

## ABSTRACT

The chemical cross-linking modifications of asymmetric 3,3',4, 4'-benzophenone tetracarboxylic dianhydride and diamino-phenylindane (BTDA-DAPI) polyimide membranes with *para*-phenylenediamine (*p*PD) have been investigated. The modification was performed by immersing BTDA-DAPI polyimide membranes in a *p*PD/methanol solution at ambient temperature for certain periods of time. The effects of immersion time and cross-linker concentrations on degree of cross-linking, physicochemical properties and gas transport properties of the membranes have been studied. The cross-linked BTDA-DAPI polyimide membranes were characterized using gel test, fourier transform infrared (FTIR), differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and x-ray diffractometer (XRD). The FTIR spectra confirmed that the cross-linking process had taken place, with the imide groups turning into amide groups during the modification process. The degree of cross-linking was increased with the increase in the immersion time and the cross-linker concentrations. It is also showed that there are small amount of insoluble materials remaining from the gel test. The XRD results revealed that the *d*-space of the polymeric chains changed after the modification due to the methanol swelling and structure tightening effects induced by cross-linking. The TGA and DSC results indicated that the degradation and glass transition temperature were sufficient for gas separation applications. The gas transport properties of the pure and cross-linked BTDA-DAPI polyimide membranes were investigated using gas permeation tests. The results showed that the cross-linked BTDA-DAPI polyimide membranes decreased the oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) permeabilities compared to the unmodified membranes. Interestingly, 10% *p*PD-120 min samples showed an impressive enhancement of selectivity for O<sub>2</sub>/N<sub>2</sub> compared to the unmodified membrane from 6.19 to 10.01 with reasonable permeability. However, less favorable CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivity have been observed after diamine cross-linking for all samples. Thus, it appears that the *p*PD is a good alternative cross-linker agent for BTDA-DAPI polyimide membrane mainly for the separation of O<sub>2</sub>/N<sub>2</sub> with 10% *p*PD and 120 minutes as the optimum cross-linker concentrations and cross-linking time, respectively.

## ABSTRAK

Pengubahsuaian rangkai silang ke atas membran 3,3',4,4'-benzofenon tetrakarboksilik dianhidrida dan diamino-fenilindana (BTDA-DAPI) poliimida tak simetri menggunakan *para*-fenilena diamina (*p*PD) telah dikaji. Teknik ini dilakukan dengan merendam membran BTDA-DAPI poliimida ke dalam larutan *p*PD/metanol pada suhu persekitaran untuk tempoh masa tertentu. Kesan masa rendaman dan kepekatan agen rangkai silang terhadap bilangan rangkai silang yang terbentuk, ciri-ciri fisiko-kimia dan ciri-ciri pengangkutan gas membran telah dikaji. Membran terhasil dicirikan dengan menggunakan ujian gel, spektroskopi inframerah transformasi fourier (FTIR), kalorimeter pengimbasan pembeza (DSC), analisis gravimetrik termal (TGA) dan x-ray difraktometer (XRD). Spektrogram FTIR menunjukkan proses rangkaian silang telah berlaku di mana kumpulan imida telah bertukar kepada kumpulan amida semasa proses pengubahsuaian. Bilangan rangkai silang terbentuk meningkat dengan peningkatan masa rendaman dan kepekatan agen rangkai silang. Ujian gel menunjukkan sebahagian kecil bahan yang tidak terlarut ditemui. Keputusan XRD menunjukkan *d-space* rantaian polimer berubah selepas pengubahsuaian kerana kesan pembengkakan metanol dan penguatan struktur yang teraruh dari proses rangkaian silang. Keputusan DSC dan TGA menunjukkan suhu penyusutan dan suhu peralihan kaca mencukupi untuk penggunaan pemisahan gas. Ciri-ciri pengangkutan gas bagi membran BTDA-DAPI poliimida yang tidak diubahsuai dan diubahsuai dikaji dengan menjalankan ujian kebolehtelapan gas. Keputusan menunjukkan kebolehtelapan gas oksigen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), karbon dioksida (CO<sub>2</sub>) dan metana (CH<sub>4</sub>) bagi membran BTDA-DAPI poliimida yang dirangkai silang lebih rendah berbanding membran yang tidak diubahsuai. Peningkatan yang sangat memberangsangkan dapat dilihat bagi sampel 10% *p*PD-120 min yang menunjukkan kememilihan O<sub>2</sub>/N<sub>2</sub> 10.01 berbanding 6.19 bagi membran yang tidak diubahsuai dengan kebolehtelapan yang munasabah. Bagaimanapun, nilai kememilihan agak rendah bagi pemisahan gas CO<sub>2</sub>/CH<sub>4</sub> dan CO<sub>2</sub>/N<sub>2</sub> untuk semua sampel yang telah diubahsuai. Oleh itu, dapatlah disimpulkan bahawa *p*PD adalah agen rangkai silang alternatif yang bagus untuk membran BTDA-DAPI poliimida khususnya untuk pemisahan gas O<sub>2</sub>/N<sub>2</sub> dengan 10% *p*PD merupakan kepekatan optimum bagi agen rangkai silang dan 120 minit merupakan masa rendaman yang optimum.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xii
	LIST OF FIGURES	xiv
	LIST OF SYMBOLS	xix
	LIST OF ABBREVIATIONS	xx
	LIST OF APPENDICES	xxii
 <b>I</b>	 <b>INTRODUCTION</b>	
1.1	Research background	1
1.1.1	Membrane Based Gas Separation	1
1.1.2	Membranes and its Application on CO <sub>2</sub> Removal	3
1.1.3	Membranes and its Application on O <sub>2</sub> /N <sub>2</sub> Separation	6
1.2	Problem Statement	7
1.3	Objectives of the Study	8
1.4	Scopes of the Study	9
1.5	Thesis Outline	10

