Tröger's Base Ladder Polymer for Membrane-Based Hydrocarbon Separation

Thesis by
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ABSTRACT

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The use of polymeric membranes for natural gas separation has rapidly increased during the past three decades, particularly for carbon dioxide separation from natural gas. Another valuable application is the separation of heavy hydrocarbons from methane (fuel gas conditioning), more importantly for remote area and off-shore applications. A new potential polymeric membrane that might be utilized for natural gas separations is a Tröger’s base ladder polymer (PIM-Trip-TB-2). This glassy polymeric membrane was synthesized by the polymerization reaction of 9, 10-dimethyl-2,6 (7) diaminotriptycene with dimethoxymethane. In this research, the polymer was selected due to its high surface area and highly interconnected microporous structure. Sorption isotherms of nitrogen (N₂), oxygen (O₂), methane (CH₄), carbon dioxide (CO₂), ethane (C₂H₆), propane (C₃H₈), and n-butane (n-C₄H₁₀) were measured at 35 °C over a range of pressures using a Hiden Intelligent Gravimetric Analyzer, IGA. The more condensable gases (C₂H₆, CO₂, C₃H₈, and n-C₄H₁₀) showed high solubility due to their high affinity to the polymer matrix. The permeation coefficients were determined for various gases at 35 °C and pressure difference of 5 bar via the constant-pressure/variable-volume method. The PIM-Trip-TB-2 film exhibited high performance for several high-impact applications, such as O₂/N₂, H₂/N₂ and H₂/CH₄. Also, physical aging for several gases was examined by measuring the permeability coefficients at different periods of time. Moreover, a
series of mixed-gas permeation tests was performed using 2 vol.% \( n-C_4H_{10}/98 \text{ vol.}\% \) \( \text{CH}_4 \) and the results showed similar transport characteristics to other microporous polymers with pores of less than 2 nm. The work performed in this research suggested that PIM-Trip-TB-2 is suitable for the separation of: (i) higher hydrocarbons from methane and (ii) small, non-condensable gases such as \( \text{O}_2/\text{N}_2 \) and \( \text{H}_2/\text{CH}_4 \).
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Chapter 1

Introduction

Global demand for energy is rising. Therefore, it is worth looking for alternative energy sources that satisfy the demand and reduce the environmental impacts like global greenhouse emissions (GHG). The required source should produce sufficient amount of high quality energy, viable economically and has environmental sustainability. One of the crucial components of the global energy supply that has fulfilled the mentioned requirement is natural gas.

Other than natural gas primary importance as a source of energy, it is also a raw material for petrochemical industry feed stock. Many researches have been considering natural gas as a potential raw material for other products such as high purity hydrogen and syngas because of the presence of high methane content in natural gas.

Even though natural gas is mainly considered as a clean fuel relative to other fossil fuels, natural gas extracted from reservoirs deposits usually is not clean and free of impurities. It consists mostly of methane as the main component but it also constitutes of considerable amounts of heavy and light hydrocarbons as well as other impurities like N₂, CO₂, H₂S, He, etc. [1]. As a result, the contaminants must be removed from natural gas to meet the standard specification of pipelines quality as a consumer fuel, control heating value, minimize equipment and pipelines corrosion and also overcome process bottle necks.
1.1 Consumption of Natural Gas

Bearing in mind recent green technology requirements in endorsing low-and zero emission through the sustainable use of available natural energy resources, natural gas grow into one of the most used, fastest and premium growing fuel of global energy consumption [2].

According to International Energy Outlook technical report that was released in May 2016, the worldwide consumption of natural gas is projected to increase by 69% from the reference year 2012 (120 trillion cubic feet) to the predicted year 2040 (203 trillion cubic feet). Natural gas remains the primary fuel for power plants and it is used as a source for hydrocarbons, residential and transportation. Figure 1.1 shows the future forecast of natural gas consumption in major sectors in the Middle East [3].

From 2012 to 2050, global consumption of natural gas in industrial sectors is expected to increase by an average of 1.7% annually, and the consumption in electric power generation will rise by 2.2% per year. These two sectors together are responsible for 73% of the total increase in global utilization of natural gas, and about 74% of the total gas consumption in 2040 due to industrial and electricity generation sectors.
1.2 Composition of Natural Gas

Natural gas supplied to the end-users differs significantly in composition than natural gas processed at the well. Treated natural gas mainly contains methane while raw natural gas varies in composition depend on type, location, and depth of the gas reservoir. Most often, natural gas extracted from the well contains methane, ethane, propane, butane, propane and higher hydrocarbons, but it also contains other impurities such as carbon dioxide, oxygen, nitrogen, hydrogen sulfide, helium and traces of other rare gases. Furthermore, the composition of the natural gas coming from the same well will vary with time because light hydrocarbons that existed in a gaseous state in the reservoir pressure will form condensates at atmospheric pressure [4, 5]. Table 1.1 displays the typical composition range of natural gas processed at the well.
Table 1.1 composition of raw natural gas [4, 5].

<table>
<thead>
<tr>
<th>Gas component</th>
<th>Chemical formula</th>
<th>Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH$_4$</td>
<td>70 – 90</td>
</tr>
<tr>
<td>Ethane</td>
<td>C$_2$H$_6$</td>
<td>5 – 20</td>
</tr>
<tr>
<td>Propane</td>
<td>C$_3$H$_8$</td>
<td>2 – 11</td>
</tr>
<tr>
<td>Butane</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>1 – 4</td>
</tr>
<tr>
<td>Pentane$^+$</td>
<td>C$_{5+}$</td>
<td>0 – 2</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO$_2$</td>
<td>0 – 11</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O$_2$</td>
<td>0 – 0.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N$_2$</td>
<td>0 – 11</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H$_2$S</td>
<td>0 – 5</td>
</tr>
<tr>
<td>Other components</td>
<td>He, Ar, Ne, Xe</td>
<td>Traces</td>
</tr>
</tbody>
</table>

Natural gas contains lower energy per unit volume as a gaseous fossil fuel relative to other fossil fuel and emits a low quantity of greenhouse gases. However, natural gas provides higher energy conversion efficiency than other hydrocarbons and it is the most hydrogen-rich fossil fuel [6].

Natural gas exist in three types of wells:

- Oil wells (associated natural gas).
- Condensate wells (associated natural gas).
- Gas wells (non-associated natural gas).
All types of raw natural gas are fed to a purification plant in order to remove ethane, propane, butane, heavier hydrocarbons and other contaminants like carbon dioxide and hydrogen sulfide from methane. Cryogenic distillation and absorption processes are the conventional methods used for gas treatments [7].

Natural gas liquids (NGL), which are hydrocarbons associated with raw natural gas, are valuable by-products of the purification of natural gas. These by-products including ethane, propane, butane and natural gas can be used in various applications such as raw materials for petrochemicals productions [4].

1.3 Conventional Process for Natural Gas Treatment

Before reaching to end users, wellhead natural gas must be processed to meet a pipeline-quality standard. The objectives of treating natural gas are producing sales gas on standards specifications, recovering valuable natural gas liquids (NGL) and meeting required heating value. Table 1.2 shows the specification of pipeline composition for natural gas.

