Polymer Molecular Sieve Membranes

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Declaration

The work presented in this dissertation was undertaken in the Department of Physics, University of Cambridge, between October 2010 and January 2014. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text. I declare that no part of this work has been submitted for a degree or other qualification at this or any other university. This dissertation does not exceed the word limit of 60,000 words set by the Physics and Chemistry Degree Committee.

Qilei Song
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Summary

Sustainable energy supply and environmental protection are the major global scientific challenges in the 21st century, such as greenhouse gas capture, natural gas production, desalination of seawater for clean water production. Membrane separation technology offers attractive energy-efficient and environmental-friendly solutions to these challenges. This PhD thesis is focused on design and fabrication of membranes from novel molecularly defined polymers and understanding their physical properties, particularly the transport properties of gas molecules in polymer membranes.

First, we demonstrate a simple approach of fabricating novel polymer nanocomposite membranes using established colloidal science. Crystalline microporous zeolitic imidazolate frameworks (ZIFs) nanocrystals are incorporated into a polyimide polymer matrix via solution mixing. The resulting nanocomposite membranes show excellent dispersion of nanoparticles, good adhesion at the interface, and enhanced gas permeability while the selectivity remain at high level.

We then fabricated membranes from novel microporous polymers, polymers of intrinsic microporosity (PIMs). Using the PIM-1 polymer as a prototype, we discovered that ultraviolet irradiation of PIM-1 membranes in the presence of oxygen induces oxidative chain scission at the surface, resulting in local densification and structural transformation of free volume elements. Consequently, the membrane become asymmetric with a more gas-selective layer formed at the surface, while the overall permeability maintains at high level.

Finally, we report a simple thermal oxidative crosslinking method to tailor the architecture of channels and free volume elements in PIM-1 polymer membrane by heat treatment in the presence of trace amounts of oxygen molecules. The resulting covalently crosslinked polymer networks offer superior thermal stability, chemical stability, reasonable mechanical strength, and enhanced rigidity. Most important of all, thermally crosslinked PIM-1 polymer membranes show significantly enhanced molecular sieving functions that yield remarkably high selectivity and high gas permeability, which surpass the upper bound that has been limiting the polymer membranes for decades. We also demonstrate that the thermal crosslinking method is effective for crosslinking of nanocomposite membranes with porous or nonporous fillers. These microporous molecular sieve membranes are promising for a wide range of molecular-level separation applications.
List of Publications

Publications produced from this PhD thesis


Other manuscripts during PhD in Cambridge (not included in this thesis)


Patent

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Chapter 1 Introduction

1.1 Background

Membrane separation technology offers attractive energy-efficient and environmental-friendly solutions to global challenges in energy and environmental processes, such as greenhouse gas capture, desalination of seawater, and sustainable energy production. The next-generation membrane materials are porous materials with well-defined size of pores that are close to the kinetic diameter of molecules, and with chemical functionality towards the chemicals. Rational design and fabrication of polymeric materials into microporous membranes for separation applications require fundamental understandings of the physical and chemical properties on a molecular level, such as their macromolecular structures, and linking the macromolecular structure with the transport of molecules at sub-nanometre scale to establish the structure-property relationship.

1.2 Scope

This thesis applies an experimental approach to study the physical properties of polymeric membranes and their gas transport properties. This is an interdisciplinary project that involves fundamental physics of molecular transport, polymer chemistry, soft matter physics, materials science, and knowledge of chemical engineering science. Extensive physical and chemical characterizations were performed to understand the structure-property relationship of nanomaterials from molecular to microscopic level.

1.3 Outline

Chapter 2 introduces the structure and function of natural biological membranes and selective channels, followed by brief introduction of state-of-the-art molecular sieving materials including zeolites, carbon molecular sieves, metal-organic frameworks, and new polymers. High-performance polymers and novel porous polymers, such as polymers of intrinsic microporosity, and thermally rearranged polymers, are reviewed. A brief introduction is given on intermolecular forces and their impact on gas transport properties of polymer membranes. Furthermore, some established theory on free volume, solution-diffusion, and gas sorption and diffusion are briefly introduced. Finally, an important scientific question is generalized in the end.
Chapter 3 presents the general experimental methods and techniques for characterization of materials, and gas sorption and permeation apparatus. A constant-volume variable-pressure method was used to evaluate the permeation properties of pure gases. Separation of mixed gas was also performed using the constant-pressure variable-volume method.

Chapter 4 investigates the fabrication of polymer nanocomposite membranes by incorporating zeolitic imidazolate frameworks nanocrystals into a conventional polyimide matrix via solution mixing. A key finding is that the incorporation of nanosized fillers could disrupt the packing of polymer chains and enhance the free volume as proved by advanced characterization techniques.

Chapter 5 reports the interesting phenomenon of photo-oxidation of Polymers of Intrinsic Microporosity (PIM-1). A prototypical PIM-1 polymer was intensively studied. The photo-oxidation occurring at the surface of the polymer membranes, results in oxidative chain scission of the polymer, and consequently densely packing of shorter chains and loss of free volume. Surprisingly, the gas selectivity became significantly improved while the overall permeability remained at high level. However, the method is not favourable in practical applications because the degraded chains are not stable in solvents. Nevertheless, this study indicated the importance of subtle chemical reactions of the polymer could result significant change of physical properties.

Chapter 6 reports a simple thermal oxidative crosslinking method to tailor the architecture of free volume elements in PIM-1 polymers by heat treatment in the presence of trace amounts of oxygen molecules. The resulting covalently crosslinked polymer networks offer superior thermal stability, chemical stability, reasonable mechanical strength, enhanced rigidity, and remarkable improvement of molecular-sieving function that yields significantly enhanced selectivity while maintaining high gas permeability. This method is also effective for nanocomposite membranes.

Chapter 7 summarizes the thesis and proposes the future work.
Chapter 2 Literature review and theory background

2.1 Introduction

This chapter starts from a brief introduction of biological membranes in nature and synthetic membranes for separations in modern industries. Some well-known molecular sieve materials are presented, including zeolites, activated carbons, carbon molecular sieves (CMS), as well as cutting-edge microporous materials including metal-organic frameworks (MOFs), covalent organic frameworks (COFs), porous organic cages (POCs), and polymers of intrinsic microporosity (PIMs). This is followed by an extensive review on PIMs, mainly on the synthetic chemistry, post-synthetic modifications, and their applications in membrane separations. The intermolecular interactions in polymers are briefly introduced and their impact on the physical properties is highlighted. Nanocomposite membranes are introduced, particularly the novel polymer/MOFs composite membranes. Finally, theories on free volume and glass transition are briefly introduced, as well as the solution-diffusion model to illustrate the mechanism of gas permeation through a polymer membrane.

Based on the review of previous research work, I conclude an important scientific question that is addressed in this PhD dissertation and brief introduction of my own approaches to solve the question.

2.2 Membranes in nature

Membranes are ubiquitous in nature and exist as selectively permeable barriers, within or around cells. Biological membranes consist of many units, such as lipid layer, protein for communication and transport of chemicals and ions. The selective transport of ions, water, molecules and compounds through biological membranes are restricted to unique-structured membrane protein channels and transporters after evolution for millions of years. The selective diffusion of molecules or ions through these channels depends on the size and charge of the substance, and is subject to various regulation mechanisms that eventually behaving as opening or closing of the channel or pores. The physical structures of the channels or pores that allow fast diffusion of ions and molecules, essentially, have a common characteristic of open cellular space and narrow gates that restrict the diffusion of solutes or ions by different mechanisms. The most well-known membrane protein channels are the water transporting channel, known as Aquaporins [1-3], and ion transport channels [4-5], the importance of which has been recognized by awards of the Nobel prize in chemistry in 2003.
2.3 Synthetic membranes for separation applications

Synthetic membranes in modern industry are selective semi-permeable barrier layers, fabricated from inorganic and organic materials, with the function of filtering different substances. Depending on the pore size, membranes are classified into different categories by their applications: particle filtration, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, pervaporation, and gas separation membranes. The size of molecules and ions diffuse through the membranes in the later three categories are in the range of subnanometer scale.

Among the wide applications of synthetic membranes, molecular-level separations are especially promising and important for global energy and environmental processes, such as natural gas purification (the major energy source in the 21st century), greenhouse gases capture, renewable H₂ separation, air separation (a multi-billion industry), and desalination of seawater for clean water production. Conventional processes for separating these gases or liquids, e.g., cryogenic distillation and adsorption-desorption processes, involve phase changes, therefore they consume significant amounts of energy. Membrane separation processes generally do not involve phase changes, therefore, they are more energy-efficient and cost-effective [6]. The first successful commercialization of membrane technology is reverse osmosis membrane for desalination of seawater since 1950s [7]. Following the success of desalination membrane, gas separation membranes have also been commercialized in chemical and energy industries since 1980s [8], for example, H₂/N₂ separation for hydrogen recovery in ammonia plant by Monsanto, separation of nitrogen from air, CO₂ and acidic gases removal from natural gas, and organic vapour removal from air or nitrogen streams. There are also some developing area, for example, separation of condensable gases (e.g. hydrocarbons) in natural gas and petrochemical industry. Membrane is also of great potential for separating CO₂ from flue gas emitted from coal-fired power plant. With the development of new combustion technology (e.g. combustion with pure O₂), there is also an urgent need for separation of O₂ from air. Therefore, research on membranes gas separation technology is of significant importance to the global energy industry.

Membrane materials are the key components in membrane separation technology. Molecular transport in membrane materials depends on several factors, mainly physical structure (pore size, fractional free volume) and chemical properties (affinity with molecules). According to the definition of International Union of Pure and Applied Chemistry (IUPAC), micropores are defined as pores with size less than 2 nm, with mesopores in the range of 2-50 nm, and macropores larger than 50 nm. As shown in Figure 2.1, with the pore size of the
membrane changes, the separation mechanism varies significantly, particularly for gas separation. Conventional dense membranes are made of polymers that pack efficiently with isolated free volume in the matrix. The gas molecules are dissolved in the polymer and diffuse slowly through the free volume depending on the thermal activation of the polymer segments. This is the usual separation mechanism for polymeric membranes. More attractive membrane materials are porous materials with interconnected free volumes or micropores. With the pores and channels interconnected at molecular dimensions (< 1 nm), the membrane would become a molecular sieve, allowing smaller gas molecules passing through the channels while blocking larger ones. When the pore size is larger (i.e. 2-50 nm) but smaller than the mean free path of gas molecules, the gas molecules would collide with the walls and the diffusion would behave as Knudsen flow. For porous membranes with even larger pore size (larger than the mean free path of gas molecules), all gas molecules could pass through without any selectivity.

Figure 2.1: Transport mechanisms of separation membranes. (A) Solution-diffusion through dense membranes used in gas separation, reverse osmosis and pervaporation, where molecules dissolve in the membranes and diffuse through; (B) Restricted diffusion or molecular sieving through precisely-defined pores and channels, used for gas separation; (C) Knudsen diffusion through pores, used in some gas separation membranes, with pore diameter \(d_p\) smaller than mean free path \(\lambda\) of gas molecules; (D) Bulk viscous flow through pores, used in ultrafiltration and microfiltration, no separation effect for gas separation, reverse osmosis, or nanofiltration.

Figure 2.2: Cross-sectional scanning electron microscopy (SEM) image of a commercial polymer membrane, with a thin dense selective layer supported by porous substrate.
Polymer membrane could be prepared in forms of flat sheet, or hollow fibre depending on the design of modules, e.g. spiral wound or hollow fibre modules. The structure of the membrane also depends on the need and purpose of tests. Thick membranes are often prepared (20-100 µm) for membrane characterization and permeation evaluation. In practical application, asymmetric membrane is prepared with a selective layer at the surface as thin as possible (<1 µm) with lower permeation resistance to enhance the permeance or flux of molecules (as shown in Figure 2.2). Similar to the asymmetric membrane, composite membrane is usually prepared with an effective thin film layer coated on a porous support [9].

With the development of nanotechnology and advanced functional nanomaterials over the past decades, there is a significant research interest in developing the next-generation nanoporous membranes for gas and liquid separation processes [10-11]. By tuning the pore size to match the kinetic diameter of chemical molecules and by tailoring chemical affinity towards specific molecules, both the permeability and selectivity properties are expected to be enhanced to an unprecedented level [10-14].

2.4 Molecular sieve materials

The term ‘molecular sieving’ refers to a particular physical property of open framework materials that could selectively sort molecules primarily based on the shape and size exclusion process. The small molecules could enter the pores or cages in the framework, while large molecules are restricted by the size and shape of the channels or apertures that link these cages. Conventional molecular sieve materials are usually inorganic materials, such as zeolites (aluminosilicate), carbon molecular sieves, activated carbons, silica, etc.

In the past decade, the materials and chemistry field have witnessed an explosive growth of interest in synthesis, design and fabrication of new-generation porous materials, such as metal-organic frameworks (MOFs) [15-17], porous organic cages (POCs) [18-19], covalent organic frameworks (COFs) [20-21], conjugated microporous polymer (CMPs)[22-23], and Polymers of intrinsic microporosity (PIMs)[24-29]. These porous frameworks are highly promising for molecular separations, gas storage, and catalysis.

Ordered framework (e.g. zeolite), from the viewpoint of condensed matter physics, is a representative type of crystalline solids with constituent atoms arranged in an orderly repeating pattern. In a broad context, molecular sieve materials are not restricted to the ordered frameworks, many other molecular sieves are formed of disordered frameworks that behave as amorphous solids (glass). The difference between crystalline and amorphous solids is exemplified by crystalline silica (quartz) and amorphous glass networks, as shown by the two-dimensional diagram in Figure 2.3. A wide range of materials can form
amorphous glasses, including metal oxides, elements, organic molecules, polymers, and metal alloys. In the amorphous solids, e.g. silica glass, long-range order is not present, although there is local ordering with respect to the tetrahedral arrangement of oxygen (O) atoms around the silicon (Si) atoms. Owing to the disordered packing of atoms, irregular pores could be formed in the amorphous frameworks, which could be used for molecular sieving of molecules [30].

![Figure 2.3: Two-dimensional schematic diagram of crystalline and amorphous glass networks. Blue: Si atoms; Red: oxygen atoms.](image)

### 2.4.1 Zeolites

Zeolites are the most well-known open frameworks, with well-defined crystalline structure forming regular shaped cages at molecular dimensions. The dimension of pores is conventionally defined by the ring size of the aperture which restricts the diffusion of molecules. For example, in a representative zeolite rho (Figure 2.4), the closed loop, built from eight tetrahedrally coordinated silicon (or aluminium) atoms and 8 oxygen atoms, form a "8-ring" that defines the aperture at 3.6 Å, which could selectively separate CO$_2$ and CH$_4$ [31], the kinetic diameters of the two molecules are 3.3 and 3.82 Å, respectively.

