

**SYNTHESIS AND CHARACTERIZATION OF  
BTDA-ODA AND BPDA-ODA MEMBRANE**

**By**

**JONG YIK CHIENG (SID: 12598)**

**Supervisor:**

**DR. OH PEI CHING**

**Dissertation submitted in partial fulfillment of  
the requirements for the  
Bachelor of Engineering (Hons)  
(Chemical Engineering)**

**MAY 2013**

**Universiti Teknologi PETRONAS  
Bandar Seri Iskandar,  
31750 Tronoh,  
Perak Darul Ridzuan.**

**CERTIFICATION OF APPROVAL**

**SYNTHESIS AND CHARACTERIZATION OF  
BTDA-ODA AND BPDA-ODA MEMBRANE**

**By**

**JONG YIK CHIENG (SID: 12598)**

**A Project Dissertation to the  
Chemical Engineering Programme  
Universiti Teknologi PETRONAS  
in partial fulfillment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
(CHEMICAL ENGINEERING)**

**Approved by,**

---

**(DR. OH PEI CHING)**

**UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK**

**May 2013**

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

---

**(JONG YIK CHIENG)**

## **ACKNOWLEDGEMENT**

First and foremost, the student would like to express his gratitude towards his Final Year Project (FYP) Supervisor, Dr. Oh Pei Ching from Chemical Department of Universiti Teknologi PETRONAS for her precious time, guidance and assistance throughout this project. Dr. Oh has been very kind and helpful in providing all the necessary information and knowledge before the student started the project. Her passion towards this field has turned to be the inspiration for the student to perform better in FYP.

Besides, the student would like to thank coordinators for FYP1 and FYP2, who have consistently provided all the students with necessary information and guidelines regarding how students are going to complete all the required paper submissions. Reminders and updates have been informed in E-learning to ensure that students are well-informed.

Apart from that, the student would like to thank the management of Universiti Teknologi PETRONAS, especially Chemical Engineering Department for providing all the necessary equipment and tools for the student's project. Well-trained technicians are available to help out students with different kinds of problems. Appreciation is shown towards STIRF Grant No.27/2012 that without this grant, this project would not have been funded.

Last but not least, gratitude is shown towards family and friends who have shown unconditional love and supports towards the student. They have provided moral support and advices to ensure that the student is able to perform and is in good condition as well.

## ABSTRACT

Recently, membrane is a separation process that has gained attention from different industries, especially membranes for gas separation processes such as removal of carbon dioxide from natural gas. From all the researches and findings, the most conventional polymeric membrane is the cellulose acetate membrane with low-cost as one of the benefits. In this research, the main focus will be on polyimide which is currently considered as a new kind of membrane with lesser reference compared with other kinds of membrane, thus it is proposed to be a replacement for cellulose acetate membrane, and a new alternative material for membrane fabrication. This research will mainly focus on the optimization of parameters of the fabrication of flat-sheet polyimide membrane using dry-wet phase inversion method. In this research, BTDA (3, 3', 4, 4' – benzophenonetetracarboxylic dianhydride) and BPDA (3, 3', 4, 4' – biphenyl tetracarboxylic dianhydride) are mixed with ODA (4, 4' – dianiline) separately to form BTDA-ODA and BPDA-ODA using DMAc (N, N – dimethylacetamide) and DMF (dimethylformamide) as the solvent. Two different solvents are used to ensure poly amic acid with better viscosity. In the coagulation bath, water is used as the initial non-solvent for the precipitation of the membrane. Characterizations to be done are by using FESEM (Field Emission Scanning Electron Microscopy) and TGA (Thermal Gravimetry Analysis). Parameters such as concentration of polymers, choices and concentration of solvent and ratio of non-solvent are adjusted to perform optimization of the membrane fabrication.

## TABLE OF CONTENT

CERTIFICATION OF APPROVAL	i
CERTIFICATION OF ORIGINALITY	ii
ACKNOWLEDGEMENT	iii
ABSTRACT	iv
TABLE OF CONTENT	v
LIST OF FIGURES	vi
LIST OF TABLES	vii
CHAPTER 1: INTRODUCTION	1
1.1. PROJECT BACKGROUND	1
1.2. PROBLEM STATEMENT	5
1.3. OBJECTIVES	6
1.4. SCOPE OF STUDIES	6
1.5. RELEVANCY AND PROJECT FEASIBILITY	6
CHAPTER 2: LITERATURE REVIEW AND THEORIES	8
2.1. CATEGORIES OF MEMBRANES	8
2.2. CARBON DIOXIDE SEPARATION AND CAPTURE	10
2.3. POLYIMIDE SYNTHESIS	11
2.4. DRY-WET PHASE INVERSION TECHNIQUE	12
CHAPTER 3: METHODOLOGY/ PROJECT WORK	15
3.1. KEY MILESTONES/ PROJECT ACTIVITIES	15
3.2. EXPERIMENTAL PROCEDURES	18
CHAPTER 4: RESULTS AND DISCUSSION	22
4.1. SYNTHESIS OF MEMBRANE	22
4.2. EFFECT OF CHOICES AND CONCENTRATION OF POLYMER SOLUTION	28
4.3. EFFECT OF CHOICES OF SOLVENT	29
4.4. EFFECT OF BINDER ADDITION	29
4.5. CHARACTERIZATION	30
CHAPTER 5: CONCLUSION AND RECOMMENDATION	35
REFERENCES	36

## LIST OF FIGURES

FIGURE 1 1: Robeson Curve	2
FIGURE 1 2: Total Energy Consumed in the U.S. – 2010	3
FIGURE 1 3: Natural Gas Use by Sector in 2010	4
FIGURE 1 4: Gas Separation Membrane Application	5
FIGURE 2 1 : (a) Isotropic Membrane (b) Anisotropic Membrane	8
FIGURE 2 2 : Schematic Diagram of Different Isotropic Membrane Morphologies	9
FIGURE 2 3 : Schematic Diagram of Different Anisotropic Membrane Morphologies	10
FIGURE 2 4 : Basic Methods to Separate Gas	10
FIGURE 2 5 : Synthesis Route via One-Step Polymerization	11
FIGURE 2 6 : Synthesis Route via Two-Step Polymerization	11
FIGURE 2 7 : Structure of BTDA-ODA	12
FIGURE 2 8 : Structure of BPDA-ODA	12
FIGURE 3 1 : Project Activities and Key Milestones	15
FIGURE 3 2 : Schematic Diagram of the General Procedure	18
FIGURE 4 1: Sample 1 – Cracked Membrane (BTDA-ODA/DMAc)	24
FIGURE 4 2: Sample 2 – Cracked and Brittle Film without binder (BTDA-ODA/DMAc)	25
FIGURE 4 3: Sample 3 – Cracked and Brittle Film with binder (BTDA-ODA/DMAc)	25
FIGURE 4 4: Sample 8 – Less-cracked Membrane (BTDA-ODA/DMF)	26
FIGURE 4 5: Sample 10 – Less-cracked Membrane (BTDA-ODA/DMAc)	26
FIGURE 4 6: Sample 12 – Membrane without Cracks (BPDA-ODA/DMF)	27
FIGURE 4 7: Sample 13 – Cracked Membrane (BPDA-ODA/DMAc)	28
FIGURE 4 8: TGA Analysis for BTDA-ODA Membrane	31
FIGURE 4 9: TGA Analysis for BPDA-ODA Membrane	32
FIGURE 4 10: Surface View of BTDA-ODA Membrane	33
FIGURE 4 11: Surface View of BPDA-ODA Membrane	33
FIGURE 4 12: Cross-sectional View of BTDA-ODA Membrane	34
FIGURE 4 13: Cross-sectional View of BPDA-ODA Membrane	34

## LIST OF TABLES

TABLE 1 1: Typical Composition of Natural Gas	3
TABLE 1 2 : Expected Experimental Process Flow	7
TABLE 3 1: Gantt chart for Final Year Project 1	16
TABLE 3 2: Gantt chart for Final Year Project 2	17
TABLE 3 3: Chemicals, Glassware and Equipment for the Experiment	20
TABLE 4 1: Details and Results for BTDA-ODA and BPDA-ODA Membranes	22



# CHAPTER 1

## INTRODUCTION

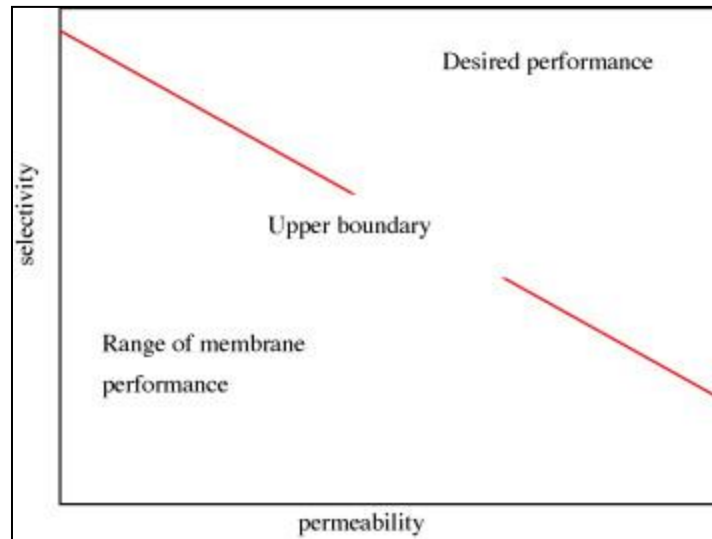
### 1.1 Project Background

#### 1.1.1 Overview of Membranes

In many industries and manufacturing plants, a variety of separation processes have been applied for separation of chemical components streams, purification of products or enhancement of process efficiency, for example, centrifugation, evaporation, extraction, filtration, distillation, and drying. Among these processes, membrane separation is one of the most commonly used processes, and this process has been active in industries even in oil and gas industries whereby it is widely used to separate carbon dioxide from the natural gas stream. According to Dortmund and Kishore [1], carbon dioxide, which falls under the category of acid gases, is usually found in the gas streams, at level as high as 80%. It turns corrosive and is able to destroy pipelines and equipment rapidly when it combines with water. Besides, it also reduces heating value of a natural gas stream and wastes pipeline capacity, especially in LNG plant. Carbon dioxide (CO<sub>2</sub>) is to be extracted to avoid freezing in low-temperature chillers. Because of these, Dortmund and Kishore [1] proposed that membranes can be used in CO<sub>2</sub> removal applications, which include natural gas sweetening and also enhanced oil recovery.

According to Biology Online [2], membrane is a thin pliable sheet of material, permeable to substances in solution, whereas Mulder [3] states that it is the heart of every membrane process and can be considered as permselective barrier between two phases, in other words, it is permeable and selective. The specialties and the main attributes for the membrane are that it can control permeation rate through the membrane, and no heating is required to undergo membrane separation processes.

Permeation rate is based on the selectivity and permeability of the membrane, and these two parameters are inversely proportional to each other according to Robeson's curve shown in **Figure 1-1**.