Separation of natural gas is quite complex and includes several process steps. The five main processes for removing natural gas impurities are:

I. Gas oil separator.
II. Condensate removal.
III. Dehydrator.
IV. Sulfur and carbon dioxide removal unit.
V. Nitrogen and mercury extractor.
VI. Fractionator (NGL separation).
Table 1.2 Natural gas composition specification for pipeline

<table>
<thead>
<tr>
<th>Component</th>
<th>Pipeline specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$+</td>
<td>950-1050 Btu / scf dew point -20 °C</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>&lt; 2 mol%</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>&lt; 4 ppm</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>&lt; 120 ppm</td>
</tr>
<tr>
<td>Inert gases (N$_2$, Ar, He, etc.)</td>
<td>&lt; 4 mol%</td>
</tr>
</tbody>
</table>

Figure 1.2 Simplified schematic of a natural gas processing plant [8].

I. Gas Oil Separator

A cylindrical vessel is used to separate crude oil from natural gas by reducing the pressure of the stream. Three phases are formed in the separator where the crude
oil is collected from the bottom and natural gas from the top. The separation occurs simply by gravity.

When wells contain high-pressure natural gas with light crude oil, a low-temperature separator (LTX) is used. In this separator, a pressure differential is utilized to cool down wetted natural gas to be separated from oil and condensate [9].

II. Condensate Removal

A mechanical separator is used to separate condensate from natural gas. In this step two main operations occur: water washing and stabilization of condensate. Water wash is used to remove salts and additives and the requirements of this step depend on the quality of associated water [8].

III. Dehydrator

The water vapor associated with natural gas is removed using dehydration processes to eliminate the formation of hydrates, corrosion problems and controlling the dew point. In this treatment step, an absorption process using ethylene glycol is used to eliminate water vapor from the natural gas stream. Alternatively, an adsorption process could be used for dehydration dry-bed towers filled with solid desiccant like activated alumina [10].

IV. Sulfur and Carbon Dioxide Removal Unit

Natural gas contains sulfur primary as hydrogen sulfide or mercaptans. Natural gas is commonly called sour gas when it contains more than 5.7 milligrams of hydrogen sulfide per cubic meter. Hydrogen sulfide is removed mainly using amine absorption. Moreover, at relatively low concentration, solid desiccants such as iron sponges could be used to remove hydrogen sulfide as well as carbon dioxide.
In the amine absorption process, the sour natural gas is contacted with amine solution in an absorption tower. Currently, two kinds of amine solvent are used to remove sulfur compounds from natural gas: monoethanolamine (MEA) and diethanolamine (DEA). The amine solvent is regenerated by heating to remove absorbed sulfur [9].

V. Nitrogen and Mercury Extractor

Nitrogen is separated from the natural gas using two processes, namely cryogenically separated from natural gas by their boiling point difference and physical absorption process. The regeneration of methane and other hydrocarbons from absorption solvent is done by reducing the pressure. Then, traces amount of inert gas can be removed using pressure swing adsorption [8].

VI. Fractionator (NGL Separation)

Natural gas liquids (NGLs) are removed from the gas stream using mainly two methods that are complicated and with high costs in construction, operation and maintenance [11].

1. Absorption Method

In this method, an absorption tower filled with oil that absorbs NGLs is used. First, the gas is passed through the absorption tower. Then, the solution of absorption oil and hydrocarbons is heated up to recover the hydrocarbons utilizing the difference in boiling points between the absorption oil and hydrocarbons.

2. Cryogenic Expander Process
In this process, a turbo expander process is used to drop the temperature of natural gas to approximately \(-84.4\) °C. The temperature drop allows ethane and heavier hydrocarbon to condense whereas methane remains in gaseous form.

After the removal of NGLs from the main stream, their components are separated using fractionation. The separation process is done by varying the volatility of different hydrocarbons and mainly consists of distillation columns arranged in the following order:

- Deethanizer tower for ethane separation.
- Depropanizer tower for propane separation.
- Debutanizer tower for butane separation.

### 1.4 Natural Gas in the Kingdom

Oil was discovered in Saudi Arabia in 1938 with estimated reserves of approximately 255,000 million barrels that is around 25% of the global oil reserves then. Associated and non-associated natural gas reserves were estimated to be approximately 177 trillion standard cubic feet (SCF) [12]. Nowadays, Saudi Arabia is the fifth natural gas producing country in the world [3]. The typical natural gas composition in the Kingdom is showed in Table 1.3 [12].

Table 1.3 Typical natural gas composition in Saudi Arabia.

<table>
<thead>
<tr>
<th>Gas component</th>
<th>Associated (mol%)</th>
<th>Khuff Gas (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>62.77</td>
<td>69.01</td>
</tr>
<tr>
<td>Ethane</td>
<td>15.07</td>
<td>5.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Propane</td>
<td>6.64</td>
<td>2.30</td>
</tr>
<tr>
<td>Butane</td>
<td>2.40</td>
<td>1.21</td>
</tr>
<tr>
<td>Pentane and heavier</td>
<td>1.12</td>
<td>0.90</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>2.80</td>
<td>5.02</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>9.20</td>
<td>3.46</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-</td>
<td>12.40</td>
</tr>
</tbody>
</table>

The petrochemical industry feedstock availability is strongly linked to the oil production level since most of the natural gas produced in the Kingdom is associated gas.

The Master Gas System (MGS) in Saudi Arabia that was initiated in 1975 with a designed total capacity of 3.6 billion SCFD consists of three parts: gas-oil separating plants, gas plants and fractionation plants. The system added a great value to the national economy because the associated gas was utilized rather than flared. The system component is showed in Figure 1.3.
1.5 Fuel Gas Conditioning

During last three decades, polymeric membranes for gas separation have become important in the natural gas industry. It has been mainly used for the separation of carbon dioxide from natural sour gas with more than 200 installed membrane units. The capacity of some of those units exceeds 100 MMSCFD [13]. The membrane type used for CO$_2$ removal application is most commonly a size-sieving, glassy polymer, cellulose tricatete (CTA). Alternatively, a rubbery membrane could be used to selectively permeate condensable gases like aromatics, C$_3$+ hydrocarbons and water vapor over non-condensable gases like methane, nitrogen, and hydrogen using rubbery polymers. This counterintuitive reverse selectivity of the rubbery polymer has been utilized in the application of C$_3$+ hydrocarbon separation from methane. This technology has been used to condition the fuel gas for gas engine and turbine used in remote areas.
The basic design for membrane system used in condensable vapors separation is shown in Figure 1.4. The natural gas feed is compressed and sent to a condenser. A portion of C_3+ hydrocarbon is collected here as a liquid. The non-condensable gases with the rest of heavy hydrocarbons are then fed to the membrane where the heavy hydrocarbons pass through as permeate and the non-condensable gases rejected as residue. The permeate hydrocarbons are recycled back to compressor [14].

![Figure 1.4 Natural gas treatment flow scheme][1]

Gas Engine Application

The use of natural gas is common for the gas engine and turbine in hydrocarbon processing industry. Generally, natural gas is the only fuel used in the operation of compressors stations in remote areas as well as offshore platforms. Raw natural gas contains higher hydrocarbons that have high heating value and dew point with low octane number. These conditions could severely damage the internal parts of the firing chamber in the gas engines. Because gas engines and turbines drive other machinery, the disruption of their operation can cause substantial revenue loss.