![Figure 2.4: A representative crystalline structure of zeolite rho.](image)
2.4.2 Metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs), are a novel class of porous polymeric materials [32-34]. The compounds are formed by coordination bonds between metal-containing units, or secondary building units (SBUs), with organic ligand molecules [35-39]. The coordination compounds could be extended to 2 or 3 dimensions, forming porous coordination polymers. The versatile combinations of SBUs and organic linkers allow the production of thousands of compounds, and the database of MOFs is still growing rapidly. A typical approach to MOFs synthesis is shown in Figure 2.5. Owing to their exceptional high surface area and porosity, MOFs are promising for a wide range of applications, including gas storage, separation, catalysis, and drug delivery, etc.

![Assembly of metal-organic frameworks (MOFs) by the copolymerization of metal ions with organic linkers. Adapted from reference [40].](image)

2.4.3 Zeolitic imidazolate frameworks (ZIFs)

Zeolitic imidazolate frameworks (ZIFs) are a sub-family of MOFs, formed by coordination bonds between metal ions and imidazole-containing organic linkers, as shown in Figure 2.6. Similar to MOFs, ZIFs have tuneable pore sizes and chemical functionality, coupled with exceptional chemical stability, and exhibit versatile structures analogous to that of inorganic zeolites [41]. For example, ZIF-8 is made from linking of zinc (II) cations and 2-methylimidazole anions, giving a sodalite topology with a pore cavity of 11.6 Å and a theoretical pore aperture of 3.4 Å [16].

Several types of ZIFs have been successfully prepared as membranes (Figure 2.6) and have demonstrated molecular sieving effect for gas separation [17, 42-52]. ZIF-8 has been demonstrated as capable of separating smaller gas molecules from larger ones, such as separation of H₂ from CH₄ (selectivity of 11-14) [44, 53], separation of H₂ from hydrocarbons [46], separation of CO₂ from CH₄ (relatively lower selectivity CO₂/CH₄ of 4-7) [42]. By similar preparation techniques, some other ZIFs, including ZIF-7 (pore aperture ~ 3.0 Å), ZIF-22 (~ 3.0 Å), and ZIF-90(~ 3.5 Å), have also been demonstrated as molecular
sieving membranes [43, 45, 47-49]. However, the selectivity of these membranes is not yet satisfactory for industrial-scale applications. The low selectivity is attributed to the flexible nature of the organic linkers and interfacial defects in the polycrystalline membranes. Although much progress has been made on zeolite membranes on the laboratory scale [54], they have not yet found industrial applications in the field of gas separation, mainly because of the challenges of fabrication at large scale without pinholes or cracks [17, 55]. Similarly, these challenges need to be resolved in the scale-up of MOF-based membranes for gas separation processes [17, 55].

![Image of synthetic pathways and structures of ZIFs and MOFs](image)

**Figure 2.6: Zeolitic imidazolate frameworks (ZIFs).** (A) Synthetic pathways of ZIFs reported by Yaghi’s group [16, 41], using a variety of imidazole-containing building blocks (B), generating open porous sodalite-like topological structure similar to that of conventional zeolites (C-D). (E) SEM image and EDX analysis of the cross-section of ZIF-8 membrane fabricated by Caro’s group [44].

### 2.4.4 Covalent organic frameworks (COFs)

Covalent organic frameworks (COFs), is another class of porous polymers formed from building blocks linked by purely covalent bonds, firstly reported by Yaghi’s group in 2005 [20]. As shown in **Figure 2.7**, the pathways of condensation reactions in COFs are very similar to the syntheses of other polymeric materials (e.g. PIMs), the difference is that COFs are generally in the crystalline state owing to its ordered molecular structure.

The first generation of COFs are two-dimensional crystalline materials, analogous to that of graphene. By tuning the size of building blocks, it was possible to tune the pore size...
from 7 to 27 Å. Later on, Yaghi’s group further synthesized 3D COFs using more rigid building blocks [21]. The 3D COFs show high surface area up to 4000 m² g⁻¹, which is much higher than that of 2D COFs (700 to 1600 m² g⁻¹). Owing to the high energy of covalent bonds, COFs polymers also show high thermal stability.

Figure 2.7: Chemical structure and synthetic pathways for covalent organic frameworks (COFs). Adapted from references [20] and [21]. (A) synthesis of COF-1, (B) COF-5, (C) crystalline structure of COF-5, (D) building block for 3D COFs, and (E-G) molecular structures of some representative 3D COFs.
2.4.5 Porous organic cages (POCs)

Porous organic cages (POCs), are another class of porous polymeric materials [18]. The representative synthetic chemistry of POCs is shown in Figure 2.8. Cage molecules are generated from the condensation of 1,3,5-triformylbenzene with diamines. Owing to the rigid shape, internal space is formed in the cages. However, the porosity also depends on the packing of these molecules, either in a crystalline state or an amorphous state depending on the monomers and the synthesis conditions [56]. Molecular dynamics simulations suggest that these cages could allow rapid diffusion of gas molecules [57]. Furthermore, these cages could also be synthesized into nanoparticles that can be incorporated into polymer, forming mixed matrix membranes [58].

![Figure 2.8: Synthetic pathways and chemical structures of porous organic cages (POCs) by cycloimination reaction of 4 trialdehydes and 6 diamine molecules. Adapted from references [18, 56].](image)

2.4.6 Conjugated microporous polymers (CMPs)

Conjugated microporous polymers (CMPs) are a sub-class of porous materials synthesized from rigid monomers in conjugation states [22-23], as shown in Figure 2.9. CMPs are normally amorphous networks rather than crystalline. CMPs are related to conjugated polymers that have been intensively studied in polymer electronics, but the network structure of CMPs makes them not soluble in solvents and difficult to process. Nevertheless, with the progress of synthetic chemistry, solution processable CMPs [59] were reported recently. These porous CMPs are related to applications in gas sorption [22], catalysis [60], light harvesting [61], and supercapacitors for energy storage [62], owing to their high surface area of CMPs (up to 1000 m²/g) and extended conjugation functions.
2.4.7 Carbon-based molecular sieves

Carbon-based materials, such as activated carbons, carbon molecular sieves (CMS), amorphous carbon [63], carbon nanotubes (CNTs) [64], and graphene [65-67], are also promising for molecular sieving materials. Activated carbons, with surface area typically about 1000 m$^2$ g$^{-1}$, have been used in a wide range of applications, including adsorbents and supports for catalysts. Activated carbons are produced from a series of steps: (i) carbonization of carbonaceous materials (such as coal and biomass) by thermal pyrolysis at high temperature (e.g. 600-1000°C) in inert atmosphere, (ii) followed by activation by controlled oxidative gasification (oxygen, steam, or CO$_2$) at high temperature (600-1200°C); (iii) further chemical activation with acid or base. Generally, activated carbons show a broad pore size distribution (trimodal distributions, from subnanometer to macropore range).

Carbon molecular sieves (CMS) are another class of carbonaceous materials that show much narrower size distribution (e.g. from 4 to 9 Å) [68]. Similar to the preparation of activated carbons, CMS materials are prepared from controlled thermal oxidative pyrolysis of carbonaceous materials, such as biomass, coal and polymers. The pore structure could be modified by subsequent treatment, such as partial gasification with steam or carbon dioxide (to open the pores), or controlled thermal cracking of hydrocarbons (to close the pores). By these delicate modifications via chemical reactions, the CMS could show selective adsorption and diffusion of molecules of different size, which is attributed to the narrow micropore size distribution. The ability to tailor the pore size distribution of CMS membranes and consequently the gas separation performance has been demonstrated in controlled oxidative pyrolysis of polymeric membrane precursors, notably by Koros and co-workers over the past two decades [69-72]. However, the presence of pore size distribution in CMS, even if narrow, results in molecular sieving selectivity that is lower than ordered frameworks such as zeolite molecular sieves.
In short summary, inorganic molecular sieves (e.g., zeolites, silica, CMS, etc), organic-inorganic frameworks (i.e., MOFs and ZIFs), and novel microporous polymeric molecules and frameworks (i.e., COFs, POCs, and CMPs) are highly promising for molecular separations due to their tuneable microporosity [54, 73]. However, these materials has some drawbacks that limit their scale up for large scale membrane separation: high cost, processability, complicated procedure of preparation, brittleness, low effective membrane area, low permeability in the case of highly selective dense membranes and difficulty of sealing at high temperatures [74]. Conversely, commercially used membranes are dominated by those made of polymers, which can be solution processed and manufactured in large scale.

2.5. Selective polymer membranes

Since the first commercial application of polymer membrane for H₂/N₂ separation (Prisms®, air Products) in ammonia plants in 1980s [6], numerous polymers have been developed, however, only a few of them have been successfully commercialized, such as polysulfone (PSF), poly(phenylene oxide) (PPO), cellulose acetate (CA), polycarbonates, and polyimides (Matrimid®) (see Appendix A). These conventional polymers are formed of disordered packed chains with very low free volume. Therefore, the gas transport through these polymers is very slow, giving considerably low gas permeability. In contrast, polymers with rigid macromolecular structures have high free volume and high permeability (Figure 2.10), such as poly(1-trimethylsilyl-1-propyne) (PTMSP) [75], Teflon® AF2400, substituted polyacetylenes [76], polyimides [77], thermally rearranged polymers [12], and PIMs [78-81].

Gas permeation in polymeric membranes is subject to a trade-off between permeability and selectivity, i.e. polymers with high selectivity present low permeability, and vice-versa. This trade-off behaviour has been summarized as an empirical upper bound relationship by Robeson in 1991 [82] and updated in 2008 [83]. The trade-off phenomenon has also been theoretically illustrated by a solution-diffusion model by Freeman [84].

Freeman predicted two strategies to enhance both the permeability and selectivity of polymeric membrane materials [84]: (i) improving the solubility selectivity (S_A/S_B), such as crosslinked poly(ethylene oxide) [85]; (ii) increasing the stiffness of polymer chains while maintaining large interchain spacing, such as rigid polyimides, thermal rearranged (TR) polymers [12, 86], and polymers of intrinsic microporosity (PIMs) [13, 26-27, 29, 81, 87-89]. These highly permeable and selective membranes have great potential arising from their low-cost solution processability (thin films or hollow fibers) that can be readily retrofitted to the existing polymer membrane industry.
Chapter 2  
Literature review and theory background

2.5.1 Polyimide polymers

Polyimides are synthesised by imidization of polyamic acid prepared from dianhydrides and diamines. Commercially available polyimides, such as Ultem® polyetherimide and Matrimid® 5218, have very low gas permeability. New polyimides containing more rigid and bulkier 6FDA units (2,2'-Bis (3,4-Dicarboxyphenyl) Hexafluoropropane Dianhydride) present much higher gas permeability and reasonable selectivity for several industrially important gas pairs [90-91]. The rigidity of the polymer chains is enhanced by the trifluoromethyl groups which restrict the rotation within the polymer backbone. Extensive reviews on polyimide polymer membrane can be found in the references[91]. These more permeable polyimides represent the second-generation polymers being commercialized in the membrane industry.
Recently, some new polyimides were synthesized using monomers with more rigid structure, which can be described as polymers of intrinsic microporosity, which will be introduced in detail in the following section on PIMs.

2.5.2 Thermal rearranged (TR) polymers

TR polymers are aromatic polymers prepared by thermal treatment of polyimides with ortho-functional groups (PIOFG) [12, 86]. Ortho-functional group can be hydroxyl (–OH), thiol (–SH), and amine (–NH$_2$) groups. The thermal treatments are usually performed at intermediate temperatures (350-450°C) in inert atmosphere, after which the polymers are transformed to aromatic, infusible, and insoluble materials. The thermal treatment method was extended to a variety of aromatic polymers with different chemical structures [86, 92-96]. A typical mechanism is shown in Figure 2.11. Advanced characterization analyses indicate that the free volume elements and their size distributions could be tuned by varying the monomer structures of precursor polymers and by using different thermal treatment protocols.

![Figure 2.11: Proposed mechanism of thermal conversion of hydroxy–imide to benzoxazole](image)

The thermal treatment transforms dense glassy polymer precursors with low free volume, to microporous polymers with interconnected microcavities with a narrow cavity size distribution. Such change of microporous structure results in highly permeable and selective membranes with exceptional gas transport properties. These TR polymer membranes exhibit excellent gas separation performance, especially in separation of light gas molecules from large molecules, such as CO$_2$/CH$_4$ separations. For example, the CO$_2$ permeability of a representative TR polymer is as high as 1600 Barrer while the CO$_2$/CH$_4$ selectivity is stable at about 50 with negligible plasticization effect at high pressure.

Thermal rearranged polymer membranes were initially studied by Park et al [12]. The thermally rearranged polymers were believed to have chemical structures as polybenzoxazoles (PBO), polybenzothiazoles (PBZ), polypyrrolone (PPL). The thermal conversion mechanism of hydroxy–imide to benzoxazole was initially proposed by Tullos...
and coworkers [97-98]. However, the mechanism remains to be debated because thermal pyrolysis-induced crosslinking is possible in the temperature range, as raised by Hodgkin *et al* [99-100].

Although the chemical mechanism is still not fully understood, TR polymers represent a unique class of materials that surpass the gas separation performance of all existing polymers. The polymer precursors have been widely used in industrial applications and are soluble in common organic solvents, so they can be easily prepared into various membrane modules, such as flat films or hollow fibers, and exposed to thermal treatment to transform to TR polymers. TR polymers are one type of the next-generation polymers for membrane separation applications.

### 2.6 Polymers of intrinsic microporosity (PIMs)

Polymers of intrinsic microporosity (PIMs), invented by Budd and McKeown [24, 26-29, 87], are a new class of microporous polymers. PIMs polymers are amorphous microporous materials with unique rigid and contorted macromolecular structure (for example, PIM-1, see Figure 2.10). Therefore, the backbone inhibits the free rotation or large scale conformational change and polymer chains cannot pack efficiently in the amorphous solid state, forming irregularly shaped free volume elements. The fractional free volume in PIM is sufficiently high that free volume elements are effectively interconnected, behaving like micropores (dimensions < 2 nm). Such high free volume allows the high solubility of small molecules owing to their dipole-dipole interactions (in particular, condensable gasses such as CO$_2$ and CH$_4$), while the ‘bottleneck’ or gates between free volume elements behave as a sieve for molecules with different sizes. Owing to the high intrinsic microporosity, the PIMs polymers are promising for a wide range of applications, such as membranes for molecular-level separations, adsorption, gas storage, and heterogeneous catalysis.