**FIGURE 1-1: Robeson Curve**

*Source: "Separation and Purification Technology" (2009)*

To further support the benefits of membrane separation, Newpoint Gas [4] states that gas treating membrane systems offer a harmless and effective option for water vapor and carbon dioxide removal from natural gas, especially in remote locations. Membrane systems are extremely adaptable to various gas volumes CO<sub>2</sub> concentrations and product-gas specification. By using membranes for removing CO<sub>2</sub>, versatility and adaptability can be achieved it is also environmentally friendly and easy to be operated.

### **1.1.2 Natural Gas**

Natural gas, being known as one of the fossil fuels or another kind of hydrocarbon, is made up of hydrogen and carbon compounds [17]. In natural gas, there are few components before it is refined, which is stated in **TABLE 1.1**.

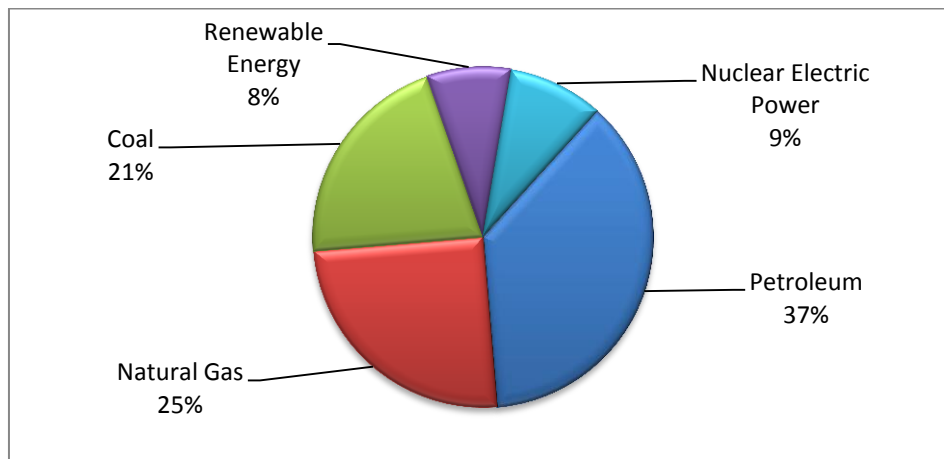
It has been utilized and consumed globally as one of the major energy sources. The main characteristics for natural gas being chosen as the main option are such as the cleanest source which produces the least pollution; and safest to be used in all

kinds of industries. **FIGURE 1-2** shows the total energy consumed in the U.S. in 2010.

**TABLE 1-1: Typical Composition of Natural Gas**

Methane	CH <sub>4</sub>	70-90%
Ethane	C <sub>2</sub> H <sub>6</sub>	0-20%
Propane	C <sub>3</sub> H <sub>8</sub>	
Butane	C <sub>4</sub> H <sub>10</sub>	
Carbon Dioxide	CO <sub>2</sub>	0-8%
Oxygen	O <sub>2</sub>	0-0.2%
Nitrogen	N <sub>2</sub>	0-5%
Hydrogen sulphide	H <sub>2</sub> S	0-5%
Rare gases	A, He, Ne, Xe	trace

Source: <http://www.naturalgas.org/overview/background.asp>

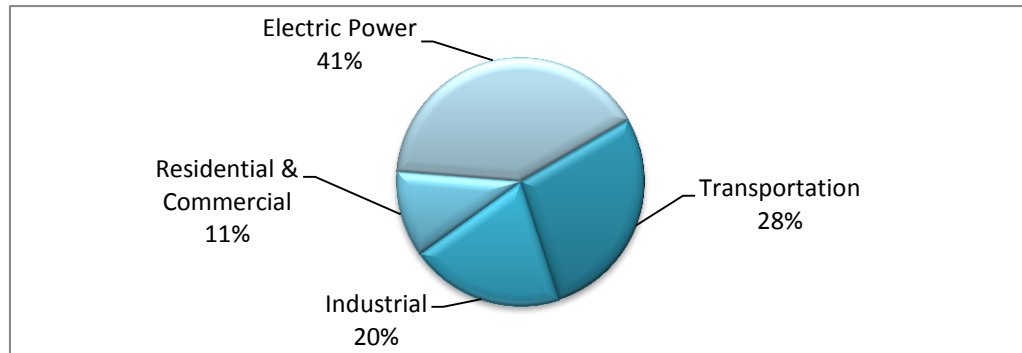


**FIGURE 1-2: Total Energy Consumed in the U.S. – 2010**

Source: EIA - Annual Energy Outlook 2010

It is clearly shown that natural gas has emerged to be one of the high demanding sources of energy, with 25% being consumed in U.S. in 2010. And from this portion, 41% of the natural gas has been used for electrical power generation. **FIGURE 1-3** portrays the natural gas use by sector. With the hasty development in industries, the natural gas consumption increases tremendously. According to BP Statistical Review of World Energy June 2013 [18], it is tabulated that the total world natural gas consumption has increased from 2522.1 billion m<sup>3</sup> to 3314.4 billion m<sup>3</sup> from the year of 2002 to 2012. This eventually provides great opportunity for natural gas research to

refine and increase the quality of natural gas. Therefore, it is vital to keep natural gas in its good quality for better performance and usage, which can be done by using gas separation. One of the common gas separations being performed is CO<sub>2</sub>/hydrocarbons in acid gas treatment and landfill gas upgrading.



**FIGURE 1-3: Natural Gas Use by Sector in 2010**

*Source: EIA – Annual Energy Outlook 2010*

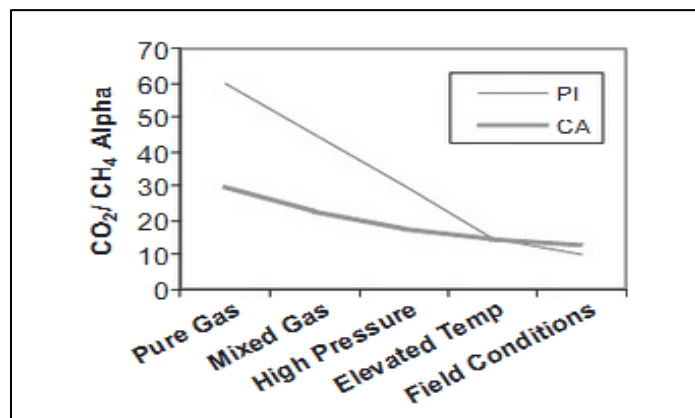
### 1.1.3 Overview of Polyimide

Polyimide (PI) is a class of thermally stable polymers that are often based on stiff aromatic backbones. It is a polymeric plastic material, engineered for long term performance at very high temperatures, in excess of 250°C for prolonged period of time, with the characteristic of thermally stable, therefore it is very suitable for industries like electronics, electrical and aerospace industries because it requires high temperature materials.

There are varieties of monomers as well as techniques available for the synthesis of polyimides. Laot [16] introduced that the most widely used procedure is the two-step poly (amic acid) process where there is a reaction between a dianhydride and a diamine at the ambient condition in a dipolar aprotic solvent. This reaction bases on the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group. After the reaction, poly (amic acid) is formed which is subsequently cyclized into final polyimide. Due to various types of monomers available, different types of polyimide are able to be produced and fabricated.

## 1.2 PROBLEM STATEMENT

In this research, the focus is on the synthesis, characterization and optimization of polyimide membrane. There are a few commonly used polymer-based membranes for carbon dioxide removal, namely cellulose acetate, polyimide, polyamide, polysulfone, polycarbonate, and polyetherimide. Cellulose acetate membrane is still the most widely used material because of the factor of low-cost when fabricating cellulose acetate membrane. However, research has shown that polyimide has a better advantage in removal process of carbon dioxide. **FIGURE 1-5** shows the separation factors for CO<sub>2</sub>/CH<sub>4</sub> using polyimide (PI) and cellulose acetate (CA).



**FIGURE 1-4: Separation Factors for CO<sub>2</sub>/CH<sub>4</sub> using PI and CA**

*Source: "Basic Principles of Membrane Technology" by Marcel Mulder (1996)*

Hence, it is decided that this research will focus on polyimide membrane. However, little emphasis was made in previous papers regarding the synthesis procedure of polyimide membrane and less focus on the optimization of the membranes for commercial purpose. Therefore, this research will mainly focus on the synthesis and the optimization of flat sheet polyimide membrane using dry-wet phase inversion method. The main parameters being focused will be the effect of polymer and solvent concentration. The best composition ratio of polymer and solvent will be optimized.

Once the membrane is fabricated and dried without much defects, it will be sent for characterization using TGA and FESEM.

### **1.3 OBJECTIVES**

There are some objectives to be achieved in this project, which are:

- To elucidate the casting solution formulation for fabrication of BTDA-ODA and BPDA-ODA membranes.
- To study the effect of polymer and solvent concentration towards the membrane properties.
- To characterize the fabricated membranes using FESEM and TGA.

### **1.4 SCOPE OF STUDIES**

There are two main scopes involved in this project, namely:

#### **A) Synthesis of the membrane**

In this project, it has been decided to synthesize a flat sheet membrane by manual casting method based on dry-wet phase inversion technique. Effect of polymer and solvent concentration towards membrane properties will be studied.

#### **B) Characterization of the membrane**

This phase assists in providing better understanding about the morphology of the membrane, including the component and the pores distribution. FESEM and TGA will be used.

### **1.5 RELEVANCY AND PROJECT FEASIBILITY**

The process timeline for this project is shown in **TABLE 1-2**, which includes the steps and duration for each step.

**TABLE 1-2: Expected Experimental Process Flow**

<b>No</b>	<b>Step</b>	<b>Duration</b>
1	Experimental setup preparation	30 minutes
2	Membrane solution preparation	24 hours – 48 hours
3	Membrane casting	30 minutes
4	Solvent evaporation time	1 hour – 24 hours
5	Coagulation process	1 hour – 24 hours
6	Drying time	24 hours – 48 hours
	<b>Total Time</b>	<b>51 hours – 146 hours</b>

From the process flow, steps such as membrane solution preparation time, solvent evaporation time, coagulation process time and drying time have a range of duration, which are suitable to be the parameter to be studied in this research a total of 15 experiments are expected to be performed throughout Final Year Project 1 and Final Year Project 2.

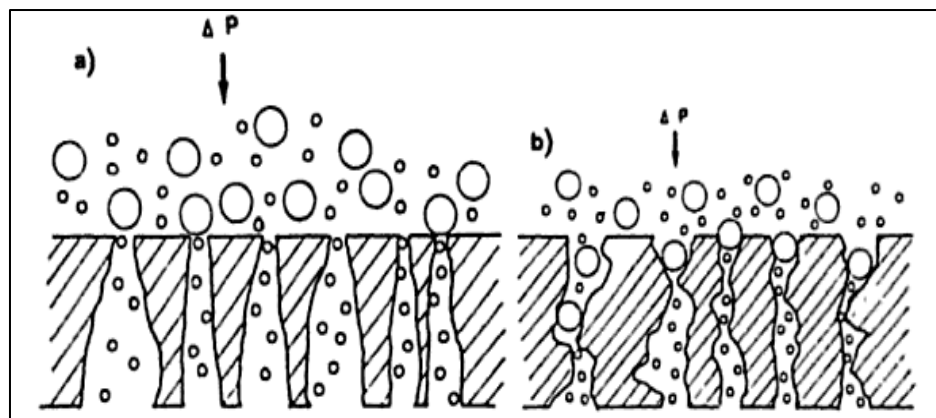
## CHAPTER 2

### LITERATURE REVIEW AND THEORIES

#### 2.1 CATEGORIES OF MEMBRANES

These are two categories of membrane according to Baker [5], namely isotropic and anisotropic membrane.