**II****LITERATURE REVIEW**

2.1	Overview of Membrane for Gas Separation	11
2.1.1	Membrane Structures	13
2.1.1.1	Symmetrical Membrane	14
2.1.1.2	Asymmetric Membrane	16
2.1.1.3	Porous Membrane	18
2.1.1.4	Non-Porous Membrane	20
2.1.2	Membrane Configurations and Fabrication Techniques	21
2.2	Gas Transport in Membranes	
2.2.1	General Gas Transport Theory	22
2.2.2	Gas Transport Mechanism in Dense and Porous Membrane	25
2.2.2.1	Solution-diffusion Model	25
2.2.2.2	Dual Mode Sorption Theory	27
2.2.2.3	Knudsen Diffusion	28
2.2.2.4	Molecular Sieving	30
2.3	Polymeric Membrane for Gas Separation	31
2.3.1	Glassy Polymeric Membrane for Gas Separation	32
2.3.2	Rubbery Polymeric Membrane for Gas Separation	37
2.4	General Steps in Preparation of Polymeric Membrane for Gas Separation	39
2.4.1	Membrane Fabrication by Phase Inversion Process	39
2.5	Approaches to Improve Membrane Performance	42
2.5.1	Thermal Treatment	42
2.5.2	Polymer Blending	44
2.5.3	Cross-linking	48

2.6	Cross-linked Polymer Research Specific to this Project	51
-----	--	----

### **III RESEARCH METHODOLOGY**

3.1	Research Design	56
3.2	Material Selection	58
	3.2.1 Polymer Matrix	58
	3.2.1.1 Polyimide	59
	3.2.3 Cross-linking Agent	60
	3.2.4 Solvent	61
	3.2.5 Test Gases	61
3.3	Preparation of Cross-linked Polyimide Membrane	62
	3.3.1 Preparation of Casting Solution	62
	3.3.2 Polyimides Membrane Formation	64
	3.3.3 Cross-linking of Polyimides Membrane	65
3.4	Characterization and Performance Testing	65
	3.4.1 Gas Permeation Test	66
	3.4.2 Attenuated Total Reflection-Fourier Transforms Infrared Spectroscopy (ATR-FTIR)	67
	3.4.3 Gel Test	68
	3.4.4 X-ray Diffraction	69
	3.4.5 Differential Scanning Calorimetry (DSC)	69
	3.4.3 Thermogravimetric Analysis (TGA)	70

#### **IV THE EFFECTS OF *p*-PHENYLENEDIAMINE MODIFICATION ON GAS TRANSPORT PROPERTIES OF BTDA-DAPI POLYIMIDE MEMBRANES**