#### 2.6.1 First-generation PIMs

The first generation PIMs were synthesized by double aromatic nucleophilic substitution polycondensation of monomers containing rigid and contorted structures. The synthetic approach is shown in Figure 2.12, along with various types of monomers. PIMs can be synthesized into either network-like insoluble polymers, or as linear soluble polymers. More details of monomer candidates are shown in Appendix B.

A typical example of linear PIMs, PIM-1, is polymerized from polycondensation of 5,5′,6,6′-tetrahydroxy-3,3′,3′-tetramethylspirobisindane and 2,3,5,6-tetrafluoroterephthalonitrile. Critical parameters to high-molecular-weight PIMs are the stoichiometric ratio of
reactants and a high degree of conversion during the step-growth reactions. The microporous PIM-1 polymer is soluble in tetrahydrofuran, chloroform, and dichloromethane, therefore, it is easy to prepare a film using traditional solution processing method. Membranes have been prepared from these polymers and tested for gas separation. Also the polymer has solubility to condensable gases, therefore, it combines both high gas permeability and selectivity over light gases. For PIM-1 membrane, initial tests showed that the permeability of CO$_2$ is as high as 2300 Barrer with CO$_2$/CH$_4$ selectivity of 18.4 and CO$_2$/N$_2$ selectivity of 25 [24, 26, 87]. The permeability order is CO$_2$ > H$_2$ > He > O$_2$ > Ar > CH$_4$ > N$_2$. Later on, it was found that the polymer matrix could be swelled in alcohols [101], introducing extra free volume after removal of solvents, consequently, the permeability could be further enhanced.

Following the initial work of Budd and McKeown, many other types of PIMs polymer have been developed by synthesizing new monomers [102-103] and modification of existing PIMs [13, 104]. The synthetic chemistry allows versatile combination of monomers with different geometry, such as tuning the angles of the contorted sites, molecular length between the contorted sites, and pendant groups on the polymer backbone. Notable monomers include 9,10-Dimethyl-9,10-ethano-9,10-dihydro-2,3,6,7-tetrahydroxyanthracene [105], 2,2',3,3'-Tetra-hydroxy-1,1'-dinaphthy l[106], hexaphenylbenzene–based monomers [107], 6,6',7,7'-tetra-hydroxy-4,4',4'-tetramethyl-2,2'-spirobischromane [108].

Generally, changing the shape and geometry of monomers (Figure 2.12 and 2.13) could tune the rigidity of the polymer backbones and consequently the gas transport properties. For example, Cardo-PIM-1 synthesised from phenazyl monomers and 9,9-bis(3,4-hydroxyphenyl)-fluorene shows much lower permeability (CO$_2$ ~430 Barrer) [78], which is attributed to the greater conformational freedom and flexibility of the polymer chain. In contrast, a more rigid spirofluorene-based PIM (PIM-SBF) shows much higher permeability [88], though the selectivity remains at a modest level. Alternatively, tuning the molecular length of the units between contorted centres also affects the molecular packing of polymer chains, and consequently the gas transport properties.

Furthermore, monomers with different pendant groups (Figure 2.14) on the backbone could also affect the packing of polymer chains. For example, disulfone-based pendant groups may act as fillers in the intrachain free volume, consequently the polymer membranes show higher gas selectivity for O$_2$/N$_2$ (3.2 to 4.2) and CO$_2$/N$_2$ (15 to 23), while the gas permeability decreases (CO$_2$ ~1000 Barrer), which is attributed to the lower fractional free volume [102-103].

The strategies to improve the separation performance of PIMs membranes can be summarized as: (i) enhancing the rigidity of polymer chain by synthesis of new monomers
[81, 88, 102-103, 109], (ii) post-synthetic modification of PIMs polymer [13, 104, 110], (iii) mixed matrix membranes [111-113], and (iv) crosslinking induced by chemical [114] or heat treatment [115]. The gas permeation properties of these PIMs polymers are slightly different from that as reported by Budd and McKeown, however, they generally show high permeability and moderate selectivity, which fall in the region that is close to the Robeson’s upper bound in 2008.

Figure 2.12: Synthetic pathway and monomers for polymers of intrinsic microporosity (PIMs) based on dibenzodioxin formation reactions. The 3D model next to the chemical formula is obtained after energy minimization. References [24, 27-29, 78, 88, 108-109, 116-118].
Figure 2.13: Synthetic pathway and monomers for polymers of intrinsic microporosity (PIMs) based on dibenzodioxin formation reactions (continued).

Figure 2.14: Visualization of PIMs monomers with different pendant groups. The chemical structures are redrawn from references [102-103].
2.6.2 Polyimides with intrinsic microporosity

Polyimides with intrinsic microporosity were synthesized following the conventional cycloimidization pathways, with rigid monomers of bis(carboxylic anhydride) and a diamine [79-80]. Two types of synthetic pathways were developed via combination of either spirobisindane-containing bis(carboxylic anhydride), or spirobisindane-containing diamine, as shown in Figure 2.15. The molecular structures of PIM-polyimides are similar to that of PIM-1 and PIM-7, with addition of imide linkages. The essential idea is incorporating the spirobisindane unit into the polymer backbone, which provides a site of contortion. Of course, the monomers are not limited to the spirobisindane-containing units.

![Figure 2.15: Synthesis of polyimides with intrinsic microporosity (PIM-PI). The synthetic pathway follows cycloimidization reaction between a bis(carboxylic anhydride) (X) and a diamine (Y). The chemical structures of monomers are redrawn from reference [79-80].](image-url)
Thermal treatment has been applied to transform PIM-polyimides. For example, Pinnau and Han’s groups [119-121], and Budd and Lee’s groups [122] independently studied the thermal treatment of polyimides containing a spirobisindane moiety (PIM-6FDA-OH) at temperature around 400-450°C. The gas transport properties of these thermally treated polymers show significant increase of CO₂ permeability while the selectivity remained stable. For example, the CO₂ permeability showed a significant increase from 100 to 675 Barrer, while the selectivity remained stable. In addition, these thermally treated membranes show robust mechanical properties. Furthermore, the PIM-PI polyimides could be transformed to carbon molecular sieve membranes. The thermal treatment protocols have significant effect on the conversion of polymers and their gas transport properties.

2.6.3 New synthetic pathways of PIMs

In the first-generation PIMs, the spirobisindane (SBI) unit and dioxane linkages are relatively flexible [123], therefore the polymer chains could still pack densely. An alternative strategy is enhancing the rigidity of polymer chains while maintaining interchain spacing [81, 88, 124]. A new synthetic pathway for PIMs containing rigid ethanoanthracene (EA) and Troger’s Base (TB) units was recently reported by McKeown’s group [81]. The polymerization pathway was inspired by the Tröger’s base (TB), bridged bicyclic amine 2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine, which was originally reported in 1887 after its serendipitous isolation from the reaction between p-toluidine and dimethoxymethane. They designed rigid aromatic diamine monomers, for example, 2,6(7)-diamino-9,10-dimethylethanoanthracene (Figure 2.16, A and C) and 5,5′,(6),(6′)-diamino-3,3′,3′-tetramethyl-1,1′-spirobisindane (Figure 2.16, B and D), for the TB polymerization reaction and generated rigid ladder polymer consisting of fused-rings.

The resulting TB-based polymers are truly ladder polymers linked by purely covalent bonds. Owing to the contorted macromolecular structure, PIM-EA-TB shows a high BET surface area of 1028 m² g⁻¹, which is higher than all the previous reported PIMs. Dense flat membranes casted from the PIM-EA-TB polymer show extraordinarily high permeability, such as H₂ permeability up to 7760 Barrer, CO₂ permeability of 5000 to 7000 Barrer, O₂ permeability of 1500 Barrer. The gas transport properties of H₂/N₂, H₂/CH₄, and O₂/N₂ gas pairs all surpass the Robeson’s upper bound, in terms of permeability and selectivity. However, CO₂/CH₄ and CO₂/N₂ gas pairs show modest selectivity of about 10, therefore the overall gas transport properties falls below the upper bound. The kinetic parameters of PIM-EA-TB, such as solubility and diffusion coefficients as derived from time-lag method, are higher or comparable to that of PIM-1. The mechanism of gas permeation in PIM-EA-TB is
still not fully understood. In conventional dense polymers, the Brownian movement of flexible chain segment allows the diffusion of gas molecules. In the case of gas permeation through PIMs, the permeation of light gas molecules is dominated by fast diffusion through the interconnected cavities, while CO₂ permeation is determined by high solubility, which is a common characteristic for PIMs polymers owing to the presence of high free volume. In addition, PIM-EA-TB also suffers from physical aging, a similar characteristic of PIMs.

![Synthetic pathway of Tröger’s base (TB)-based PIMs.](image)

**Figure 2.16:** Synthetic pathway of Tröger’s base (TB)-based PIMs. (A) PIM-EA-TB, (B) PIM-SBI-TB. DMM, dimethoxymethane; TFA, trifluoroacetic acid. Chemical structures are redrawn from reference [81]. (C) Molecular model of PIM-EA-TB and (D) PIM-SBI-TB, derived from Chemdraw after energy minimization.

### 2.6.4 Post-synthetic modifications of PIMs

While chemists are smart to design and invent new synthetic chemistry, it is also useful to find simple ways to change the chemical structure of existing PIMs polymers via post-synthetic modifications. Current studies have been focused on the modification of nitrile groups in PIMs polymer, such as hydrolysis to carboxylic acids, reaction of sodium nitride to tetrazole groups, reaction with P₂S₅ to thioamides, and reaction of hydroxylamine to amidoximes, as shown in Figure 2.17.
These approaches are effective for modification of PIM-1, most of the resulting polymers generally show enhanced selectivity at the trade-off of permeability. One notable modification is tetrazole-substituted PIMs (TZPIMs). Du et al. [13] introduced tetrazole groups into the polymer networks of PIM-1, which functionalized polymer matrix shows high solubility of CO₂ and forms narrower cavity size. Similarly, other substituted groups, such as carboxylic acid and thioamides, could also introduce hydrogen bonding into the polymer matrix, which significantly reduces the surface area probed by nitrogen and limit the diffusion of large molecules. These modifications highlight the significant impact of intermolecular interactions on the packing of polymer chains and their physical properties. The hydrogen bonding and their impact on physical properties will be introduced in detail in the following section.

Figure 2.17: (A) Post-synthetic modification of nitrile group in PIM-1 polymer. (B) Hydrolysis to carboxylic acids [104], (C) reaction of sodium nitride to tetrazole groups [13], (D) reaction with P₂S₅ to thioamides [110], (E) reaction of hydroxylamine to amidoximes [125].

2.7 Intermolecular forces in polymers

While polymer chemistry elegantly defines the combination of atoms and molecules as building blocks to individual polymer molecules, the physics of polymers defines the dynamic changes of states, and intermolecular forces between the macromolecules control the properties of the polymer, a key area of soft matter physics.

In 1991, Pierre-Gilles De Gennes gave his Nobel lecture entitled ‘Soft Matter’ [126]. In the first two paragraphs, he highlighted the two major features of soft matter:
'What do we mean by soft matter? Americans prefer to call it “complex fluids”. This is a rather ugly name, which tends to discourage the young students. But it does indeed bring in two of the major features:

1) **Complexity.** We may, in a certain primitive sense, say that modern biology has proceeded from studies on simple model systems (bacteria) to complex multicellular organisms (plants, invertebrates, vertebrates...). Similarly, from the explosion of atomic physics in the first half of this century, one of the outgrowths is soft matter, based on polymers, surfactants, liquid crystals, and also on colloidal grains.

2) **Flexibility.** I like to explain this through one early polymer experiment, which has been initiated by the Indians of the Amazon basin: they collected the sap from the hevea tree, put it on their foot, let it “dry” for a short time. And, behold, they have a boot. From a microscopic point of view, the starting point is a set of independent, flexible polymer chains. The oxygen from the air builds in a few bridges between the chains, and this brings in a spectacular change: we shift from a liquid to a network structure which can resist tension - what we now call a rubber (in French: caoutchouc, a direct transcription of the Indian word). What is striking in this experiment is the fact that a very mild chemical action has induced a drastic change in mechanical properties: a typical feature of soft matter.

Of course, with some other polymer systems, we tend to build more rigid structures…'

Interestingly, the example mentioned in the lecture, **vulcanization of natural rubber**, highlights the importance of intermolecular forces introduced by chemical crosslinking on the physical properties of polymers. The intermolecular forces in polymers can be divided into noncovalent interactions and covalent crosslinking. The noncovalent interactions include: (i) hydrogen bonding, (ii) dipole-dipole interactions, and (iii) van der Waals forces. Among these intermolecular forces, hydrogen bonding and covalent crosslinking are strong interactions that could significantly alter the physical properties of polymer membranes. Hence, we only focus on the introduction of hydrogen bonding and covalent crosslinking in polymers, and particularly their impact on the packing of polymer chains and structure of free volume, and molecular sieving properties.

### 2.7.1 Hydrogen bonding

A hydrogen bond is the electromagnetic interaction between polar molecules where hydrogen is bound to a highly electronegative atom, such as N, O, F, and S. The hydrogen bonds can occur between molecules (intermolecular) or within different groups of a single molecule (intramolecular). Hydrogen bonding plays an important role in controlling the intermolecular forces within polymer molecules, and consequently the structural control of molecular packing of polymer chains and their physical properties.

A well known polymer is polyamide (e.g. Nylon 6,6, shown in Figure 2.18), in which the intermolecular hydrogen bonding between carbonyl groups and –NH in amide groups of adjacent linear chains leads to formation of crystalline sheets, linked by van der Waals forces.
Such dense packing of sheets results in high mechanical strength and low gas permeability. In fact, polyamides have been used for fabricating reverse osmosis (RO) membranes for desalination of seawater since 1977, based on interfacial polymerization reaction of meta-phenylenediamine (MPD) with trimesoyl chloride. Most commercially used RO membranes are based on similar synthetic chemistry, therefore, such intermolecular interactions are important factors that affect the packing of polymer chains and water transport properties.

Figure 2.18: Hydrogen bonding in polyamide (Nylon 6,6).

In PIMs polymers, hydrogen bondings have been mainly introduced by modification of the nitrile groups to other functional groups, such as hydrolysis to carboxylic acids, reaction with sodium nitride to tetrazole groups, reaction with P$_2$S$_3$ to thioamides, and reaction with hydroxylamine to amidoximes, as introduced in Section 2.6.4. In these modified polymers, the polymer chain length, molecular weight distribution and backbone structure are not altered; therefore they serve as excellent candidates for studying the effect of intermolecular interactions on the free volume and molecular sieving properties.

