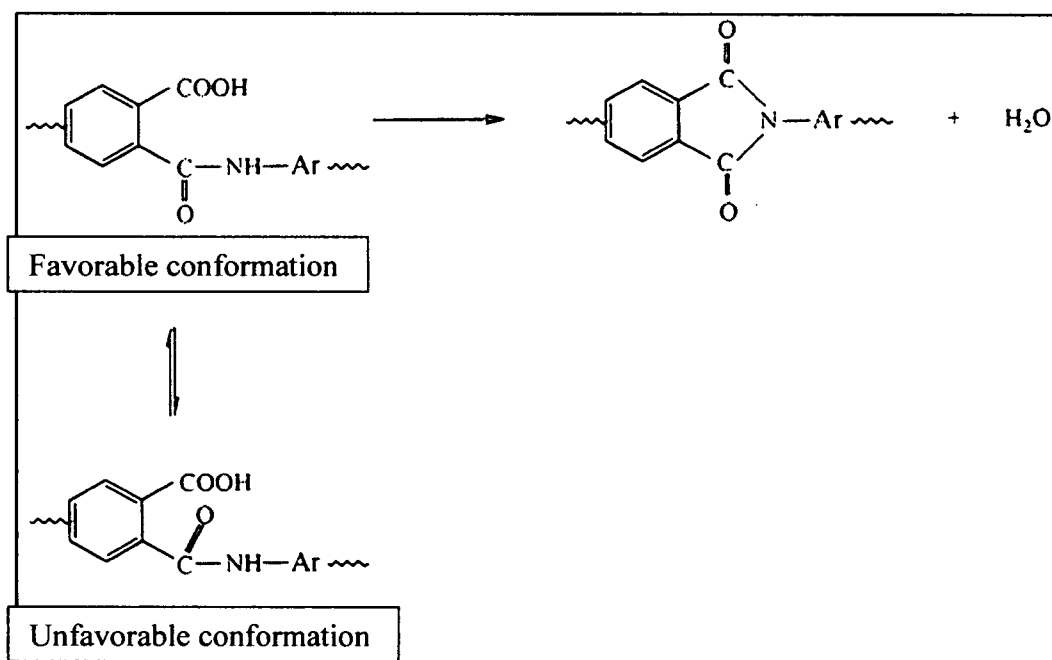

Figure 12 : Conformations of poly (amic acid)

In the glassy state, residual solvent molecules also hinder attainment of imidization favoring conformations by forming intermolecular hydrogen bonds with the reactive groups. (Dunson, 2000). This resulted in the final polyimide products with uncyclized amid acid which are hydrolytically unstable and cause chain degradation.

CHAPTER 3

METHODOLOGY

1. CHEMICALS AND GLASSWARES

Table 4 : Chemicals and Glasswares

Type	Number	Name	Amount
Chemical	1	PMDA	50g
	2	ODA	50g
	3	DMAc	1l
	4	DMF	1l
	5	Calcium Chloride	10g
Glassware and apparatus	6	Mixing beaker	500ml
	7	Mixing beaker	250ml
	8	Two necked round bottomed flask	50ml
	9	Vacuum extension	1
	10	Glassware clamp	3
	11	Retort Stand	1
	12	Water bath	1
	13	Petri Dish	4
	14	Glass plate	1
	15	Hot plate stirrer	1
Equipment	16	Oven	
	17	Vacuum Oven	
	18	Degassifier	
	19	Casting machine	

2. PROCEDURE

2.1 Drying of chemicals and glassware

1. An amount of PMDA and ODA are put in two different petri dishes.
2. Each petri dish is covered with an aluminium foil with holes to prevent contamination in the oven.
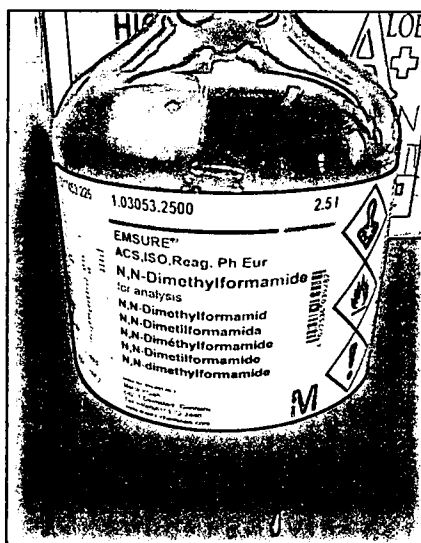3. The chemicals are then dried in an oven at 100 °C for one day.

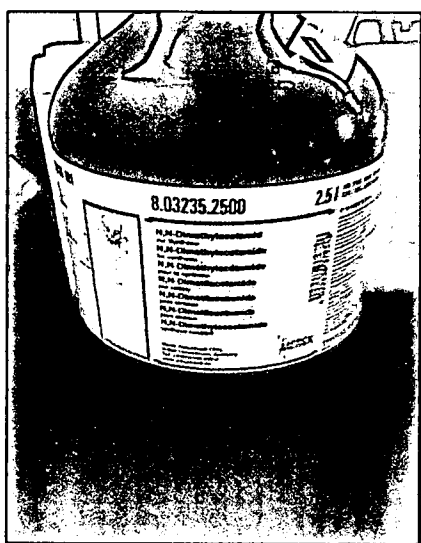Figure 13 : Dimethylformamide (DMF)
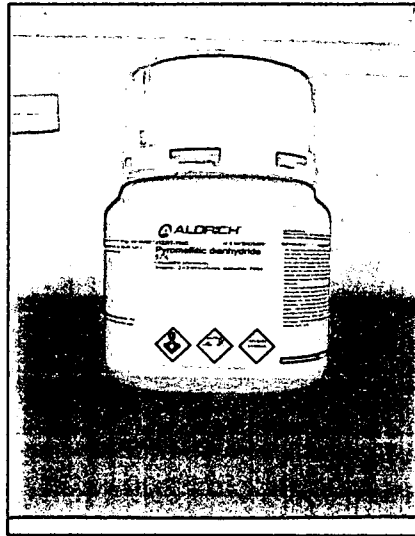

Figure 14 : Dimethyacetamide (DMAc)

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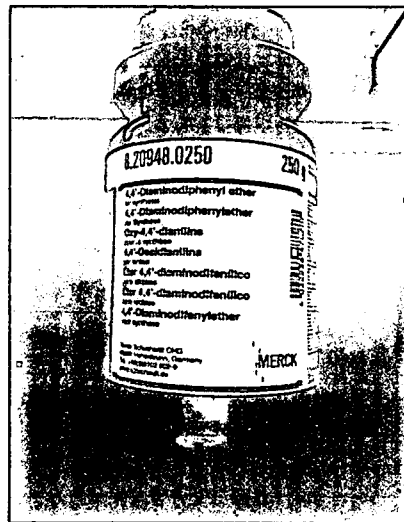Figure 15 : Pyromellitic Dianhydride (PMDA)