Based on Baker [5], isotropic membrane has a uniform composition structure throughout, and they can be porous or dense. The resistance to mass transfer in these membranes is determined by the total membrane thickness. A decrease in membrane thickness results in an increased permeation rate. The difference of isotropic and anisotropic membrane is portrayed in **FIGURE 2-1**.



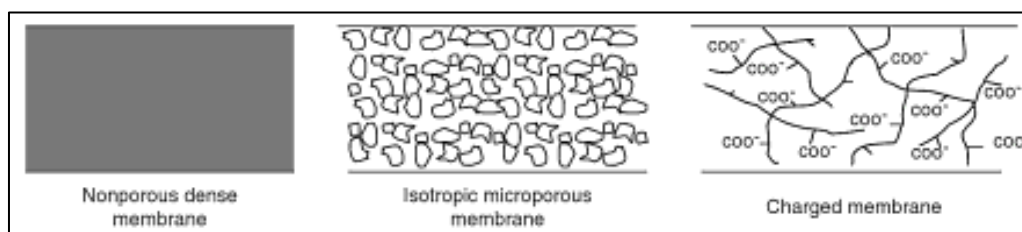
**FIGURE 2-1 : (a) Isotropic Membrane (b) Anisotropic Membrane**

*Source: "Handbook of industrial membrane technology" by Porter M. C. (1990)*

There are three kinds of isotropic membranes, namely microporous membranes, non-porous but dense membrane, and electrically charged membranes. Based on Separation Process website [6], microporous membrane is a polymer film with



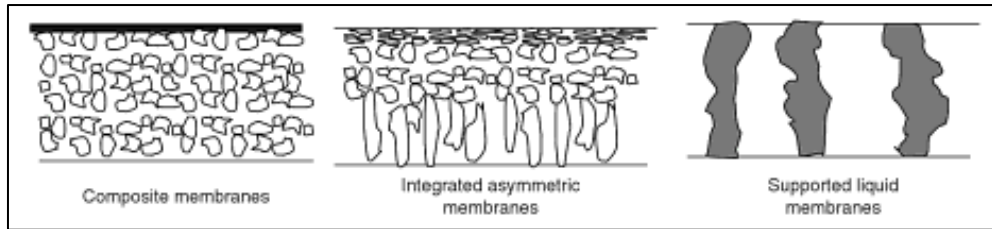
cylindrical pores or capillaries, whereas nonporous but dense membrane is a dense film through which permeates are transported by diffusion under the driving force of pressure, concentration, or electrical potential gradient. For electrically charged membrane, it is known as ion-exchanged membrane because it binds anions in the surrounding fluids. **FIGURE 2-2** shows the different morphologies of three isotropic membranes in schematic diagram form [7].



**FIGURE 2-2 : Schematic Diagram of Different Isotropic Membrane Morphologies**

*Source: "Membrane and desalination technology" by Wang, L. K. et al (2010)*

For anisotropic membranes, they consist of a number of layers, each with different structures and permeability. According to Separation Process website [8], a typical anisotropic membrane has a relatively dense, extremely thin surface layer supported on an open much thicker porous substructure. Under this category there are also three kinds of anisotropic membrane, namely Loeb-Sourirajan membrane, interfacial composite membrane, and also liquid membrane. Loeb-Sourirajan membrane, also known as integrated asymmetric membrane, consists of a single material membrane, but the porosity and pore size change in different layers of the membrane. Interfacial composite membrane consists of a thin dense film of highly cross-linked polymer formed on the surface of a thicker microporous support. For liquid membrane, it has become increasingly significant in the context of facilitated transport, which utilizes the carriers to selectively transport components such as metal ions at relatively high rate across membrane interface. **FIGURE 2-3** shows the different morphologies of anisotropic membranes [7]. So in this project, the main membrane being focused on is isotropic microporous membrane.



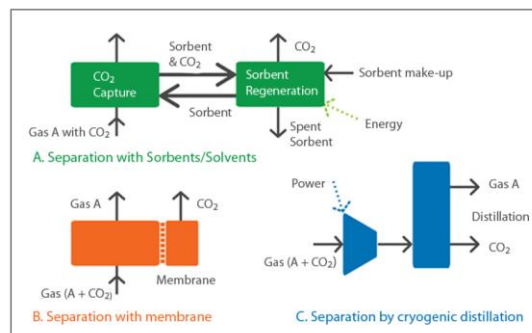
**FIGURE 2-3 : Schematic Diagram of Different Anisotropic Membrane Morphologies**

Source: “Membrane and desalination technology” by Wang, L. K. et al (2010)

## 2.2 CARBON DIOXIDE SEPARATION AND CAPTURE

In oil and gas industries, the production of flue gas has been a problem to the environment whereby greenhouse gases are produced. Examples of greenhouse gases are carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrogen oxide (NO<sub>x</sub>) and ozone (O<sub>3</sub>). As combustions are involved in all sorts of industries, CO<sub>2</sub> is one of the main products being produced and emitted from the chimney. Therefore, separating and capturing of CO<sub>2</sub> serves as one of the alternatives to reduce the emission of CO<sub>2</sub> into the atmosphere. Another reason for CO<sub>2</sub> separation and capture, according to Howard Herzog (1999)[20], is that “it provides attention as a possible economic source of CO<sub>2</sub>, especially to be used in enhanced oil recovery (EOR) operation whereby CO<sub>2</sub> is injected into reservoirs to increase the mobility of the oil.”

Here, it can be seen that CO<sub>2</sub> still has its economical values in industries. To separate CO<sub>2</sub> from the gas stream, there are a few methods being used, namely separation with sorbents, separation with membrane and separation by cryogenic distillation. **FIGURE 2-4** shows the basic methods to separate gas in diagram form.



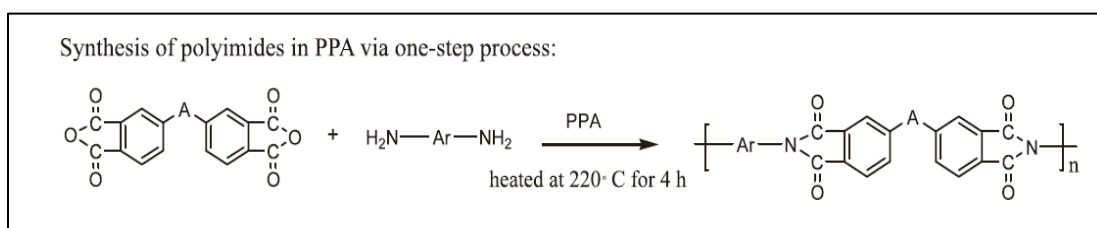
**FIGURE 2-4: Basic Methods to Separate Gas**

Source: [http://www.co2captureproject.org/pdfs/3\\_basic\\_methods\\_gas\\_separation.pdf](http://www.co2captureproject.org/pdfs/3_basic_methods_gas_separation.pdf)

## 2.3 POLYIMIDE SYNTHESIS

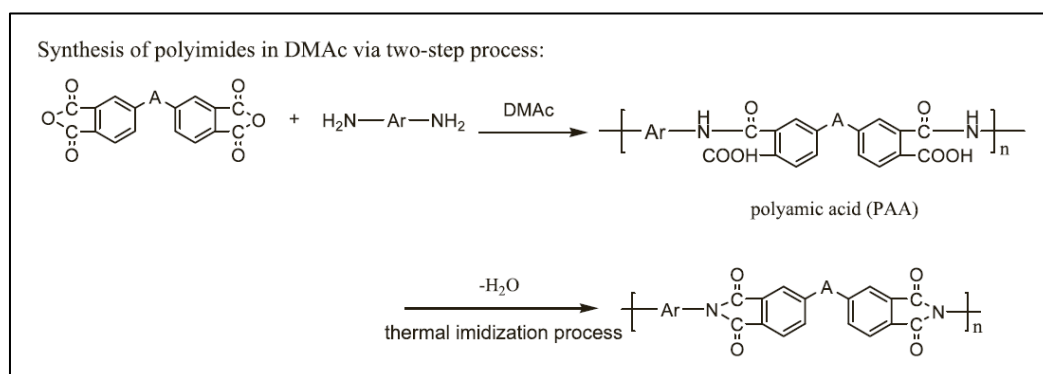
According to Jin et al. [11], there are two main synthetic routes to produce polyimides, namely two-step and one-step polymerization. In the conventional two-step polymerization, the poly (amic acid) is first synthesized from dianhydride and diamine in a polar aprotic solvent such as N, N-dimethylformamide (DMF), dimethylacetamide (DMAc) or N-Methyl-2-pyrrolidone (NMP). This poly (amic acid) solution is then processed into products such as films or fibers.

As for one-step polymerization, direct polycyclization method is used to prepare polyimides derived from tetracarboxylic acid anhydrides and various diamines, and this has been reported by Vinogradova and Vygodskii et al [9]. In this method, nitrobenzene, ditolylmethane or sulfolane are used as solvents. Later, Kuznetsov et al. developed one-step synthesis method to prepare aromatic polyimides and copolyimides with reasonably high molecular weight in carboxylic acid media such as molten benzoic acid. However, this method needs toxic carcinogen solvents. Therefore, two-step polymerization method is used. **FIGURE 2-5** and **FIGURE 2-6** shows the two main synthesis routes to produce polyimides [11].



**FIGURE 2-5: Synthesis Route via One-Step Polymerization**

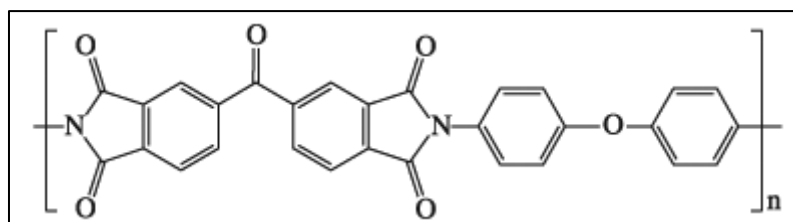
Source: "Homogeneous one-pot synthesis of polyimides in polyphosphoric acid" by Jin et al (2009)



**FIGURE 2-6: Synthesis Route via Two-Step Polymerization**

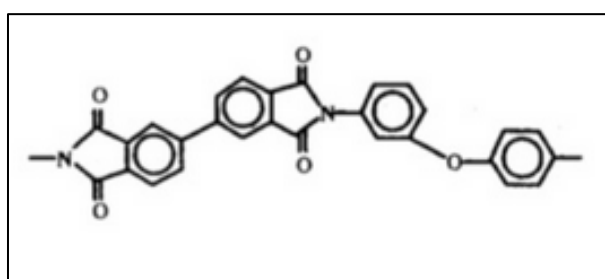
Source: "Homogeneous one-pot synthesis of polyimides in polyphosphoric acid" by Jin et al (2009)

In this research, there are two different polyimide membranes will be studies, BTDA-ODA and BPDA-ODA membrane. **FIGURE 2-7** and **FIGURE 2-8** show the chemical equation of the product of the reaction of BTDA-ODA and BPDA-ODA respectively.