Figure 2.19: Hydrogen bonding in carboxylated PIM polymer chain. Adapted from references [104, 127]. The loosely packed unmodified PIM-1 polymer chains could be tightened by the hydrogen bonding (dashed lines), which is thermally reversible upon increase or decrease of temperature.

The hydrogen bonds introduce intramolecular or intermolecular interactions, as shown in the schematic diagram in Figure 2.19, forming impermanent networks from independent rigid polymer chains. In carboxylated PIMs, the nitrile groups are modified to carboxylic acid groups by hydrolysis reactions. The carboxylic acid groups would form hydrogen bonding with the ether linkages in the backbone or dimmers between carboxylic acid groups. In another similar study by Budd’s group, the nitrile groups were modified to thioamide groups,
which also introduce hydrogen bondings (Figure 2.20). The hydrogen bonding is reversible depending on the change of temperature. At elevated temperatures, the hydrogen bonds are weaker and the network structure is broken. These hydrogen bonded networks are not soluble in chlorinated solvents but become soluble in polar aprotic solvents, such as DMF, DMAc, and NMP.

Figure 2.20: Hydrogen bonding in Thioamide-PIM polymer matrix. (A) Possible intramolecular (\(-\text{NH}_2\) with ether linkages) and intermolecular (=S with \(\text{NH}_2\)) hydrogen bonding in TA-PIM polymer reported by Mason et al in Budd’s group[110]. (B) An energy minimized molecular model of TA-PIM fragment containing 10 repeating units. Hydrogen bonds are noted by dashed blue and grey lines.

The modifications of nitrile groups to carboxylic acid or thioamide groups resulted in a loss of surface area and free volume. This is mainly attributed to the intramolecular and intermolecular interactions induced by hydrogen bonding between functional groups. The denser packing of polymer chains leads to higher selectivity at significant decrease in permeability. In the case of thioamide-PIM, further ethanol treatment could enhance the CO\(_2\) permeability to 1120 Barrer, while the selectivity of CO\(_2\)/N\(_2\) selectivity maintains as high as to 30.

The most prominent modification of PIMs is the tetrazole-substituted PIMs (TZPIMs). Du et al. [13] performed chemical modification of nitrile groups in PIM-1 to tetrazole groups, which results in two-fold effect: (1) high CO\(_2\) solubility due to the presence of tetrazole groups; (2) enhanced rigidity of polymer network linked by hydrogen bonding introduced by the tetrazole groups. Molecular modelling suggests that hydrogen bonding is formed between the tetrazole groups with the dioxane linkages (Figure 2.21), which tightens the packing of polymer chains, whilst the bulkier tetrazole groups could maintain large intrachain spacings. Owing to the higher CO\(_2\) solubility and enhanced rigidity, the polymer shows higher selectivity of CO\(_2\) over N\(_2\) (ideal CO\(_2\)/N\(_2\) gas selectivity about 30) while the CO\(_2\) permeability (2500-3000 Barrer) remains at remarkable levels compared to the raw PIM-1
(CO\textsubscript{2} permeability of 6500 Barrer and selectivity of 19). The hydrogen-bonded CO\textsubscript{2}-philic polymer networks perform even better for separation of CO\textsubscript{2}/N\textsubscript{2} mixture with selectivity as high as 40. However, the performance of TZPIMs remains to be improved for separation of condensable gas molecules (CO\textsubscript{2} and CH\textsubscript{4}), which only shows modest selectivity (~15).

![Figure 2.21: Hydrogen bonding in TZ-PIMs polymer matrix. (A) Molecular simulation of unmodified PIM-1. (B) Molecular simulation of tetrazole-substituted PIM-1 (TZ-PIM), showing the hydrogen bonding formation between tetrazole groups with the dioxane linkages of the backbone. Adapted from reference [13].](image)

### 2.7.2 Covalent crosslinking

Covalent cross-linking of polymer is the process of chemically linking polymer chains by covalent bonds. After covalent crosslinking, the polymer molecules cannot slide over each other so easily and the resulting polymer network becomes tougher and less flexible. Such crosslinked network may become more resistant to plasticization due to the sorption of condensable gas molecules (e.g. CO\textsubscript{2}), therefore covalent crosslinking are a favourable approach to stabilize polymeric membranes.

Covalent crosslinking bonds are usually formed by chemical reactions between various functional groups of polymer chains and reagents. A well-known example of covalent crosslinking of polymer is the crosslinking of natural rubber by sulphur or oxygen molecules as shown in Figure 2.22, discovered as vulcanization in the 19\textsuperscript{th} century though the rubber curing history can be dated back to prehistoric time. In modern polymer chemistry, it is possible to define the functional groups in polymers that allow covalently crosslinking and post-crosslinking. Other widely used methods are mixing the monomers or polymer chains with crosslinking reagents (or crosslinker), which would initiate chemical reactions and form crosslinks. Detailed reviews on covalent crosslinking with various functional groups can be
Examples of functional groups include: (i) primary amines \((-\text{NH}_2\)) (ii) carboxyls \((-\text{COOH})\); (iii) thiols \((-\text{SH})\); and (iv) carbonyls \((-\text{CHO})\). For each of these functional groups, there are several types of reagents that could form covalent crosslinking. A notable example is covalent crosslinking of polyimides containing pendant carboxylic acid groups, involving the reactions of ethylene glycol with the carboxylic acid groups via the monoesterification, followed by a second step of heat treatment to crosslink the polymer chains via a transesterification reaction [129], as shown in Figure 2.23.

Figure 2.22: Schematic diagram of covalent crosslinking of polymer via a vulcanization reaction. Initially, the independent linear polymer chains are entangled but not covalently crosslinked. The reactions chemically link adjacent segments leading to formation of a crosslinked network. In the case of vulcanization of natural rubber, the crosslinking points are sulphur bridges.

Figure 2.23: Crosslinking of carboxylic acid-containing copolyimides with ethylene glycol. Two steps are involved: (1) reaction of carboxylic acid groups with ethylene glycol, (2) crosslinking via transesterification. Adapted from reference [129].

Another well-known example in polymer membrane field is the covalent crosslinking of polyimides with diamines, via the transformation of imide to amide groups. Polyimides membranes have been patented by Du Pont since 1988 [130], later on the company further disclosed the modification of polyimide with amine solution to enhance the selectivity of gas separation and resistance to chemicals [131]. Extensive follow-up studies have indicated a possible mechanism of reversible covalent crosslinking reactions between the imide groups...
and amine groups. Researchers in Chung’s group studied the chemical crosslinking modification of polyimide membranes by diamine solutions, and proposed a mechanism of reaction of imide groups with amino groups forming amide groups [132-133], as schematically shown in Figure 2.24. They found that such chemical crosslinking leads to significant drop in permeability while the selectivity maintain constant. The decrease of permeability was attributed to the reduction in free volume, chain mobility and interstitial chain space after cross-linking.

![Proposed mechanism of chemical crosslinking of polyimide polymer with p-xyylene diamine](image)

Figure 2.24: Proposed mechanism of chemical crosslinking of polyimide polymer with p-xyylene diamine [132-133].

Covalent crosslinking reactions are generally irreversible, however, in some cases covalent crosslinking bonds can be reversible under external stimulus, such as thermal treatment, light irradiation, or catalysts. Well known examples of reversible covalent crosslinking include the thermally reversible Diels-Alder (DA) and retro-Diels-Alder (RDA) reactions [134-136] at low temperature (<150°C) (Figure 2.25). The monomers containing functional groups such as furan or maleimide could form a unique structure by two carbon-carbon bonds through the DA reaction. Upon heating, the polymer can break down to original monomers through the RDA reaction pathway. The DA/RDA reactions have been used to crosslink polymer chains by linking the pendant groups [136], or polymerize polymers from monomers through the successive DA reactions forming the backbone [137].
Figure 2.25: General mechanism of Diels–Alder cycloaddition reaction. (a) Diels-Alder (DA) and retro-Diels-Alder (RDA) reactions [138]. A and B need not to be connected, C and D can be connected to each other through any group. (b) An example of DA/RDA reactions involving furan and maleimide functional groups [136].

Another example of reversible covalent crosslinking system is the thiol-based polymers, which containing disulfide bonds that can be reversibly crosslinked through oxidation and reduction reactions. Under oxidizing conditions, the thiols (-SH) groups of each polymer chain (or monomer) could form disulfide (-S-S-) bridges, crosslinking the materials to polymer [139]. Under reducing conditions, the disulfide bonds break down and form to original monomers.

In addition, crosslinking can also be induced by heat, irradiation, or UV light. For example, UV light is very efficient for crosslinking poly(ethylene oxide) [85]. A detail review on photo-induced crosslinking or degradation of polymers can be found in the reference [140]. In some cases, these covalent crosslinking processes are possibly also associated with the degradation of polymers, such as chain scission or radicals-induced degradation.

Thermal crosslinking at intermediate temperature (<450°C) are also used in crosslinking polymers. For example, Koros and co-workers found the crosslinking of carboxylic acid-containing 6FDA-based polyimides annealed at temperatures close to the glass transition temperature (375°C)[141]. The authors performed various characterization techniques and ruled out the possible mechanisms including charge transfer complexing, oligomer cross-linking, decomposition, and dianhydride formation. The decarboxylation reaction removes the pendant acid group creating a phenyl radical capable of attacking other portions of the polyimide forming covalent aliphatic and aryl crosslinking bonds. Later on, Du et al [115] also studied thermal crosslinking of carboxylic acid-containing PIMs prepared from hydrolysis of PIM-1. The authors proposed a possible crosslinking pathway involving aryl radical-induced thermal decarboxylation and crosslinking, as shown in Figure 2.26.
Figure 2.26: Possible mechanism of decarboxylation-induced crosslinking of carboxylic acid-containing PIMs polymer. Possible crosslinking sites on the carboxylated PIMs: (1) through the methyl, (2) Biphenyl radicals, and (3) at the cleaved CH$_3$ site. The structures are adapted from reference [115].

Generally, covalent crosslinking converts the flexible polymer chains to rigid polymer networks, consequently the mechanical properties are changed depending on the degree of crosslinking. In polymer membrane field, covalent crosslinking are useful for enhancing the rigidity of polymer network, consequently improving the selectivity of molecular separation, and resistance to gas plasticization and solvent. The covalent crosslinked polymer networks would also become useful for separation of liquid fuels (e.g. pervaporation) and separation of chemicals and solvents (e.g. nanofiltration), which are becoming important for industrial applications.
2.8 Mixed matrix membranes (MMMs)

Mixed matrix membrane, known as mixing molecular sieves into polymer matrix (Figure 2.27), has been an active area of research over the past decade. The gas separation performance of conventional dense polymers is limited by the slow diffusion of gas molecules through the isolated free volume elements. The approach of mixed matrix membrane was proposed to enhance the gas separation performance of dense polymers by adding highly permeable and selective molecular sieves [142-143]. Mixed matrix membranes of polymer and conventional molecular sieves, such as zeolites and carbon molecular sieves, have always been compromised by the interfacial defects, poor dispersion and aggregation of fillers [144-145].

Figure 2.27: A schematic diagram of mixed matrix membrane containing dispersed fillers in a continuous polymer matrix. In the dashed circle, the molecular structure of ZIF-8 [16] is included as an example of molecular sieve material.

The physical and chemical properties of inorganic fillers could be tuned to enhance the gas transport in the matrix [146]. Various types of inorganic fillers have been incorporated into polymer matrix aiming to improve the gas permeability and selectivity. Mixed matrix membranes are expected to combine the molecular sieving effect of fillers and processability of polymers. Therefore, they could be readily scaled up for industrial applications using the established fabrication techniques for polymer membranes [147].

The Maxwell model was initially presented by Maxwell in 1873 describing the specific resistance ($K$) of a heterogeneous medium consisting of a substance of specific resistance $k_C$, containing dispersed small spheres of specific resistance $k_D$, with a volume fraction of $\phi_D$ [148]:

$$K = k_C \left[ \frac{2k_D + k_C + \phi_D (k_D - k_C)}{2k_D + k_C - 2\phi_D (k_D - k_C)} \right]$$

(2-1)

where $k_C$ is the resistance of the continuous medium, $k_D$ is the resistance of the dispersed spheres. The model assumes that the spheres are discontinuous that they do not interfere with each other, and the volume fraction is low.
The gas permeability through a membrane under the driving force of concentration gradient is analogous to the electrical conductivity \((\sigma=1/k)\) through a heterogeneous media. Therefore, the Maxwell model can be modified to describe the gas permeability:

\[
\frac{1}{P_{eff}} = \frac{1}{P_C} \left[ 2 \left( \frac{1}{P_D} + \frac{1}{P_C} \right) + \phi_D \left( \frac{1}{P_D} - \frac{1}{P_C} \right) \right] - \frac{2}{P_D} \left( \frac{1}{P_C} - \frac{1}{P_D} \right)
\]

where \(P_{eff}\) is the effective permeability of the composite membrane, \(P_C\) and \(P_D\) represent the permeability of the continuous phase (polymer) and dispersed phase (filler), respectively. The equation can be simplified as:

\[
P_{eff} = P_C \left[ \frac{P_D + 2P_C - 2\phi_D(P_C - P_D)}{P_D + 2P_C + \phi_D(P_C - P_D)} \right]
\]

With the known permeability, the ideal selectivity of gas pairs could also be predicted. The model is applicable to diluted suspensions of spherical particles in a matrix without consideration of non-ideal cases, such as the particle size distribution, shape, interfacial voids, aggregation of particles, pore blockage, and enhanced rigidity of surrounding polymer chains due to intermolecular interactions.

Ideally, addition of highly permeable and selective fillers could potentially enhance the overall permeability and selectivity of the resulting composite membrane to significant levels. Unfortunately, mixing amorphous polymer with fillers has always been complicated with phase separation and defects at the interface, which is the critical issue in mixed matrix membranes. In addition, the loading of fillers can not exceed certain limit due to the potential aggregation and poor mechanical properties. These issues have limited the practical applications of mixed matrix membranes.