A flow diagram of the membrane system used for raw natural gas fuel conditioning for gas engine is shown in Figure 1.5 [13]. The feed gas is compressed from 100 psig to 1000 psig and then is cooled in an air-cooled aftercooler. The C_{4+}
hydrocarbons are condensed and recovered as liquids. The remaining gas is sent to the membrane unit for further removal of $C_4+$ hydrocarbon to increase the quality of the fuel gas used for combustion in the engine. Table 1.4 shows the composition and condition of typical natural gas feed and conditioned fuel gas.

![Flow diagram of fuel gas conditioning for gas engine](image)

Figure 1.5 Flow diagram of fuel gas conditioning for gas engine [13].

Table 1.4 typical feed and conditioned gas for gas engine [13].

<table>
<thead>
<tr>
<th>Process conditions</th>
<th>Feed gas</th>
<th>Conditioned gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>35</td>
<td>33</td>
</tr>
<tr>
<td>Pressure (psig)</td>
<td>1000</td>
<td>985</td>
</tr>
<tr>
<td>Total flow (MMSCFD)</td>
<td>0.95</td>
<td>0.5</td>
</tr>
<tr>
<td>Component (mol %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.3</td>
<td>0.6</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>CH₄</td>
<td>72.5</td>
<td>81.2</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>9.5</td>
<td>9</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>9.9</td>
<td>7.1</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>2.4</td>
<td>0.9</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>2.5</td>
<td>0.9</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Water</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>Fuel heating value (Btu/scf)</td>
<td>1464</td>
<td>1316</td>
</tr>
<tr>
<td>Octane number</td>
<td>114</td>
<td>116</td>
</tr>
<tr>
<td>Hydrocarbon dew point (°C)</td>
<td>35</td>
<td>4</td>
</tr>
</tbody>
</table>

Gas Turbine Application

The use of gas turbines is increasing in the gas processing industry particularly on offshore platforms for power generation and compression drivers. These turbines are
frequently powered by associated raw natural gas. This type of natural is typically rich in heavy hydrocarbon and at relatively low pressure [15]. The process flow diagram of the typical system for fuel gas conditioning for gas turbines is shown in Figure 1.6 [13]. The natural gas feed is compressed from 35 psig to 285 psig and then cooled down in a condenser. The heavy hydrocarbons are recovered as liquids. The rest of the gas still contains a significant amount of heavy hydrocarbons that may damage the turbine. Therefore, the gas is sent to a membrane unit to remove the remaining heavy hydrocarbons and to meet the specification of the fuel gas. The performance of the membrane system is shown in Table 1.5.

Another benefit of the membrane system is to recover heavy hydrocarbons in the form of liquid. The value of these hydrocarbons can easily justify the capital cost of the membrane system. Typically 60 to 90% of C$_3$+ hydrocarbons are recovered that usually provide feedback time for the capital cost of less than a year [13].

![Figure 1.6 Typical fuel gas conditioning system for gas turbine [13].](image-url)
Table 1.5 Typical performance of gas turbine conditioning system.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dew point of the feed gas (°F)</td>
<td>100</td>
</tr>
<tr>
<td>Ambient temperature (°F)</td>
<td>100</td>
</tr>
<tr>
<td>Dew point of the conditioned gas (°F)</td>
<td>60</td>
</tr>
<tr>
<td>Heavy hydrocarbon removal (%)</td>
<td>60</td>
</tr>
<tr>
<td>Recovered C$_3$+ hydrocarbons (gallons/day)</td>
<td>21,300</td>
</tr>
<tr>
<td>Typical payback time (months)</td>
<td>12</td>
</tr>
</tbody>
</table>

Figure 1.7 Gas turbine conditioning system [13].

1.6 Membrane-Based Gas Separations

The proceeding chapter of this work reviewed the milestones in the development of membrane-based gas separation. A journey that took more than a century to transfer the fundamental observations to commercialized industrial products.
In 1850, Graham for the first time described gas permeation through dense, non-porous, rubbery membranes by a solution/diffusion mechanism. The mechanism consists of three steps: 1) sorption of the gas into the membrane surface, 2) diffusion of the gas along a concentration gradient from the feed to the permeate side, 3) desorption of the gas from the other side of the membrane.

Figure 1.8 Milestones in the development of membrane-based gas separations [16].

As shown in Figure 1.8, it took more than one century from Graham’s experimental work to the commercialization of membranes for gas separation applications. In the 1940s and 1950s, Amerongen [17] and Barrer [18] explained the mechanism of the transport across a membrane in a more fundamental and scientific framework. Much of the research required for development of materials, membranes and modules for gas separation resulted from early work on seawater desalination. In 1961, Loeb and Sourirajan found a simple procedure for the formation of thin defect-free asymmetric membranes with high flux for water desalination applications. The cellulose acetate
membrane was composed of a very thin selective layer atop a highly porous support made by a phase inversion process [19].

Many companies such as DuPont, Union Carbide and Monsanto tackled low flux issues with engineering-based solutions. Researchers from Union Carbide formed multiple thin selective layers atop a microporous substrate, revealing the composite membrane concept [20]. In 1977, DuPont introduced a new innovative technique that was increasing the membrane flux by using membranes spun in hollow fiber geometry that achieved high surface area to volume ratio with up to 10,000 ft²/ft³. In 1980, as shown in Figure 1.9, a new innovative approach of “caulked” composite membranes was introduced by Monsanto [21], which was the basis for their PRISM membrane system that was used in the tuning of the H₂:CO ratio in syngas applications [22].

![Figure 1.9 Caulked thin-film composite membrane](image)

Three factors are important in controlling and improving membrane-based gas separation applications [16]:

• Membrane material selection.
• Formation of the membrane.
• Membrane system module.

Currently, hundreds of polymers have been developed and tested on the laboratory scale; however, only around ten of these polymers have been used commercially for gas separation as shown in Table 1.6. Membranes are utilized commercially in large scale for natural gas purification, hydrogen recovery and air separation [22].

Table 1.6 Existing membranes used commercially for gas separation [16].

<table>
<thead>
<tr>
<th>Separation application</th>
<th>Material used</th>
<th>Module used</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂/N₂</td>
<td>Polyimide</td>
<td>Hollow fiber</td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>Polysulfone</td>
<td>Hollow fiber</td>
</tr>
<tr>
<td>CO₂</td>
<td>Cellulose acetate</td>
<td>Hollow fiber or Spiral</td>
</tr>
<tr>
<td>VOC/N₂</td>
<td>Silicone rubber</td>
<td>Spiral</td>
</tr>
<tr>
<td>H₂O/Air</td>
<td>Polyimide</td>
<td>Capillary</td>
</tr>
</tbody>
</table>

Potential Advantages of Membrane-Based Gas Separations

There are several advantages of membrane technology over the conventional technologies for natural gas purification [23]:

• No rotating equipment is required in membrane technology. Because of that membrane-based gas separation require less energy and maintenance.

• Membrane systems have relatively small foot-print which is particularly significant for off-shore platforms. Furthermore, membrane units are modular that make the
expansion simpler and less expensive than conventional gas separation processes.

- In the off-shore application, long distance transport of the natural can be avoided by installing on-site membrane unit since they are compact. This can reduce the cost significantly because using costly pipeline for the transport of corrosive acid gas is eliminated as well as the cost of gas compression.

Because of these major advantage, membrane-based technology has been growing in the last decades. Currently, more than 200 membrane plants have been installed globally for natural gas treatment [16].