**FIGURE 2-7: Structure of BTDA-ODA**

Source: "Processing of high performance composites based on peek by aqueous suspension" by Liliana B. N. et al (2010)



**FIGURE 2-8: Structure of BPDA-ODA**

Source: "BPDA-PDA polyimide: synthesis, characterization, aging and semiconductor device passivation", by Sombel, D. (2012)

## 2.4 DRY-WET PHASE INVERSION TECHNIQUE

According to Mulder [3], phase inversion is a process whereby a polymer is transformed in a controlled manner from a liquid to a solid state. This method has been used to prepare various kinds of polymeric membranes since 1960, and yet many aspects in the process are still not clarified clearly, which is the complete analysis of skin layer formation at initial stage of phase inversion.

In this technique, based on Mulder [3], it relies on the phase separation of polymer solutions producing porous polymer films. This mechanism can be subdivided into three categories depending on the parameter that induce demixing, temperature induced phase separation (TIPS) whereby heat will be exchanged and demixing can

be induced; reaction induced phase separation (RIPS) whereby the original polymer solution can be subjected to a reaction which cause phase separation; and also diffusion induced phase separation (DIPS) whereby the phase when polymer solution is contacted with vapor or liquid, diffusional mass exchange will lead to a change in local composition of polymer film and demixing can be induced.

In this research, the main technique being focused is the dry-wet phase inversion technique. According to Khulbe et al [10], this dry-wet phase inversion technique was used by Loeb and Sourirajan in their development of the first cellulose acetate membrane for seawater desalination. Through this method, they have prepared a polymer solution by mixing polymer and solvent. After the mixing process the mixture is then casted on a suitable flat surface using a casting knife with the desired thickness. After a partial evaporation of solvent the casted membrane is immersed in a non-solvent medium named the coagulation bath which consists of the non-solvents like water. With this, precipitation of the polymer membrane can be done.

There are several techniques to perform precipitation according to Mulder [3], which includes solvent evaporation, vapor phase, immersion, controlled evaporation and thermal method.

#### **2.4.1 Precipitation by solvent evaporation**

The simplest technique for preparing phase inversion membranes whereby the polymer is dissolved in a solvent and the polymer solution is casted on a suitable support, e.g. a glass plate or another kind of support which may be porous or non-porous. The solvent is allowed to evaporate in an inert atmosphere in order to include water vapor, allowing a dense homogeneous membrane to be obtained. Instead of casting, it is also possible to deposit the polymer solution on a substrate by dip-coating or by spraying, followed by evaporation.

#### **2.4.2 Precipitation from vapor phase**

A cast film, consisting of a polymer and a solvent, is placed in a vapor atmosphere where the vapor phase consists of a non-solvent saturated with the same solvent. The high solvent concentration in the vapor phase prevents the evaporation of solvent from the cast film. This leads to a porous membrane without top layer. With

immersion precipitation an evaporation step in air is sometimes introduced and if the solvent is miscible with water, precipitation from the vapor will start at this stage.

### **2.4.3 Precipitation from immersion**

Most commercially available membranes are prepared by immersion precipitation: a polymer solution, which consists of polymer and solvent, is casted on a suitable support and immersed in a coagulation bath containing a non-solvent. Precipitation occurs because of the exchange of solvent and non-solvent. The membrane structure ultimately obtained results from a combination of mass transfer and phase separation.

### **2.4.4 Precipitation by controlled evaporation**

Precipitation by controlled evaporation was being used in early years whereby the polymer is dissolved in a mixture of solvent and non-solvent. Since the solvent is more volatile than the non-solvent, the composition shifts during evaporation to a higher non-solvent and polymer content. This leads to the formation of a skinned membrane.

### **2.4.5 Thermal precipitation**

A solution of polymer in a mixed or single solvent is cooled to enable phase separation to occur. Evaporation of the solvent often allows the formation of a skinned membrane this method is frequently used to prepare microfiltration membrane.

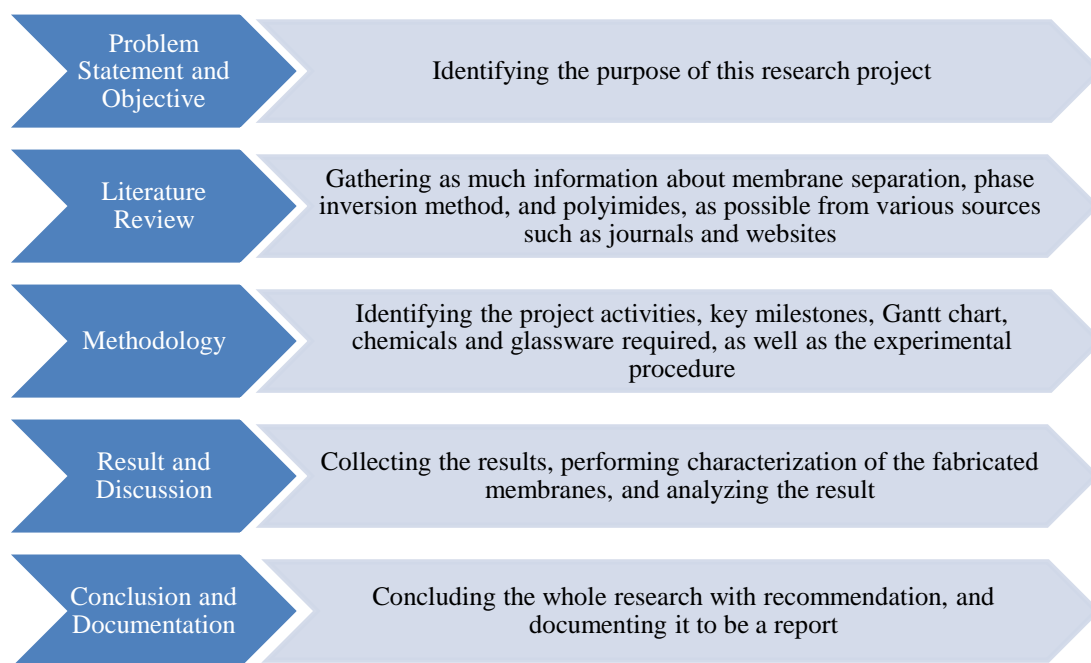
In this experiment, the technique being focused and used will be precipitation from immersion whereby the polymer solution will be inserted into the coagulation bath with non-solvent, which has been mentioned in [12].

## CHAPTER 3

### METHODOLOGY/ PROJECT WORK

#### 3.1 KEY MILESTONES/ PROJECT ACTIVITIES

Several key milestones for this research project must be achieved in order to meet the objective of this project, which is shown in **FIGURE 3-1**:



**FIGURE 3-1 : Project Activities and Key Milestones**

**TABLE 3-1** and **TABLE 3-2** show the Gantt chart for Final Year Project 1 and Final Year Project 2. The process is currently parallel with Gantt chart. For experimental work, it has been started in Final Year Project 1 so that there will be longer time for the optimization work.

**TABLE 3-1: Gantt chart for Final Year Project 1**

NO	DETAILS	WEEK														Study Week	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14		
1	Selection of Project Title	■	■	■													
2	Meeting with Supervisor			■	■	■	■	■	■	■	■	■	■	■	■	■	
3	Preliminary Research Work and Literature Review			■	■	■											
4	Submission of Extended Proposal						●										
5	Preparation for Oral Proposal Defense							■	■								
6	Oral Proposal Defense Presentation								■	■							
7	Detailed Literature Review								■	■	■	■	■	■	■	■	
8	Experimental Lab Work - Membrane solution preparation and casting - Solvent evaporation - Precipitation and drying of membrane												■	■	■		
9	Preparation of Interim Report			■	■	■	■	■	■	■	■	■	■	■	■		
10	Submission of Interim Draft Report															●	
11	Submission of Interim Final Report																●



**TABLE 3-2: Gantt chart for Final Year Project 2**

NO	WEEK DETAILS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	After Final Exam
		1	Meeting with Supervisor	■	■	■	■	■	■	■	■	■	■	■	■	
2	Project Work Continues			■	■	■	■	■	■	■	■	■	■			
3	Submission of Progress Report								●							
4	Pre-SEDEX											●				
5	Submission of Draft Report												●			
6	Submission of Dissertation (Soft Bound)													●		
7	Submission of Technical Paper														●	
8	Oral Presentation														●	
9	Submission of Project Dissertation (Hard Bound)															30 <sup>th</sup> September 2013

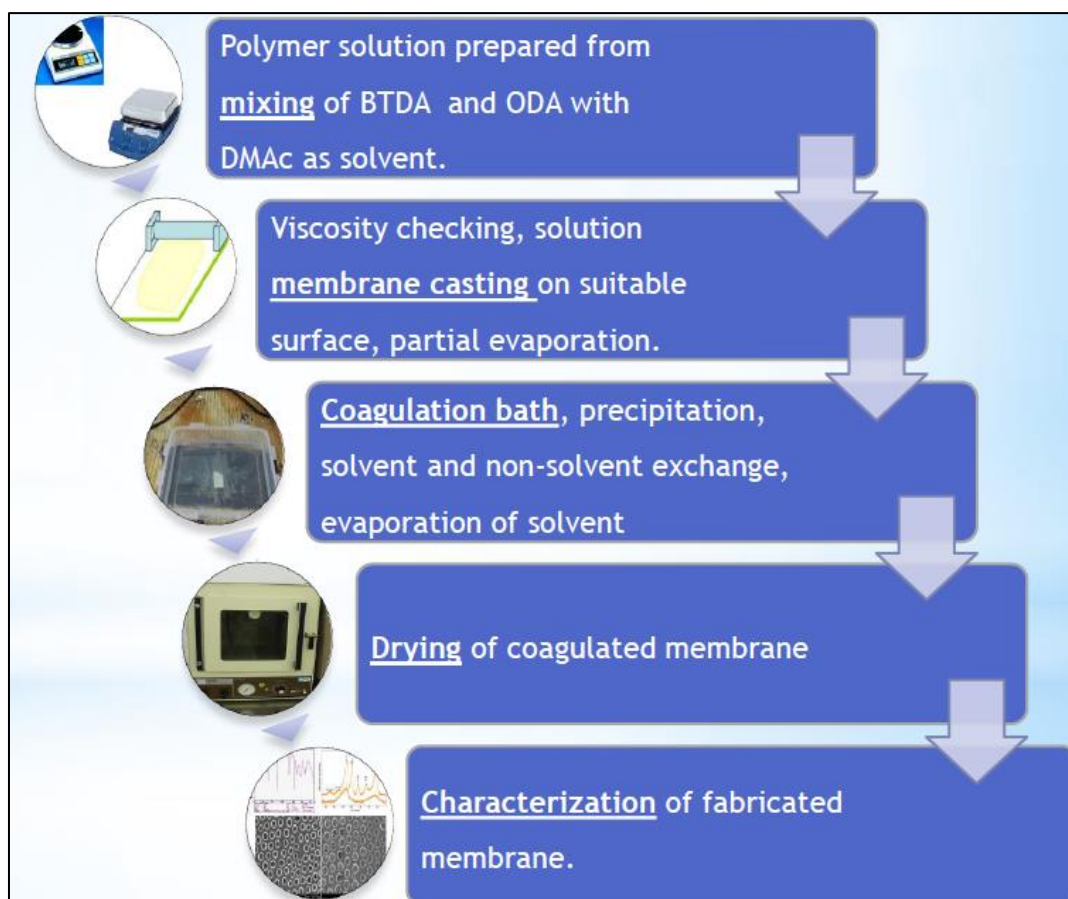
● Suggested Milestones



Process

### 3.2 EXPERIMENTAL PROCEDURES

**FIGURE 3-2** shows the general experiment procedures that have been implemented in this research which applies to BTDA-ODA and BPDA-ODA membrane preparation.