Another critical issue in development of mixed matrix membranes is the mechanism of gas transport. This is particularly important when the size of fillers is scaled down to nanoscale or comparable to that of polymer chains. Over the past decade, numerous studies have indicated that incorporation of nonporous nanoparticles into polymer matrix could disrupt the packing of polymer chains, which results in increase of free volume elements, or defects at the interface with lower selectivity. Such membranes behave as hierarchically porous materials, with diffusion path shortened and adsorption is kinetically enhanced. Therefore, the selectivity of solubility-favoured vapours and hydrocarbons over light gas is enhanced, known as reverse-selective.
New microporous open frameworks, such as metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and porous organic cages, are also potential candidates for mixed matrix membranes. These novel porous polymeric materials would have better compatibility with polymer chains, owing to the organic nature of the linkers. Furthermore, the functional groups of organic linkers allow the possibility of physical or chemical crosslinking with polymer chains via intermolecular interactions, which is distinctively different from conventional inorganic molecular sieves (e.g. zeolite, activated carbon, etc). Therefore, the polymer/MOFs composite membranes have been an active area of research in the past several years [149-156]. Again, incorporation of nanoscale MOFs into polymer matrix would revisit the challenge of phase separation and the argument about the gas transport pathways, e.g. through the filler, or the interface between the filler and polymer phase.

2.9 Glass transition temperature and free volume theory

The thermodynamic state of materials is generally distinguished between the first and second order transitions. For the first order transition, the first derivatives of the Gibbs free energy exhibit discontinuity. In the case of second order transitions, the free energy function itself and the first derivatives are continuous, while the second partial derivatives of the function (e.g. heat capacity, compressibility, and the thermal expansion coefficient) are discontinuous. The glass transition temperature, $T_g$, is subject to the experimental conditions, for example, the cooling rate from an equilibrium state (liquid) to a nonequilibrium state (glass). The glass transition temperature is normally determined by measuring the change of heat capacity as a function of temperature, whereas the point of discontinuity of heat capacity indicates the experimental $T_g$. Specifically, amorphous polymers transit from glassy state to liquid or rubbery state at temperature above the glass transition temperature, and show viscous liquid like properties. The glass transition is related to the cooperative movement of polymer segments in long range and in short range. Below the glass transition temperature, the entangled polymer chains only allow local movement of segments, which is related to the presence of free volume.

In 1960, Fujita proposed that the total volume of polymer consists of three components [157-158]: (i) the occupied volume of macromolecules; (ii) the interstitial free volume, (iii) hole free volume. This is schematically shown in Figure 2.28. Many other explanations were developed to illustrate the free volume theory and glass formation, though they all have shortcomings. These theories assume that the liquids contain a certain amount
of free volume, which provides space that permits the motion of adjacent segments. The fractional free volume is defined as:

$$\frac{v_f}{v} = f_g + \alpha_f (T - T_g)$$  \hspace{1cm} (2-4)$$

Where $f_g$ is the fractional free volume at the glass transition temperature, and $\alpha_f$ is the expansion coefficient of the free volume.

Fujita's free volume theory [157-158] and other similar theories [159-160] are based on the equation developed by Doolittle. Doolittle equation is an semi-empirical equation for viscosity of liquids [161]:

$$\eta = A \exp \left( \frac{Bv_0}{v_f} \right)$$  \hspace{1cm} (2-5)$$

where $v_0$ and $v_f$ are occupied and free volumes, respectively. $A$ and $B$ are numerical constants.

The fractional free volume (FFV) in conventional glassy polymers are calculated using an empirical equation following the Bondi’s method [162]:

$$FFV = \frac{V_{FFV}}{V_{sp}} = \frac{V_{sp} - 1.3V_{vdW}}{V_{sp}}$$  \hspace{1cm} (2-6)$$

Specifically, the occupied free volume in polymers is related to the van der Waals volume ($V_{vdW}$) of the polymer chains.

This equation is widely used in characterizing the FFV of polymer in the polymer membrane research field, however this empirical equation only give roughly estimated values. Using this method, the FFV of PIM-1 could be as high as 0.26. Experimentally, the FFV could be determined by different techniques, such as positron annihilation lifetime spectroscopy (PALS), and gas sorption measurements.

![Schematic diagram of free volume in polymers and dependence with temperature](image)

**Figure 2.28: Schematic diagram of free volume in polymers and dependence with temperature.**

$T_g$: glass transition temperature. At slower cooling rate, the $T_g$ decreases to $T_g'$. 

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2.10 Gas sorption in porous glassy polymers

Amorphous glassy polymer can be assumed as heterogeneous material consisting of a continuous domains of polymer chain and domains of microcavities (holes). These microcavities are present in isolated state in dense polymer matrix, or interconnected in microporous polymers. The gas sorption in glassy polymers is always described by the dual mode sorption model. The dual mode sorption model is defined as the combination of sorption following the Henry’s law (dissolution in continuous chain matrix) and Langmuir sorption model (sorption in the cavities or free volume elements).

The gas concentration ($C$) in the polymer as a function of pressure is described as:

$$C = C_D + C_H = k_D p + \frac{C_H^b p}{(1 + b p)}$$

where $C$ is the gas concentration, $C_D$ is the gas concentration by dissolution, $C_H$ is the gas concentration due to hole saturation, $k_D$ is the Henry’s law dissolution constant, $p$ is the pressure, $C'_H$ is the Langmuir capacity constant, and $b$ is the hole affinity constant.

The gas solubility is defined as:

$$S = \frac{C}{p} = k_D + \frac{C'_H b}{(1 + b p)}$$

The dual mode sorption model does not include parameters that fundamentally correlate with the properties of polymer, gas molecules, and their interactions. Furthermore, the model is too simple to consider the broad size distribution of pores in amorphous polymers. Nevertheless, the model conceptually explains the gas sorption behaviour in polymers. It should be noted that the sorption of gases in polymers may also induce structural changes. For example, gas sorption in glassy polymer are subject to the plasticization effect which originates from the swelling of the polymer upon sorption of condensable gases (e.g. CO$_2$ and hydrocarbons), which could result in poor selectivity of the membrane and consequently change of gas separation performance.

2.11 Gas permeation and diffusion through polymer membranes

For polymeric membrane, the gas permeation is usually described by a solution-diffusion mechanism. Generally, the gas permeation follows three steps: (1) absorption of gas molecules into the polymer at the high pressure side by chemical affinity or solubility; (2) gas diffusion within the polymer matrix under the driving force of concentration gradient; and (3) gas desorption from permeate side (low pressure). The diffusion of gas molecules is the rate-limiting step of gas permeation through a membrane.
The diffusion equation is described by Fick’s law:

\[ J = -D \nabla C \]  \hspace{1cm} (2-9)

where \( J \) is the rate of transfer per unit area of section per unit time, \( C \) is the concentration of diffusing substances.

Hence, in the case of diffusion along one direction, the concentration would change with time expressed as the Fick’s second law, assuming the diffusion coefficient is constant:

\[ \frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} \right) \]  \hspace{1cm} (2-10)

where \( D \) is the gas diffusion coefficient in the membrane. In polymeric and heterogeneous materials, the diffusion coefficient would be a function of position and depend on the concentration, so a more accurate equation is expressed as:

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D(x) \frac{\partial C}{\partial x} \right) \]  \hspace{1cm} (2-11)

Under steady state, the concentrations remain constant at all positions by time, and the diffusion coefficient is constant:

\[ \frac{d^2 C}{dx^2} = 0 \]  \hspace{1cm} (2-12)

The integration form of equation (2-12) with the boundary conditions, \( x = 0 (C = C_2) \) and \( x = l (C = C_1) \), gives:

\[ \frac{C_2 - C}{C_2 - C_1} = \frac{x}{l} \]  \hspace{1cm} (2-13)

Therefore, the rate of mass transfer could be expressed as:

\[ J = -D \frac{dC}{dx} = \frac{D(C_2 - C_1)}{l} \]  \hspace{1cm} (2-14)

In the case of gas permeation, the steady-state permeability of gas through the membrane (see previous Equation 2-2) is defined as:

\[ P = \frac{J \times l}{(p_2 - p_1)} \]  \hspace{1cm} (2-15)

where \( p_2 \) and \( p_1 \) are the upstream (i.e., high) and downstream (i.e., low) pressures, respectively. The permeability coefficient is expressed in Barrer, where 1 Barrer = \( 1 \times 10^{-10} \) cm\(^3\) (STP) cm cm\(^{-2}\) s\(^{-1}\) cmHg\(^{-1}\). Combining equations (2-14) and (2-15), the permeability is expressed as:
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\[ P = D \frac{C_2 - C_1}{p_2 - p_1} \]  

(2-16)

where \( D \) is the concentration-averaged effective diffusion coefficient in the range \( C_1 - C_2 \):

\[ D = \frac{1}{C_2 - C_1} \int_{C_1}^{C_2} D_{\text{eff}} dC \]  

(2-17)

where \( D_{\text{eff}} \) is the local effective diffusion coefficient. However, it is difficult to measure the local gas diffusivity directly. Gas permeability and solubility could be derived from the experiments measurements using constant volume variable pressure method, where the permeate pressure at downstream is far lower than the feeding pressure, \( p_1 \ll p_2 \), consequently, the concentration gradient could assumed to be \( C_1 \ll C_2 \), therefore, the permeability can be simplified as:

\[ P = \frac{DC_2}{p_2} = D \times S \]  

(2-18)

where \( S = \frac{C_2}{p_2} \) is the apparent sorption coefficient or solubility of diffusion substance in the polymer (related to Equation 2-8). Therefore, by measuring the gas permeability at an upstream pressure of \( p_2 \) and solubility at a pressure of \( p_2 \), the average gas diffusivity \( D \) could be derived.

The ideal selectivity of a membrane for gas A over gas B could be simply calculated from the ratio of their pure gas permeability:

\[ \alpha_{A/B} = \frac{P_A}{P_B} = \left[ \frac{D_A}{D_B} \right] \left[ \frac{S_A}{S_B} \right] \]  

(2-19)

where \( D_A/D_B \) is the diffusivity selectivity, equal to the ratio of the diffusion coefficients of gases A and B, respectively. The ratio of the solubility coefficients of gases A and B, \( S_A/S_B \), is the solubility selectivity. Normally, for membranes with diffusivity dominates, small gas molecules pass through much faster. While for those polymer with high solubility selectivity, the permeability of gas molecules or organic vapours is much higher than smaller gas molecules.

2.12 Scientific questions

Literature review indicates that molecular-scale design of novel microporous polymeric materials and understanding their structure-property relationship are interesting and important scientific questions. In particular, rational design and fabrication of these novel materials for functional applications requires a fundamental understanding of their physical
and chemical properties at the molecular level, such as their macromolecular structure, packing of polymer chains, intermolecular interactions, and link the molecular structure with their pore structure and molecular transport physics over multi-magnitudes of scale. Therefore, I defined the scope of my PhD thesis on novel porous polymeric materials, fabrication of membranes, and study their molecular transport properties. Theoretical analysis is very challenging owing to the complexity of the polymer materials. Instead, this thesis is focused on the experimental approach corroborated with computational simulations.

![Chemical structure, molecular model and 3D molecular simulation of PIM-1 (A-C) and PIM-EA-TB (D-F).](image)

**Figure 2.29:** Chemical structure, molecular model and 3D molecular simulation of PIM-1 (A-C) and PIM-EA-TB (D-F). The molecular model of polymer chain segments have been energy minimized, but not reaching the equilibrium state. The size of amorphous cell (C) is 31.8×31.8×31.8 Å, containing 4 PIM-1 chains with each consisting of 10 repeating units, with bulk density of 1.050 g cm$^{-3}$. The size of cell (D) is 30.1×30.1×30.1 Å, consisting of 4 PIM-EA-TB polymer chains each consisting of 15 repeating units. The density is 1.040 g cm$^{-3}$.

The common characteristics of PIMs polymers are the inefficient packing of rigid polymer chains and heterogeneous distribution of interconnected free volume or microporosity, as exemplified by the two representative polymers, PIM-1 and PIM-EA-TB shown in **Figure 2.29**. The gas permeation in PIMs polymer matrices could still be illustrated by the solution-diffusion model, that is, the sorption of gas is governed by the amount and
topologies of free volume elements while the diffusion is limited by the size of the interconnected gates or channels. In terms of the size distribution and topologies of free volume elements, more quantitative measurements by advanced techniques (e.g. PALS) are necessary. Our molecular simulation indicates that the EA and TB units are indeed more rigid than the SBI or dioxane units in PIM-1, however, the shorter length of repeating unit of PIM-EA-TB seems to give smaller intrachain spacing. The free volume elements probed by CO$_2$ molecules in PIM-EA-TB appear to be less uniform than that in PIM-1, which may illustrate the low selectivity for CO$_2$/CH$_4$.

From the perspective of soft matter physics, amorphous polymer chains interact by relatively weak noncovalent interactions such as van der Waals forces or entanglements, and easily slide over each other. At the microscopic level, the amorphous nature of PIMs polymer chains results in a broad size distribution of free volume elements (4 to 10 Å) with different topologies existing in all the PIMs polymers, which compromises their separation performance, i.e. poor molecular selectivity, physical aging and plasticization. In particular, for industrially and environmentally important gases, such as separations of CO$_2$/CH$_4$ and hydrocarbons in natural gas industry, all of which have high solubility in glassy polymers. All of the existing PIMs polymers have only shown modest selectivity for CO$_2$/CH$_4$ separations. Therefore, tailoring the distribution, size, and architecture of channels and free volume elements is critical to achieve substantial increase of diffusivity selectivity via molecular sieving function. Understanding the structure-property relationship of PIMs and further tuning their properties and functions is an interesting and important scientific question, which will be studied in this PhD thesis.

![Figure 2.30: Two-dimensional schematic diagrams of representative materials studied in this PhD thesis. (A) Dense glassy polymer with low free volume (e.g. polyimide), (B) amorphous microporous polymer with high interconnected free volume (e.g. PIM-1), (C) porous and crystalline organic framework with ordered micropores and channels (e.g. ZIF-8).](image)
Three representative types of polymers will be studied in this thesis, as schematically shown in Figure 2.30: (i) dense glassy polymer containing low free volume (e.g. polyimide); Matrimid® 5218 was selected owing to its commercial availability and well-studied gas transport properties. (ii) Amorphous microporous polymer containing interconnected free volume (e.g. cutting-edge PIMs); Specifically, PIM-1 was selected owing to its unique properties, simple synthetic chemistry, and commercial availability of monomers. (iii) Crystalline microporous frameworks (e.g. MOFs and ZIFs) with well-defined pore structure. ZIF-8 was selected as prototypical filler owing to its easy synthesis in the form of nanoparticles, well-defined micropore structure, and high thermal stability during the thermal processing of polymer composites.