1.7 Polymeric Membranes for Gas Separation

Polymeric membranes are exclusively used in natural gas processing and purification mainly because of their relatively low cost and ease of manufacturing [24, 25]. Inorganic membranes show good performance on the laboratory scale. However, they cannot compete with polymeric materials due to their high cost, weak mechanical properties and difficulty in reproducible fabrication [24].

Polymeric membranes can be classified generally as either glassy or rubbery and they can be used in different applications [26]. Glassy polymers are rigid and the dominant factor that determines the overall selectivity is the gas diffusivity ratio. The gas diffusion coefficient mainly depends on gas molecular size. Therefore, glassy membranes are typically used to permeate smaller gas molecules such as CO₂ and to reject larger gas molecules like propane and butane [27, 28], as shown in Figure 1.10.
On the other hand, rubbery polymers are soft and flexible and the main factor in determining the selectivity of the membrane is the ratio of the gas solubility coefficients which reflect the gas condensability of the gas components. Thus, rubbery membranes used to preferential permeate larger, more condensable gas like $C_3+$ hydrocarbons and reject methane as the residue [11, 27] as shown in Figure 1.11. This behavior is considered as counter-intuitive because membrane filters usually allow smaller particles to pass through and reject the larger one.

![Figure 1.10 Typical gas permeability order in glassy polymers [27].](image1)

![Figure 1.11 Typical gas permeability order in rubbery polymers [27].](image2)

In general, the selectivity of the membrane is a function of diffusivity and solubility coefficients ratio of two gases. Usually, most membrane-based gas separation systems depend on diffusivity selectivity; nevertheless, specific industrial and environmental applications are based on solubility selectivity [7].
1.8 Polymers of Intrinsic Microporosity (PIMs)

Polymers of intrinsic microporosity (PIMs) are a new interesting class of glassy polymers that have interconnected pores with sizes that less than 2 nm. Therefore, they possess high surface area of 200-1000 m²/g [29]. PIMs were first introduced by Budd and McKeown in 2002 at the University of Manchester. Most of the PIMs are based on ladder polymers that have a rigid spirobisindane unit, which causes inefficient chain packing, thus creating microporosity. They are thermally stable, rigid amorphous solids and are often soluble in common solvents [30, 31].

PIM-1 is the prototype of polymers of intrinsic microporosity that shows relatively high gas permeability and moderate selectivity above the Robeson upper bound for many important gas pairs [31]. Figure 1.12 shows the chemical structure of PIM-1.

![Chemical structure of PIM-1](image)

Figure 1.12 a) Chemical structure of PIM-1. b) Molecular model of PIM1 [32].
Chapter 2

Theoretical Background

2.1 Amorphous Glassy Polymers

When cooling a polymer from the rubbery state, a transition occurs to a more rigid state at the glass transition temperature ($T_g$). As shown in Figure 2.1, the transition state appears as a change in the slope of the specific volume against temperature. When a polymer is below $T_g$, the chain packing is disrupted causing the formation of an “excess free volume” in the solid state [33]. The excess free volume is often expressed as a fractional free volume (FFV), given by:

$$ FFV \equiv \frac{\nu - \nu_0}{\nu} $$

(1)

Where $\nu$ is the specific volume (cm$^3$/g) and $\nu_0$ is the theoretical volume occupied by the polymer chains that can be estimated using group contribution theory.
2.2 Solution-Diffusion Model

Gas transport through isotropic, non-porous polymeric materials is often described by the solution-diffusion mechanism [34]. As shown in Figure 2.2, the mechanism contains three process steps:

1. Gas molecules are first adsorbed on the surface of the high-pressure side of the membrane.
2. Diffusion of gas molecules across the membrane thickness down a concentration gradient.
3. Desorption of gas molecules from the low-pressure side of the membrane.

Figure 2.1 Specific volume of a polymer in the rubbery and glassy state [33].
2.3 Permeability

Generally, diffusion is defined as the net transfer of molecules from a higher concentration area to a lower concentration area through random motion [35].

Gas diffusion through a membrane can be described by Fick’s law as:

\[ J = -D \left( \frac{dc}{dc} \right) \]  

(2)

where, \( J \) is gas flux through the membrane, \( D \) is the Diffusion coefficient and \( \left( \frac{dc}{dc} \right) \) is the concentration gradient across the membrane.

When the diffusion coefficient is constant, Fick’s law becomes:

\[ J = D \frac{C_0 - C_1}{l} \]  

(3)

where \( C_0 \) and \( C_1 \) are upstream and downstream gas concentrations, respectively, and \( l \) is membrane thickness.

At low pressure, gas concentration in the membrane can be expressed by Henry’s law:
\[ C = S \cdot p \]  
\[ \text{(4)} \]

where \( S \) is the solubility constant and \( p \) is gas pressure.

By substituting equation (4) into equation (3) yields:

\[ J_i = D_i \cdot S_i \frac{(p_{io} - p_{il})}{l} = P \frac{(p_{io} - p_{il})}{l} \]  
\[ \text{(5)} \]

Thus, gas permeability is the product of solubility coefficient and diffusion coefficient of the gas molecule [7].

\[ P = D \cdot S \]  
\[ \text{(6)} \]

The permeability coefficient is often expressed in Barrers, where 1 Barrer = \( 1 \times 10^{-10} \text{cm}^3 (\text{stp}) \cdot \text{cm/cm}^2 \cdot \text{s} \cdot \text{cmHg} \)

### 2.4 Selectivity

Membrane selectivity is a major factor for characterizing the performance of membranes used in gas separation. It determines the gas purity and recovery that can be achieved for a given separation. The ideal selectivity of a membrane for gas pairs is defined as the permeability ratio of the two gases:

\[ \alpha_B^A = \frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \]  
\[ \text{(7)} \]

where \( \frac{D_A}{D_B} \) is the diffusivity or mobility selectivity and \( \frac{S_A}{S_B} \) is the solubility selectivity.

The diffusivity selectivity is linked to the ratio of the molecular sizes of a gas pair, whereas the solubility selectivity is linked to the relative condensability of the two gases; generally, the solubility of a gas increases with increased condensability.
2.5 Dual-Mode Sorption Model

Gas sorption provides a qualitative investigation of the physical microstructure (chain mobility, chain packing) of amorphous polymers. In rubbery polymers, sorption isotherms for gas molecules typically follow Henry’s law [36]:

\[ C_D = K_D \cdot p \]  \hspace{1cm} (8)

where \( K_D \) is the solubility coefficient of the gas molecule in the dense polymer.

