DESIGN OF MOLECULAR CONFIGURATION

OF POLYIMIDE NANOCOMPOSITE

MEMBRANE FOR CO₂/N₂ SEPARATION

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DESIGN OF MOLECULAR CONFIGURATION OF POLYIMIDE

NANOCOMPOSITE MEMBRANE FOR CO₂/N₂ SEPARATION

by

TAN PENG CHEE

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LIST OF ABBREVIATIONS

6FDA	4,4'-(hexafluoroisopropylidene)diphthalic anhydride
6FpDA	4,4'-(hexafluoroisopropylidene)dianiline
APTES	(3-aminopropyl)triethoxysilane
APTMS	(3-aminopropyl)trimethoxysilane
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
BAFM	α,α-bis(4-amino-3,5-dimethylphenyl)-1-(4'- fluorophenyl)methane
BAPAF	2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane
BAPM	α, α -bis(4-amino-3,5-dimethylphenyl)-1-phenylmethane
BATFM	α, α -bis(4-amino-3,5-dimethylphenyl)-1-(3',4',5'-trifluorophenyl)methane
BDA	Benzidine
BDC	1,4-benzenedicarboxylate
BET	Brunauer-Emmett-Teller
BisP	4,4'-(1,4-phenylenediisopropylidene) bisaniline
BTC	Benzene-1,3,5-tricarboxylate
BTDA	Benzophenone-3,3',4,4'-tetracarboxylic dianhydride
CFC	Chlorofluorocarbon
CNT	Carbon nanotube
COMPASS	Condensed-phase optimized molecular potentials for atomistic simulation studies
CVFF	Consistent-valence forcefield
DABA	3,5-diaminobenzoic acid
DAM	2,4,6-trimethyl- <i>m</i> -phenylenediamine
DAP	2,4-diaminophenol dihydrochloride
DLS	Dynamic light scattering

DMMDA	3,3'-dimethyl-4,4'-diaminodiphenylmethane	
DPPD	3,8-diphenylpyrene-1,2,6,7-tetracarboxylic dianhydride	
DPt	3,8-di(4-tert-butylphenyl)pyrene-1,2,6,7-tetracarboxylic dianhydride	
EDX	Energy dispersive X-ray	
EMT	Hexagonal Faujasite	
FAU	Cubic Faujasite	
FESEM	Field emission scanning electron microscopy	
FFV	Fractional free volume	
GC	Gas chromatograph	
GCMC	Grand canonical Monte Carlo	
GDP	Gross domestic product	
GHG	Greenhouse gases	
GONRs	Graphene oxide nanoribbons	
GPC	Gel permeation chromatography	
HBD	Hydrogen bond donation	
Hmim	2-methylimidazole	
IR	Infrared	
MD	Molecular dynamics	
MFC	Mass flow controller	
<i>m</i> -HAB	4,4'-dihydroxybiphenyl-3,3'-diaminobiphenyl	
MOF	Metal organic framework	
MSD	Mean square displacement	
<i>m</i> -TDA	2,4-toluenediamine	
MWCNT	Multi-walled carbon nanotube	
NMP	1-methyl-2-pyrrolidinone	
NPT	Constant number of particles, pressure and temperature	

NVT	Constant number of particles, volume and temperature
o-BAT	1,4-bis(2-aminophenoxy)triptycene
ODA	4,4'-oxydianiline
ODPA	4,4'-oxydiphthalic anhydride
PAA	Polyamic acid
<i>p</i> -BAT	1,4-bis(4-aminophenoxy)triptycene
PCFF	Polymer-consistent forcefield
PDI	Polydispersity index
<i>p</i> -DMPD	2,5-dimethyl-1,4-phenylenediamine
PEBA	Polyether-block-amide
PEBA 1657	Poly(amide-6-b-ethylene oxide)
PES	Polyethersulfone
PFDAB	2-(perfluorohexyl)ethyl-3,5-diaminobenzoate
<i>p</i> -HAB	3,3'-dihydroxy-4,4'-diaminobiphenyl
PI	Polyimide
PIM	Polymers of intrinsic microporosity
PMDA	Pyromellitic dianhydride
<i>p</i> -PDA	1,4-phenylenediamine
PSf	Polysulfone
SO ₃ H-MCM-41	Sulfonic acid functionalized ordered mesoporous silica spheres
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilica
THF	Tetrahydrofuran
UiO-66	Universitet i Oslo-66
XRD	X-ray diffraction
ZIF	Zeolitic imidazolate framework

LIST OF SYMBOLS

Α	Area of membrane sample	cm^2
а	Slope of mean square displacement versus time plot	Ų/ps
$\alpha_{a/b,B}$	Binary gas selectivity	dimensionless
$\alpha_{a/b,I}$	Ideal selectivity	dimensionless
С	Concentration of ZIF-8 units	mol/cm ³
C_i	Gas concentration in polymer matrix	cm ³ (STP)/cm ³ polymer
C_o	Equilibrium concentration of ZIF-8 units	mol/cm ³
D	Gas diffusivity	cm ² /s
D_o	Pre-factor of diffusivity	cm ² /s
D_s	Diffusion coefficient of solid particle	m ² /s
dp/dt	Permeation rate	cmHg/s
ΔE	Binding energy of membrane system	kcal/mol
ΔG_{v}	Gibbs free energy per unit volume	J/m ³
Δp	Differential pressure	cmHg
E_a	Electron affinity	dimensionless
Ecomplex	Total energy of a membrane system comprising of different components	kcal/mol
E_d	Diffusion activation energy	kcal/mol
$E_{\it individual}$	Energy of individual component present in a particular membrane system	kcal/mol
k	Boltzmann constant	J/K
l	Membrane thickness	cm
l _c	Initial membrane casting thickness	μm
М	Mass of membrane or polyimide chain	g
M_w	Molecular weight	g/mol