Figure 2.31: A roadmap of molecular sieve materials for gas separation membranes. The main graph (F) shows the upper bound plots of gas pair selectivity versus permeability for gas separation membranes. Black and red lines: upper bound of polymer membrane summarized by Robeson in 1991[82], and 2008[83], respectively. Grey regions: conventional dense polymers; Yellow regions: Zeolites and MOFs; Green region: PIMs polymers; Red regions: performance for polymer molecular sieves (PMS) achieved by chemical modification of a prototypical PIM-1 polymer. Novel molecular sieve materials can be classified into disordered and ordered frameworks, are represented by PIMs (A-C) or MOFs materials (D-E). (A) An ideal molecular model of a PIM-1 polymer chain segment. (B) A molecular dynamics simulation of an amorphous cell of PIM-1 polymer chains (four polymer chains inside, each containing of 10 repeating units). The grey surface indicates the van der Waals surface, green surface is the Connolly surface with probe radius of 1.65 Å (kinetic radius of a CO₂ molecule). (C) A two-dimensional (2D) schematic illustration of the interconnected free volume elements in PIM-1 polymer membranes with hour-glass shaped structure. (D) A 3D structure of ZIF-8 crystal [16], as an example of ordered molecular sieves (e.g. zeolites and MOFs). (E) A 2D schematic diagram of molecular sieving of ordered molecular sieves.
This PhD dissertation aims to achieve the following objectives:

(i) Design and fabrication of membrane materials, and understand the packing of polymer chains, formation of microporosity, and interactions in the complex heterogeneous polymer/nanoparticles materials.

(ii) Understand the structure of novel polymer of intrinsic microporosity.

(iii) Modify the pore structure of PIMs polymers and understand the structure-property relationship.

(iv) Measure the transport properties of gas molecules in polymeric membranes.

Another scientific challenge addressed in this thesis is to push the limit of gas separation performance to surpass the Robeson’s upper bound of polymeric membranes (Figure 2.31). The pioneering invention of PIMs by Budd and McKeown has redefined the limit of Robeson’s upper bound. Any mild change of the PIMs polymer matrix via chemical reactions would lead to significant change of physical properties including the molecular transport properties, which is a well-known characteristic of soft matter.

It should be noted that during my PhD research I observed many interesting phenomena with these novel microporous polymers and explored their applications, including catalytic hydrogenation of PIM-1, in situ polymerization of polydopamine on PIM membranes, electroluminescence and light emitting of PIM-1 thin film, photoresist, carbonization, actuation of PIMs induced by rapid adsorption and desorption of solvents, ion transport properties of PIM-1 membranes and desalination, chemical crosslinking, composite membranes, and synthesis of novel network-type PIMs. The results are related to this thesis, but are not included due to incomplete understanding and word limit of the thesis.

In this PhD dissertation, instead of designing new synthetic chemistry, we focus on design and fabrication of polymer membranes from molecularly defined nanomaterials and study their physical properties and particularly the molecular transport properties. In particular, we aim to tailor the structure of interconnected microcavities in PIMs membranes by chemical modifications to produce selective sieves that could significantly improve the selectivity in gas separation, whilst aiming to understand the science of the materials behind the molecular sieving function.

2.13 References


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Chapter 3 Materials and methods

3.1 Materials

3.1.1 Polymers

Commercially available glassy polyimide, Matrimid® 5218 (see Figure 3.1) was kindly provided by Huntsman Advanced Materials. The molecular weight of the as-received polymer was $M_n = 44,000$ g/mol with a polydispersity index of 1.84, as analysed by gel permeation chromatography (GPC) calibrated by polystyrene standards.

The PIM-1 polymer was synthesized following the method invented by Budd and McKeown [1], and a recipe by Guiver and co-workers [2]. A one-step polycondensation via a double aromatic nucleophilic substitution from purified monomers, 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirosindane (TTSBI, 10.213 g, 30 mmol, Alfa Aesar) and 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN, 6.003 g, 30 mmol, Matrix Scientific), was performed in the presence of K$_2$CO$_3$ (8.292 g, 60 mmol, Aldrich) in anhydrous dimethylformamide (200 mL, Alfa Aesar). After the mixture has been stirred at 60°C for about 48 h, the polymer was purified by dissolving in chloroform and re-precipitation from methanol, filtered and dried in a vacuum oven at 110°C for overnight.

Figure 3.1: Chemical structures of Matrimid® 5218, PIM-1, and ZIF-8.
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Materials and methods

The ZIF-8 nanocrystals were synthesized following the rapid room-temperature synthesis method reported by Cravillon et al.[3] In a typical synthesis, a solution of 3 g (10 mmol) of Zn(NO$_3$)$_2$·6H$_2$O (Alfa Aesar) in 100 mL of methanol and another solution of 6.6 g (80 mmol) of 2-methylimidazole [C$_4$H$_6$N$_2$, Sigma-Aldrich] in 100 mL of methanol were prepared and then mixed by vigorously stirring for 1 h at room temperature. After 1 h stirring, the resulting ZIF-8 nanocrystals were separated by centrifugation, followed by washing with methanol twice and with chloroform once and finally re-dispersed as colloids in fresh chloroform for use in membrane preparation. As control samples, two batches of ZIF-8 nanocrystals were dried under vacuum at 60°C and 230°C and stored dry for further analysis. The yield of ZIF-8 was about 40 mol% based the ideal molar conversion of zinc.

3.1.2 Preparation of polymer membrane

The polymer was dissolved in a solution of chloroform (1-2 wt%) and nondissolved particles were removed by filtration through PTFE filters (0.45 or 1.0 um) or by centrifugation at 12,000 rpm for 30 min. For preparation of pure polymer membranes, the concentration of polymer solution was further adjusted to 8-10 wt% by bubbling pure N$_2$ to slowly evaporate excess solvent. The polymer solution was then briefly ultrasonicated for 1 min to remove gas bubbles. Then, polymer solution was cast on clean glass substrate in a glove box. After the solvent has been slowly evaporated at room temperature in two days, the free-standing membrane was removed from glass substrate, and exposed to methanol soaking for overnight and dried in air. After, the membrane was dried in a vacuum oven at 120°C for 24 h. Nanocomposite membranes were prepared from the polymer/nanoparticle colloidal mixtures following the same protocol of solution casting and post treatment.

3.1.3 Preparation of polymer nanocomposite membrane

Two types of nanoparticles were used as fillers: (1) porous zeolitic imidazolate framework (ZIF-8) nanocrystals, (2) nonporous inorganic nanoparticles (SiO$_2$, TiO$_2$, etc).

The ZIF-8 nanocrystals with diameter of 60-100 nm were dispersed in chloroform were then mixed with polymer solution and maintained magnetic stirring in a glass vial for two days. After, the mixture was bubbled with pure N$_2$ to slowly evaporate excess solvent until suitable polymer concentration was reached (8-10 wt%). After brief sonication to remove the gas bubbles, the solution of colloidal mixture was cast on clean gas substrate to form nanocomposite membranes, following the same procedure as that of pure polymer.

The fumed silica nanoparticles have an average primary particle size of 12 nm (99.8% trace metals basis, Sigma Aldrich) with specific surface area of 175-225 m$^2$/g as claimed by
the company. The size of primary particles were confirmed by SEM and STEM, however, aggregation of 200-300 nm was always observed even though we tried to disperse them (e.g. ultrasonic shear mixing). Such aggregated nanoparticles were dispersed in a solution of chloroform and mixed with diluted PIM-1 polymer solution and the resulting mixtures were thoroughly stirred for two days. Extra solvent was removed by evaporation to reach suitable concentration (8-10 wt%) for solution casting.

The volume fraction $\phi_D$ of the dispersed phase in the mixed matrix membrane is defined as

$$\phi_D = \frac{m_D / \rho_D}{m_D / \rho_D + m_C / \rho_C}$$

(3-1)

where $m$ and $\rho$ refer to the mass and density of the continuous phase (polymer) and dispersed phase (filler), respectively. denoted by subscripts “C” and “D”.

3.1.4 Preparation of polymer thin films

Thin films were prepared by spin coating of diluted PIM-1 solution in chloroform (0.8-2 wt%) on clean silicon wafer or glass substrate. A series of samples were spin-coated on clean glass substrate at speed of 2000 rpm for 60 s at an acceleration speed of 1500 rpm, giving an initial thickness of ~100 nm. The thickness of films was tuned by varying the concentration of polymer solution and spinning speed.

3.2 Characterization

3.2.1 Morphology

Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) were performed using a Hitachi S5500 microscope. Samples were prepared by freeze-fracture of membranes and subsequent sputter-coating with a thin layer of gold.

3.2.2 X-ray diffraction and scattering

Wide angle X-ray diffraction (XRD) was performed with a Bruker D8 X-ray diffractometer operated at 40 mA and 40 kV using Cu Kα radiation with a step of 0.02° per second. The membrane sample was attached onto a sample holder with a single crystal silicon substrate. For the nanocomposite membrane containing ZIF-8, the average crystallite size of ZIF-8 is calculated from the Scherrer equation [4].
3.2.3 Density

The density values of polymer membranes were measured using a Micromeritics Accupyc 1340 helium pycnometer, equipped with a 1 cm³ insert. Typically, sample masses of 100-200 mg were used and the values quoted are the mean and standard deviation from a cycle of 15 measurements. Before density measurements, all samples were degased thoroughly under vacuum at 150 °C for 5 hours to remove gas and moisture adsorbed in the polymer matrix.

It should be noted that the density of polymer membranes measured by helium pycnometer was calculated as the ratio of mass to the volume, both of which are measured values. The volume is the amount of three-dimensional space inaccessible to the gas used. For polymers such as PIMs containing interconnected free volume, the volume measured is close to the occupied volume of macromolecules. Those isolated free volume elements or frozen pores that are not connected to the surface may be included in the measured volume. Then the measurement in this case also depends on the permeability of helium into the isolated free volume elements. Therefore, the density measured by the helium pycnometer could slightly deviate from the true density of the polymer, but it can be assumed as skeleton density of the polymer.

The apparent bulk density was measured from the ratio of weighed mass and volume. The weight is measured from balance. The volume is calculated from the product of thickness and size of the films. The volume includes the volume of polymer chains, interstitial volume and interconnected holes. Therefore, the calculated density is the bulk value.

3.2.4 Molecular weight distribution

The molecular weight and molecular weight distribution are fundamental properties of polymeric materials. Gel permeation chromatography (GPC), a type of size exclusion chromatography (SEC), is an established method for quantifying the molecular weight distribution. The key unit of a GPC is a column packed with porous gel beads. As shown in Figure 3.2A, for polymers with a distribution of molecular weights passing through the column, the smaller polymer molecules can penetrate into the pores and it takes more time to elute from the column, while conversely the large polymer molecules are excluded from the pores quickly. Therefore, the polymer molecules are separated by their size or hydrodynamic volume (Figure 3.2B). In this study, the molecular weight of polymer was analyzed by a GPC (Model GPC-50, Polymer Laboratories) equipped with a refractive index (RI) detector. The GPC was operated with a column set of 2 × PLgel 5 µm MIXED-D (Agilent Tech.), and column set length of 550 mm in chloroform effluent at a flow rate of 0.30 mL min⁻¹, operated
at temperature of 30°C. The column was first calibrated with polystyrene standards (with Mw from 392,553 to 671 g mol\(^{-1}\)). Diluted polymer solution in chloroform (concentration of 0.10 mg mL\(^{-1}\), volume 20.0 µL) was injected in each run. The molecular weight distribution is calculated from the linear calibration curve. The polydispersity (PDI) is calculated from the ratio of the weight average molecular weight (\(M_w\)) to the number average molecular weight (\(M_n\)).

Figure 3.2: (A) A schematic diagram of GPC column separation of particles of different size, and (B) a typical calibration curve of size versus retention volume.

3.2.5 Infrared spectroscopy

FTIR spectra were measured with a NICOLET spectrometer (iS10, Thermo Scientific) in the transmission mode, or using the Bruker Tensor 27 Infrared Spectrometer, equipped with an attenuated total reflectance (ATR) cell in the reflection mode. The wave length range is within 400-4000 cm\(^{-1}\), with a spectral resolution of 0.24 cm\(^{-1}\) and 64 scans. The ZIF-8 nanoparticles were prepared in KBr pellets.

In the case of some UV irradiation experiments, PIM-1 thin films were dip-coated on NaCl plates and exposed to UV irradiation, then measured with a NICOLET spectrometer (iS10, Thermo Scientific) in transmission mode.

3.2.6 Gel fraction analysis

The crosslinked polymer films were heated at 120°C under vacuum for overnight to remove the moisture and with the mass measured immediately. Then the films were soaked in volatile solvent chloroform for two days, with the insoluble film or gel removed from the
solution by filtration or by centrifugation, washed with methanol and dried at 120°C under vacuum. After, the mass was recorded again to quantify the fraction of crosslinked part. The solutions containing dissolved polymer were used for GPC measurements to quantify the evolution of molecular weight distribution. The solubility of crosslinked polymer films was also examined using other common solvents, or acid and alkaline solutions.

### 3.2.7 Thermal conductivity

The thermal conductivities of PIM-1 membranes and PIM-1/ZIF-8 nanocomposite membranes were measured using a hot disk thermal constants analyzer, at 25°C and atmospheric pressure. An encapsulated Ni-spiral sensor was sandwiched between two pieces of flat thick membranes (thickness of 2 mm, diameter of 20 mm, solution-cast using the same solution for preparation of dense membranes). The output of power was 0.05 W and measurement time was 5 seconds. The final thermal conductivity was averaged from 4-6 measurements. Both pure PIM-1 and representative nanocomposite membranes were measured. The thermal conductivity of PIM-1 polymer is about 0.23 W m\(^{-1}\) K\(^{-1}\), which is in the normal range of conventional polymers (0.1-0.3 W m\(^{-1}\) K\(^{-1}\)). Therefore, the heat transfer properties during thermal treatment of PIM-1 membranes should be similar to that of conventional polymer films.

The thermal conductivity of ZIF-8 was also measured. ZIF-8 nanocrystals were dried at 120°C under vacuum and pelletized. The thermal conductivity of ZIF-8 is not known in the literature. Here, the ZIF-8 pellet shows an apparent value of 0.19 W m\(^{-1}\) K\(^{-1}\) at 295 K, which is likely an underestimation of the intrinsic value due to the presence of voids between the crystals. The thermal conductivity of MOF-5 single crystal gives an intrinsic low value of \(\sim 0.3\) W m\(^{-1}\) K\(^{-1}\) at 300 K [5].