4.1	Cross-linking Modification of Polymeric Membrane for Gas Separation	71
4.2	Experimental	
4.2.1	Materials and Membrane Preparation	74
4.2.2	Cross-linking of Polyimides Membrane	74
4.2.3	Characterization	75
4.3	Results and Discussion	
4.3.1	Effects of Immersion Time on Physical Properties of the Membrane and Degree of Cross-linking	76
4.3.2	Cross-linking Mechanism	80
4.3.3	Effects of Immersion Time on Thermal Properties of Cross-linked BTDA-DAPI Polyimide Membranes	82
4.3.4	Effects of Immersion Time on <i>d</i> -space of Cross-linked BTDA-DAPI Polyimide Membranes	86
4.3.5	Effects of Immersion Time on Gas Transport Properties of Cross-linked BTDA-DAPI Polyimide Membranes	92
4.4	Conclusions	101

#### **V CHEMICAL CROSS-LINKING MODIFICATION OF BTDA-DAPI POLYIMIDE MEMBRANE USING *p*-PHENYLENEDIAMINE FOR GAS SEPARATION: EFFECTS OF CROSS-LINKER CONCENTRATIONS**

5.1	Cross-linking of Gas Separation Membranes	
-----	---	--

	with <i>p</i> -phenylenediamine	103
5.2	Experimental	
	5.2.1 Materials and Membrane Preparation	105
	5.2.2 Cross-linking of Polyimides Membrane	106
	5.2.3 Characterization and Performance	
	Testing of Modified Polyimides Membrane	106
5.3	Results and Discussion	
	5.3.1 Effects of Cross-linker Concentrations	
	on Degree of Cross-linking	107
	5.3.2 Effects of Cross-linker Concentrations	
	on Thermal Properties of Cross-linked BTDA-	
	DAPI Polyimide Membranes	113
	5.3.3 Effects of Cross-linker Concentrations	
	on <i>d</i> -space of Cross-linked BTDA-DAPI	
	Polyimide Membranes	118
	4.3.5 Effects of Cross-linker Concentrations	
	on Gas Transport Properties of Cross-linked	
	BTDA-DAPI Polyimide Membranes	124
5.4	Conclusions	130

## **VI                    GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK**

6.1	General Conclusions	132
6.2	Recommendations for Future Work	134

<b>REFERENCES</b>	136
-------------------	-----

<b>APPENDICES</b>	145
-------------------	-----

<b>LIST OF PUBLICATIONS</b>	154
-----------------------------	-----

## **CHAPTER I**

### **INTRODUCTION**

#### **1.1 Research Background**

##### **1.1.1 Membrane Based Gas Separation**

The first scientific observation related to gas separation was encountered by J.K Mitchell in 1831. However, the most remarkable and influential contribution to membrane gas separation technology was the systematic study by Thomas Graham in 1860. Only in 1980, membrane gas separation has rapidly become a competitive separation technology when the serial production of commercial polymeric membrane was implemented by Cynara (now part of Natco), Separex (now part of UOP), GMS (now part of Kvaerner) and Generon (now part of MG) (Baker, 2002). Membrane separation processes provide several advantages over other conventional separation techniques (e.g., cryogenic distillation and adsorption processes). First, the membrane process is a viable energy-saving alternate for CO<sub>2</sub> separation, since it does not require any phase transformation. Second, the necessary process equipment is very simple with



no moving parts, compact, relatively easy to operate and control, and also easy to scale-up (Powell et al., 2006).

There are many opportunities to extend markets for membrane gas separation. In some cases, the membrane materials, membrane configuration, and preparation routes are inadequate to fully exploit these new fields. A broad range of materials was investigated and different improvements were achieved by the time in this field. Today, much of the research work is being addressed to the investigation of new materials and to the development of new membrane structures that can exhibit both higher selectivity and permeability to specific gases.

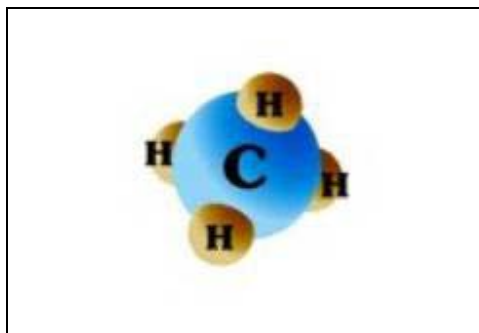
Polymers are currently the dominant materials for gas separation membranes due to their high separation efficiency, low operating costs and simple operating procedures. The development of novel polymer membranes with higher gas permeabilities and selectivities has received a lot of attention. Recently, there is a lot of papers reported on a variety of polymeric materials that have been investigated to fabricate membrane-based gas separation system. Surprisingly, only eight or nine polymer materials have been used to make at least 90% of the total installed gas-separation membrane-based systems (Kookos, 2002; Bernardo et al., 2009). The main rubbery and glassy polymers employed for gas separation membranes are listed in Table 1.1 (Bernardo et al., 2009).