Ν	Number of diffusing molecules	dimensionless
η	Viscosity	Pa·s
Ω	Atomic volume	m ³
P_a	Pure gas permeability of gas <i>a</i>	Barrer
P_b	Pure gas permeability of gas <i>b</i>	Barrer
P _{bf}	Pure gas permeability obtained from bubble flow permeation method	Barrer
P _{br}	Pure gas permeability obtained from barometric permeation method	Barrer
P/P_o	Relative pressure	dimensionless
Р	Gas permeance	GPU
\mathcal{P}_{a}	Permeance of gas a	$cm^{3}(STP)/(cm^{2}\cdot s\cdot cmHg)$
р	Operating pressure	bar
p_d	Downstream pressure	Pa
p_i	Sorbent pressure	cmHg
ρ	Membrane density	g/cm ³
R	Universal gas constant	cm ³ ·cmHg/mol·K
r	Radius of diffusing particle	m
r^*	Minimum size to form a stable ZIF-8 nucleus	m
r(0)	Initial position vector of gas molecule	Å
<i>r</i> (<i>t</i>)	Final position vector of gas molecule over time interval <i>t</i> .	Å
S_i	Solubility of gas <i>i</i>	cm ³ (STP)/(cm ³ ·cmHg)
σ	Supersaturation	dimensionless
Т	Temperature	°C or K
T_g	Glass transition temperature	°C
t	Simulation run time	ps
μ	Dipole moment	D

μ_x	Dipole moment in <i>x</i> direction	D
μ_y	Dipole moment in <i>y</i> direction	D
μ_z	Dipole moment in <i>z</i> direction	D
V	Downstream reservoir volume	cm ³
V _{ds}	Volume of dope solution	mL
V_e	Specific volume of sample	cm ³ /g
V_o	Volume occupied by polymer chains	cm ³ /g
V_T	Total membrane volume	μm^3
V_w	Van der Waals volume	cm ³ /g
<i>॑</i> V	Permeate flow rate	cm ³ /s
x _a	Mole fraction of gas a in feed stream	dimensionless
x_b	Mole fraction of gas b in feed stream	dimensionless
Уa	Mole fraction of gas <i>a</i> in permeate stream	dimensionless
y_b	Mole fraction of gas b in permeate stream	dimensionless
γ	Surface energy of ZIF-8 formed	J/m ²

REKA BENTUK KONFIGURASI MOLEKUL MEMBRAN NANOKOMPOSIT POLIIMIDA UNTUK PEMISAHAN CO₂/N₂

ABSTRAK

Aplikasi luas membran poliimida (PI) untuk pemisahan CO₂ perindustrian telah dihadkan oleh keseimbangan intrinsik antara kebolehtelapan dan kememilihan. Sehubungan itu, kajian ini menerokai reka bentuk molekul polimer PI dan pembangunan membran nanokomposit PI/partikel kerangka imidazolat zeolitik-8 (ZIF-8) untuk meningkatkan prestasi pemisahan gas. Secara prinsipnya, berat molekul asid poliamik (PAA) dan PI yang sepadan sangat bergantung pada kereaktifan monomer yang dikawal oleh halangan sterik gantian monomer tetapi bukan sifat electroniknya. Ia juga didapati bahawa perilaku reologi dan berat molekul PAA boleh bertindak sebagai garis panduan untuk menyaring protokol sintesis membran yang sesuai untuk struktur PI tertentu. Khususnya, PAA dengan kelikatan yang tinggi (>81 cP) dan berat molekul yang tinggi (\geq 5.39 Mg/mol) adalah prasyarat untuk membentuk membran PI tanpa kecacatan melalui penuangan larutan PI yang diimidai secara kimia. Ia juga mendapati bahawa kesan kesekerjaan antara konfigurasi atom dan kekutuban monomer harus dipertimbangkan dalam menganalisa pecahan isipadu bebas (FFV) membran PI. Suatu monomer dengan struktur tak sesatah dan kekutuban yang rendah adalah lebih baik untuk mencapai membran PI dengan FFV yang tinggi. Membran 4,4'-(heksafluoroisoproilidena)diftalik anhidrida (6FDA)-2,4,6-trimetil-*m*-fenilen diamina (DAM):asid 3,5-diaminobenzoik (DABA) (3:2) yang menpunyai FFV tinggi pada 0.212 telah menunjukkan prestasi pemisahan yang terbaik antara struktur PI yang dikaji. Ia mempunyai kebolehtelapan CO₂ sebanyak 63 Barrer (0.60 GPU) dan kememilihan CO₂/N₂ setinggi 57 dalam ujian penelapan pada 3 bar. Simulasi dinamika molekul (MD) juga dijalankan untuk meramalkan kelakuan pengangkutan gas membran PI. Sesungguhnya, kebolehharapan model PI yang dibina menggunakan *Materials Studio* telah disahkan kerana kebolehtelapan CO₂ dan N₂ yang diramalkan hanya berbeza daripada keputusan ujikaji dengan faktor 1.86 dan 1.76 masing-masing. Kemudian, ZIF-8 telah diletakkan di atas membran PI yang disokong oleh alumina melalui penyalutan celup untuk menghasilkan membran nanokomposit PI/ZIF-8. Keberkesanan (3-aminopropil)trietoksisilan (APTES) untuk meningkatkan keserasian antara alumina-PI-ZIF-8 telah diramal dengan menggunakan simulasi molekul berdasarkan pengiraan tenaga pengikat. Hasil simulasi juga disahkan selanjutnya dengan ujikaji. Dalam pemisahan gas perduaan, telapan CO_2 dan kememilihan CO_2/N_2 yang optimum adalah 93.47 GPU dan 7.50 dengan penyalutan celup ZIF-8 sebanyak 5 kali. Secara keseluruhan, kajian ini memberikan gambaran asasi tentang peranan reka bentuk molekul dan membran nanokomposit PI/ZIF-8 dalam penyesuaian prestasi pemisahan gas membran. Kajian pada masa hadapan boleh ditumpukan kepada permukaan ZIF-8 pengubahsuaian untuk mengurangkan kecenderungan penggumpalan ZIF-8 dan seterusnya menambahbaik prestasi pemisahan gas membran nanokomposit PI/ZIF-8.