**FIGURE 3-2: Schematic Diagram of the General Procedure**

Firstly, the polymer solution is prepared by measuring the weight of BTDA and ODA with the mass ratio of 1.6: 1. It is to ensure that the weight percentage of polymer in the solution is equal to or more than 20% to ensure the desired viscosity. Since BTDA has lower solubility than ODA, therefore BTDA is added first into the solvent to prevent formation of lumps of monomers inside the solvent. When all the BTDA is dissolved in DMAc, ODA is slowly added into the solution.

When all the solutes are dissolved in the solvent, it is stirred for another 24 hours. After the stirring period, the solution is degassed for 3 hours. Then the solution is cast

using a casting knife on a glass plate. These procedures are repeated by replacing BTDA with BPDA, with the mass ratio of 1.4: 1 for BPDA and ODA, and being stirred in DMF as the solvent.

Once the membrane is cast, it is left on the table for solvent evaporation for 1 hour to remove excessive solvents inside the membrane. After solvent evaporation process, the glass plate is slowly inserted into the coagulation bath with water as the non-solvent to promote immersion precipitation. This is the process whereby the membrane starts to form and harden, and the result of the membrane can be observed clearly once the glass plate is slide into the coagulation bath. After precipitation process for one day, the membrane can be extracted out from the coagulation bath and left on the table for drying process. Besides immersion precipitation, dry method is also performed by leaving the membrane on the glass plate to be dried with the atmospheric air.

Throughout these procedures, dehumidifiers are used to absorb the moisture of the air, because the moisture will result in cracking of the membrane during the precipitation process. Besides, anhydrous calcium chloride is also put inside the three-necked round bottom flask to absorb the moisture inside the flask during the stirring process.

### **3.2.1 Chemicals, Glassware and Equipment of the Experiment**

**TABLE 3-3** shows the chemicals, glassware and equipment needed during preparation of the polymer solution, membrane casting, precipitation, and characterization of membrane.

**TABLE 3-3: Chemicals, Glassware and Equipment for the Experiment**

<b>No.</b>	<b>Name of Chemicals</b>	<b>Obtained from</b>
1	BTDA (3, 3', 4, 4' – benzophenone tetracarboxylic dianhydride)	Sigma-Aldrich
2	BPDA (3,3',4,4' – biphenyl tetracarboxylic dianhydride)	Sigma- Aldrich
3	ODA (4,4' – oxydianiline)	Merck
4	DMAc (N, N – dimethylacetamide)	UTP
5	DMF (dimethylformamide)	UTP
6	Ethanol	UTP
7	Anhydrous calcium chloride	UTP
8	Anhydrous glycerol	UTP
<b>No.</b>	<b>Name of Glassware and Equipment</b>	<b>Obtained from</b>
1	Three-neck round bottom flask and stoppers	UTP
2	Casting Knife	UTP
3	Glass plates	UTP
4	Magnetic stirrer and stirring plate	UTP
5	Beaker	UTP
6	Measuring balance	UTP
7	Crucible	UTP
8	Measuring cylinder	UTP
9	Spatula	UTP
10	Stirring rod	UTP
11	Rotary Evaporator	UTP
12	Dehumidifiers	-
13	Coagulation bath basin	-

### 3.2.2 Characterization of the fabricated membrane

The recommended characterization methods for fabricated membrane include:

#### A. *Field Emission Scanning Electron Microscopy (FESEM)*

- a. Have very high resolution which is obtained by the field emitter technology and the column which allows the resolution to reach an ultra-high resolution electron image at over 1 million times.
- b. Able to identify very small micro-structural details of sample.
- c. Widely being used in nano-material research, electronics, new materials development, biology, genetics, etc.

***B. Thermal Gravimetric Analysis (TGA)***

- a. Provides a graph of mass loss versus temperature over the range of 25°C to 1200°C.
- b. Widely being used in polymer science, inorganic chemistry, fuel science and geology.
- c. Can characterize mass losses of a material, and where the losses are in discrete steps.
- d. Can offer quantitative data on the course of decomposition.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 SYNTHESIS OF MEMBRANE

TABLE 4-1 shows the tabulation of details and results of the experiments for BTDA-ODA and BPDA-ODA membranes.

**TABLE 4-1: Details and Results for BTDA-ODA and BPDA-ODA Membranes**

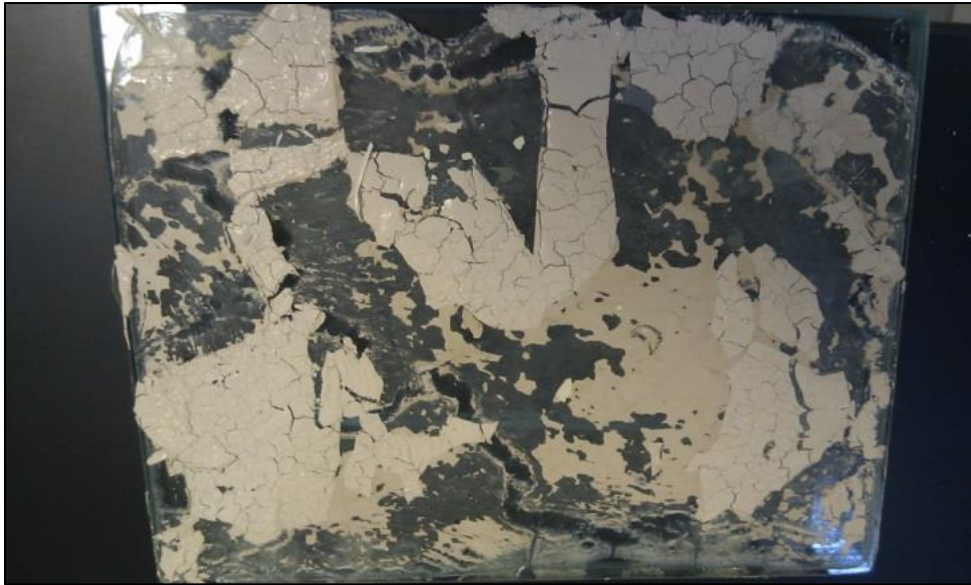
Sample No	BTDA-ODA Composition (wt%)	Solvent (mL)		Coagulation bath	Result
		DMF	DMAc		
1	20%	N/A	10	Water	Cracked
2	23%	N/A	30	N/A (use air)	Cracked and Brittle
3	23% + 2% Binder	N/A	30	N/A (use air)	Cracked and Brittle
4	23% + 2% Binder	N/A	30	Water	Cracked
5	24% + 2% Binder	N/A	30	N/A (use air)	Shrunk
6	24% + 2% Binder	N/A	30	Water : Ethanol (1:1)	Cracked
7	21% + 3% Binder	N/A	30	Ethanol	Less cracks
8	21% + 3% Binder	30	N/A	Water	Less cracks
9	21% + 3% Binder	N/A	30	Water	Less cracks
10	23% + 3% Binder	N/A	30	Water: Ethanol (1:1)	Less cracks
11	25%	30	N/A	Water	Less cracks
Sample No	BPDA-ODA Composition (wt%)	Solvent (mL)		Coagulation bath	Result
		DMF	DMAc		
12	18%	30	N/A	Water	Without cracks
13	20%	N/A	30	Water	Cracked
14	23% + 3% Binder	N/A	30	Water	Cracked

In the first objective of the research, which is to synthesize polyimide membrane from BTDA and ODA in DMAc, several attempts have been made. At this stage, the parameter being altered is the concentration of BTDA-ODA in terms of wt. % based on the solution. Due to the low viscosity of the solution after stirring, at third attempt, binder is introduced to bind both BTDA and ODA so that polymerization will occur and polymer can be formed.

After a few attempts, the membrane can be casted but it still cracks. Therefore, BPDA-ODA membrane is introduced, and as a result, a better membrane can be obtained.

#### **4.1.1 Sample 1 - Cracked Membrane (BTDA-ODA Membrane)**

**FIGURE 4-1** shows the cracked membrane Sample 1 after drying process. This membrane occurs at the stage of membrane precipitation when the membrane on the glass plate is inserted into the coagulation bath. This is usually obtained when the viscosity of the membrane is not up to the required viscosity. When it is not viscous, it is hard for the membrane to be casted on the glass plate. Besides, when the polymers are not completely reacted to form polymer during polymerization, this will lead to less viscosity for the polymer solution, and membrane cannot be casted. Another reason for the cracked membrane to occur can be that the non-solvent in the coagulation bath is not suitable. Lastly, membrane cracking can also occur during the drying process whereby the environment around the membrane changes. When the drying process is incomplete, there will be leftover solvents in the membrane and this can lead to the cracking of membrane in drying at higher temperature due to higher volatility of the solvent.



**FIGURE 4-1: Sample 1 – Cracked Membrane (BTDA-ODA/DMAc)**

#### **4.1.2 Sample 2 and Sample 3 - Cracked and Brittle Film (BTDA-ODA Membrane)**

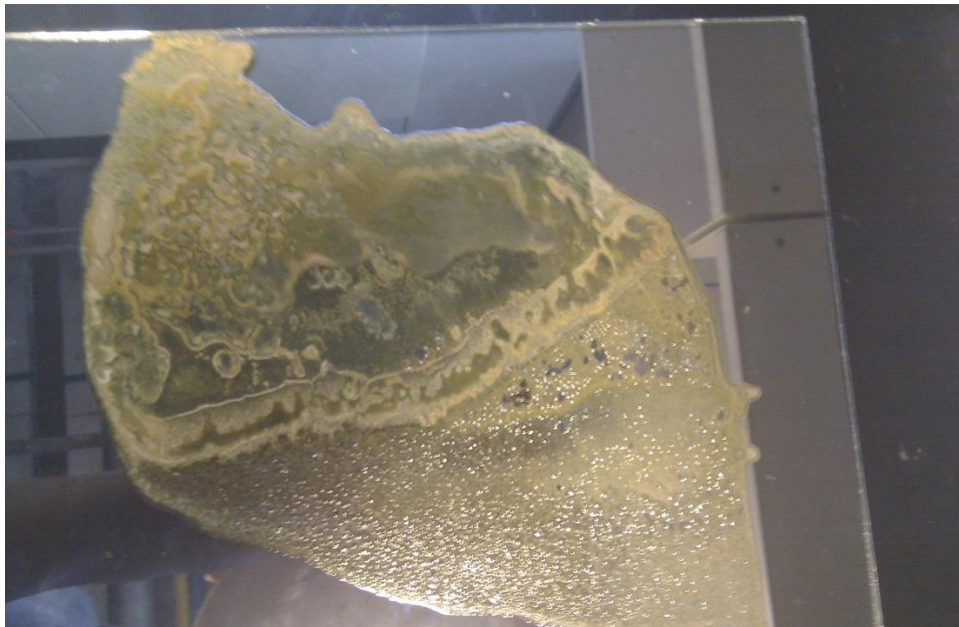
In this attempt, since the viscosity of 20% polymer based on the solution does not reach the desired value, the weight percentage of polymer in the solution is increased to 23% to increase the viscosity of the solution. Under this condition, the thickness of the membrane is only 30  $\mu\text{m}$ . Therefore, a brittle film is formed instead of a membrane. One of the reasons is that the surface of the table is slightly slanted, therefore the solution, after being casted, will flow slowly to one side. Besides, manual casting is performed and the membrane is not spread evenly. The amount of polymer solution on the glass plate should be increased before casting the membrane. **FIGURE 4-2** shows sample 2 in photo form.