Figure 16 : Oxydianiline (ODA)

2.2 Poly (amic acid) preparation

1. Weight 20g of DMAc or DMF and pour into a mixing bottle.
2. Put a magnetic stirrer, close the cap and stir the solvent.
3. Weight an amount of ODA to give 30 weight percent and add slowly into the solution.
4. Stir until completely dissolve.
5. Weight an amount of PMDA to 30 weight percent and add slowly into the solution.
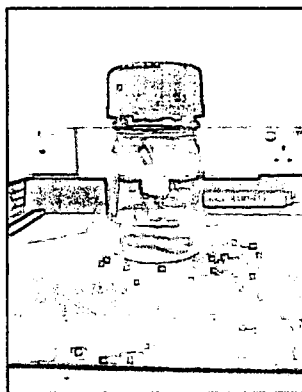6. Stir until completely dissolve and uniformly mix.

Figure 17 : Solution Stirring at Room Temperature

2.3 Calculation of weight percent

$$\frac{weight\ of\ solid}{weight\ of\ solid\ +\ weight\ of\ solvent} = solid\ weight\ percent$$

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2.4 Polyimide preparation (Imidization)

1. The poly (amic acid) solution is degased using ultrasonic degasifier to remove gas inside the solution.
2. The poly (amic acid) solution is poured and spread over a clean glass plate.
3. Immersed the glass plate in water.
4. Once the membrane peel itself from the glass plate, take out from the water and dry for 24 hours.
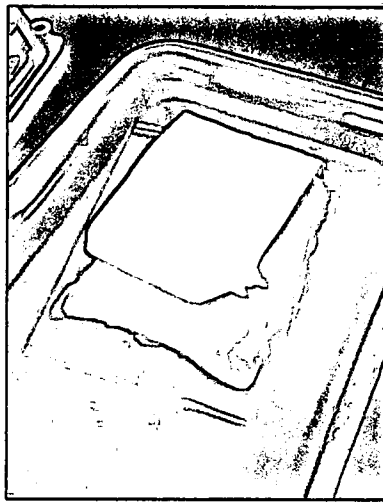
Figure 18 : Wet Phaisng

3. CHARACTERIZATION

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is used to confirm the functional groups in the polyimide oligomers. FTIR utilizes the light absorption characteristics of the sample. FTIR will capture how well the sample absorb light at each wavelength. FTIR band occurring at approximately 1780-, 1730-, 1375- and 720 cm^{-1} confirms the presence of imide functional group in polyimide oligomers (Dunson, 2000).

3.2 Scanning Electron Microscopy (SEM)

SEM analyze the morphology of the surface and the cross section of the membrane.

CHAPTER 4

RESULT AND DISCUSSION

1. EXPERIMENTAL RESULT

Table 5 : Run Data

Run	Monomer weight percent	Stirring Temperature, °C	Stirring Duration, hr	Curing Method	Result
1	9	80	24	Oven 200 °C	Not viscous/burn
2	9	80	24	Oven 100 °C	Not viscous/shrink
3	20	Room	24	Oven 100 °C	Not viscous/brittle
4	20	Room	2-3	Oven 100 °C	Viscous/brittle
5	25	Room	2-3	Wet phasing	Viscous/crack
6	30	Room	2-3	Wet phasing	Very viscous/membrane
7	35	Room	2-3	Wet phasing	Very viscous/membrane
8	30	room	2-3	Dry phasing	Very viscous/brittle

Figure 19 : Burnt Membrane

Figure 20 : Shrunk Membrane
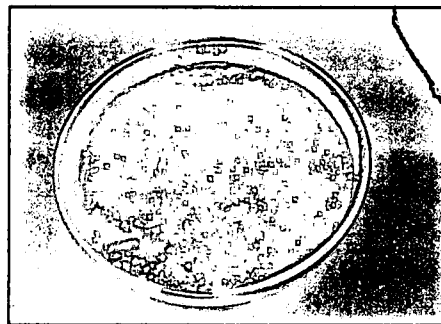
Figure 21 : Brittle Membrane
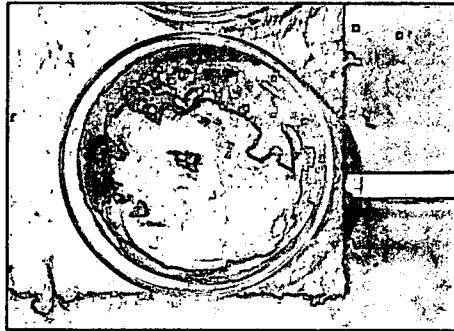
30
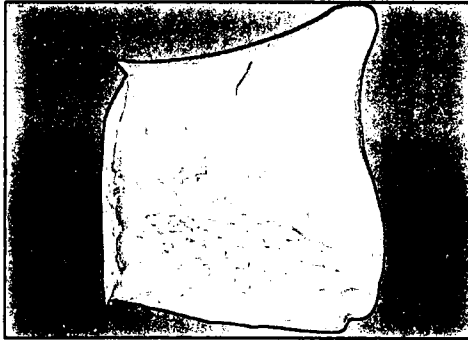
Figure 22 : Good membrane via wet phasing