DESIGN OF MOLECULAR CONFIGURATION OF POLYIMIDE NANOCOMPOSITE MEMBRANE FOR CO₂/N₂ SEPARATION

ABSTRACT

The application of polyimide (PI) membrane for industrial carbon dioxide (CO₂) removal has been restricted by its intrinsic trade-off between permeability and selectivity. In view of this, this study explores the molecular design of PI polymer and the development of PI/zeolitic imidazolate framework-8 (ZIF-8) nanocomposite membrane aiming to improve the gas separation performance. Principally, the molecular weight of polyamic acid (PAA) and its corresponding PI depend strongly on the monomer reactivity, which is dominantly controlled by the steric hindrance of monomers' substituent instead of their electronic nature. It was also found that the rheological behavior and molecular weight of PAA could act as a guideline to screen the suitable membrane synthesis protocol for a particular PI structure. Specifically, a PAA with high viscosity (> 81 cP) and high molecular weight (\geq 5.39 Mg/mol) is the prerequisites in forming a defect-free PI membrane via casting of chemically imidized PI solution. It was found in this work that the synergistic effect of both atomic configuration and polarity of monomer needs to be taken into consideration in analyzing the fractional free volume (FFV) of a PI membrane. A monomer with nonplanar structure and low polarity is highly preferable to attain a PI membrane with high FFV. 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)-2,4,6-trimethyl*m*-phenylenediamine (DAM):3,5-diaminobenzoic acid (DABA) (3:2) membrane with a high FFV of 0.212 showed the best separation performance among the PI structures studied. It possessed a CO_2 permeability of 63 Barrer (0.60 GPU) and CO_2/N_2 selectivity of 57 at 3 bar of permeation test. Molecular dynamics (MD) simulation was also performed to predict the gas transport behavior of PI membrane. Indeed, the reliability of the PI model developed using Materials Studio software was validated as the predicted CO₂ and N₂ permeability only differed from the experimental results by a factor of 1.86 and 1.76, respectively. Later, ZIF-8 particles were deposited on top of the alumina-supported PI membrane via dip-coating to produce PI/ZIF-8 nanocomposite membrane. The effectiveness of (3-aminopropyl)-triethoxysilane (APTES) in improving the compatibility between alumina-PI-ZIF-8 was predicted using molecular simulation based on the binding energy. The simulation result was also further verified experimentally. In binary gas separation, an optimum CO₂ permeance and CO₂/N₂ selectivity were found at 93.47 GPU and 7.50, respectively at 5 times of ZIF-8 dip-coating. In overall, this work provides a fundamental insight into the role of molecular design and PI/ZIF-8 nanocomposite membrane in tailoring the membrane gas separation performance. Future research can be focused on the surface modification of ZIF-8 to minimize the tendency of ZIF-8 agglomeration and hence further improve the gas separation performance of PI/ZIF-8 nanocomposite membrane.

CHAPTER ONE

INTRODUCTION

This chapter provides an overview on the research background of this study. First of all, the polyimide (PI) membrane, which is a promising material for carbon dioxide (CO₂) removal, is introduced with highlight on its structural flexibility. In addition, the advancement of nanocomposite membrane for gas separation is briefly discussed. This chapter also emphasizes the problem statement of this work based on the latest development of PI membrane. Subsequently, the research objectives, scope of study and thesis organization are presented.

1.1 Polyimide (PI) Membrane for CO₂ Removal

The remarkable increase of global temperature, generally known as global warming, has alerted the public on the alarmingly increasing emission rate of greenhouse gases (GHG) such as CO₂, methane (CH₄), nitrous oxide and hydrofluorocarbon into the atmosphere (Songolzadeh et al., 2014). In particular, CO₂ is the major contributor of anthropogenic GHG and is responsible for approximately 67 % of the total greenhouse effect (Zhang et al., 2014). Generally, CO₂ emission is mainly originated from the combustion of fossil fuels. The CO₂ concentration in flue gas or exhaust stream varies from as low as 3 mol% to about 45 mol% depending on the type of fossil fuel and the process involved (Songolzadeh et al., 2014, Khalilpour et al., 2015). Without proper implementation of global warming mitigation policies, the global GHG emission is predicted to increase by 25-90 % in 2030 relative to 2000, which is equivalent to CO₂ concentration of 600-1550 ppm in the atmosphere (Leung

et al., 2014). In view of this, an efficient CO_2 removal technology is an immediate necessity.

Among the CO₂ removal technologies available, amine absorption stands as the most mature technology (Tian et al., 2018). However, the regeneration of amine absorbent is an energy intensive process. Besides, the amine absorbent degrades into toxic substances, which are harmful to human health and environment (Leung et al., 2014). Out of these considerations, membrane technology emerges as an attractive alternative for CO₂ removal as it offers process simplicity, lower capital and operating cost, higher energy efficiency and it is also a solvent-free process (Qiu et al., 2013, Heck et al., 2017, Zhang et al., 2017b). Recent research reveals that membrane technology is competitive with other technologies such as amine absorption and pressure swing adsorption for CO₂ removal due to the advancement of material that substantially improves the membrane gas separation performance (Khalilpour et al., 2015).

More recently, aromatic PI, which consists of a rigid backbone, appears to be a promising membrane material and has captured a lot of research interest due to its excellent intrinsic gas separation properties as well as high chemical, thermal and mechanical stability (Tong et al., 2015, Yoshioka et al., 2017). In general, the gas transport across the PI membrane is governed by the solution-diffusion mechanism (Vanherck et al., 2013). Thus, a PI structure with high gas solubility and diffusivity is strongly desirable to attain a membrane with higher gas permeability and selectivity. Fundamentally, the gas solubility is controlled by the condensability of gas penetrant, the interaction between polymer and gas penetrant as well as the free volume in the membrane matrix (Wind et al., 2003, Comesaña-Gandara et al., 2017). Meanwhile, the gas diffusivity is primarily dependent on the polymer packing and the size of gas penetrant (Wind et al., 2003, Comesaña-Gandara et al., 2017). In fact, a PI structure can be derived from various dianhydride-diamine combinations. Owing to the flexibility of PI, structural alteration can be performed easily by manipulating the combinations of dianhydride and diamine monomers in a systematic manner. This allows the improvement of gas solubility and/or gas diffusivity by imparting changes to the properties of the resulting membrane such as free volume and polymer packing. In particular, the incorporation of monomers with bulky group, flexible linkage or specific functional group, for example the carboxylic acid group into the PI backbone are the common practices in the molecular architecture of PI in order to enhance the membrane gas separation performance (Park et al., 2003, Amutha et al., 2015, Shin et al., 2018).