![Diagram of sorption model](image)

**Figure 2.3** The dual-mode sorption model for glassy polymers.

On the other hand, the gas sorption isotherms in glassy polymers are always concave to the pressure axis. As shown in Figure 2.3, this kind of isotherms can be rationalized by the dual-mode sorption model that is a combination of two modes: (1) a fast initial rise at low pressure following the Langmuir isotherm as a result of non-equilibrium excess free volume and (ii) slow steady rise in sorption at high pressure.
following Henry’s law due to dissolving of gas molecules in the equilibrium structure of the polymer. The dual-mode model is described by [37, 38]:

\[ C = C_D + C_H = K_D \cdot p + \frac{c_H' \cdot bp}{1 + bp} \]  

(9)

where \( C \) is the total concentration, \( C_D \) is the gas concentration resulting from Henry’s law mode, \( C_H' \) is the gas concentration in the excess free volume due to the Langmuir mode. \( K_D \) represents Henry’s law constant, \( C_H' \) is the hole-filling constant, and \( b \) is the affinity of the gas to the polymer parameter.
Chapter 3

Experimental Section

3.1 PIM-Trip-TB-2 Synthesis

The PIM-Trip-TB-2 ladder polymer (Fig. 3.1) was prepared by the polymerization reaction of 9,10-dimethyl-2,6(7)-diaminotriptycene (0.5 g, 1.6 mmol) under stirring with dimethoxymethane (0.70 mL, 8 mmol). Trifluoroacetic acid (5 ml) was added dropwise over a period of 15 minutes, and the solution was then stirred vigorously under nitrogen atmosphere for 20 h at room temperature. The highly viscous orange solution was quenched with aqueous ammonium hydroxide solution (20%, 100 ml) and stirred vigorously for another 10 h. The resulting polymer was filtered, washed with water and purified by reprecipitation from chloroform/methanol mixture twice and then dried under vacuum at 130 °C to give the desired product (0.53 g, 95% yield) as pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.17 (br s, 6H), 3.91(br m, 4H), 4.46 (br s, 2H), 6.66-7.13 (br m, 8H). BET surface area = 940 m$^2$ g$^{-1}$. TGA analysis: (Nitrogen), initial weight loss due to thermal degradation commences at $T_d$ 450 °C. The ladder polymer was kindly prepared by Dr. Bader Ghanem who is a Research Scientist in the Advanced Membranes and Porous Materials Center (AMPMC) at KAUST.
3.2 Preparation of PIM-Trip-TB-2 Membrane

Isotropic PIM-Trip-TB-2 films were prepared by slowly pouring 2 wt.% chloroform solution of the ladder polymer on a flat-bottomed glass petri dish. Then, it was covered with a glass plate for slowing down solvent evaporation. The film was first dried at room temperature for two days. After that, the film was dried in a vacuum oven at 120 °C for 16 hours. Then, the film was immersed in methanol at ambient temperature for 8 hours. Finally, the film was dried once more in a vacuum oven at 120 °C for 16 hours prior to gas permeation tests. The density of PIM-Trip-TB-2 film was calculated using Archimedes' principle. The calculated density was 1.21 g/cm³.

3.3 BET Surface Area

A Brunauer-Emmett-Teller (BET) surface area test was performed using a Micromeritics ASAP 2020. Physisorption isotherm and pore size distribution were obtained using nitrogen at 77 K, as shown in Figure 3.2.

As shown in Figures 3.2, the PIM-Trip-TB-2 has a very high BET surface area of 942 m²/g, almost identical to that of poly (1-trimethylsilyl-1-propyne) (PTMSP) (949
m²/g) [39], confirming that PIM-Trip-TB-2 has a highly interconnected microporous structure. Furthermore, the N₂ sorption uptake at very low relative pressure (p/p₀ < 10⁻⁵) is significantly higher in PIM-Trip-TB-2 relative to PTMSP, as shown in Figure 3.3.

As the pore size distribution analyses shown in Figure 3.4 indicate, the porous texture of PIM-Trip-TB-2 consists of a bimodal distribution with larger micropores > 10 Å promoting permeability and smaller ultramicropores < 7 Å improving diffusion selectivity. This is starkly different from PTMSP that characterized by a less tightly packed microstructure with a significant fraction of larger micropores and much smaller fraction of ultramicropores. Thus, PTMSP is one of the highest permeable known polymers with low permanent gas selectivity as well as unparalleled reverse-selectivity for vapor/gas separations [40].

The tightened but highly interconnected microstructure with pore size smaller than 7 Å is the basis for the transport dominated by diffusion in PIM-Trip-TB-2 and its ability to combine high permeability with high selectivity for some important commercial gas pairs separations, such as O₂/N₂, H₂/N₂ and H₂/CH₄.
Figure 3.2 Nitrogen adsorption isotherms for PTMSP [39] and PIM-Trip-TB-2 measured at 77 K.

Figure 3.3 Low-pressure region of nitrogen adsorption isotherms for PTMSP [39] and PIM-Trip-TB-2 measured at 77 K to elucidate ultramicroporosity.
3.4 Thermal Gravimetric Analysis (TGA)

The thermal stability of PIM-Trip-TB-2 was obtained using thermal gravimetric analysis TGA (TA Instruments Q5000). The polymer film sample was loaded into a platinum pan and introduced to the apparatus under a 10 mL/min nitrogen purge. Initially, the sample was heated up to 100 °C and held constant for two hours; then the sample was heated up from 100 to 800 °C at a rate of 10 °C/min. The thermal degradation of PIM-Trip-TB-2 started at around 450 °C, as illustrated in Figure 3.5.
3.5 Gravimetric Gas Sorption

The gas solubility of PIM-Trip-TB-2 was determined using a Hiden Intelligent Gravimetric Analyzer IGA (Hiden Isochema, UK). A simplified schematic of the apparatus is shown in Figure 3.6. The apparatus was used to measure high-pressure gas sorption isotherms up to 20 bar for PIM-Trip-TB-2 powder sample.

First, a 50 mg of PIM-Trip-TB-2 powder sample was mounted in the apparatus and degassed under high vacuum at 35 °C for 24 hours until stabilization of the sample weight reading. After that, the desired gas was introduced to the apparatus by stepwise pressure increase by ramping of 100 mbar/min until the desired pressure was reached. After attaining equilibrium, weight uptake of the sample was recorded. Then, the next pressure point was set, and the mentioned process was continued until completing the full isotherm for a given gas.
3.6 Pure-Gas Permeation System

The pure-gas permeation properties measurements for an isotropic 80-µm-thick PIM-Trip-TB-2 film were conducted using the constant-pressure/variable-volume method, as illustrated in Figure 3.7.

The permeation experiments were conducted at a feed pressure of 6 bar and the permeate pressure was atmospheric. The order of gas permeation experiments was helium, hydrogen, nitrogen, oxygen, methane and carbon dioxide. The feed and permeate side of the system were always purged with the desired gas before the permeation measurement. The flow rate of permeate was measured using a bubble flow meter.

The steady-state permeability, \( P \), determined by the constant-pressure/variable-volume method is given by:

\[
P = \frac{l}{p_2 - p_1} \frac{273 \ p_{atm}}{TA \ 76} \left( \frac{dV}{dt} \right)
\]  

(10)
where \( l \) is the membrane thickness, \( p_1 \) is the downstream atmospheric pressure (cmHg), \( p_2 \) is the feed pressure (cmHg), \( T \) is the absolute gas temperature (K), \( A \) is the membrane film area (cm\(^2\)), \( p_{atm} \) is the atmospheric pressure (cmHg), and \( \left( \frac{dv}{dt} \right) \) is the steady-state permeate flow rate (cm\(^3\)/s).