Figure 23 : Brittle membrane via dry phasing

2. CHARACTERIZATION RESULT

2.1 Fourier Transform Infrared Spectroscopy

FTIR will determine the polyimide synthesize via the absorbance of light at different wavelength. Different bond inside the polyimide absorb different wavelength of light. The FTIR band of 1780-, 1730-, 1375- and 720 cm^{-1} confirms the presence of imide functional group in polyimide oligomers.
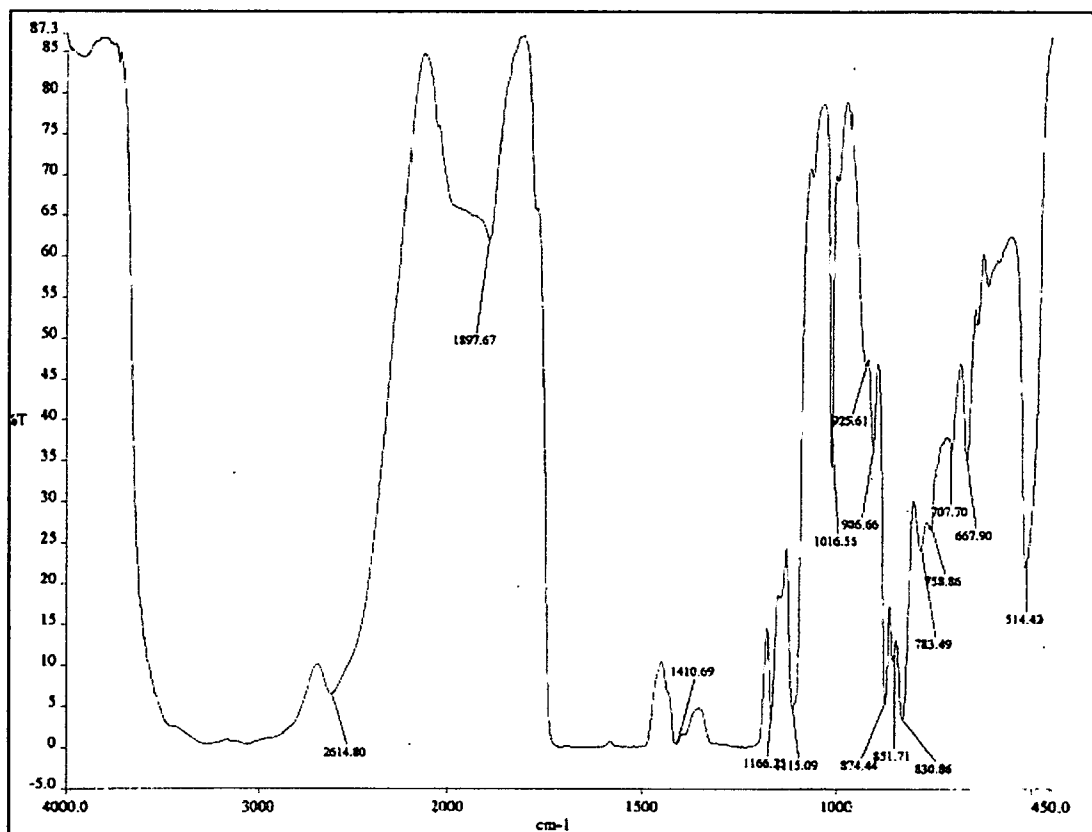
Figure 24 : FTIR result
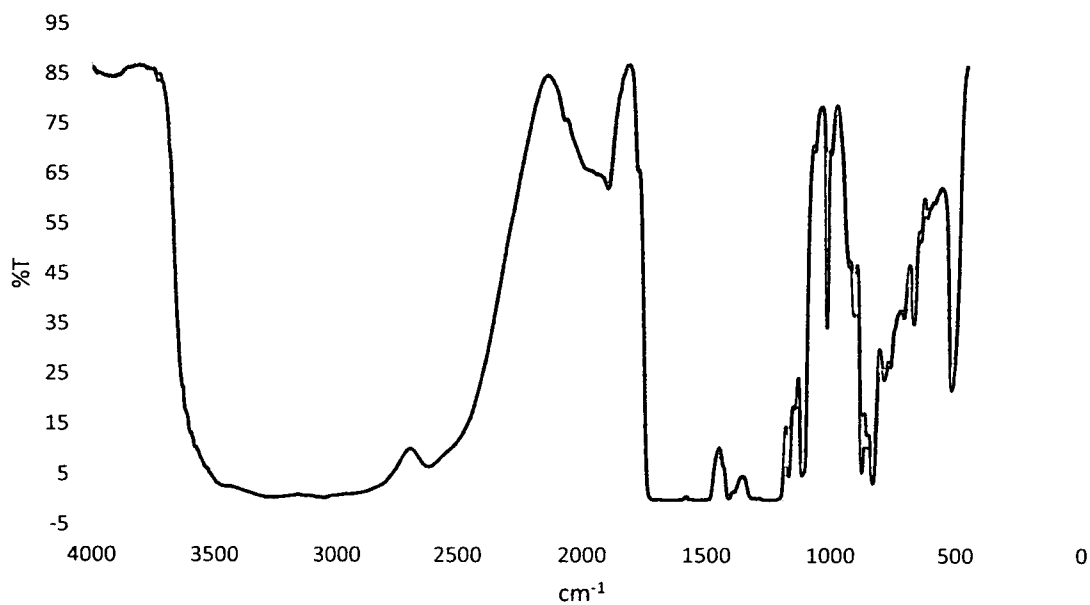
Figure 25 : FTIR result - Excel generated

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2.2 Scanning Electron Microscopy