**Table 1.1:** Glassy and rubbery polymers used in industrial membrane gas separation

<b>Rubbery polymers</b>	<b>Glassy polymers</b>
Poly(dimethylsiloxane)	Cellulose acetate
Ethylene oxide/propylene oxide -amide copolymers	Polyperfluorodioxoles
	Polycarbonates
	Polyimides
	Poly(phenylene oxide)
	Polysulfone

### 1.1.2 Membrane and its Application for CO<sub>2</sub> Removal

Natural gas is considered as a “cleaner” source of energy than traditional fossil fuels since it has much higher hydrogen to carbon ratio by comparison as shown in Figure 1.1. Natural gas is a fuel source that has an annual world market value of over \$22 billion. Though, natural gas contains small concentrations of various impurities, the focus of natural gas purification is typically on acid gas removal. This includes carbon dioxide, hydrogen sulfide, hydrogen chloride, and sulfur dioxide. These acid gases can corrode pipelines, as well as lower the overall energy value of the natural gas (Hillock, 2005). Generally, pipeline specifications limit the CO<sub>2</sub> concentration to 2 mole percent and the H<sub>2</sub>S concentration to 4 ppm (Lee et al., 1995). Natural gas compositions and pressures vary widely by geographical location (Wind et al., 2003b). Table 1.2 shows the typical composition of natural gas wells. As shown in Table 1.2, carbon dioxide accounts for the largest amount of impurities in many wells and must be reduced to less than 2% to meet sales specification.



**Figure 1.1:** A methane molecule

**Table 1.2:** Typical composition of natural gas

Gas components	Chemical formula	Composition
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	Ar, He, Ne, Xe	trace

There are several technologies that had been applied in CO<sub>2</sub> separation including absorption, adsorption, membrane separation and cryogenic separation. Chemical and/or physical absorption processes are widely used in the petroleum, natural gas and chemical industries for the separation (or capture) of CO<sub>2</sub>. However this process gives limited CO<sub>2</sub> loadings and significant energy requirements resulting from the reaction stoichiometry and the heat of reaction, respectively. Adsorption processes are based on significant intermolecular forces between gases and the surfaces of certain solid materials such as molecular sieves and activated carbon. The inherent advantage of

adsorption processes is their relatively simple although unsteady state operation, however the capacity and CO<sub>2</sub>-selectivity of available adsorbents is low. For cryogenic processes, the basic advantage is that, provided the CO<sub>2</sub> is properly conditioned, high recovery of CO<sub>2</sub> and other feed constituents is possible. However, cryogenic processes are inherently energy intensive (Meisen and Shuai, 1997).

Membrane separation of CO<sub>2</sub> from light hydrocarbons has met with considerable success in the petroleum, natural gas and chemical industries because of the inherent simplicity resulting from steady state operation, absence of moving parts and modular construction (Meisen and Shuai, 1997). Monsanto is largely responsible for the commercial success of gas separation membranes. They used these membranes for recovery of hydrogen in their own ammonia plants for several years before introducing the product to industry. Other suppliers of commercial gas separation membranes include Dow, Dupont, Grace, and Separex, with more recent announcements by Union Carbide and Ube (Schendel et al., 1984).

Membranes are an excellent candidate for removing carbon dioxide from methane at the high concentration levels. Also, due to their modular nature, membranes can be added, as required, as the CO<sub>2</sub> concentration rise. The CO<sub>2</sub> can be produced at intermediate pressure to reduce compression costs for reinjection. Therefore, membranes can be effectively used for bulk removal of CO<sub>2</sub> so that the remaining gas can be processed in existing equipment. In fact, this option is already being chosen by several CO<sub>2</sub> flood operators (Schendel et al., 1984)

### 1.1.3 Membrane and its Application for O<sub>2</sub>/N<sub>2</sub> Separation

Membrane-based air separation is relatively new but is likely to be important since nitrogen and oxygen is the second and third most produced chemicals, respectively in the world (Ghosal and Freeman, 1994). The production of nitrogen-enriched air using membrane is important in inert gas blanketing of fresh fruits and vegetables and inflammable liquids. Membrane-produced nitrogen is particularly attractive for inerting applications because this application does not require very pure nitrogen. While the production of pure oxygen is important to some medical uses and oxygen-enriched air for enhanced combustion, respectively. Compared to the conventional technology for air separation (cryogenic distillation and ambient temperature adsorption), membrane units are more attractive due to their compactness and portability (Combee and Nieh, 2007).