The Maxwell equation was used to predict the effective thermal conductivity \(k_{\text{eff}}\) of nanocomposite membranes using the as measured apparent data:

\[
k_{\text{eff}} = k_C \left[ \frac{k_D + 2k_C - 2\phi(k_C - k_D)}{k_D + 2k_C + \phi(k_C - k_D)} \right]
\]

(3-2)

Where \(k_C\) and \(k_D\) are the thermal conductivity of continuous phase (polymer) and dispersed phase (fillers), respectively. \(\phi\) is the volume fraction of fillers. The experimental thermal conductivity of nanocomposite membranes is lower than the prediction by Maxwell equation, which is due to the presence of voids and cavities at the interface (not considered in the model).
3.2.8 Optical spectroscopy

UV–visible absorption spectra of PIM-1 thin film (~100 nm, as measured by SEM) were measured using a Hewlett Packard 8453 UV-Vis spectrometer, with an operating spectral range of 190–1000 nm. Steady-state photoluminescence excitation measurements were taken on CARY Eclipse fluorescence spectrophotometer, at an excitation wavelength of 420 nm.

3.2.9 Mechanical properties

Tensile tests of polymer films were carried out at a home-made stretcher machine. Polymer films with thickness in the range of 50-80 μm were cut into thin slices with an effective length of ~20 mm and a width of ~2 mm, with the accurate value determined from high-resolution photos and calibrations from known length. The films were stretched for 0.02 mm in each step with a relaxation time of 30 s, giving an apparent strain rate of ~4×10⁻⁵ s⁻¹. The average value of Young’s modulus was derived from the initial slope. The tensile strength at break and elongation at break were measured and compared.

Nanoindentation of surfaces of polymer membranes were performed at ambient temperature using a sharp Berkovich tip in the continuous stiffness measurement (CSM) mode on an MTS NanoIndenter® XP (MTS Corp., Eden Prairie, MN). The indenter axes were aligned normal to the membrane planes. The average values of the Young’s modulus ($E$) and hardness ($H$) are calculated as a function of surface penetration depth ($h$) using the dynamic CSM mode over depths of 100–1000 nm, with a series of 20 measurements at different locations. This is accomplished by continuously monitoring the change of the elastic contact stiffness ($S_e$) determined from the $P$-$h$ curves, then the reduced modulus ($E_r$) was extracted from the equation [6]:

$$E_r = \frac{\sqrt{\pi} S}{2\beta \sqrt{A_c}}$$  \hspace{1cm} (3-3)

where $A_c$ is the contact area under load (based on the calibrated tip area function) and $\beta$ is a constant that depends on the geometry of the indenter ($\beta = 1.034$ for a Berkovich tip). Oliver and Pharr [7-8] proposed that the sample elastic modulus can be derived from the reduced modulus assuming isotropic elastic properties, which is normally not the case for single crystals. Similarly here the polymer films are asymmetric materials. To account for the effects of anisotropy in materials, it has been shown that the modulus obtained from nanoindentation of a single crystal is more appropriately represented as an “indentation modulus” [9-10], given by:
where ν and E are Poisson’s ratio and elastic modulus, respectively; and the subscripts i and s refer to the indenter and test material, respectively. The indenter properties used in this study are $E_i = 1141$ GPa, and Poisson’s ratio for the indenter is $\nu_i = 0.07$. Both elastic modulus from the orthogonal orientations were calculated using $\nu_s = 0.3$.

### 3.2.10 Dynamic mechanical thermal analysis

The glass transition temperatures ($T_g$) of the membranes were measured by a dynamic mechanical thermal analyzer (DMA, Gearing Scientific Ltd.). A piece of $\sim 3\times5$ mm membrane was sandwiched in a stainless steel envelope (Triton Technology Material Pocket) which was then mounted in the analyzer. Then the sample was heated from room temperature to $400^\circ C$ at a heating rate of $10^\circ C$ min$^{-1}$ under a dynamic force with a single frequency oscillation of 1 Hz and at an amplitude of 50 µm. The storage modulus, phase angle and tan delta (ratio of storage modulus to loss modulus) were measured as functions of temperature and $T_g$ was calculated from the peak of tan delta. For each sample, two or three pieces of film were tested and gave good reproducibility of $T_g$ ($\pm 2^\circ C$).

### 3.2.11 Positron annihilation lifetime spectroscopy (PALS)

The local free volume of Matrimid® based membranes was measured using an established technique, positron annihilation lifetime spectroscopy (PALS) [11-12], in collaboration with Dr. Mina Roussenova in Prof. Ashraf Alam’s group at University of Bristol. The source of positrons was provided by $\text{^{22}Na}$, and PALS experiments were performed using a fast-fast coincidence system [11-12]. The membranes used for the PALS experiments were cut into $1 \times 1$ cm squares and were stacked on top of each other to produce a thickness of $\sim 1.1$ mm, enough to stop $\sim 99\%$ of the incident positrons. The lifetime measurements were carried out in an air-tight copper sample holder at 25 $^\circ C$, with at least 5.5 million counts for all spectra. In molecular materials, a substantial fraction of the injected positrons form positronium (Ps), a metastable positron-electron bound state. The “pick-off” lifetime, $\tau_{po}$, of the more abundant and longer lived ortho-positronium provides a highly accurate correspondence to the average molecular hole size, $r_h$, which can be calculated via the following semi-empirical equation:

$$
\tau_{po} = 0.5 \left[ 1 - \frac{r_h}{r_h + \Delta r} + \frac{1}{2\pi} \sin \left( \frac{2\pi r_h}{r_h + \Delta r} \right) \right]^{-1} \text{ns}
$$

(3-5)
here, 0.5 ns is the spin-averaged lifetime of the Ps [11-12] and the positronium wave function may overlap with the wave functions of molecular electrons within a layer $\delta r$ of the potential well. [13-14] The lifetime spectra were analysed using the Life Time fitting routine [15] (version 9.1) and a four finite lifetime component analysis yielded the optimum fit to the experimental data.

### 3.3 Gas sorption measurements

#### 3.3.1 Low pressure gas sorption

Low pressure gas sorption was performed using a Micromeritics ASAP 2020 instrument with the sorption pressure up to 1 bar, in collaboration with Prof. Tony Cheetham’s group (Department of Materials Science and Metallurgy, University of Cambridge). Dense polymer membranes (~0.1 g) with thickness of ~50 µm were cut into small pieces, loaded into the apparatus and degassed at 120 °C under high vacuum (<10$^{-6}$ bar). After the mass being measured, the samples were further degassed under high vacuum for at least 4 h prior to the gas sorption measurements. Nitrogen adsorption-desorption isotherms were measured at 77 K and 273 K, respectively. The sorption isotherms of CO$_2$ and CH$_4$ were also measured at 273 K. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) model and the pore size distribution was derived from non-local density functional theory (NLDFT) model from N$_2$ isotherms at 77 K, or from CO$_2$ sorption isotherms at 273 K when the sorption of N$_2$ was subject to kinetic control.

#### 3.3.2 High-pressure gas sorption

Pure gases of H$_2$ (99.9995 vol.%), CO$_2$ (99.995 vol.%), O$_2$ (99.6 vol.%), N$_2$ (99.9995 vol.%) and CH$_4$ (99.5 vol.%) (BOC, UK) were used for the gas sorption and permeation experiments. The high-pressure pure-gas sorption properties were measured using a dual-volume pressure-decay apparatus developed in our lab, as shown in Figure 3.3, at pressure up to 35 bar and isothermal room temperature of 22°C. The system consists of a sample cell containing the polymer films and a charge cell connecting to the gas cylinder. The pressures of sample cell and gas charging chamber are measured continuously by two pressure transducers (Keller PAA33X, 0-35 bar) connected to a data acquisition system. The data measured by our system is comparable to the data reported by other groups [16].
A batch of polymer films were heated at 120°C under high vacuum for 12 h. After measurement of the mass, the films were loaded in the sample cell and further evacuated for 12 h prior to sorption measurements. A certain amount of gas was then introduced into the sample chamber; the gas sorption in the polymer resulted in the decrease of pressure in the sample chamber and finally reached to equilibrium. The amount of gas sorption was calculated from the mass balance of gas molecules based on the equation of gas states, using the equilibrium pressure calibrated with compressibility factors:

\[
    n_{p,m} = n_{p,m-1} + \left[ \frac{p_{c,m-1}V_c}{RTZ_{c,m-1}} + \frac{p_{s,m-1}(V_s - V_p)}{RTZ_{s,m-1}} \right] - \left[ \frac{p_{c,m}V_c}{RTZ_{c,m}} + \frac{p_{s,m}(V_s - V_p)}{RTZ_{s,m}} \right]
\]

where \( V_c, V_s, \) and \( V_p \) are the volumes of the charge cell, sample cell, and polymer sample, respectively. The subscripts \( m \) and \( m-1 \) represent the properties at the step \( m \) and \( (m-1) \), respectively. \( Z \) refers to the compressibility factor of the gas at pressure \( p \) and temperature \( T \).

From these sequential measurements, the gas sorption isotherms can be obtained. The solubility coefficient \( (S) \) as a function of pressure can be calculated and described by a dual mode model:

\[
    S = \frac{C}{P} = k_D + \frac{C_s b}{1 + bp}
\]

where \( C \) is the concentration, \( p \) is the pressure, \( k_D \) is the Henry’s law constant, \( C_s \) is the Langmuir capacity constant, and \( b \) is the Langmuir affinity constant. The measurements followed the sequence of \( \text{H}_2, \text{O}_2, \text{N}_2, \text{CH}_4, \) and \( \text{CO}_2 \). The samples were thoroughly evacuated between measurements of each gas.

### 3.4 Gas permeation measurements

#### 3.4.1 Transient permeation kinetics

When a membrane is exposed to a gas pressure at the feeding side, there is a transient gas sorption period during which the gas concentration gradient changes with time and
position in the membrane before the gas permeation reaches steady state. The diffusion equation, defined by the Fick’s second law (Section 2.11), could be solved based on the initial conditions, boundary conditions and inherent properties of diffusion coefficient. The gas diffusion coefficient is assumed to be independent on concentration. Therefore, the amount of gas, $Q_t$, passing through the membrane with thickness of $l$ as a function of time could be expressed as:

$$Q_t = \int_0^l D \left( \frac{\partial C}{\partial x} \right) \, dx = \frac{DlC_2}{l} - \frac{lC_2}{6} - \frac{2lC_2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2l^2}{l^2}\right)$$

(3-8)

When the gas permeation reaches steady state, the equation could be approximate to:

$$Q_t = \frac{DlC_2}{l} (t - \frac{l^2}{6D})$$

(3-9)

In practical method, the cumulative flux could be recorded by pressure increase in a closed chamber, as presented in Figure 3.4. The intercept of the steady-state region of $Q_t$ with the time axis is defined as the time lag $\theta$. Therefore, the diffusion coefficient ($D$) for a specific gas can be derived from the thickness of the membrane and the time lag ($\theta$):

$$D = \frac{l^2}{6\theta}$$

(3-10)

The above theoretical analysis was developed by Daynes in 1920. In 1939, Barrer and coworkers reported a system to measure the time lag and steady-state flow in polymers. Using this established technique, permeability, diffusivity and solubility can be estimated from a single experiment [17-18].

Figure 3.4: A representative pressure-time profile of gas permeation for a Matrimid® polymer membrane obtained from the time-lag method. The dashed lines represent the linear fitting of the pressure increase in pseudo-steady state. Gas permeation test condition: feeding pressure of 4 bar at room temperature (22°C).
3.4.2 Single gas permeation method

A home-made membrane separation system was used to measure the pure gas permeation properties, as shown in Figure 3.5. A stainless steel membrane holder (Millipore) was used as the membrane cell where the membrane was supported on filter paper and a porous metal disk at the bottom. The mass transfer resistance of the support is far less compared to that of the polymer film so that the measured gas flux reflects the inherent gas permeation properties of the membrane. The membrane was sealed by a viton o-ring (instead of silicone o-ring which gave high gas leakage). The effective area of the membrane available for gas diffusion is 12.6 cm² or 2.2 cm².

Figure 3.5: Schematic diagram of pure gas permeation apparatus. P: pressure gauge or transducer; T: temperature controller. The membrane cell could be placed in a temperature controlled box. In this study, the gas permeation was performed at room temperature of 22°C. Note: the tube volume from the gas cylinder to the membrane cell is sufficient to maintain the feeding pressure during the gas permeation, alternatively the gas is provided by the cylinder with the regulator open and maintaining the pressure.

The permeate volume includes the space in the gas sampling cylinder, tube connections, valves and the membrane cell. The stainless steel gas sampling cylinder (Swagelok, 75 and 500 cm³) can be switched to provide reasonable volume depending on the permeability of the membrane. The rate of increase of permeate pressure could be adjusted by the volume. For a low-permeability gas, only tube volume is enough to measure the pressure increase rate. The volume ($V_0$) of tubing and the dead volume in the cell could be calibrated by the mass balance of gases that behave qualitatively like an ideal gas (i.e. helium or nitrogen) at low pressure using standard known cylinder volume of $V_1$ or $V_2$. For example, the gas in the tube volume $V_0$ with an initial pressure of $P_0$ can be released into the cylinder $V_1$, with the measured pressure drop to $P_1$. The unknown volume $V_0$ can be calculated from the equation $P_0V_0=P_1(V_0+V_1)$. 


The pure gas was supplied from the gas cylinders with pressure measured by a digital manometer (Keller LEO 2 Ei, absolute pressure 0-31 bar). For the dense membrane, the rate of gas permeation is quite slow, and the permeate pressure is usually set to be lower than 50 mbar with the feeding pressure constant at 4 bar. Therefore, the effective pressure difference between the feeding and permeate could be assumed as constant.

Pure gas permeation tests were carried out at temperature of 22°C and feed pressure of 4 bar, using the constant-volume pressure-increase apparatus. In a typical run, the membrane was loaded in the cell and both upstream and downstream were evacuated at least two hours (up to overnight) with a vacuum pump (Edwards RV3) prior to measurement of each gas. Then the leak rate was checked by measuring the increase of permeate pressure with the valve connecting the vacuum pump closed. Normally, the leaking rate is negligible with good sealing and evacuation. Then the feed gas was introduced and the feed and permeate pressure were recorded by pressure transmitters (Keller PAA 33X, Accuracy of 0.01% F.S.) connected to a data acquisition system, until the permeate pressure reached steady state (the slope of pressure increase, \( \frac{dp}{dt} \), became constant). The steady state could be verified by evacuating the downstream briefly and measuring the slope of the permeate pressure again.