Surface

Figure 26 : Surface at 1k magnification

PI   F L   D6.1 x2.0k   30 um
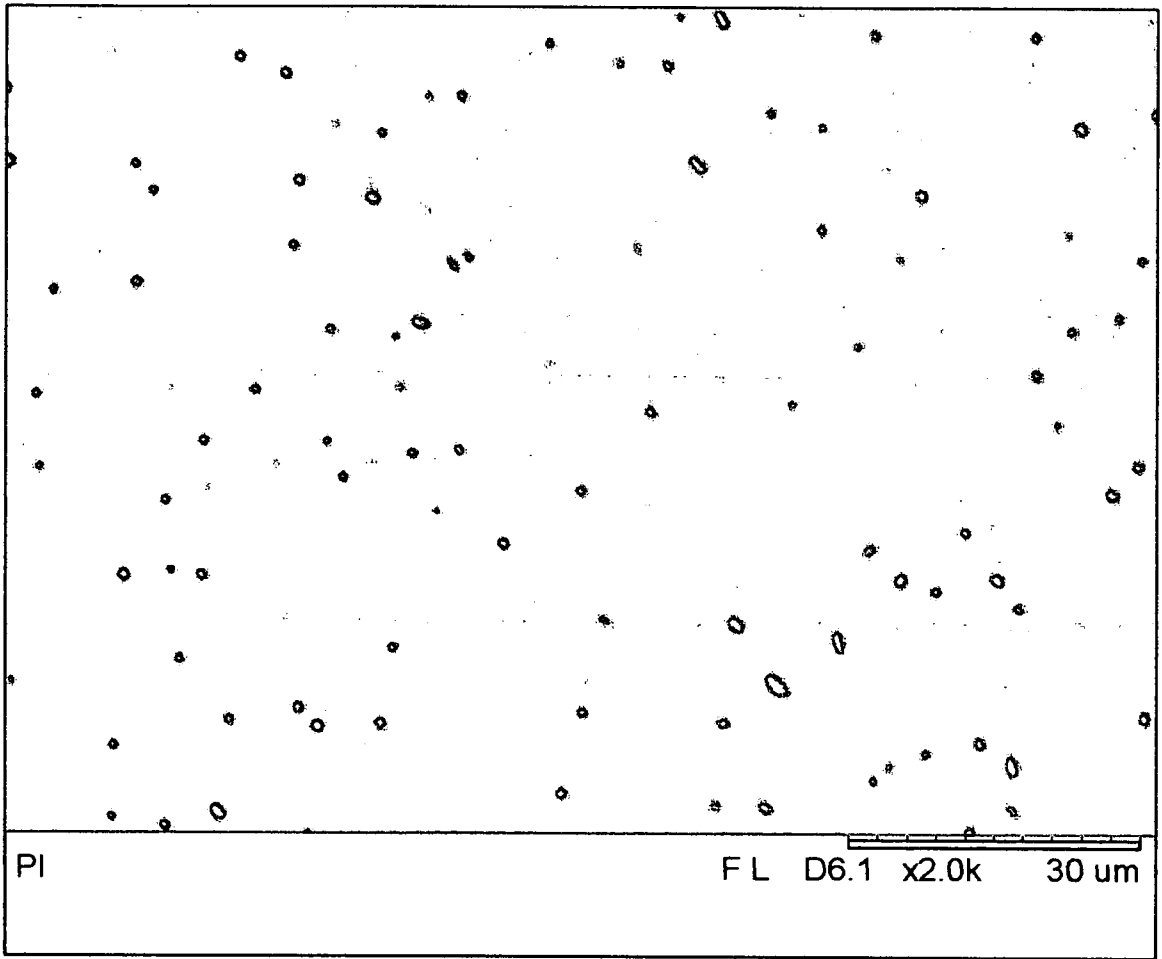
Figure 27 : Surface at 2k magnification
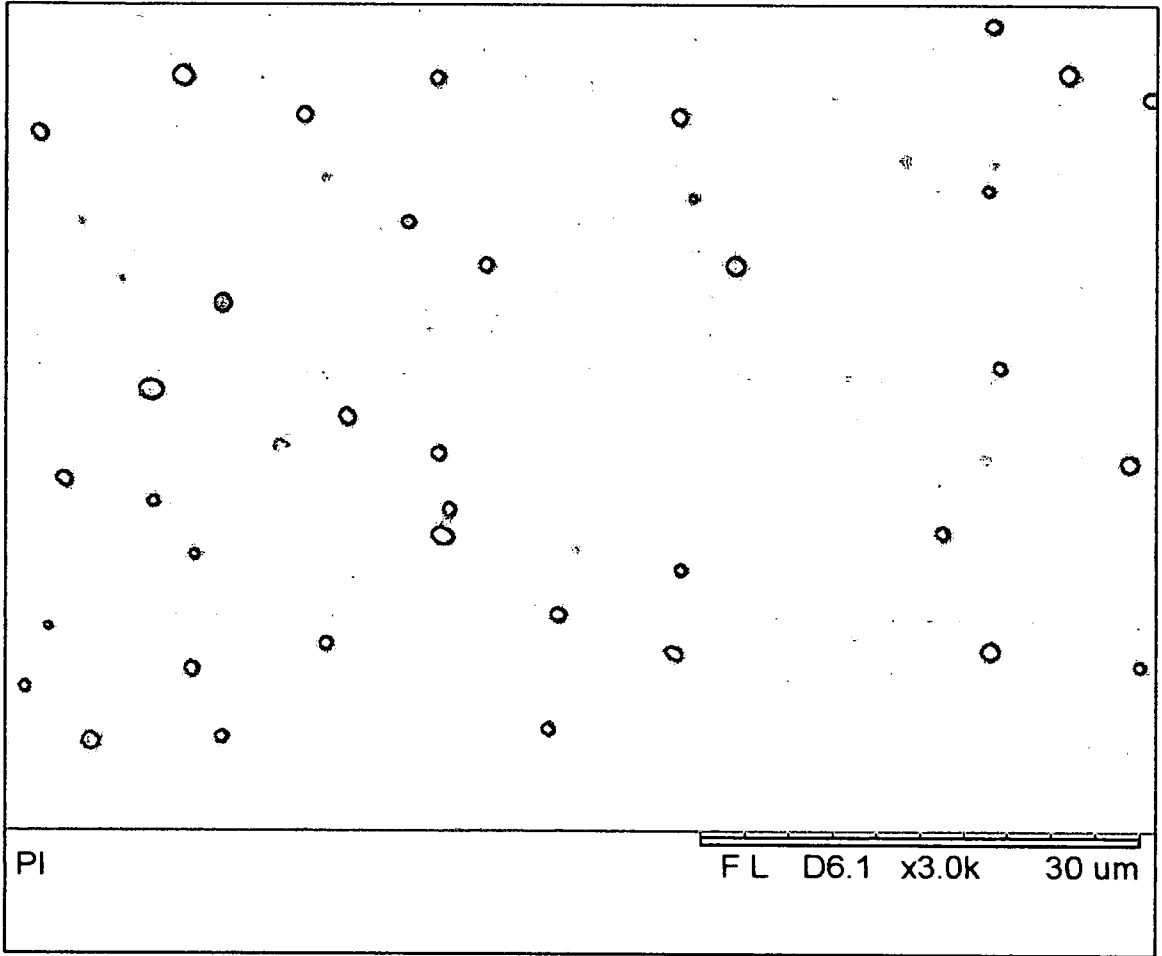
Figure 28 : Surface at 3k magnification
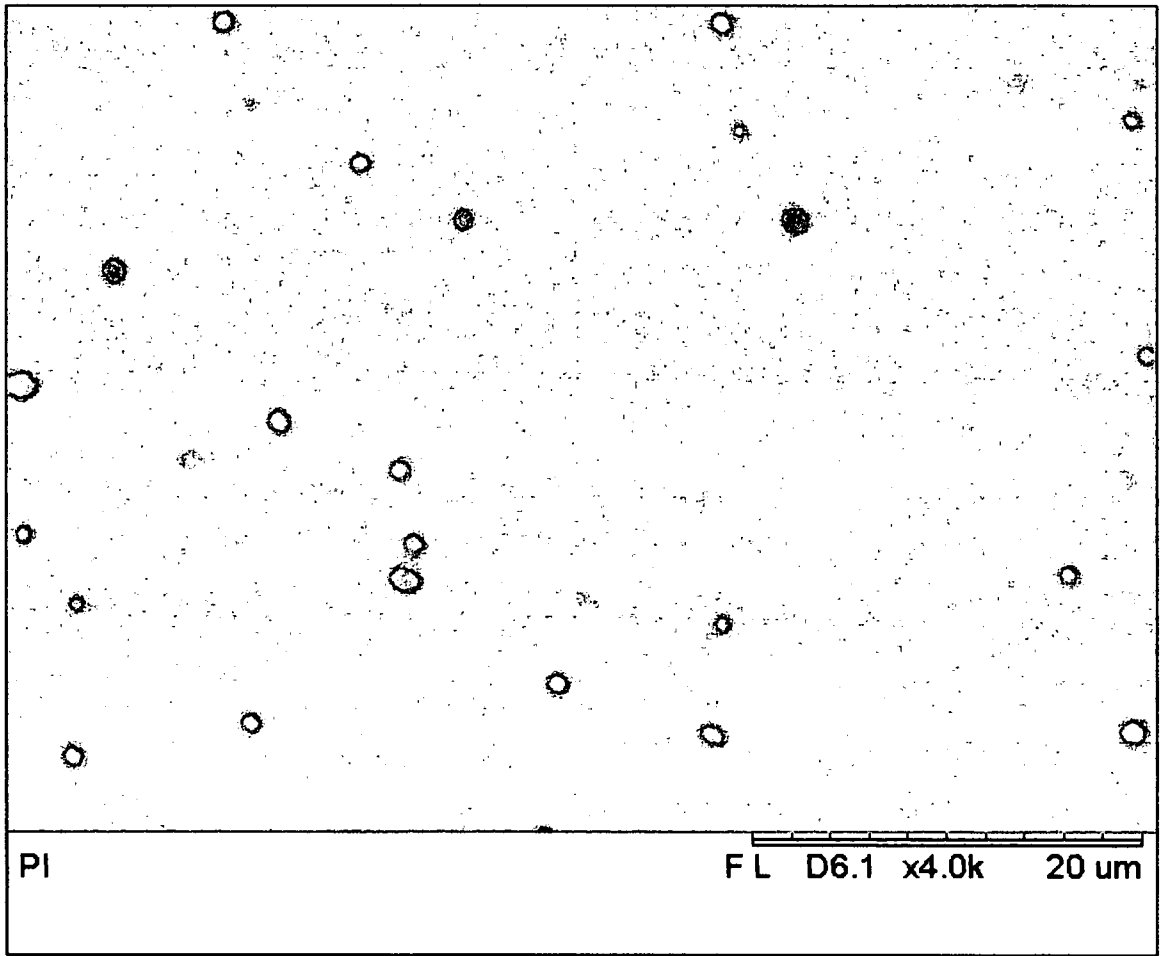
Figure 29 : Surface at 4k magnication