For sample 3, binder is introduced to promote and improve polymerization of BTDA and ODA to ensure both monomers reacted to form polymer. Elasticity of the membrane can be promoted as well. **FIGURE 4-3** shows sample 3 in photo form.





**FIGURE 4-2: Sample 2– Cracked and Brittle Film without binder (BTDA-ODA/DMAc)**



**FIGURE 4-3: Sample 3 - Cracked and Brittle Film with binder (BTDA-ODA/DMAc)**

### 4.1.3 Sample 8 and Sample 10 - Less-cracked Membranes (BTDA-ODA Membrane)

For less-cracked membranes, there are a few changes occurred. Firstly, the usage of drying agent has been implemented whereby anhydrous calcium chloride has been inserted in one of the columns in three-necked round bottom flask to absorb the moisture in the flask during stirring process. Besides, new BTDA powder has been used instead of the old BTDA powder. This is due to contamination of air moisture and other impurities in the old BTDA powder, which will reduce the viscosity of the solution. Therefore, all the monomer powders are dried before being used. With this, the thickness can reach until 100  $\mu\text{m}$ . **FIGURE 4-4** and **FIGURE 4-5** show sample 8 and sample 10 respectively.



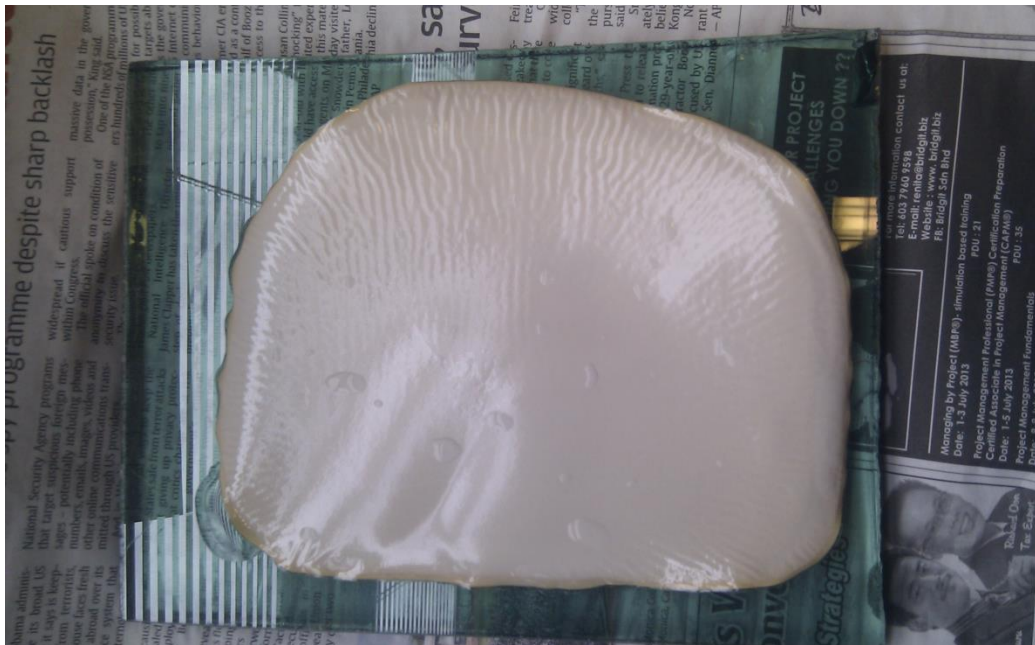
**FIGURE 4-4: Sample 8 – Less-cracked Membrane (BTDA-ODA/DMF)**



**FIGURE 4-5: Sample 10 – Less-cracked Membrane (BTDA-ODA/DMAc)**

#### 4.1.4 Sample 12 - Membrane without Cracks (BPDA-ODA Membrane)

For this result, BPDA is used instead of BTDA, and DMAc is replaced with DMF. This is because the dissolving rate is slower using DMAc [26]. Therefore, a change in monomer and solvent has been done. By using 18wt% of BPDA-ODA, stirred in DMF, the solution is viscous enough to be casted on the glass plate and therefore a smooth membrane is obtained. **FIGURE 4-6** shows sample 12.



**FIGURE 4-6: Sample 12 - Membrane without Cracks (BPDA-ODA/DMF)**

#### 4.1.5 Sample 13- Cracked Membrane (BPDA-ODA Membrane)

For this part of the experiment, DMF is changed back to DMAc to observe the quality of the membrane. When DMAc is used, the membrane cannot be formed as complete as using DMF as the solvent. Therefore, cracks are formed. **FIGURE 4-7** shows sample 13.



**FIGURE 4-7: Sample 13 - Cracked Membrane (BPDA-ODA/DMAc)**

#### **4.2 EFFECT OF CHOICES AND CONCENTRATION OF POLYMER SOLUTION**

In this experiment, the range of concentration being tested is from 20% until 25% for BTDA-ODA membrane and 18% until 23% for BPDA-ODA membrane. Throughout the experiment, the stirring time, degassing time and evaporation time remain fixed.

According to the observation, the concentration for BTDA-ODA membrane best performs at 23%. The membrane is formed, but the elasticity is absent whereby the membrane cracks during the drying process with the air. With this concentration, the thickness of the membrane can reach 100  $\mu\text{m}$ .

By changing the concentration to 20% and 21%, the solution can only be casted at 30  $\mu\text{m}$ , and after the precipitation process in coagulation bath, the membrane cannot be lifted up from the glass plate. As a result after the drying process, no membrane is formed; instead powdery surface is formed on the glass plate.

When the concentration is changed to 25%, the viscosity actually remains the same compared with 23wt%, but the membrane casted has more cracks compared with 23wt% polymer concentration during precipitation process.

As for BPDA-ODA membrane, 18wt% of polymer concentration is the optimum concentration for a membrane to be casted. When the concentration increases, the membrane eventually cracks when the membrane is inserted into the coagulation bath.

Therefore, the best combination of monomers for the membrane casting is BPDA-ODA membrane, with the concentration of 18wt%.

### **4.3 EFFECT OF CHOICES OF SOLVENT**

From the experiment, there are two different solvents being used, DMAc and DMF. For all the samples using DMAc, the solution is not viscous enough to be casted on the glass plate. Only when the concentration of BTDA-ODA increases to 25%, then it can be casted at 130 $\mu$ m. As for DMF, at 21% it contains better viscosity for casting process and the viscosity is at the best state a 23wt% of polymer concentration. As for BPDA-ODA, when DMF is replaced with DMAc, even when the polymer concentration increases, the casting solution is not too viscous compared with casting solution using DMF. As for the result, the membrane cracks.

One of the reasons is that DMF is having a better solubility and dissolving capacity [26]. Therefore, during the stirring process, the monomers dissolve faster in DMF, whereas there is difficulty in dissolving the monomers in DMAc, which it promotes formation of lumps of monomers in the solution.

Therefore, DMF is a better choice compared to DMAc.

### **4.4 EFFECT OF BINDER ADDITION**

In this experiment, binders are added to enhance its elasticity so that it can undergo the separation process of carbon dioxide if it is used for carbon dioxide separation under a certain pressure. This is also to maintain the structure of polyimide membrane. In this experiment, anhydrous glycerol is added into the solution at the concentration of either 2wt% or 3wt%. When 2% is used, the membrane is cracked more frequent.

When the concentration of binder increases from 2% to 3%, the membrane has lesser cracks. Therefore, the optimum concentration for binder to be used is 3wt%.