To achieve an improved gas separation performance, a proper selection of monomers is necessary in the molecular design of PI. By integrating different monomers with distinct structure into the PI backbone, an extreme gas separation performance can be resulted. For instance, a PI membrane comprising of 4,4'- (hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 2,4,6-trimethyl-*m*-phenylenediamine (DAM) monomers possessed a high CO₂ permeability of 847 Barrer but low CO₂/CH₄ selectivity of 18 only (Qiu et al., 2013). On the contrary, a high CO₂/CH₄ selectivity of 62.2 but low CO₂ permeability of 12.5 Barrer was observed by replacing the DAM with 3,5-diaminobenzoic acid (DABA) monomer in preparing the PI membrane (Qiu et al., 2013). As different PI structures can result in diverse gas transport properties, a detailed insight into the correlation between the monomer characteristics and membrane properties is of strong interest to maximize the effectiveness of molecular design in screening a PI structure with better gas separation performance.

1.2 Nanocomposite Membrane

Unfortunately, the gas separation performance of PI membrane has generally reached a limit in spite of its continuous improvement due to the nature of permeability-selectivity trade-off (Ordoñez et al., 2010, Shahid et al., 2015). This limitation has barricaded the practical application of PI membrane for industrial gas separation. The development of nanocomposite membrane, which consists of nanoparticles or fillers dispersed in the polymer matrix (Liu et al., 2018b), has shed light on the possibility of pushing the gas separation performance of PI membrane beyond the Robeson's 2008 upper bound plot. By incorporating the fillers with inherently higher gas separation performance than the pristine membrane is achievable (Xu and Chung, 2017). Furthermore, the nanocomposite membrane retains the good processability of polymer matrix (Peydayesh et al., 2017).

In essence, the filler enhances the gas separation efficiency of a nanocomposite membrane via several ways. First of all, the filler with particular size of framework pore can act as a molecular sieve. With the size discrimination ability, the filler favors the transport of the smaller gas penetrant while hindering the passage of other larger components across the membrane (Goh et al., 2011). As a consequence, a nanocomposite membrane with higher gas selectivity can be obtained. Furthermore, a filler with specific surface property is able to promote its interaction with the gas penetrant hence increasing the gas solubility in membrane (Li et al., 2009b). In most of the research, the filler is dispersed uniformly within the polymer matrix. In such case, the existence of filler modifies the polymer packing and hence affecting the gas permeability significantly (Goh et al., 2011).

In spite of the promising separation performance of nanocomposite membrane, the incompatibility between filler and polymer remains the major challenge in synthesizing a defect-free nanocomposite membrane with enhanced gas separation performance (Zhang et al., 2017c, Ilyas et al., 2018). Indeed, polymer-filler incompatibility leads to the agglomeration of fillers and promotes the formation of interfacial defects (Ismail et al., 2009, Ordoñez et al., 2010). Such defects unavoidably lower the separation efficiency of the resulting nanocomposite membrane.

In view of the polymer-filler incompatibility concern, zeolitic imidazolate framework-8 (ZIF-8) has gained much research interest nowadays for the synthesis of nanocomposite membrane. In particular, ZIF-8 consists of both organic ligand and inorganic ion. The organic ligand of ZIF-8 plays a vital role in promoting its interaction with the polymer, thus, minimizing the interfacial defects (Ordoñez et al., 2010). Besides, ZIF-8 possesses a framework pore of 3.4 Å (Kida et al., 2013). Its pore size, which is in close proximity to the kinetic diameter of common gases, makes it ideal for gas separation especially for the separation of CO_2 (3.3 Å) from other gases such as N_2 (3.64 Å) and CH_4 (3.8 Å) based on the size discrimination (Li et al., 2008b). Owing to the high porosity, ZIF-8 also exhibits a high CO_2 adsorption capacity (Venna and Carreon, 2009). The role of ZIF-8 in improving the gas separation performance of a nanocomposite membrane will be further discussed in Chapter two.

1.3 Problem Statement

Generally, PI membrane has superior gas separation performance than the conventional polysulfone (PSf) and cellulose acetate membranes. Besides, the membrane morphology and gas separation performance of most polymeric membranes are typically controlled by varying the membrane formulation such as polymer concentration and phase inversion process. One of the specialties of PI membrane is its structural flexibility. This indicates that the gas transport properties of PI membrane can be tailored effectively starting from its structure by selecting different monomer combinations to produce PI membrane with specific desired properties. As of today, thousands of PI structures are available due to the diversity of dianhydride and diamine monomers. This makes the selection of appropriate monomer for PI synthesis a very difficult task. With a detailed understanding on the relationship between PI properties and monomer chemistry, particularly on the aspect of monomer electronic nature (nucleophilicity and electrophilicity), polarity and atomic configuration, it is easier and more efficient in designing the molecular structure of a PI polymer. Each specific PI structure with desirable gas transport properties can then be used to produce PI membrane for various industrial gas separation applications.

Principally, the procedure involved in synthesizing a membrane is tedious and time-consuming. Worse still, owing to the existence of thousands of PI combinations, it is technically impossible to have a universal synthesis protocol of PI membrane attributed to their different processability. Generally, PI membrane can be synthesized using different approaches such as casting of chemically imidized PI solution or thermal imidization of polyamic acid (PAA). However, up to now, no proper guideline on the selection of PI membrane synthesis protocol is available in the scientific literature. Since PAA acts as the precursor of PI, its rheological behavior and molecular weight can be correlated to the membrane synthesis protocol to provide a simple means in the selection of membrane synthesis protocol.

Up to this point, the overall process of PI molecular design, including the PI synthesis, membrane fabrication and gas separation performance evaluation, is laborious and involves a lot of trial and error. Moreover, the success of obtaining a

new PI structure with excellent gas transport behavior is not guaranteed in spite of the high chemical and time consumption. Hence, it is of interest to predict the gas transport behavior such as the gas diffusivity and solubility of a PI structure beforehand via the aid of simulation. With the establishment of a reliable PI model, the materials and time-consuming experimental work can be minimized in future. Instead, only the PI structure that demonstrates a promising gas separation performance in simulation is synthesized and analyzed experimentally.