Cross Section
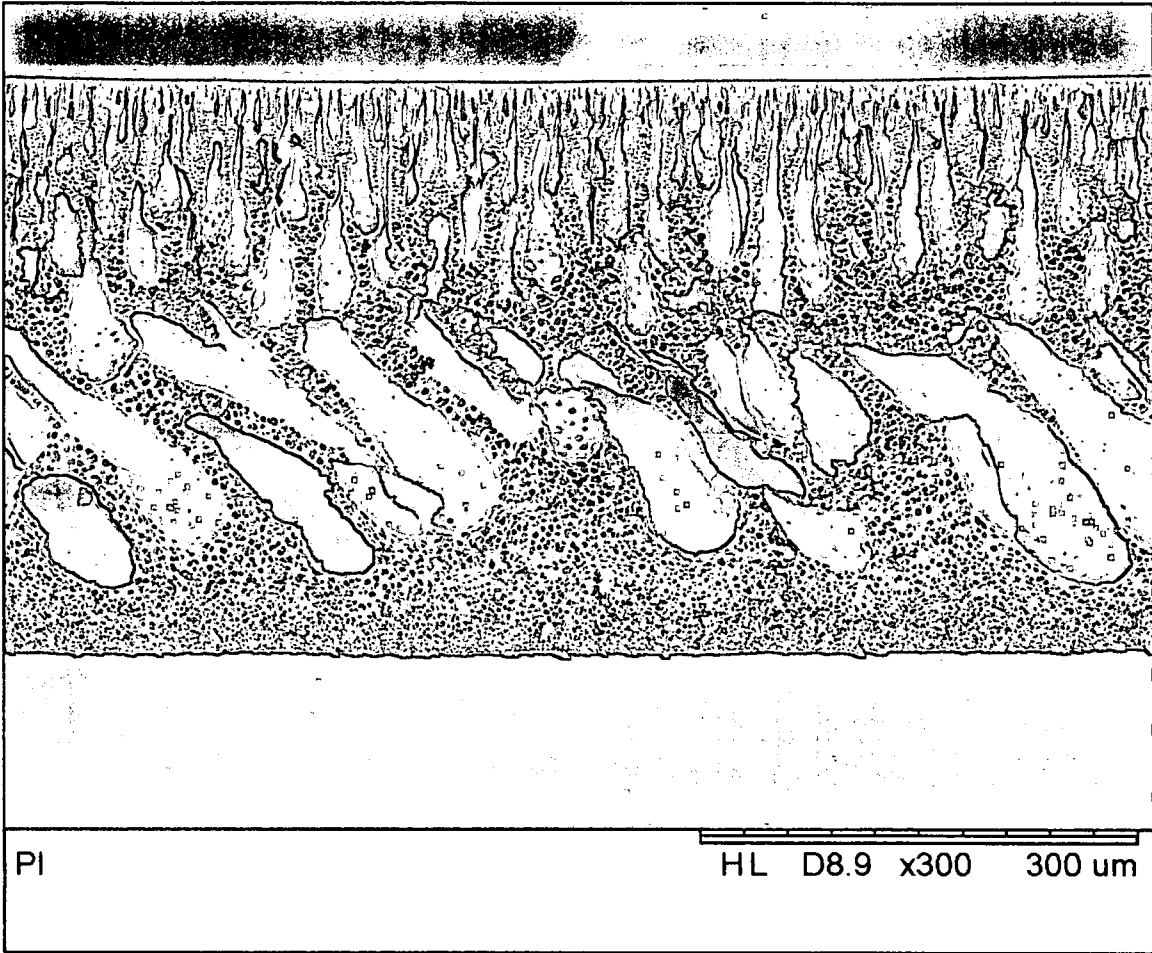
Figure 30 : Cross section at 300 magnification
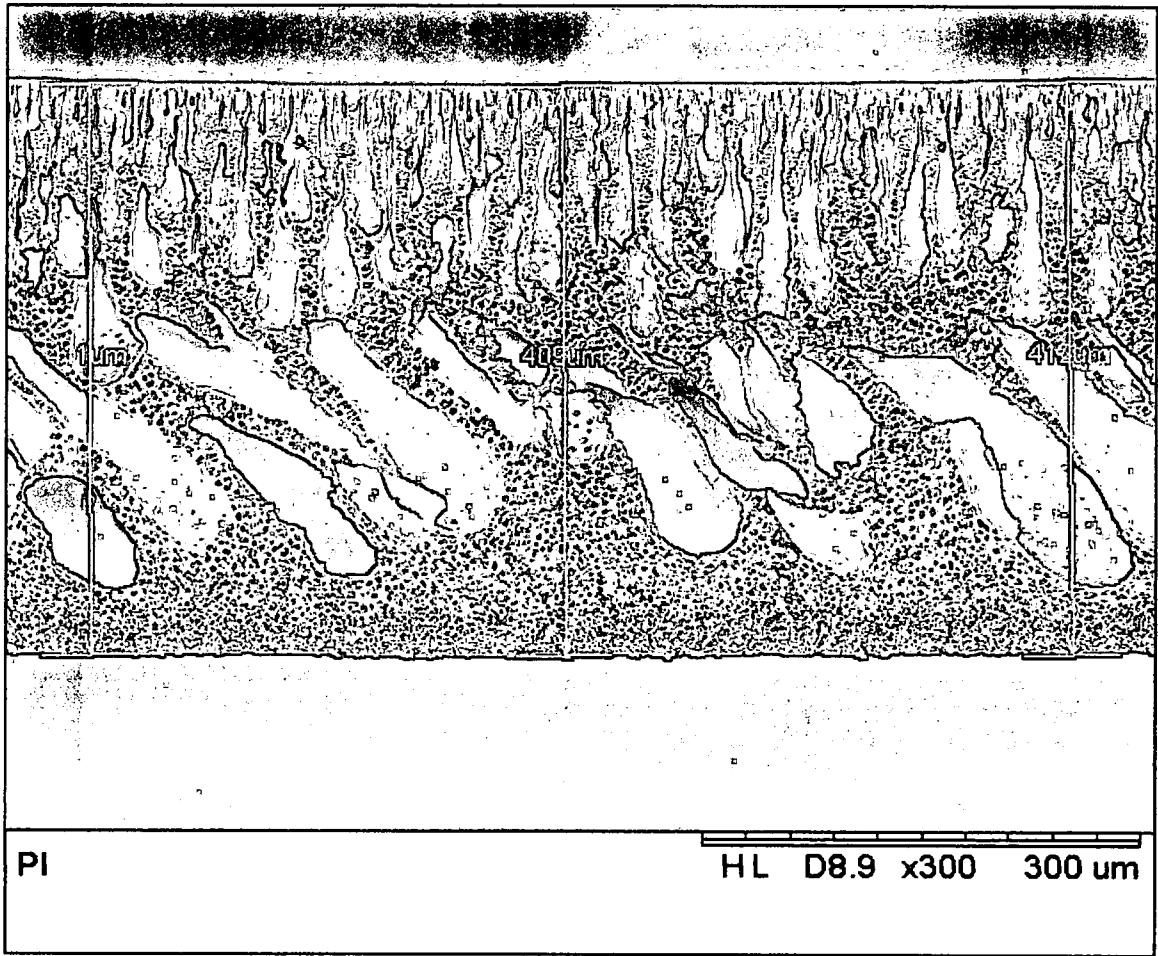
Figure 31 : Cross section at 300 magnification with thickness