Because air already contains 80% nitrogen, and nitrogen remains on the residue side of the membrane, production of essentially pure nitrogen from air is comparatively easy. Producing oxygen by a membrane separation process is more difficult because some nitrogen always permeates with the oxygen, producing oxygen-enriched air rather than pure oxygen. The process was developed to the early commercial stage during the 1980s using silicone rubber and ethyl-cellulose membranes, but the performance of these membranes was not good enough to make the process competitive. Therefore, the outlook for this application could improve with the development of material with higher selectivities.

## 1.2 Problem Statement

Membrane separation process has become one of the most exciting and significant new unit processes to have appeared in many years. Developing membrane technology for gas separation is challenging, but economically rewarding from industrial prospect (Shao et al., 2005a; Hacıoğlu et al., 2003; Ismail and Yaacob, 2006). Currently, the immediate challenges faced by existing membrane technology in gas separation can essentially be summarized into a few key areas (Koros and Mahajan, 2000). Achieving higher selectivity for the relevant application with at least equivalent productivity is the first of these challenges. Second challenge is maintaining these properties in the presence of complex and aggressive feeds (e.g. high temperature and high concentrations of CO<sub>2</sub>). Among many polymeric materials for gas separation, polyimides has been found to possess high gas permeability as well as high intrinsic selectivity in comparison to polycarbonate, polysulfone and other materials (Shao et al., 2004b). By applying polyimide membrane in gas separation application, the first challenges mentioned earlier can be defeated. However, polyimide still facing with the trade-off relationship effects, which is the limit for achieving the desired result of a high separation factor combined with a high permeability.

According to Freeman's theory (Cocepiere-Gomez et al., 2007) polymeric membranes can be induced to perform closer or beyond the upper bound through any of the following mechanisms: (a) by improving the solubility selectivity and (b) by increasing the polymer chain stiffness while simultaneously the interchain spacing increases up to a limit, to avoid losing mobility-selectivity. In the meantime, cross-linking modification of polyimides has received much attention since it appears to provide a promising approach toward improving selectivity and chemical and plasticization resistance in the presence of aggressive feeds (Liu et al., 2003a). The cross-linking modification tends to increase chain packing/stiffness and inhibits the

intra-segmental and inter-segmental mobility (by forming cross-linked networks and hydrogen bonds), resulting in higher gas selectivity (Xiao et al., 2007).

Thus, by fabricating cross-linked polyimide membrane, membrane with an improvement in chemical and plasticization resistance and simultaneously with higher gas selectivity can be obtained. Cross-linking can be achieved by thermal, ion beam and UV irradiation treatment, or by reactions with added chemicals (Kim et al., 2006b; Wind et al., 2003a). Currently, the chemical cross-linking approach seems to be an important method and has been widely studied by many researchers (Wind et al., 2003a; Shao et al., 2008; Tin et al., 2003). These approaches seem to be promising because not only they enhance the gas separation performance but also possess the advantages such as the simplicity of treatment and the availability to all kinds of aromatic polyimides (Tin et al., 2003, Shao et al., 2005a).