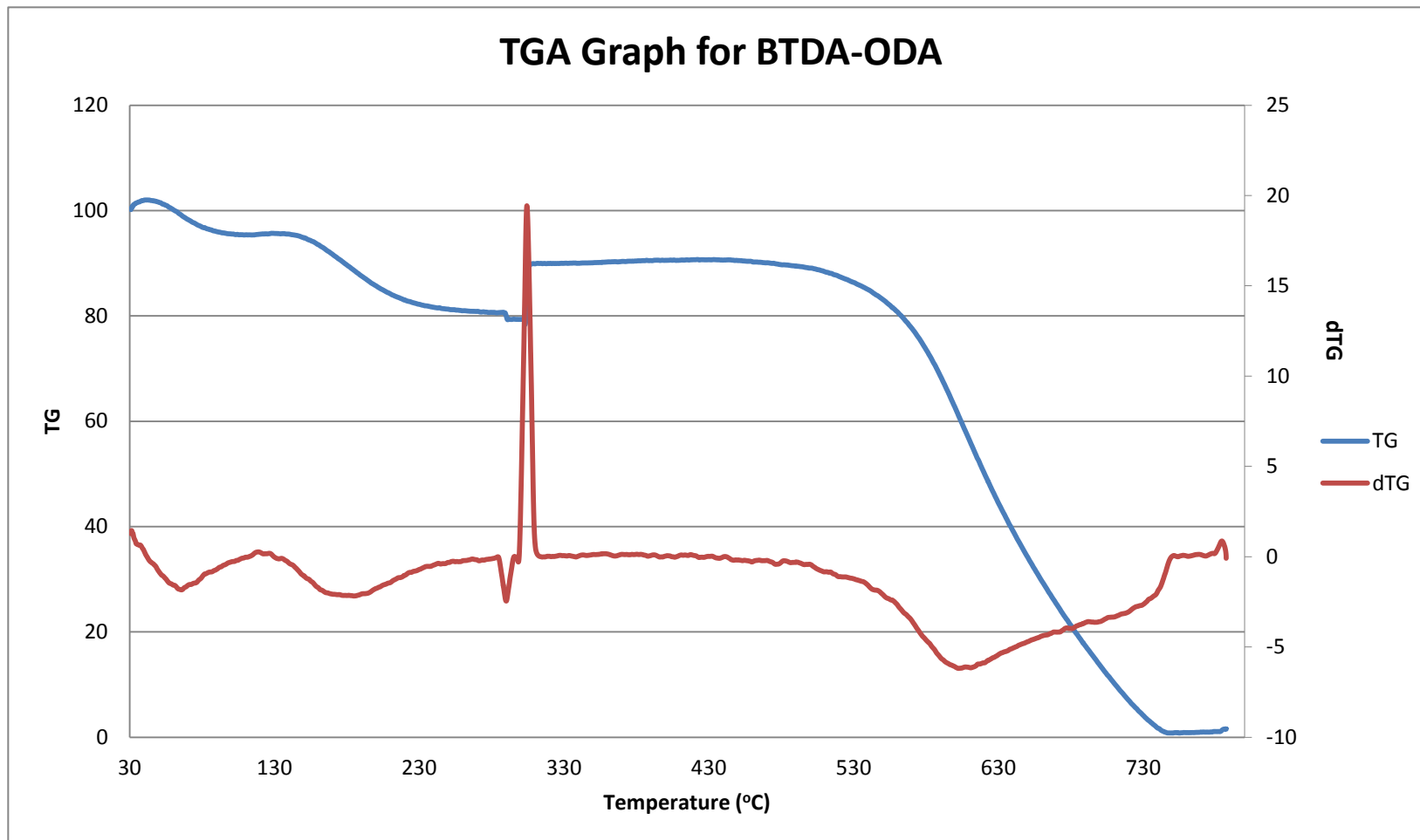
## 4.5 CHARACTERIZATION

### 4.5.1 TGA Analysis

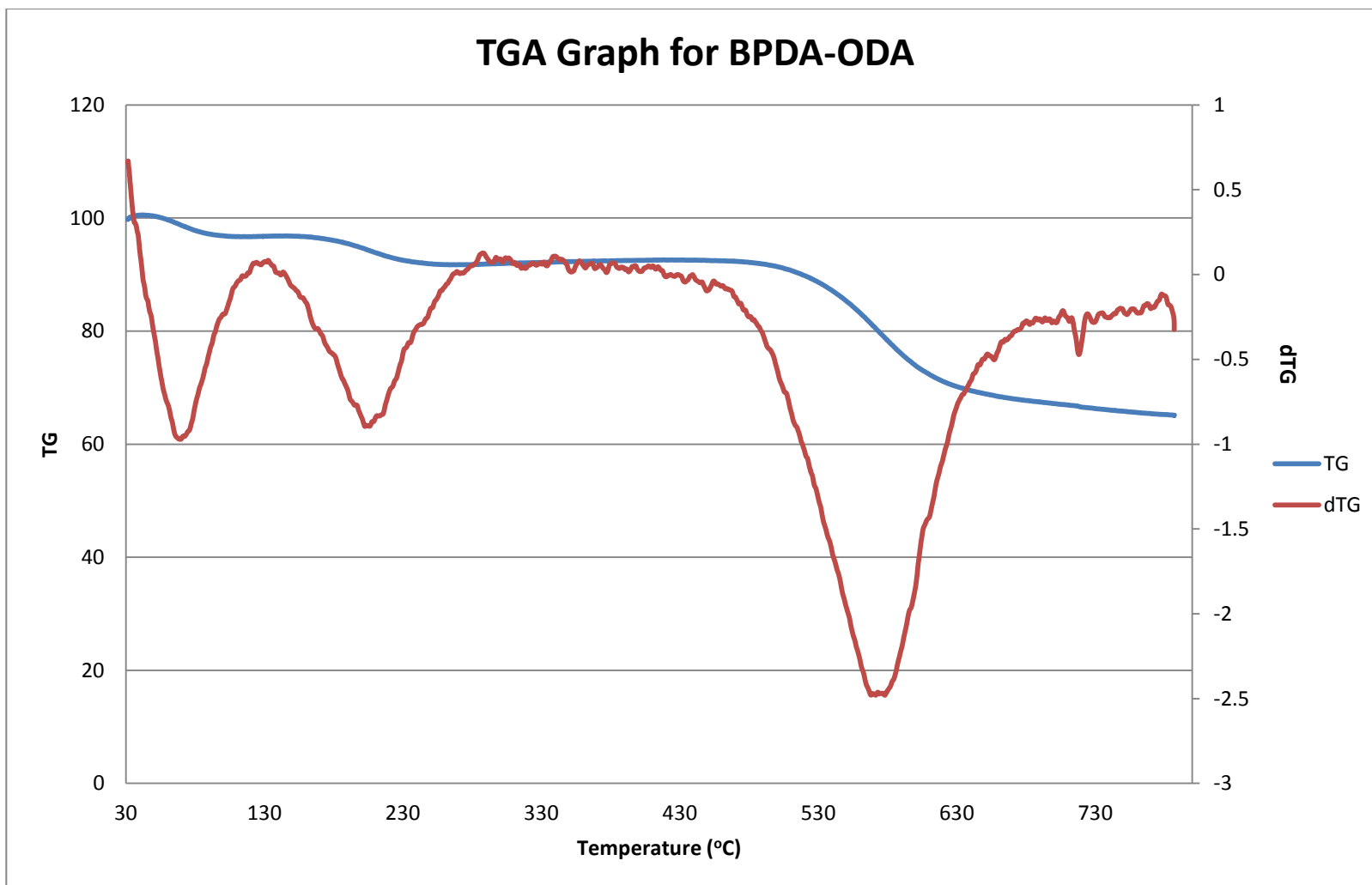
For BTDA-ODA membrane, there is a slight weight loss around 80°C until 150°C; whereas from 150°C until 300°C, the weight loss increases. But from 300°C until 308°C, there is a negative weight loss, whereby there is weight gain from the sample. This can be due to chemical reactions with gaseous substances with the formation of non-volatile compounds, and also physical transition which adsorption of gaseous substances on samples occurs [24]. From 500°C onwards, the sample undergoes drastic weight loss until 787°C.

As for BPDA-ODA, there is a slight weight drop from 80°C until 300°C, which can be due to residual imidization [25]. From 500°C onwards, there is a drastic weight loss as well, but compared with BTDA-ODA, the weight loss is much lesser than BTDA-ODA's weight loss.

Therefore, BPDA-ODA is a better membrane to withstand temperature as high as 780°C. **FIGURE 4-8** and **FIGURE 4-9** shows the TGA analysis graph for BTDA-ODA membrane and BPDA-ODA membrane respectively.



**FIGURE 4-8: TGA Analysis for BTDA-ODA Membrane**

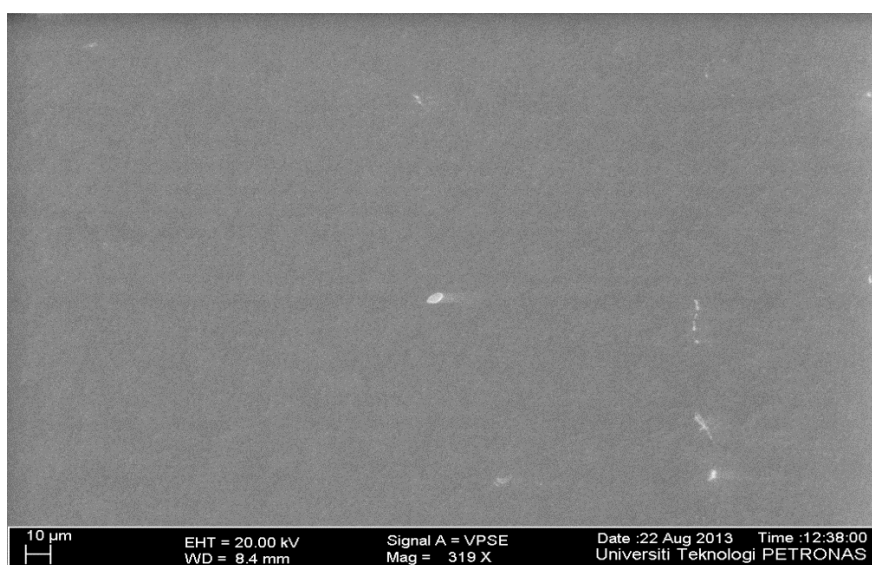


**FIGURE 4-9: TGA Analysis for BPDA-ODA Membrane**



#### 4.5.2 FESEM Analysis

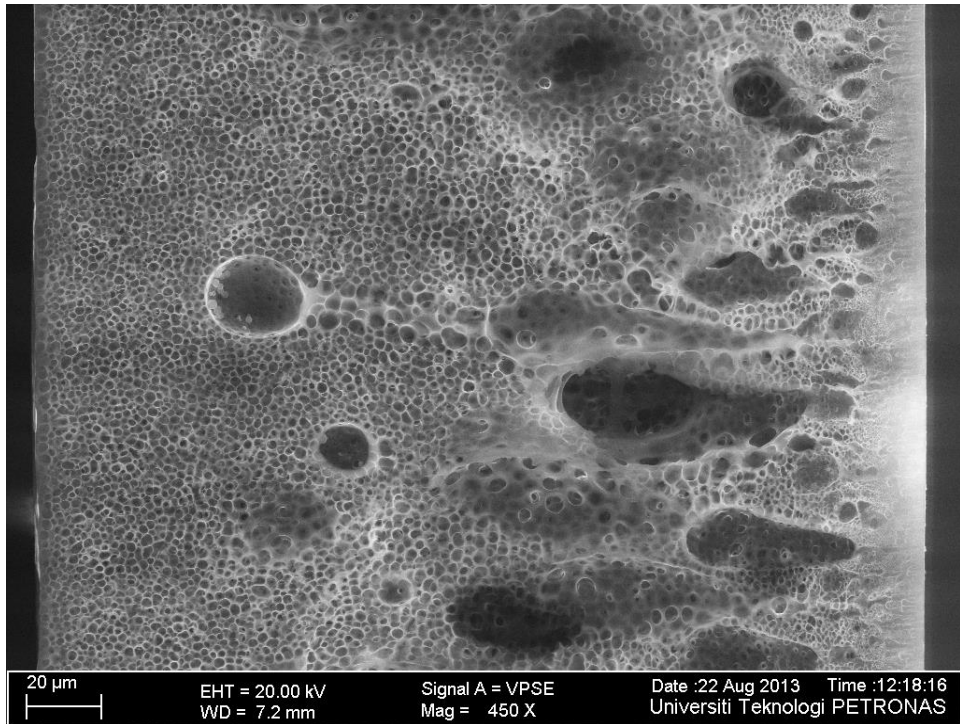
The surface view of both BTDA-ODA and BPDA-ODA membrane are as shown in **FIGURE 4.10** and **FIGURE 4.11**. From the surface view of the membranes, the impurities on the surface are much smaller in BPDA-ODA membrane, which is less than  $2\mu\text{m}$ ; whereas the impurities on BTDA-ODA membrane can be seen at  $10\mu\text{m}$ . **FIGURE 4-12** and **FIGURE 4-13** shows the cross-sectional view of BTDA-ODA and BPDA-ODA membrane respectively. From the cross-sectional view, BPDA-ODA membrane has a better morphology because there are less large pores, which are the air bubbles; whereas from BTDA-ODA membrane, large pores can be seen from the cross-sectional area.