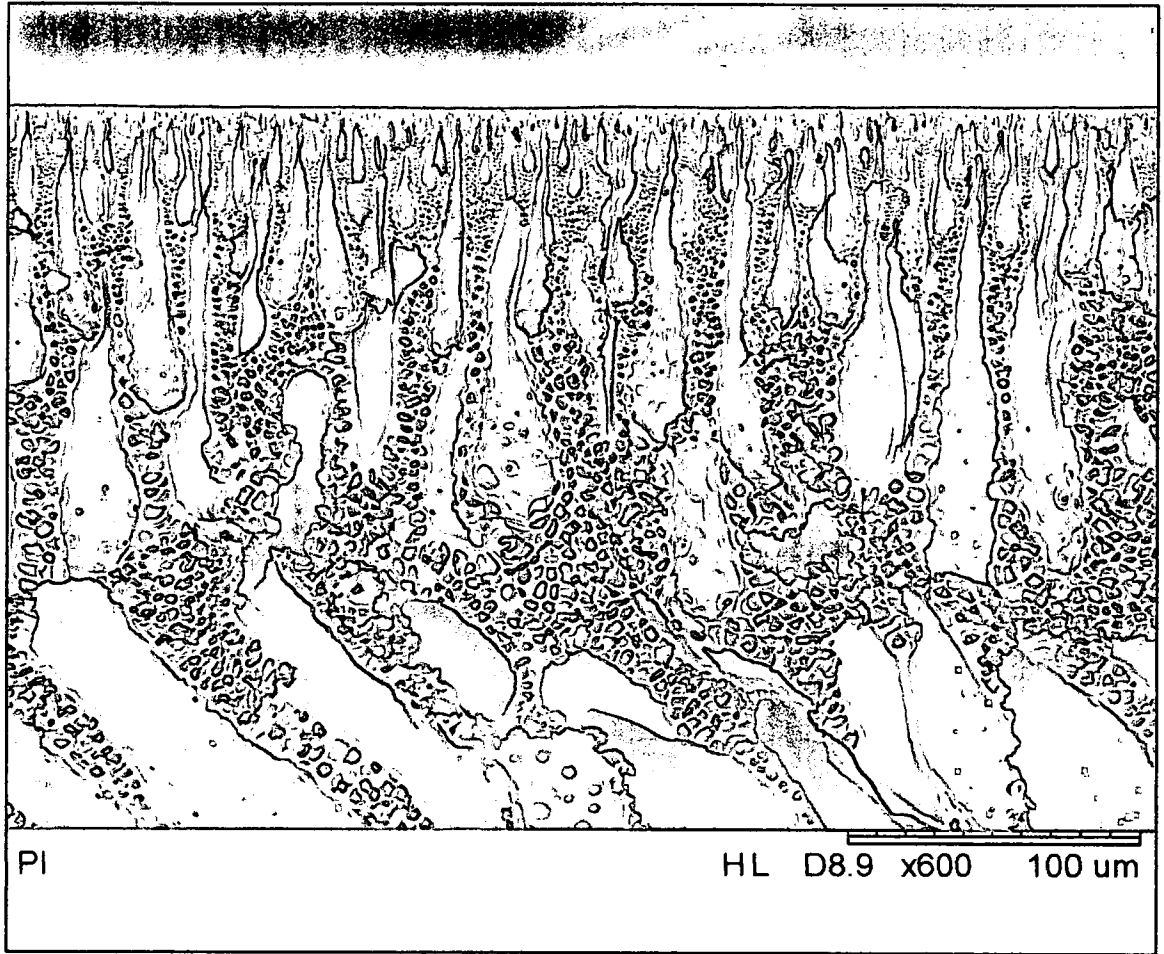
Figure 32 : Cross section at 600 magnification
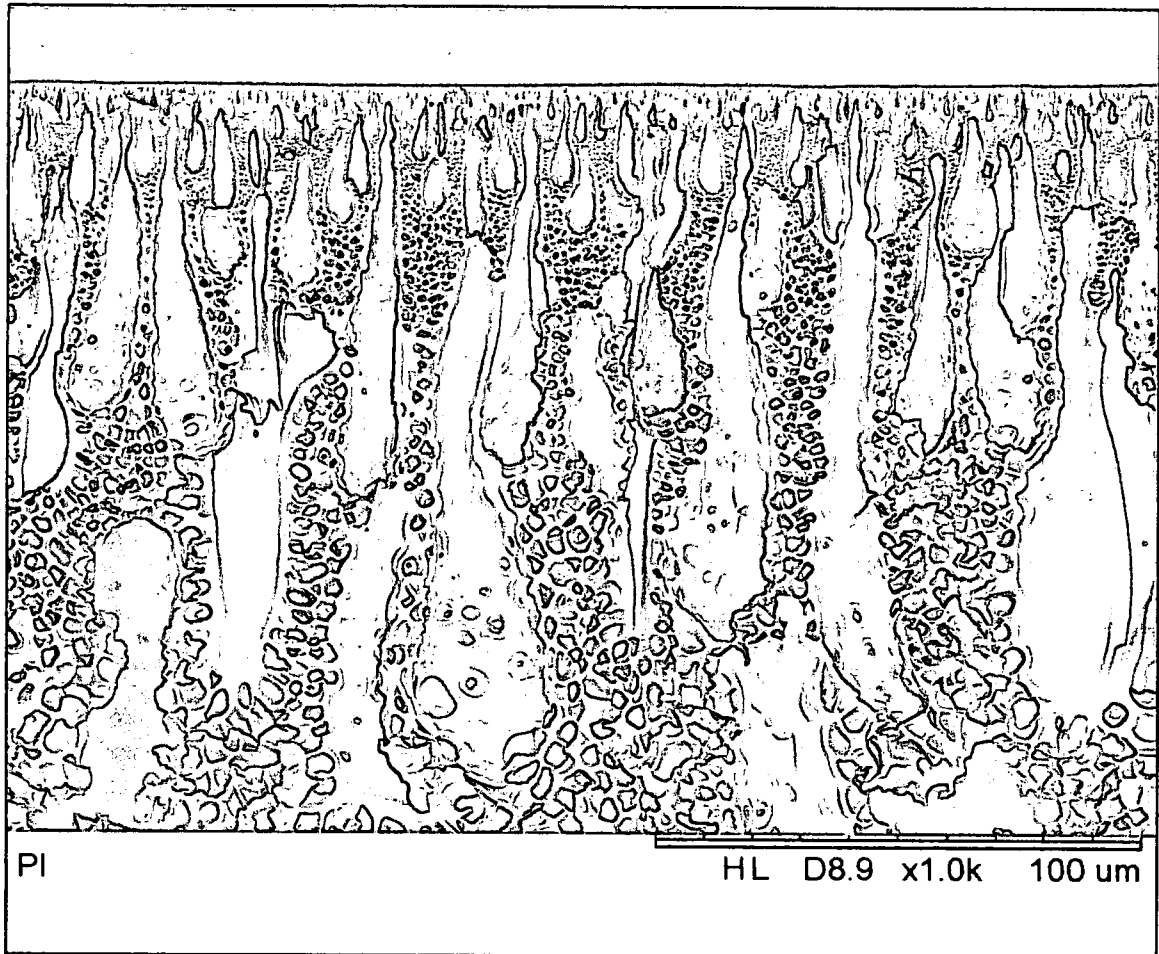
Figure 33 : Cross section at 1k magnification