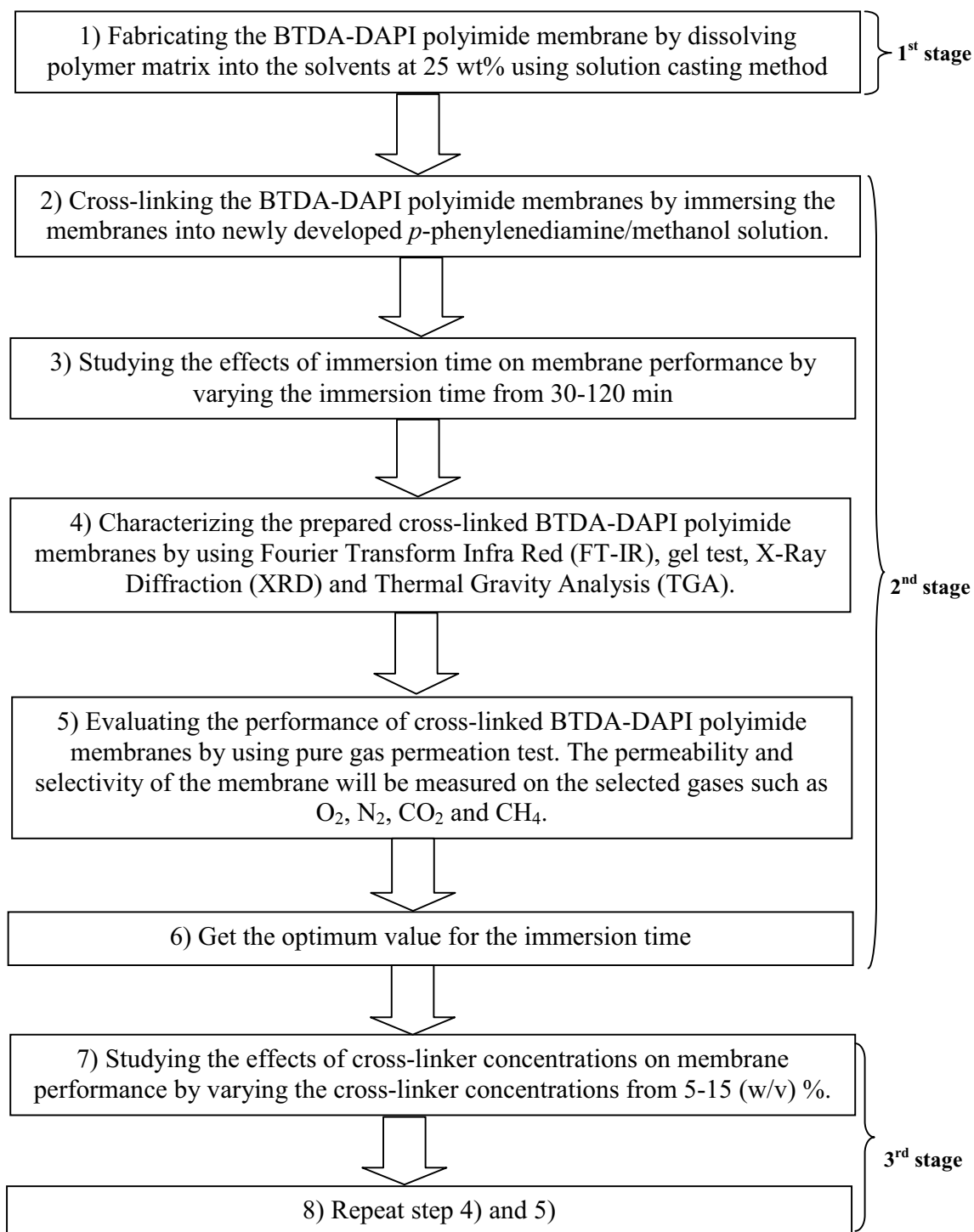
### **1.3 Objectives of the Study**

Based on the problem statement, the objectives of this study are:

- 1) To develop a new cross-linked BTDA-DAPI polyimide membrane for gas separation
- 2) To investigate the effects of cross-linker concentration and immersion time on the degree of cross-linking.
- 3) To investigate the effects of cross-linking on the physicochemical properties of the membrane their separation performance.

## 1.4 Scopes of the Study

In order to achieve the above mentioned objectives, the following scopes of work have been drawn:





## **1.5 Thesis Outline**

The body of the thesis was divided into six main chapters. Chapter one presents brief description of the research background, including the problem statement, objectives and scope of the study. Chapter two provides the comprehensive literature review on membrane-based gas separation and their potential modification technique to improve membrane performances. Detailed descriptions of research methodology and characterizations method carried out in this study were then presented in Chapter three. This is subsequently followed by the results and discussion on the effects of applying p-phenylenediamine as cross-linker agents into BTDA-DAPI polyimide membranes for gas separation in Chapter four. Chapter five continued with the discussion on the effects of cross-linker concentrations on polyimide membrane performance. The thesis ends at Chapter six, summarizes the concluding remarks on this study and recommendations for future works.