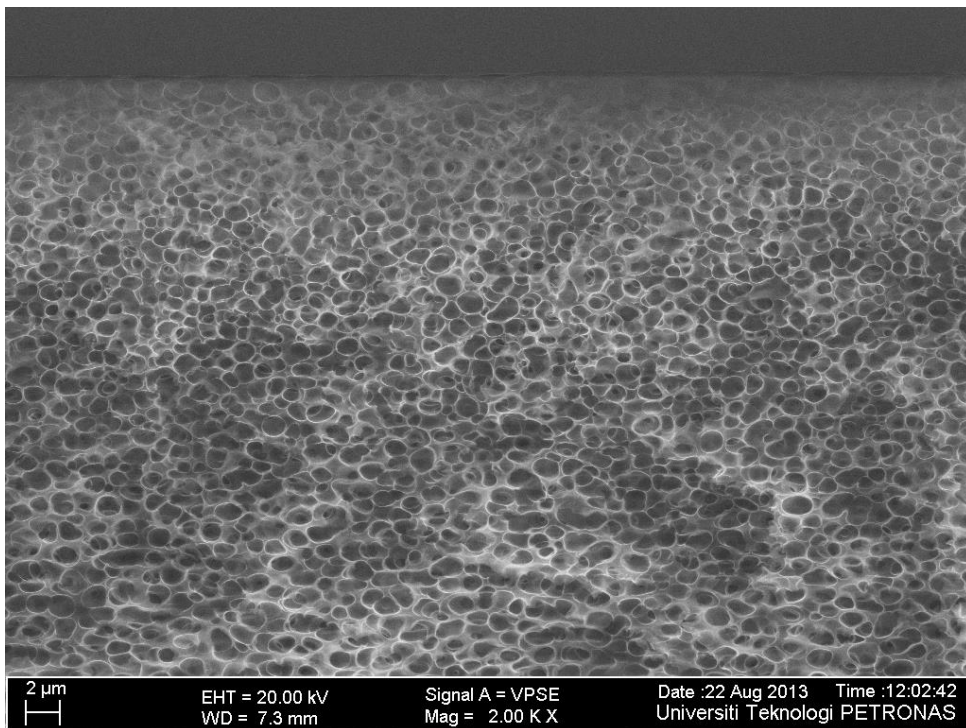
**FIGURE 4-10: Surface View of BTDA-ODA Membrane**



**FIGURE 4-11: Surface View of BPDA-ODA Membrane**



**FIGURE 4-12: Cross-sectional View of BTDA-ODA Membrane**



**FIGURE 4-13: Cross-sectional View of BPDA-ODA Membrane**

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATION**

From this research, we can conclude that BPDA-ODA membrane has a more promising result compared to BTDA-ODA membrane. Several factors have been studied in the research, such as choice and concentration of polymer, binder addition, choice and concentration of solvent. After several experiments, the optimum polymer concentration is 23wt% for BTDA-ODA and 18wt% for BPDA-ODA. Addition of 3% binder is encouraged to strengthen the condition of the membrane. Finally, TGA analysis has been performed and it shows that the synthesized membrane has high heat resistance and it is suitable to be used for high temperature process. This research will be able to contribute by providing a better quality membrane for a more effective membrane separation.

There are some recommendations in this research. First of all, the polymers should be added bit by bit instead of adding into the solvent in a huge amount. This is to prevent the polymers from hardening and ended up disrupting the stirring process. Secondly, the surrounding must be dry to ensure that the mixing solution does not contain much moisture this will lead to cracking of the membrane when it is inserted into the coagulation bath for precipitation. Thirdly, more combination of monomers can be tested to come out with a better membrane. Addition of monomer into the current polymer combination can be performed as well. Fourthly, the materials are to be dried in an oven before being used to ensure the moisture being evaporated. Last but not least, more characterization tests are performed in order to understand more about the morphology of the membrane.

## REFERENCES

- [1] Dortmund, D., Doshi, K. (1999). *Recent developments in CO<sub>2</sub> removal membrane technology*.
- [2] *Biology online*. (n.d.). Retrieved from <http://www.biology-online.org/dictionary/Membrane>
- [3] Mulder, M. (1996). *Basic principles of membrane technology*. (Second ed.). Netherlands: Kluwer Academic Publishers.
- [4] Newpoint Gas, LP. (n.d.). *Carbon dioxide removal: Membrane separation*. Retrieved from [http://www.newpointgas.com/naturalgas\\_carbondioxide.php](http://www.newpointgas.com/naturalgas_carbondioxide.php)
- [5] Baker, R. W. (2012). *Membrane technology and applications*. (3rd ed.). John Wiley.
- [6] *Membrane classification*. (n.d.). Retrieved from [http://www.separationprocesses.com/Membrane/MT\\_Chp02a.htm](http://www.separationprocesses.com/Membrane/MT_Chp02a.htm)
- [7] Wang, L. K., Chen, J. P., Hung, Y., & Shamma, N. K. (2010). *Membrane and desalination technology*. London: Humana Press. Retrieved from [http://books.google.com.my/books?id=CMOBQ8ijJbwC&pg=PA50&lpg=PA50&dq=isotropic+microporous+membrane&source=bl&ots=j56hMNAida&sig=0OGXUnHcuN1zXq2hAFCzOqNH\\_SY&hl=en&sa=X&ei=-5xUeX6HIz8rAeol4GIDw&ved=0CF4Q6AEwBw#v=onepage&q=isotropic%20microporous%20membrane&f=false](http://books.google.com.my/books?id=CMOBQ8ijJbwC&pg=PA50&lpg=PA50&dq=isotropic+microporous+membrane&source=bl&ots=j56hMNAida&sig=0OGXUnHcuN1zXq2hAFCzOqNH_SY&hl=en&sa=X&ei=-5xUeX6HIz8rAeol4GIDw&ved=0CF4Q6AEwBw#v=onepage&q=isotropic%20microporous%20membrane&f=false)
- [8] *Membrane classification*. (n.d.). Retrieved from [http://www.separationprocesses.com/Membrane/MT\\_Chp02b.htm](http://www.separationprocesses.com/Membrane/MT_Chp02b.htm)

- [9] Vinogradova S. V., Vygodskii Y. S., Korshak V. V., “Features of polyimide synthesis by one-step high-temperature polycyclization.” *Vysokomolekulyarnye Soedineniya, Seriya A*, 12 (9) (1970), page 1987-1993.
- [10] Khulbe, K. C., Feng, C. Y., & Matsuura, T. (2008). *Synthetic polymeric membranes: Characterization by atomic force microscopy*. Springer Laboratory.
- [11] Jin, L., Qinghua, Z., Yuan, X., Qingming, X., & Dajun, C. (2009). *European polymer journal. Homogenous one-pot synthesis of polyimides in polyphosphoric acid*, 2805-2811. Retrieved from <http://www.sciencedirect.com/science/article/pii/S001430570900319X>
- [12] Zhang J., Lu J., Liu W., Xue, Q. Separation of CO<sub>2</sub> and CH<sub>4</sub> through two types of polyimide membrane. *Thin Solid Films* 340 (1999), page 106-109.
- [13] Xingzhong, F., Zheng, W., Zhenghua, Y., Lianxun, G., Qingxuan, L., & Mengxian, D. (n.d.). (2003). Retrieved from <http://www.sciencedirect.com/science/article/pii/S0032386103001812>
- [14] Youn Kook, K., Bum Park, H., & Moo Lee, Y. (n.d.). (2005). Retrieved from <http://www.sciencedirect.com/science/article/pii/S0376738805001195>
- [15] Be Cheer, N., & Ahmad Fauzi, I. (n.d.). (2000). Retrieved from [http://eprints.utm.my/5255/1/NBeCheer2000\\_APreliminaryStudyOfFlatSheetAsymmetricMembrane.pdf](http://eprints.utm.my/5255/1/NBeCheer2000_APreliminaryStudyOfFlatSheetAsymmetricMembrane.pdf)
- [16] Laot, C. M., Dr. Ravi Saraf, Dr. Eva Marand, Dr. Garth L. Wilkes, Dr. Richey M. Davis, Dr. Herve Marand. “Gas transport properties in polycarbonate – Influence of the cooling rate, physical aging, and orientation” (2001).
- [17] *Overview of Natural Gas*. (n.d.). Retrieved from NaturalGas.org: <http://www.naturalgas.org/overview/overview.asp>
- [18] BP Statistical Review of World Energy June 2013. (2013, June). Retrieved from BP: [http://www.bp.com/content/dam/bp/pdf/statistical-review/statistical\\_review\\_of\\_world\\_energy\\_2013.pdf](http://www.bp.com/content/dam/bp/pdf/statistical-review/statistical_review_of_world_energy_2013.pdf)

- [19] Abedini, R., & Nezhadmoghadam, A. (2010, April 30). Application of Membrane in Gas Separation Processes: Its Suitability and Mechanisms. Retrieved June 15, 2010, from VÚRUP, a.s:  
[http://www.vurup.sk/sites/vurup.sk/archivedsite/www.vurup.sk/pc/vol52\\_2010/issue2/pdf/pc\\_2\\_2010\\_abedini\\_069.pdf](http://www.vurup.sk/sites/vurup.sk/archivedsite/www.vurup.sk/pc/vol52_2010/issue2/pdf/pc_2_2010_abedini_069.pdf)
- [20] Herzog, H. (1999, August). An Introduction to CO<sub>2</sub> Separation and Capture Technologies. Retrieved from The Engineering Resource: [http://www.engineering-resource.com/Files/introduction\\_to\\_capture.pdf](http://www.engineering-resource.com/Files/introduction_to_capture.pdf)
- [21] Cryogenic Separation. (n.d.). Retrieved from Student's Webpage @ Chemical Engineering & Chemistry: [http://students.chem.tue.nl/ifp24/techn\\_cryo.htm](http://students.chem.tue.nl/ifp24/techn_cryo.htm)
- [22] Sombel, D., M.-L., L., & Rabih, K. (2012, 12 19). *Bpda-pda polyimide: Synthesis, characterizations, aging and semiconductor device passivation*. Retrieved from Intech: <http://www.intechopen.com/books/high-performance-polymers-polyimides-based-from-chemistry-to-applications/bpda-pda-polyimide-synthesis-characterizations-aging-and-semiconductor-device-passivation>
- [23] Burakowski Nohara, L., Leali Costa, M., Angelo Alves, M., Ferreira Koyama Takahashi, M., Lu í Nohara, E., & Cerqueira Rezende, M. (2010, May 24). Processing of high performance composites based on peek by aqueous suspension. Retrieved from SciELO Brazil: [http://www.scielo.br/scielo.php?pid=S1516-14392010000200020&script=sci\\_arttext](http://www.scielo.br/scielo.php?pid=S1516-14392010000200020&script=sci_arttext)
- [24] Widmann, G. (2001, January). UserCom. *Interpreting TGA Curves*. Schwerzenbach, Switzerland: Mettler Toledo.
- [25] Revathi, P. (2013). Synthesis and Characterization of Polyimides based on BPDA, BTDA, ODPDA and ODA. In *Development and characterization of mesoporous terpolyimide nanocomposites with low dielectric constant* (pp. 48-80).
- [26] Ma, P., & Chen, M. (2003). Chemical Engineering Data. *Solid-Liquid Equilibrium of Terephthalic Acid in Several Solvents*, 334-337.

[27] Rafiq, S., Man, Z., Maulud, A., Muhammad, N., & Maitra, S. (2011). Effect of Varying Solvents Compositions on Morphology and Gas Permeation Properties on Membranes Blends for CO<sub>2</sub> Separation from Natural Gas. *Journal of Membrane Science*, 444-452.