3. DISCUSSION

3.1 Weight Percent

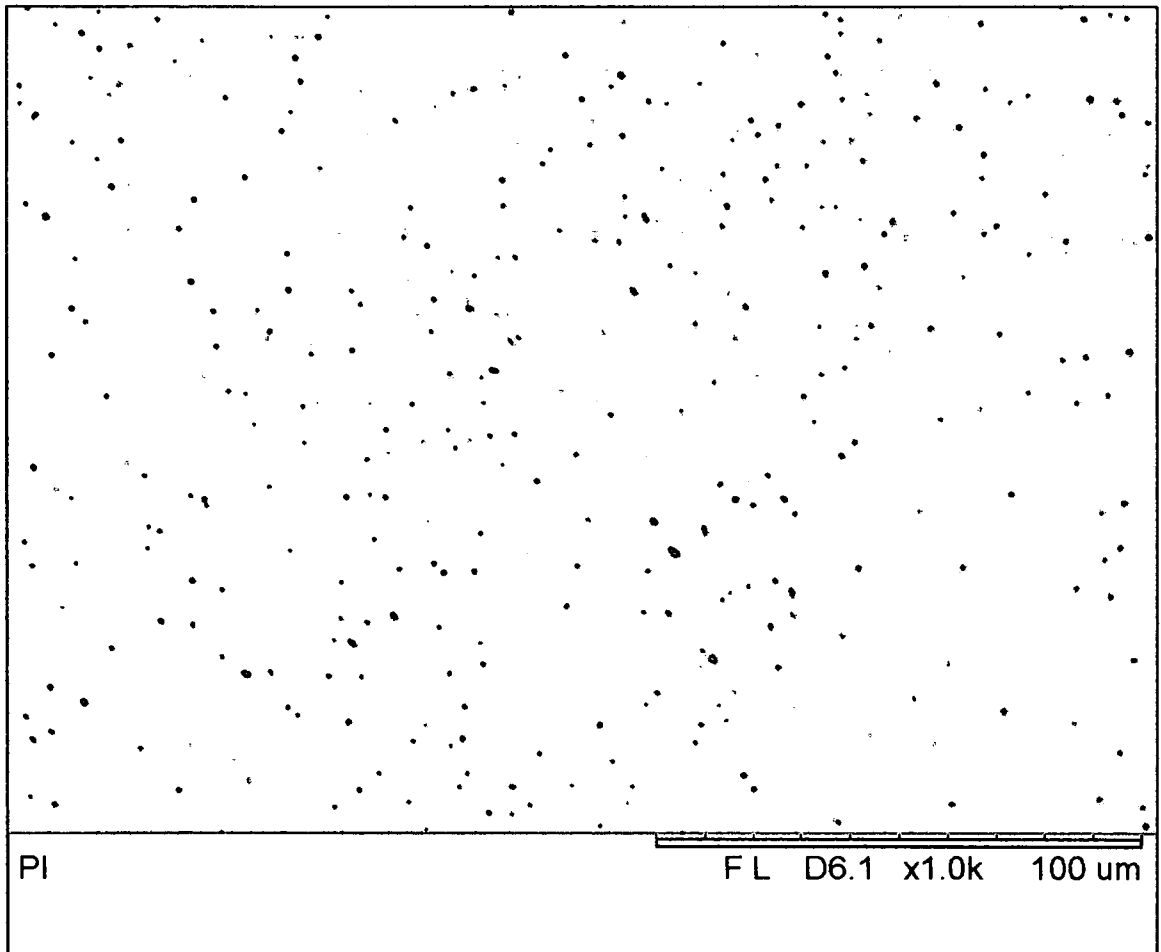Weight percent plays an important roles in polymerization. The higher amount of weight percent will yield polyimide with longer chain as there are more monomers to react. Too high amount of weight percent of solid on the other hand can yield in a very viscous poly (amic acid) solution. Very viscous solution are hard to be process eventhough the polymerization chain is longer. Lower weight percent result in low viscosity which the polymer chain is not long enough. Short molecular chain are not favourable.