After obtaining an optimized PI structure from the molecular design study, it is highly recommended to incorporate fillers into the PI matrix to produce a PI nanocomposite membrane with better gas separation performance than the pristine PI membrane (Shahid and Nijmeijer, 2017, Ahmad et al., 2018a). However, the synthesis of a defect-free nanocomposite membrane is usually constrained by the incompatibility between the organic polymer and inorganic filler such as zeolite. The polymer-filler incompatibility always causes the formation of interfacial defect and particle agglomeration, which eventually lowers the membrane gas separation performance. In view of this, ZIF-8 particle is more beneficial as it consists of organic ligand in its structure, which enhances its compatibility with the organic polymer. The gas separation performance of a nanocomposite membrane is significantly affected by its synthesis conditions. For instance, high loading of fillers in polymer matrix usually leads to particle agglomeration and thus lowers the membrane gas separation performance. Meanwhile, a thicker dense membrane layer is expected to possess higher diffusion resistance for gas penetrant to transport across the membrane. Thus far, the synergistic effect of filler (in this work, ZIF-8 loading is referred) and thickness of membrane (PI base layer) on the gas transport properties of PI/ZIF-8 nanocomposite membrane is still unclear and hence requires a systematic investigation.

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1.4 Research Objectives

The ultimate aim of this project is to develop a PI/ZIF-8 nanocomposite membrane for CO_2 removal. The research objectives for this study are as follows:

- 1. To investigate the correlation between the monomer chemistry and PI property via the molecular design of PI polymer.
- To evaluate the gas separation performance of structurally distinct PI membranes synthesized through chemical and thermal imidization approaches.
- To predict the sorption and diffusion behavior of gas molecules across the PI membrane using molecular dynamics (MD) simulation.
- 4. To develop a PI/ZIF-8 nanocomposite membrane with improved fillerpolymer compatibility for CO_2/N_2 binary gas separation using dip-coating technique.

1.5 Scope of Study

The molecular design of PI is performed by incorporating different dianhydrides and diamines with various bridging groups or substituents into the PI backbone. 6FDA, benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) and 4,4'-oxydiphthalic anhydride (ODPA), which consists of -C(CF₃)₂-, -C=O-, and -O-bridging group, respectively, are chosen as the dianhydride monomers for this study. Similarly, several diamines with different chemical structure such as 4,4'- (hexafluoroisopropylidene)dianiline (6FpDA, -C(CF₃)₂-), DAM (-CH₃) and DABA (-COOH) are selected to be incorporated into the PI backbone. In total, four monomer combinations are formulated in this work, namely 6FDA-DAM:DABA (3:2), 6FDA-6FpDA:DABA (3:2), BTDA-DAM:DABA (3:2) and ODPA-6FpDA:DABA (3:2).

Each monomer combination consists of one dianhydride and two diamines, in which the molar ratio between the two diamines is 3:2. The PI is formed via a two-step reaction: polymerization of dianhydride and diamines to produce PAA followed by chemical imidization to convert the PAA to PI. The properties of PAA and PI are characterized by viscosity measurement, gel permeation chromatography (GPC) as well as attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and correlated to the monomer chemistry.

Thereafter, the PI membrane with different structures are formed using two synthesis protocols, which are the casting of 10 wt.% chemically imidized PI solution and thermal imidization of the casted PAA layer. The formation of defect-free PI membrane via the two methods is correlated to the properties of PAA precursor as well as the monomer structure. Single gas permeation test of CO₂ and N₂ is carried out from 1 bar to 6 bar in order to assess the gas separation performance of the four PI membranes in terms of the permeability and selectivity. The gas separation performance of different PI membranes is interpreted from the aspect of monomer dipole moment, membrane density and fractional free volume (FFV). Subsequently, the PI structure with the best separation performance is subjected to FFV tuning by simple thickness adjustment of the casted membrane from 400 µm to 1300 µm.

With the aid of Materials Studio software, the gas transport properties of PI membrane are predicted using MD simulation. First of all, the reliability of small model system is validated by evaluating the simulated density. High-temperature Arrhenius extrapolation approach is adopted for predicting the gas diffusivity. In this approach, a series of high temperature simulations (900 K to 1200 K) are performed to obtain the gas diffusivity at high temperatures. Afterward, the gas diffusivity at 298 K is estimated using Arrhenius equation of diffusivity by extrapolating the linear plot

between natural logarithm of diffusivity, $\ln [D(T)]$ and reciprocal temperature, 1/T. Meanwhile, the gas solubility in PI matrix is predicted using the Sorption module of Materials Studio software. The simulated gas permeability is then obtained by the multiplication of the simulated diffusivity and solubility and is compared to that of the experimental result.

Lastly, PI/ZIF-8 nanocomposite membranes are fabricated by incorporating ZIF-8 particles into 6FDA-DAM:DABA (3:2) PI. The effects of solvent (deionized water and methanol), concentration of 2-methylimidazole linker, Hmim (Zn:Hmim equals to 1:8 and 1:70) and reaction time (1 min to 4 min) on the size of ZIF-8 particles are investigated. Besides, the stability of ZIF-8 particles over the storage period is evaluated. The ZIF-8 particles are also characterized using dynamic light scattering (DLS), X-ray diffraction (XRD), nitrogen adsorption-desorption analysis and transmission electron microscopy (TEM). Thereafter, ZIF-8 particles with preferable size are then chosen to be deposited above the PI layer to produce a PI/ZIF-8 nanocomposite membranes. As polymer-filler incompatibility is one of the major concerns in forming a defect-free PI/ZIF-8 nanocomposite membrane, APTES is used as a linker to promote the interaction between alumina-PI-ZIF-8. The effectiveness of APTES as a linker in improving the adhesion between alumina-PI-ZIF-8 is predicted by calculating the binding energy of the membrane system via molecular simulation. The simulation results are further verified experimentally. The morphology of the PI/ZIF-8 nanocomposite membrane is observed using field emission scanning electron microscopy (FESEM) coupled with energy dispersive X-ray (EDX) spectroscopy. Besides, the binary gas separation performance of PI/ZIF-8 nanocomposite membrane with different PI loadings (3 and 3+2 layers), ZIF-8 loadings (2, 5 and 7 layers) and

ZIF-8 types (self-synthesized and commercial) is evaluated using two gas mixtures with composition of $80:20 \text{ CO}_2/\text{N}_2$ and $50:50 \text{ CO}_2/\text{N}_2$ at feed pressure of 6 bar.

1.6 Thesis Organization

This thesis is organized into five chapters. Chapter one provides an overview on the research background of this study. The problem statement is outlined based on the recent development of PI membrane for CO_2 removal. Thereafter, research objectives and scope of study are formulated to address the problem statement. Lastly, the organization of this thesis is summarized to provide a brief description of its content.