The pure-gas selectivity of gases A and B was calculated by:

\[
\alpha_{AB} = \frac{P_A}{P_B} \quad (11)
\]

### 3.7 Mixed-Gas Permeation System

The mixed-gas permeation measurements of PIM-Trip-TB-2 were carried out at 35 °C with 2 vol.% \( n \)-butane/98 vol.% methane. The permeation experiments were conducted at feed pressures of 2, 4, 6, 8, and 10 bar, respectively. The feed flow rate to permeate flow rate ratio, known as stage cut, was always kept below 0.01. Under these conditions, the composition of the residue was essentially equal to the feed composition. The mixed-gas permeability coefficient was calculated by:

\[
P = \frac{x_{perm} \cdot l}{(p_2x_{feed} - p_1x_{perm}) \cdot 273 \cdot p_{atm} \cdot \frac{T}{A} \cdot 76 \cdot \left( \frac{dv}{dt} \right)} \quad (12)
\]

where \( x_{perm} \) and \( x_{feed} \) are the mol fractions of the desired gas in the permeate and feed side, respectively, \( p_1 \) is the downstream atmospheric pressure (cmHg), \( p_2 \) is the feed pressure (cmHg), \( l \) is the membrane thickness, \( T \) is the absolute gas temperature (K), \( A \) is the membrane film area (cm\(^2\)), \( p_{atm} \) is the atmospheric pressure (cmHg), and \( \left( \frac{dv}{dt} \right) \) is the steady-state permeate flow rate (cm\(^3\)/s). The gas mixture selectivity was calculated using Equation (11).
Figure 3.7 Process flow diagram of constant-pressure/variable-volume permeation system.
Chapter 4

Results and Discussion

4.1 Gas Sorption

Sorption isotherms of N\textsubscript{2}, O\textsubscript{2}, CH\textsubscript{4}, CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, and n-C\textsubscript{4}H\textsubscript{10} were obtained at 35 °C using an Intelligent Gravimetric Analyzer (IGA) and the results are presented in Figures 4.1-4.6. All sorption isotherms were concave to the pressure axis as described by dual-mode sorption model which is the typical trend for glassy polymers.

Sorption isotherms for PIM-Trip-TB-2 were compared with sorption isotherms for PIM-1 obtained at 25 °C [41]. PIM-Trip-TB-2 displayed higher gas uptake than PIM-1 for all tested gases, as presented in Figures 4.1-4.6. It is suggested that this resulted from the higher BET surface area of PIM-Trip-TB-2 (942 m\textsuperscript{2}/g) compared to PIM-1 (768 m\textsuperscript{2}/g) [39].

Sorption for non-condensable gases, which have very low normal boiling points, (N\textsubscript{2}, O\textsubscript{2} and CH\textsubscript{4}) was much lower than relatively condensable gases indicating that non-condensable gases interact weakly with PIM-Trip-TB-2. The sorption isotherms for relatively condensable gases displayed a much more definite non-linear dual-mode behavior that is typical for conventional low-free-volume glassy polymers, such as polycarbonate.

The gas sorption tests were performed at pressures up to 20 bar. However, for C\textsubscript{3}H\textsubscript{8} and n-C\textsubscript{4}H\textsubscript{10} the tests were performed at pressure up to 7 and 2 bar, respectively, due to vapor pressure limitation. As shown in Figures 4.1-4.6, sorption follows the order of gas condensability, that is N\textsubscript{2}<O\textsubscript{2}<CH\textsubscript{4}< CO\textsubscript{2}< C\textsubscript{2}H\textsubscript{6}<C\textsubscript{3}H\textsubscript{8}<n-C\textsubscript{4}H\textsubscript{10}. 
Figure 4.1 Sorption isotherms of $\text{N}_2$ in PIM-1 at 25 °C [41] and in PIM-Trip-TB-2 at 35 °C.

Figure 4.2 Sorption isotherms of $\text{O}_2$ in PIM-1 at 25 °C [41] and in PIM-Trip-TB-2 at 35 °C.
Figure 4.3 Sorption isotherms of CH₄ in PIM-1 at 25 °C [41] and in PIM-Trip-TB-2 at 35 °C.

Figure 4.4 Sorption isotherms of CO₂ in PIM-1 at 25 °C [41] and in PIM-Trip-TB-2 at 35 °C.
Figure 4.5 Sorption isotherms of C$_2$H$_6$ in PIM-1 at 25 °C [41] and in PIM-Trip-TB-2 at 35 °C.

Figure 4.6 Sorption isotherms of C$_3$H$_8$ in PIM-1 at 25 °C [41] and C$_3$H$_8$ and n-C$_4$H$_{10}$ in PIM-Trip-TB-2 at 35 °C.
The average solubility coefficient $S$ can be determined using the dual-mode expression as follows (Figures 4.7-4.9):

$$\bar{S} = \frac{c}{p} = k_D + \frac{C_H' b}{1 + b p}$$

(10)

The dual-mode parameters $C_H'$, $k_D$ and $b$ were obtained using a non-linear regression curve fitting method for N$_2$, O$_2$, CO$_2$, CH$_4$, C$_2$H$_6$, C$_3$H$_8$, and n-C$_4$H$_{10}$ in PIM-Trip-TB-2. The dual-mode parameters used to fit the experimental sorption results (Figures 4.1-4.6) are listed in Table 4.1.

Table 4.1 Dual-mode gas sorption parameters of PIM-Trip-TB-2 at 35 °C.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$K_D$ [cm$^3$(STP)/cm$^3$.bar]</th>
<th>$C_H'$ [cm$^3$(STP)/cm$^3$]</th>
<th>$b$ [1/bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>0.9</td>
<td>38.8</td>
<td>0.12</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.4</td>
<td>40</td>
<td>0.10</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>4.1</td>
<td>112.9</td>
<td>0.89</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.9</td>
<td>65.4</td>
<td>0.35</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>4.16</td>
<td>110</td>
<td>1.5</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>16.5</td>
<td>199.5</td>
<td>2.25</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>16.7</td>
<td>250.7</td>
<td>5.9</td>
</tr>
</tbody>
</table>

The values of $K_D$ are increasing with gas condensability which is consistent with the typical trend for gas sorption in glassy polymers in the Henry sorption isotherm regions.

The Langmuir capacity parameters $C_H'$ represents the sorption capacity of the excess free volume in glassy polymers. n-C$_4$H$_{10}$ displayed the highest $C_H'$ value because it is the most condensable gas among tested gases.
Figure 4.7 Solubility coefficients of N$_2$, O$_2$, and CH$_4$ in PIM-Trip-TB-2 at 35 °C.

Figure 4.8 Solubility coefficients of CO$_2$ and C$_2$H$_6$ in PIM-Trip-TB-2 at 35 °C.
4.2 Pure-Gas Permeation Properties

Pure-gas permeation properties of a PIM-Trip-TB-2 film (80 µm) were obtained experimentally at 35 °C and 5 bar pressure difference using the constant-pressure/variable-volume method. The pure-gas permeability coefficients for He, H₂, N₂, O₂, CH₄, CO₂, C₂H₆, C₃H₈, and n-C₄H₁₀ are presented in Table 4.2 and compared with the permeation properties of PIM-1 [42] and PTMSP [40].

Hydrogen showed the highest permeability coefficient among other low-condensable gases in PIM-Trip-TB-2, including CO₂, which is uncommon behavior in very high BET surface area glassy polymers, such PIM-1 and PTMSP. This indicates that the diffusivity selectivity is dominant and PIM-Trip-TB-2 has good sieving capacity. This behavior is particularly interesting because it combines the behavior of low-free-volume, highly selective commercial polymeric membranes and high free volume, high permeable conventional PIMs.