3.2 Stirring Temperature

High temperature helps to dissolve the solids faster, but as the process is reversible and an amount of water is available the high temperature degrade the poly (amic acid) formed faster. Poly (amic acid) can react with water to form carboxylic group. High temperature promotes the formation of carboxylic acid. The best temperature is room temperature, as the monomer is slowly dissolve the formation of carboxylic group is slow down significantly. The reaction is exothermic and helps in the dissolving of the monomers.

3.3 Stirring Duration

Long stirring result in low viscosity. As observed, the viscosity reduced over time of stirring. Since the process is reversible and a small amount dianhydride is available. The solution can degrade back over time. Small amount of water exist in the solution, this water over time react with the poly (amic acid) to form carboxylic group even at room temperature. Therefore, overnight stirring is not favourable. Optimize duration of stirring is between two to three hours until the solution is uniformly mix and viscous.

3.4 Curing

Curing at high temperature yield a brittle membrane. The membrane cracks into tiny pieces. Quick rise in temperature causes the membrane to crack. The best curing is via the wet phasing by removing the solution by submerging in water.

3.5 Fourier Transform Infrared Spectroscopy

Figure 24 and Figure 25 shows the result of FTIR. From the graph, we can see peaks at around 1780-, 1730-, 1375- and 720 cm^{-1} which confirms the presence of imide monomers (Ghosh & Mittal, 2000). The characteristic N-H stretching vibrations of amino groups in poly (amic acid) at around 3300 - 3500 cm^{-1} were not observed in the FTIR spectrum, implying that the polymer was fully imidized (Wang, Wang, Yang, & Fan, 2013).

3.6 Scanning Electron Microscopy

The morphology of the surface of the membrane as in Figure 26 to Figure 29 shows a great number of pores. These pores allow for the separation to occur. Figure 30 to Figure 33 shows the cross sectional morphology of the membrane. The thickness of the membranes is around 400 micrometer. As can be seen, the morphology is of finger-like shape pores. The membrane is not dense and therefore can allow for separation to occur.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

1. CONCLUSION

Polyimide synthesis is a tricky process as a lot of parameters need to be consider. In order to synthesis the polyimide, an intermediate poly (amic acid) need to first be formed. This can be formed by reacting the polyimide in a polar aproctic solvent. The poly (amic acid) formed must be of certain viscosity. This is because the high viscosity means longer chain of polymerization. The process of synthesis itself is self-supporting, which is exothermic and autocatalyst. The PMDA and ODA polyimide is synthesizable with 30 to 35 weight percent of monomer, stirring at room temperature for a few hours and directly casting into membrane. The best curing method is via wet phasing as other method yield polymer with severe cracking.

2. RECOMMENDATION

For further expansion of the project, further analysis of the polyimide can be done by using different characterization machine. The project itself can be varied by incorporating different polyimide as for comparison. Deeper research can also be done to alter the structure of the polyimide to make it more suitable for specific purposes of the industry. In order for the project to be able for later studies, more awareness on the subject itself need to be taken into account. Students need to be more exposed on the high end polymer in class instead of just the commercially known polymer. These can be achieve by introducing a subtopic of these high end polymer and also to increase the number of literature available about these polymers.

REFERENCES

Bhargava, P. (2007). *High Temperature Properties of HFPE-II-52 Polyimide Resin and Composite.*

Biron, M. (2004). *Thermosets and Composites.* United Kingdom: Elsevier Advanced Technology.

Brown, P. J., Ying, S., & Yang, J. (2002). Morphological Structure of Polyetherketone Membranes For Gas Separations Prepared By Phase Inversion. *AUTEX Research Joural.*

Carraher, C. E. (2010). *Introduction to Polymer Chemistry.* Boca Raton: CRC Press.

Clark, J. (2000). *ChemGuide.* Retrieved from Understanding Chemistry: http://www.chemguide.co.uk/mechanisms/nucsubmenu.html

Ding, Y., Bikson, B., & Nelson, J. K. (2002). Polyimide Membrane Derived from Poly (amic acid) Salt Precursor. *Macromolecules*, 905-911.

Dunson, D. L. (2000). *Synthesis and Characterization of Thermosetting Polyimide: Oligomers for Microelectronics Packaging.* Virginia: Author.

Ghosh, M. K., & Mittal, K. L. (2000). *Polyimides: Fundamentals and Applications.* New York: Marcel Dekker Inc.

Hung, D. L., Ho, T.-I., Liaw, D.-J., & Liaw, B.-Y. (1999). Synthesis and
      Characterization of Polyimides Containing 4,4' Hexafluoroisopropylidene-
      Bisphtalic. *Artigo Tecnigo Centifigo*, 78-81.

Kononova, S. V., Gubanova, G. N., Romashkova, K. A., Korytkova, E. N., & Timpu,
      D. (n.d.). Polyamide-Imide Membranes of Various Morphology – Features of
      Nano-Scale Elements of Structure.

Luo, Y., Li, B., Liang, L., & Tan, B. (2011). Synthesis of cost-effective porous
      polyimides and their gas storage properties. *The Royal Society of Chemistry
      2011*.

Wang, H., Wang, T., Yang, S., & Fan, L. (2013). Preparation of thermal stable porous
      polyimide membranes by phase inversion process for lithium-ion battery.
      Polymer, 6339-6349.

APPENDICES

Appendix 1 – Gantt Chart FYP I

Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of project topic														
Finding literature review														
Requisition of chemical and apparatus														
Preparation of extended proposal														
Submission of extended proposal														
Preparation for proposal defence														
Proposal defence														
Preparation for draft interim report														
Submission of draft interim report														
Correction of interim report														
Final interim report submission														

Appendix 2 – Gantt Chart FYP II

Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project work continues														
Submission of progress report														
Project work continues														
Pre - SEDEX														
Submission of draft report														
Submission of dissertation (soft bound)														
Submission of technical paper														
Oral presentation														
Submission of project dissertation (hard bound)														