A comprehensive review on the current project is provided in Chapter two. The adverse impacts of increasing CO_2 emission into the atmosphere are first discussed. The potential of PI membrane for CO_2 removal and its permeability-selectivity tradeoff limitation are also highlighted. Subsequently, the past research findings on the molecular design of PI are summarized to understand the effect of structural alteration on the gas transport properties of the resulting membrane. In addition, the synthesis routes available for PI membrane are outlined. In view of the advancement of computational modeling, Chapter two also reviews the use of MD simulation in predicting the membrane is discussed along with the major concern of polymer-filler incompatibility. Chapter two ends with the research gaps that highlight the importance of this project.

Chapter three describes the materials and methodology of this research. All materials and chemicals used throughout the project are listed in detail. A research flow diagram is provided to illustrate the overview of experimental works. Besides, the detailed description of experimental procedure for PI synthesis, membrane fabrication, characterization and permeation test are presented clearly. Furthermore, this chapter also describes the simulation procedure involved in the model construction as well as the prediction of gas solubility and diffusivity.

The core findings of this study are reported in Chapter four. All results and discussion are presented in four sections according to the research objectives outlined in Section 1.4. This chapter starts with the synthesis and characterization of PI polymer with different structures by incorporating distinct dianhydride and diamine monomers into the PI backbone. Next, the success of membrane formation via either the casting of chemically imidized PI solution or the thermal imidization of PAA precursor is correlated to the rheological behavior and molecular weight of PAA. Meanwhile, the gas separation performance of PI membrane with different structures is evaluated in terms of the permeability and selectivity. Subsequently, the reliability of the PI model constructed using MD simulation is validated by comparing the simulated gas permeability to that of the experimental result. The last section of this chapter reveals the formation of PI/ZIF-8 nanocomposite membranes along with their binary gas separation performance. In addition, the stability of membrane system at different PI and ZIF-8 loadings is assessed via the prediction of binding energy using molecular simulation.

Lastly, Chapter five summarizes the important findings of this study in correspondence to the research objectives in Section 1.4. Based on the current research findings, several recommendations are proposed for future research work.

CHAPTER TWO

LITERATURE REVIEW

This chapter reviews the literature related to the current project. In section 2.1, the potential and limitation of PI membrane for CO₂ removal in mitigating global warming are discussed. Next, the past researches on the molecular design of PI in improving the membrane gas separation performance are summarized in Section 2.2. Two common synthesis protocols of PI membrane are then presented in Section 2.3. Meanwhile, Section 2.4 discusses the conditions required for the construction of a reliable polymer model as well as the gas transport properties prediction of PI membrane via MD simulation. The development of nanocomposite membrane is reviewed in Section 2.5 with emphasis on the incompatibility issue between polymer and filler. Lastly, the research gaps are also highlighted.

2.1 Membrane Technology for CO₂ Removal

The current section discusses the severe impact of global warming as well as the emergence of membrane technology for CO_2 removal in mitigating global warming. Specifically, the potential of PI membrane for CO_2 removal is highlighted along with its limitation.

2.1.1 Concern of Global Warming

Global warming has attracted an unprecedented attention particularly on the notably escalating rate of CO_2 emission to the atmosphere over the past century. CO_2 , as one of the main GHGs, is capable of trapping heat within the atmosphere and hence leading to severe greenhouse effect and unpredictable climate change. Owing to the

rapid growth of population, urbanization and industrial development, intensive exploitation of fossil fuels has inevitably contributed to huge amount of CO₂ emission (Dai et al., 2012, Scholes et al., 2012, Jiang et al., 2013, Ramírez-Santos et al., 2017, Wang et al., 2019). It has been reported that the CO₂ emission increases significantly from 9.43 Gton C (1 Gton C equal to 1 million metrics tons of carbon) in 1961 to 34.65 Gton C in 2011 (Shuai et al., 2017). As of today, the CO₂ level in air has exceeded 400 ppm as compared to 280 ppm during pre-industrial time (Akhshik et al., 2018, Chen et al., 2018).

In essence, the adverse effects of global warming can be evaluated from the perspective of environment, human well-being and economy. According to the report of Intergovernmental Panel on Climate Change, the global temperature is predicted to increase by 1.1-6.4 °C in 2100 (Solomon et al., 2007). Meanwhile, 0.18-0.59 m of sea level rise is also projected (Solomon et al., 2007). Both changes will inevitably disrupt the equilibrium of ecosystem and cause the loss of biodiversity. The global food supply will also be affected by the reduction of crop yield under the abrupt increment of global temperature (Zhao et al., 2017). In addition, the United Nations Office for Disaster Risk Reduction reported that the extreme climate change has caused the death of 600,000 people and injured 4.1 billion people over the last two decades (Shuai et al., 2017). From the economic aspect, it is anticipated that the annual Gross Domestic Product (GDP) growth, an indicator to gauge the economic health of a country, of developing countries will reduce by 10 % by 2100 as a result of climate change (Zoundi, 2017).

The severe impact of global warming has raised the awareness on the reduction of CO_2 emission worldwide. In this context, Malaysia has participated actively in intergovernmental cooperation on reduction of CO_2 emission. In particular,

Malaysia joined the United Nations Climate Change Summit in 2009 where Malaysia pledged to reduce the CO₂ emission by 40 % in 2020 relative to 2005 (Rahim and Raman, 2017). Malaysia also participated in the Paris Agreement 2016 that has ultimate aim to control the global temperature rise within 1.5 °C since pre-industrial time (Masson-Delmotte et al., 2018, Gambhir et al., 2019). To achieve this, the global CO₂ emission needs to be reduced by 45 % from 2010 to 2030. Moreover, it is preferable that a net zero CO₂ emission can be achieved by 2050 (Masson-Delmotte et al., 2018). Unfortunately, up to 2015, the increment of global temperature has reached 0.93 °C due to human activities (Millar et al., 2017). The tense situation has urged the need of an efficient CO₂ removal technology in order to mitigate the global warming effectively.