Figure 4.9 Solubility coefficients of C₃H₈ and C₄H₁₀ in PIM-Trip-TB-2 at 35 °C.
Table 4.2 Comparison of pure-gas permeability coefficients in PIM-Trip-TB-2, PTMSP and PIM-1.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability (Barrer*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PIM-Trip-TB-2</td>
</tr>
<tr>
<td>He</td>
<td>2200</td>
</tr>
<tr>
<td>H₂</td>
<td>6015</td>
</tr>
<tr>
<td>O₂</td>
<td>1140</td>
</tr>
<tr>
<td>N₂</td>
<td>195</td>
</tr>
<tr>
<td>CH₄</td>
<td>385</td>
</tr>
<tr>
<td>CO₂</td>
<td>4150</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1500</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>7000</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>29800 @ 2 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>35 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>5 bar</td>
</tr>
</tbody>
</table>

Pure-gas permeability coefficients for hydrocarbons increased with increasing gas condensability (CH₄<C₂H₆<C₃H₈<n-C₄H₁₀) indicating reverse-selectivity for vapor/gas separations.

PIM-Trip-TB-2 exhibits excellent gas separation performance in comparison to PIM-1 for several high-impact applications. The polymer displays high O₂/N₂ selectivity of around 6 which meets the target required for outcompeting cryogenic distillation for nitrogen enrichment of air application [43]. Furthermore, the polymer shows high hydrogen separation performance (H₂/N₂ and H₂/CH₄) as shown in Tables 4.3 and 4.4.
Table 4.3 Comparison of gas/nitrogen selectivities in PIM-Trip-TB-2, PTMSP and PIM-1.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability Selectivity Gas / N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PIM-Trip-TB-2</td>
</tr>
<tr>
<td>He</td>
<td>11.2</td>
</tr>
<tr>
<td>H₂</td>
<td>30.8</td>
</tr>
<tr>
<td>O₂</td>
<td>5.6</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Table 4.4 Comparison of gas/methane selectivities in PIM-Trip-TB-2, PTMSP and PIM-1.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability Selectivity Gas / CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PIM-Trip-TB-2</td>
</tr>
<tr>
<td>He</td>
<td>5.5</td>
</tr>
<tr>
<td>H₂</td>
<td>15.6</td>
</tr>
<tr>
<td>O₂</td>
<td>3</td>
</tr>
<tr>
<td>CO₂</td>
<td>17.5</td>
</tr>
</tbody>
</table>

4.3 Average Diffusion Coefficient Calculations

Because the permeability and solubility coefficients were obtained experimentally, the average diffusion coefficients for N₂, O₂, CO₂, CH₄, C₂H₆, C₃H₈, n-C₄H₁₀ were
determined from equation 6. Table 4.5 shows the average diffusion coefficients in PIM-Trip-TB-2 at 35 °C and 5 bar.

The order of magnitude of the diffusivity of gas molecules depends on the size of the permeating gas molecule and the nature of the membrane material. In general, the diffusivity increases as the gas molecule size decrease [44]. However, the results showed increasing of the diffusivity of the hydrocarbons with increasing molecule size. This result suggested that penetrant-induced dilation of the polymer matrix increased with hydrocarbons solubility led to increasing of the diffusivity with gas solubility increase.

Table 4.5 Pure-gas permeability, diffusivity and solubility coefficients for PIM-Trip-TB-2 (80 µm) at 35 °C and 5 bar.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability [Barrer]</th>
<th>Solubility [10^-2 cm^3(STP)/cm^3 cmHg]</th>
<th>Diffusivity [10^-8 cm^2/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N_2</td>
<td>195</td>
<td>5.1</td>
<td>38.2</td>
</tr>
<tr>
<td>O_2</td>
<td>1140</td>
<td>6.3</td>
<td>180.95</td>
</tr>
<tr>
<td>CH_4</td>
<td>385</td>
<td>13.8</td>
<td>27.8</td>
</tr>
<tr>
<td>CO_2</td>
<td>4150</td>
<td>32</td>
<td>129.6</td>
</tr>
<tr>
<td>C_2H_6</td>
<td>1500</td>
<td>37</td>
<td>40.5</td>
</tr>
<tr>
<td>C_3H_8</td>
<td>7000</td>
<td>70.9</td>
<td>98</td>
</tr>
<tr>
<td>n-C_4H_{10}</td>
<td>29800 @ 2 bar</td>
<td>152</td>
<td>196</td>
</tr>
</tbody>
</table>

Table 4.6 Permeability, solubility, diffusivity selectivities of gas/N_2 in PIM-Trip-TB-2.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability selectivity</th>
<th>Solubility selectivity</th>
<th>Diffusivity selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O_2</td>
<td>5.6</td>
<td>1.2</td>
<td>4.7</td>
</tr>
<tr>
<td>CH_4</td>
<td>1.9</td>
<td>2.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>
### 4.4 Pressure Dependence Permeation Test

Permeability coefficients for propane and $n$-butane obtained as a function of pressure are shown in Figure 4.10. The pressure dependence of propane permeability followed typical dual-mode behavior, that is, an increase in pressure resulted in a decrease in $C_3H_8$ permeability. Interestingly, plasticization of the PIM-Trip-TB-2 membrane was not evident for propane permeation. On the other hand, the permeability of $n$-butane increased significantly from 13,000 to 30,000 Barrer by increasing the pressure from 1.25 to 2 bar. This result suggested that penetrant-induced dilation of the polymer matrix resulted in plasticization and, hence, creation of larger micropores in PIM-Trip-TB-2. As a result, the diffusion coefficient as well as permeability of $n$-butane increased significantly.

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability Coefficient</td>
<td>21.3</td>
<td>7.7</td>
<td>35</td>
</tr>
<tr>
<td>(Barrer)</td>
<td>6.3</td>
<td>7.3</td>
<td>13.9</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>1.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>
4.5 Physical Aging Test

Physical aging is the relaxation of non-equilibrium free volume in glassy polymers due to several possible mechanisms [45]. It is known that reduction of permeability is more significant in high free volume, highly permeable polymers [46].

The physical aging of a PIM-Trip-TB-2 film with the thickness of 80 µm was studied intermittently over a period of 75 days with He, H₂, N₂, CO₂ and CH₄. The permeability coefficients of the PIM-Trip-TB-2 film after storage of 14, 40 and 75 days, respectively, are shown in Table 4.7. The results show that the permeability coefficients in PIM-Trip-TB-2 decreased significantly with time whereas selectivities increased only slightly for all gas pairs except CH₄/N₂. For example, the O₂ permeability decreased from 1140 for the 14 days old sample to 720 Barrer after storage of 75 days. However, the O₂/N₂ selectivity increased only from 5.6 to 5.9.
Table 4.7 Gas permeability coefficients for 14-, 40-, and 75-days-old PIM-Trip-TB-2 film at 35 °C and 5 bar.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability (Barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14 days aged film</td>
</tr>
<tr>
<td>He</td>
<td>2200</td>
</tr>
<tr>
<td>H₂</td>
<td>6015</td>
</tr>
<tr>
<td>O₂</td>
<td>1140</td>
</tr>
<tr>
<td>N₂</td>
<td>195</td>
</tr>
<tr>
<td>CH₄</td>
<td>385</td>
</tr>
<tr>
<td>CO₂</td>
<td>4150</td>
</tr>
</tbody>
</table>