2.1.2 Potential of PI Membrane for CO₂ Removal

The success of membrane technology for CO₂ separation strongly hinges on the development of new membrane materials with excellent gas transport properties. Among the thousands of membrane materials, PI has stood out as an attractive candidate. Relative to the conventional PSf and cellulose acetate membranes, PI membrane generally demonstrates superior gas separation properties as summarized in Table 2.1. Besides, PI possesses high thermal stability, a feature essential for industrial CO₂ removal. The aromatic structure in the PI backbone (Figure 2.1) contributes strongly to the PI chain rigidity, which increases its glass transition temperature, T_g (Vanherck et al., 2013). Since CO₂ is highly soluble and tends to plasticize a polymeric membrane (Qiu et al., 2011), PI with higher T_g or stiffer chain is beneficial for CO₂ separation as it helps to avoid the glassy-rubbery transformation of the membrane under high CO₂ concentration. Such a glassy-rubbery transformation causes a drastic loss in the membrane selectivity and hence deteriorates the membrane gas separation performance (Wind et al., 2002, Qiu et al., 2011). Generally, the T_g of a PI membrane ranges from 280 to 400 °C (Vanherck et al., 2013). In view of this, PI membrane is highly preferable for industrial CO₂ removal as the industrial processes typically operate at high temperature. Since a gas separation membrane should be able to withstand high pressure and cope with aggressive feed streams, the excellent mechanical strength and chemical resistance offered by the PI membrane (Kratochvil and Koros, 2008, Tong et al., 2015) further affirm its capability for industrial CO₂ removal.

Polymeric	CO ₂ permeability	Ideal CO ₂ /N ₂	Reference
membrane	(Barrer)	selectivity	
PSf	5.6	24	Zhu et al. (2018)
PSf	6.16	12.39	Tavasoli et al. (2018)
Cellulose acetate	2	22	Sanaeepur et al. (2016)
Cellulose acetate	15	10	Mubashir et al. (2018)
PI	134	23	Park et al. (2014b)
PI	125.4	22.8	Kim et al. (2018)

Table 2.1: Comparison between the gas separation performance of PI membranes and conventional membranes.



Imide group

Figure 2.1: General structure of aromatic PI.

The industrial application of PI membrane has been pioneered by Du Pont Co. (USA) in 1962, in which the PI membrane was used for the separation of helium from natural gas (Xiao et al., 2009, Chen et al., 2015). Later in 1986, Ube Industries (Japan) launched an ammonia production pilot plant that utilized an asymmetric PI hollow fiber membrane for the recovery of hydrogen gas from the synthesis gas (Ohya et al., 1996). In the production of natural gas, PI membrane is also widely used in the separation of CO_2 from CH₄ to obtain a fuel gas with increased calorific value. For example, Ube PI membrane has been adopted in the CO_2 separation from a landfill gas consisting of mainly CO_2 and CH₄ (Rautenbach and Welsch, 1993, Ohya et al., 1996). The implementation of PI membrane in the pilot plant is illustrated in Figure 2.2.



Figure 2.2: Implementation of PI membrane in separation of CO_2 from CH_4 (Rautenbach and Welsch, 1993).

The landfill gas with a flow rate of $200 \text{ m}^3(\text{STP})/\text{h}$ was first fed into adsorbers to remove trace components such as H₂S and chlorofluorocarbon (CFC) (Figure 2.2). The outlet gas was then further purified by five Ube hollow fiber PI membranes (total membrane area of 700 m²) to produce natural gas with CH₄ concentration of approximately 90 vol%. Meanwhile, UOP LLC (USA) had patented a PI membrane for CO_2/CH_4 separation. Indeed, the PI membrane achieved CO_2 permeability of 50 Barrer and CO_2/CH_4 selectivity of 15 at 50 °C and 8 bar (Liu et al., 2013). The implementation of PI membrane by Du Pont Co., Ube Industries and UOP LLC for gas separation thus further justifies its potential for industrial CO_2 removal.

2.1.3 Permeability-Selectivity Trade-Off of PI Membrane

In principle, a gas separation membrane should acquire both high permeability and high selectivity in order to reduce the membrane area requirement and to ensure high purity of the separated gas streams (Ayala et al., 2003). However, the permeability and selectivity performance of a polymeric membrane are contradictive by nature. As demonstrated by the Robeson upper bound plot (Figure 2.3), there is always a trade-off between permeability and selectivity, i.e., a high selectivity membrane concomitantly possesses low permeability and vice versa (Robeson, 2008). This trade-off phenomenon can be explained by the gas transport process across the polymeric membrane. For instance, a densely packed membrane with smaller size of free volumes offers less diffusion pathways for the gas penetrants. At the same time, the free volumes of smaller size act as molecular sieves to restrain the transport of larger gas molecules across the membrane. Therefore, membrane selectivity is greatly improved with the sacrifice of membrane permeability.



Figure 2.3: Robeson plot showing the permeability-selectivity trade-off of a polymeric membrane.

The permeability-selectivity trade-off is one of the major concerns that restricts the widespread application of PI membrane for industrial CO₂ removal. Substantial research efforts have been directed at surpassing this upper bound limit in order to produce a PI membrane with separation performance in the commercially attractive region as illustrated in Figure 2.3. The unsatisfactory separation efficiency of PI membrane has motivated extensive research on enhancing the gas selectivity and the membrane permeability. Several methods have been proposed to improve the gas separation performance of a PI membrane including polymer blending (Chatzidaki et al., 2007, Hosseini et al., 2008, Shahid and Nijmeijer, 2017, Escorial et al., 2018), embedding nanoparticles into the polymer matrix (Li et al., 2009a, Dorosti et al., 2011, Peydayesh et al., 2017, Liu et al., 2018b) and molecular design of PI (Hsiao and Chen, 2002, Saeed and Zhan, 2006, Tong et al., 2015, Zhang et al., 2017a, Sulub-Sulub et al., 2018). This study focused on the modification of PI backbone structure and the integration of filler into the PI matrix to produce a PI membrane with enhanced gas separation performance.

2.2 Molecular Design of PI

Generally, the gas separation performance of a polymeric membrane depends inherently on the polymer chemical structure (Qiu et al., 2013, Oral et al., 2014, Pakizeh and Hokmabadi, 2017). Hence, molecular design of PI is the simplest and most facile method for the tuning of PI membrane gas transport properties. Structural flexibility is one of the most interesting features of PI. In general, PI is synthesized from the reaction between dianhydride and diamine monomers. Owing to the diversity of monomers' chemical structure, a wide variety of PIs with different physical properties and chemical characteristics can be obtained by varying the monomer combination (Xiao et al., 2009). With proper structural alteration, it is hence possible to produce a PI membrane with better gas separation performance that surpasses the Robeson upper bound plot. In this section, the structural modification of PI in past researches and their correlation with the PI properties as well as the gas separation performance are highlighted. Table 2.2 shows the structure of the monomers discussed.

Fundamentally, any structural alteration that inhibits effective polymer packing and chain mobility tends to increase the gas permeability without significant loss of selectivity (Coleman and Koros, 1990). In view of this, fluorinated PI with $-C(CF_3)_2$ - linkage such as those containing 6FDA and 6FpDA monomers, gains much research interest compared to other categories of PI (Abdulhamid et al., 2017, Ahmad et al., 2018b, Jusoh et al., 2018). In particular, the bulky $-C(CF_3)_2$ - groups in the PI backbone tend to disrupt the polymer packing yielding a membrane with high FFV and thus high gas permeability (Cui et al., 2011, Chua et al., 2014). Despite the great improvement of gas permeability, the membrane selectivity is not significantly compromised as the introduction of $-C(CF_3)_2$ - linkage also leads to stiffer PI chains due to the restricted torsional motion of the neighboring phenyl rings (Qiu et al., 2011,

Chua et al., 2014).

Table 2.2: Structure of the commonly used monomers (Tanaka et al., 1992a, Gao and Lu, 1995, Kim et al., 2000, Park et al., 2003, Tong et al., 2015, Liu et al., 2016, Weidman et al., 2017, Shin et al., 2018, Sulub-Sulub et al., 2018).

Monomer		Structure
6FDA	4,4'-(hexafluoroisopropylidene) diphthalic anhydride	
6FpDA	4,4'-(hexafluoroisopropylidene) dianiline	H_2N H_2N H_2N H_2N H_2N H_2N H_2 H_2N
BAFM	α, α-bis(4-amino-3,5- dimethylphenyl)-1-(4'- fluorophenyl)methane	H_3C H_2N CH_3 H_3C CH_3 H_3C CH_3 H_3C CH_3 H_3C
BAPAF	2,2-bis(3-amino-4- hydroxyphenyl)hexafluoropropane	H ₂ N HO C C C C F ₃ C NH ₂ OH
BAPM	α,α-bis(4-amino-3,5- dimethylphenyl)-1-phenylmethane	H ₃ C H ₂ N H ₃ C H ₃ C H ₃ C CH ₃ CH ₃
BATFM	α,α-bis(4-amino-3,5-dimethyl phenyl)-1-(3',4',5'- trifluorophenyl)methane	H_3C H_2N CH_3 H_3C F F CH_3 H_3C H_3C CH_3

Table 2.2: Continued.

Monomer		Structure	
BDA	Benzidine	H ₂ N-O-NH ₂	
DABA	3,5-diaminobenzoic acid	H ₂ N NH ₂	
DAM	2,4,6-trimethyl- <i>m</i> -phenylenediamine	H ₂ N H ₃ C CH ₃ NH ₂ CH ₃	
DAP	2,4-diaminophenol dihydrochloride	H ₂ N HO •2HCl	
DPt	3,8-di(4-tert-butylphenyl)pyrene- 1,2,6,7-tetracarboxylic dianhydride		
<i>m</i> -HAB	4,4'-dihydroxybiphenyl-3,3'- diaminobiphenyl	H ₂ N HO OH NH ₂	
<i>m</i> -TDA	2,4-toluenediamine	H ₂ N CH ₃ NH ₂	

Table 2.2: Continued.

Monomer		Structure
o-BAT	1,4-bis(2-aminophenoxy) triptycene	H ₂ N NH ₂
ODA	4,4'-oxydianiline	H_2N NH_2
<i>р</i> -ВАТ	1,4-bis(4-aminophenoxy) triptycene	H ₂ N-O-O-O-NH ₂
<i>p</i> -DMPD	2,5-dimethyl-1,4- phenylenediamine	H ₂ N H ₃ C
p-HAB	3,3'-dihydroxy-4,4'- diaminobiphenyl	H ₂ N - NH ₂ HO OH
PFDAB	2-(perfluorohexyl)ethyl-3,5- diaminobenzoate	H ₂ N NH ₂ NH ₂ O ^C OCH ₂ CH ₂ C ₆ F ₁₃
PMDA	Pyromellitic dianhydride	
p-PDA	1,4-phenylenediamine	

The gas transport properties of a series of fluorinated and non-fluorinated PI membranes were reported by Tanaka et al. (1992a). The $-C(CF_3)_{2-}$ groups were incorporated into the PI backbone via the introduction of 6FDA or 6FpDA (Table 2.2).

It was found that the PI membrane with higher fluorine content had an inhibited chain packing and higher gas permeability. For example, the CO₂ permeability of 6FDA-ODA membrane (fluorine content = 14×10^{-3} mol/cm³) was 4.7 times higher than that of PMDA-ODA membrane (fluorine content = 0 mol/cm³). When the fluorine content of PI membrane was further increased by substituting ODA with 6FpDA, the 6FDA-6FpDA membrane (fluorine content = 24×10^{-3} mol/cm³) showed an even higher CO₂ permeability (207 % increment) than the 6FDA-ODA membrane. It was worth noting that with such a huge increment of permeability, only 22% reduction in CO₂/CH₄ selectivity was observed.

Besides the commonly reported $-C(CF_3)_2$ - group-containing PI, Kim et al. (2000) introduced another PI with fluorinated alkyl side group by incorporating a fluorinated diamine, namely PFDAB (see Table 2.2), into the PI backbone. As the fluorinated alkyl side group reduced the molecular interaction between PI chains, a PI membrane with increased FFV was obtained. Hence, the PFDAB-containing PI membrane has achieved a higher CO₂ permeability compared to the non-fluorinated PI membrane. Similarly, only slight selectivity loss was noticed.

Apart from the popularly researched fluorinated PI, the effect of bulky methyl substituent on gas permeability and selectivity has also been investigated. Shin et al. (2018) synthesized a series of PIs containing various methyl-substituted diamines. It was reported that the bulky methyl group inhibited the PI chain packing effectively. Hence, the FFV of the resulting PI membrane increased with the number of methyl substituents in diamine structure, i.e., *p*-DMPD > *m*-TDA > *p*-PDA (Table 2.2). Unsurprisingly, the CO₂ permeability of the *p*-DMPD-containing PI membrane was 3 and 12 times higher than the *m*-TDA- and *p*-PDA-containing PI membranes respectively (Shin et al., 2018). Similarly, monomers containing other bulky groups