Table 4.8 Gas/nitrogen selectivity for 14-, 40-, and 75-days-old PIM-Trip-TB-2 film at 35 °C and 5 bar.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability Selectivity Gas / N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14 days aged film</td>
</tr>
<tr>
<td>He</td>
<td>11.2</td>
</tr>
<tr>
<td>H₂</td>
<td>30.8</td>
</tr>
<tr>
<td>O₂</td>
<td>5.6</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>21.3</td>
</tr>
</tbody>
</table>

4.6 Mixed-Gas Permeation Properties

A PIM-Trip-TB-2 film (80 µm) was tested with a gas mixture containing 2 vol.% \( n \)-butane and 98 vol.% methane at 35 °C and feed pressures of 2, 4, 6, 8, and 10 bar,
respectively, as shown in Figures 4.11 and 4.12. As expected from its microporous texture, the polymer was more permeable to \( n \)-butane than methane similar to PTMSP and PIM-1 [40, 42, 47]. These high BET surface area polymers exhibit unusual vapor/gas mixed-gas permeation properties because they have very high excess free volume, interconnectivity of free volume elements and large chain spacing.

The permeation results for a gas mixture 2 vol.% \( n \)-butane in methane at 35 °C and feed pressure of 10 bar are presented in Table 4.8. PIM-Trip-TB-2 had an \( n \)-butane permeability of 1890 Barrer and methane permeability of 140 Barrer. This is an indication that the selectivity of \( n \)-butane/methane in PIM-Trip-TB-2 was dominated by solubility selectivity. The methane permeability in PIM-Trip-TB-2 was reduced from 385 Barrer in pure-gas measurement to 140 Barrer in a mixture with \( n \)-butane. The methane blocking effect by co-permeation of the larger and considerably more condensable \( n \)-butane is a typical characteristic of microporous polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
<th>Mixed-gas/ pure-gas methane permeability ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n-C_4 H_{10} )</td>
<td>CH(_4)</td>
<td>( n-C_4 H_{10} / CH(_4) )</td>
</tr>
<tr>
<td>PIM-Trip-TB</td>
<td>1890</td>
<td>140</td>
<td>13.5</td>
</tr>
<tr>
<td>PIM-1 [42]</td>
<td>4200</td>
<td>175</td>
<td>24</td>
</tr>
<tr>
<td>PTMSP [40]</td>
<td>53500</td>
<td>1800</td>
<td>30</td>
</tr>
<tr>
<td>PMP [48]</td>
<td>7500</td>
<td>530</td>
<td>14</td>
</tr>
<tr>
<td>PDMS [49]</td>
<td>12900</td>
<td>1250</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 4.9 Mixed-gas permeation properties of microporous, glassy PIM-Trip-TB-2, PIM-1, PTMSP, PMP and rubbery PDMS. Feed composition: 2 vol.% \( n-C_4 H_{10} / 98 \) vol.% CH\(_4\) at 25 °C for all except PIM-Trip-TB-2 at 35 °C.
Figure 4.11 Mixed-gas CH₄ and C₄H₁₀ permeability of PIM-Trip-TB-2 as a function of pressure at 35 °C. Feed composition: 2 vol.% n-C₄H₁₀ and 98 vol.% CH₄.

Figure 4.12 Mixed-gas n-C₄H₁₀/CH₄ selectivity of PIM-Trip-TB-2 as a function of pressure at 35 °C. Feed composition: 2 vol.% n-C₄H₁₀ and 98 vol.% CH₄.
4.7 Mixed-Gas Long Term Permeation

A long-term permeation test was performed for the PIM-Trip-TB-2 film (80 µm). The results for a 2 vol.% \textit{n}-C_{4}H_{10}/CH_{4} feed mixture are shown in Figures 4.13 and 4.14. The gas permeability coefficients obtained during the \textit{n}-butane/methane mixture test in PIM-Trip-TB-2 were time dependent. \textit{n}-Butane permeability increased 2-fold from 1100 Barrer at the beginning to around 1600 Barrer at steady-state condition after 12 hours. This time-dependent increase in \textit{n}-butane permeability was probably caused by slow dilation of the polymer matrix due to preferential sorption of \textit{n}-butane. On the other hand, the methane permeability of 120 Barrer remained essentially constant over the same time interval. As a result, the mixed gas \textit{n}-butane/methane selectivity increased from 9 to 13.5 at steady-state condition.

![Figure 4.13 Mixed-gas CH\textsubscript{4} and \textit{n}-C\textsubscript{4}H\textsubscript{10} permeability of PIM-Trip-TB-2 as a function of permeation time at 35 °C. Feed composition: 2 vol.% \textit{n}-C\textsubscript{4}H\textsubscript{10} and 98 vol.% CH\textsubscript{4}.](image-url)
Figure 4.14 Mixed-gas CH₄ and C₄H₁₀ selectivity of PIM-Trip-TB-2 as a function of permeation time at 35 °C. Feed composition: 2 vol.% n-C₄H₁₀ and 98 vol.% CH₄.

Chapter 5

Conclusions

PIM-Trip-TB-2 is a thermally stable (up to 450 °C) glassy polymer of intrinsic microporosity. The BET surface area of the polymer determined using nitrogen sorption at 77 K was 942 m²/g, which is similar to PTMSP demonstrating that the polymer has a highly interconnected microporous structure. NLDFT analysis of nitrogen sorption in PTM-Trip-TB-2 demonstrated of a bimodal pore size distribution with larger micropores > 10 Å promoting permeability and smaller ultramicropores <7 Å improving diffusion selectivity.

Sorption isotherms for PIM-Trip-TB-2 were concave to the pressure axis and were fitted with the dual-mode model for all tested gases. PIM-Trip-TB-2 displayed higher gas uptake than PIM-1 for all gases. As expected, sorption for less-condensable
gases was much lower than for condensable gases indicating that non-condensable gases interacted weakly with PIM-Trip-TB-2. The sorption isotherms for condensable gases displayed a very strong non-linear dual-mode behavior.

Interestingly for a high free volume, high BET surface area glassy polymer, hydrogen showed higher permeability than carbon dioxide in PIM-Trip-TB-2 indicating good size sieving capability. Therefore, this unique polymer combines the behavior of low free volume, highly selective commercial polymeric membranes and high free volume, high permeable conventional PIMs. Furthermore, Trip-TB-2 demonstrated increased permeability of hydrocarbons with increasing condensability of the penetrant.

Mixed-gas permeation experiments using a 2 vol.% $n$-$C_4H_{10}$/98 vol.% CH$_4$ feed demonstrated that PIM-Trip-TB-2 displayed similar transport characteristics to other microporous structured polymers like PTMSP and PIM-1. The latter two polymers have shown the highest $n$-$C_4H_{10}$/CH$_4$ selectivity of all known polymers together with very high $n$-$C_4H_{10}$ permeability. Although PIM-Trip –TB-2 has extremely high surface area of 942 m$^2$/g even higher than that of PIM-1 (760 m$^2$/g), the polymer displayed lower $n$-butane/methane selectivity and lower $n$-butane mixed-gas permeability. This result was probably due to the tighter microporous structure of PIM-Trip-TB-2 relative to those of PIM-1 and PTMSP.
References