The gas permeability (\( P \)) is calculated based on the following equation:

\[
P = \frac{Vl}{A} \frac{T_0}{p_f p_0 T} \left( \frac{dp}{dt} \right)
\]  

(3-11)

where \( P \) is the permeability of the gas through the membrane, expressed in Barrer (1 Barrer=10^{-10} \text{ cm}^3(\text{STP})\text{ cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}), V \) is the permeate volume (\text{cm}^3), \( l \) is the thickness of membrane (\text{cm}), \( A \) is the effective area of the membrane (\text{cm}^2), \( p_f \) is the feed pressure (\text{cmHg}), \( p_0 \) is the pressure at standard state (76 \text{ cmHg}), \( T \) is the absolute operating temperature (K), \( T_0 \) is the temperature at standard state (273.15 K), \( \frac{dp}{dt} \) is the slope of pressure increase in the permeate volume at pseudo-steady state (\text{cmHg s}^{-1}).

Then the solubility (\( S \)) can be derived from:

\[
S = \frac{P}{D}
\]  

(3-12)

The above calculations of solubility and diffusion coefficient were subject to the concentration gradient during the gas permeation, therefore they could deviate from the intrinsic value. Alternatively, the solubility is derived from the gas sorption measurements and the diffusion coefficients are calculated from the permeability (\( D=P/S \)).

The ideal selectivity (\( \alpha_{A/B} \)) of gas pairs, A and B, is defined as:
\[
\alpha_{A/B} = \frac{P_A}{P_B} = \left[ \frac{D_A}{D_B} \right] \left[ \frac{S_A}{S_B} \right]
\]

(3-13)

where \(D_A/D_B\) is the diffusivity selectivity and \(S_A/S_B\) is the solubility selectivity.

3.4.3 Mixed gas permeation

The mixed gas permeation properties were measured in another membrane cell using the constant-pressure variable-volume method. The schematic diagram of the apparatus is shown in Figure 3.6. The principle of measurement of mixed-gas permeability is similar to that of pure gas permeation as described above. The compositions of feed and permeate gas mixtures were measured by a gas chromatograph (Shimadzu, model 2014) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) calibrated by certified gas mixtures (Scientific and Technical Gases LTD, UK). The feeding gases were mixed by controlling the pure gases flow rate with two mass flow controllers (EL flow, Bronkhorst). The total feeding pressure was adjusted by the back pressure regulator with the gas flow rate constant. Alternatively, certified gas mixtures (BOC, UK) of \(\text{CO}_2/\text{CH}_4\) (50/50 vol.%) and \(\text{CO}_2/\text{N}_2\) (50/50 vol.%) were used. The feed pressure is up to 35 bar at room temperature (22°C). The feed flow rate was controlled by a metering valve (Swagelok) and measured by a flow meter (Aldrich). The flow rate of permeate was measured using a soap bubble flow meter (Aldrich). In some cases, helium was used as the sweep gas for the permeate side because the thermal conductivity is different from that of permeate gas, therefore, the concentration can be easily detected in the TCD in gas chromatograph. The flow rate of upstream feeding gas was maintained high enough to provide good mixing of gas mixtures and overcome the effect of external mass transfer of the gas permeation from the bulk to the interface of the film, here it is characterized by stage cut, an empirical definition in the membrane field, which is defined as the ratio of permeate gas flow rate to the feed gas flow rate, typically it is set to less than 1 or 2 vol%.

By measuring the permeate flow rate \((Q_P)\) and gas compositions with GC, the permeability of the gas specie \(i\) through the membrane, \(P_i\), is calculated as:

\[
P_i = \frac{Q_p x_{p,i}}{A(p_f x_{f,i} - p_p x_{p,i})}
\]

(3-14)

where \(x_{p,i}\) is the volume fraction of component \(i\) in the permeate gas; \(x_{f,i}\) is the volume fraction of species \(i\) in the feed gas; \(A\) is the effective area of membrane (cm\(^2\)); \(l\) is the thickness of membrane (cm); \(p_f\) is the feed pressure (cmHg); \(p_p\) is the permeate pressure (cmHg). In some experiments, when the permeate flow rate was too low to be accurately measured by the soap bubble flow meter, carrier gas (helium) was used to sweep the
permeate gas with flow rate controlled by a mass flow controller (Bronkhorst Ltd, model EL flow). With the permeability of each species, the selectivity is calculated from $\alpha_{A/B} = P_A / P_B$.

![Fig. 3.6: Schematic diagram of a mixed-gas permeation apparatus.](image)

3.4.4 Uncertainty analysis

The uncertainties of all measurements reported in this thesis were estimated using a standard propagation of errors analysis, unless specified otherwise. The error of the calculated permeability mainly originated from the variation of membrane thickness; for this study, the uncertainties of gas permeability at the moment of test are within ±5%, and selectivity within ±7%.

3.5 Molecular dynamics simulation

Molecular dynamics (MD) simulations were performed with the Materials Studio software package (Accelrys Inc, CA, USA). In one amorphous cell, four PIM-1 polymer chains with 10 repeating units were constructed at 298 K. For the thermally oxidized and crosslinked polymers, the reaction mechanisms are very complicated. Here, we use the MD simulation primarily to understand the intermolecular interactions (e.g. hydrogen bonding), and packing of short polymer segments. To mimic the oxidative chain scission, 20 short chains containing two repeating units of PIM-1 with oxidised groups (e.g. carboxylic acid groups, -COOH) were constructed in another amorphous cell at 298 K as well. For those covalently crosslinked polymers, due to the difficulty to analyze the chemical structure, they were not simulated. The Berendsen algorithm with a decay constant of 0.1 ps was used to control the temperature and pressure of each cell. The specific procedures are as follows: (1) energy minimization; (2) 50 ps NVT-MD simulation at 600 K; (3) 50 ps NPT-MD simulation at 600 K at 1 bar; (4) 50 ps NPT-MD simulation at 298 K at 1 bar; (5) 50 ps NPT-MD...
simulation at 298 K at 10 bar with a step of 1.0 fs; (6) 50 ps NVT-MD at 298 K; (7) 50 ps NPT at 298 K at 1 bar. The Ewald summation method was used to calculate the non-bond interactions with an accuracy of 0.001 kcal/mol. Hydrogen bonding was automatically monitored by the software based on a list of hydrogen-bonding scheme (N, O, S, and Halogens).

3.6 References

Chapter 4 Zeolitic Imidazolate Frameworks based nanocomposite membranes

4.1 Introduction

Zeolitic imidazolate frameworks (ZIFs) have shown molecular sieving effect in the membrane form with high permeability owing to their ordered framework structure and microporosity [1-11]. However, their gas selectivity for various gas pairs is generally not high enough for practical applications, owing to the flexible nature of the aperture rings and defects due to formation of polycrystalline phases. The most critical issue is the scale-up of the MOFs membranes owing to the difficulty of manufacture in large scale, similar to zeolite membranes [12-13].

The application of MOFs crystals in polymer nanocomposite membranes is a promising strategy to enhance the gas separation performance. However, there have been many scientific challenges that limit the practical applications of mixed matrix membranes. Existing studies on polymer/MOFs composite membranes, such as MOF-5 [14], Cu–BPY–HFS (Cu–4,4′-bipyridine–hexafluorosilicate) [15], Cu$_3$(BTC)$_2$ (BTC = 1,3,5-benzenetricarboxylate) [16], ZIF-8 [17] showed that the gas permeability was enhanced whilst the selectivity maintained approximate to that of the pure polymer in most cases. However, the large size of crystals (> 100 nm), aggregation of crystals, and poor interfaces between MOFs and polymer matrix, suggested that interfacial defects could give an illusory enhancement of permeability whilst the inherent gas permeation properties of the composite membranes were not clear. Both the size and uniformity of the ZIFs nanoparticles as well as their effective dispersion in polymer matrix remain to be improved. The only notable high-performance polymer/MOFs composite membranes were reported by Bae et al. [18] on ZIF-90/polyimide (Ultem® polyetherimide, Matrimid®, and 6FDA-DAM) composite membranes. The ZIF-90/6FDA-DAM membrane exhibited higher CO$_2$ permeability of 720 Barrer with a CO$_2$/CH$_4$ selectivity of 37. Using similar techniques, Zhang et al.[19] reported high C$_3$H$_6$/C$_3$H$_8$ separation performance of a ZIF-8/6FDA-DAM mixed matrix membrane. These studies have shown that there are several outstanding issues pertaining to polymer/MOFs nanocomposite membranes: (i) controlled synthesis of the sub-micrometer MOFs nanoparticles, (ii) defect-free interface between polymers and MOFs, and (iii) controlled dispersion of MOFs within the polymer.

In this study, using ZIF-8 as a model of ZIFs, a well-studied polyimide, Matrimid®, as the model polymer matrix and a novel direct solution mixing of components to ensure a well-
dispersed, highly loaded mixed matrix membrane. The nanocomposite membranes were characterized with various techniques to understand the physical and chemical properties. Pure gas permeation tests with industrially important gas molecules (H₂, CO₂, O₂, N₂ and CH₄) showed enhanced permeability of the mixed matrix membrane with negligible losses in selectivity. The effect of incorporation of ZIFs in the composite membrane on the mechanism of gas transport was elucidated. Positron annihilation lifetime spectroscopy (PALS) indicated that an increase in free volume in the polymer phase with ZIF-8 loading. In the mean time, the rapid diffusion of gas through the cages of ZIF-8 also contributed to an increase in the gas permeability of composite membranes. Overall, the gas transport properties of the composite membranes could be complicated by the facilitated transport in the ZIF-8 crystals, interfacial defects owing to the disrupted packing of polymer chains, and intermolecular interactions between polymer and ZIFs crystals. The processing strategy reported here can be extended to fabricate other polymer nanocomposite membranes.

4.2 Experimental

The ZIF-8/Matrimid® 5218 polymer nanocomposite membranes were prepared using the solution-casting method, as described in detail in Chapter 3 (Section 3.1.3). The loadings of ZIF-8 nanoparticles were at 5, 10, 20, 30, and 40 wt%. The membranes were annealed in the temperature range of 60-300°C, in a vacuum oven. The vacuum pressures for most samples were below 10⁻³ mbar, except that the batch annealed at 300°C was performed in a high temperature oven with vacuum pressure at 1 mbar. After, these membranes were characterized with various techniques and their pure gas permeation properties were measured in the home-made apparatus. The thickness of final pure and composite membranes varied within the range of 40-70 µm, depending on the loading of ZIF-8 and annealing conditions as measured by a micrometer (HITEC, Model 190-00, 0-25 mm, resolution 1µm).

4.3 Results and discussion

4.3.1 Characterization of ZIF-8 nanocrystals

The physical and chemical properties of as-synthesized ZIF-8 nanoparticles were routinely characterized by various techniques. Pure ZIF-8 nanocrystals show an average particle size of ~70 nm, with high crystallinity, and high microporosity (Sₐ>1300 m²/g). XRD pattern of the ZIF-8 nanocrystals, as shown in Figure 4.1, matches well with the previous reports and the theoretical pattern [20-21]. The average crystallite size of ZIF-8 nanocrystals is around 70 nm as calculated from the broadening of the peaks using the
Scherrer equation, which is in agreement with the direct observation of particle size by SEM and STEM. This size is slightly bigger than that observed in nanocomposite membranes, possibly because of the aggregation of ZIF-8 nanocrystals accompanied with covalent bonding of Zn-imidazole on the particle surface during annealing process, as proposed by Cravillon et al. [21]

Figure 4.1: X-ray diffraction patterns of ZIF-8 nanocrystals. The simulated pattern is also included [20].

Figure 4.2: N₂ adsorption isotherms of the ZIF-8 nanoparticles at 77 K. The samples were annealed at 60°C and 230°C for 18h, respectively. The inset shows the pore size distribution calculated by NLDFT model. Micropores were evacuated at 60°C under high vacuum of 10⁻⁶ bar for 24 h.
Figure 4.2 shows the nitrogen adsorption isotherms at 77 K and pore size distribution of ZIF-8 nanoparticles. The BET surface area and micropore volume of the ZIF-8 nanocrystals are as high as 1645 m$^2$ g$^{-1}$ and 0.70 cm$^3$ g$^{-1}$, respectively, after activation by removal of solvent under vacuum. Annealing at higher temperature of 230°C, the ZIF-8 nanocrystals show slightly lower surface area (1358 m$^2$/g) and smaller micropore volume (to 0.58 cm$^3$ g$^{-1}$). Such a decline in microporosity was possibly due to the decomposition of some ZIF-8 nanoparticles at higher activation temperature [22], but we confirmed that the microporous structure was maintained. The pore size distribution as estimated from a non-local density functional theory (NL-DFT) model gave a pore diameter of 10.8 Å, which is consistent with the pore diameter (11.6 Å) of the sodalite cage in ZIF-8 crystal [20].

4.3.2 Characterisation of the nanocomposite membranes

The Matrimid®/ZIF-8 composite membranes were also characterized with various techniques. We observed that the membranes with high loading of ZIF-8 became dark yellowish after annealing at temperature above 200°C while similar phenomenon was observed for ZIF-8 nanoparticles, possibly due to the degradation of ZIF-8 [22]. Yet the membranes were still transparent and flexible, as shown in Figure 4.3. The apparent density of the composite membranes varied between 1.1 and 1.2 g cm$^{-3}$ (Table 4.1), which is approximate to the theoretical density as calculated based on the loading of ZIF-8 nanoparticles.

![Image](image.png)

Figure 4.3: Photos of (a) Matrimid® 5218 and (b) Matrimid®/ZIF-8 nanocomposite membrane with 20wt% loading. The diameter of membrane is 47 mm.

The morphologies of ZIF-8 nanocrystals nanocomposite membranes were observed with SEM. We carried out control experiments on fabrication of membranes using dried nanoparticles which became not readily re-dispersible in solvent. As shown in Figure 4.4, for the membrane using dried ZIF-8 nanoparticles (20 wt% loading), we can see the aggregation
of ZIF-8 nanoparticles and poor adhesion at the ZIF-8/polymer interface. In some other trial and error experiments, we also observed the poor dispersion if the nanoparticles had been aged in methanol or chloroform for several days instead of using newly prepared ones. Such aggregation is consistent with the initial report by Cravillon et al. [21] and further confirmed in recent studies by Yang et al [23] and Liu et al[24]. Using as-synthesized ZIF-8 nanoparticles, we can obtain good dispersion and adhesion of ZIF-8 nanocrystals within the polymer matrix (up to ZIF-8 loading level of 30 wt%). Large clusters or aggregates of ZIF-8 particles were not observed in SEM. The “sieve in a cage” morphology [25-26] was not seen under these optimised conditions. At higher loading of 40 wt%, the polymer appears to be still continuous as observed in SEM although the membrane became brittle and cracked into small pieces, which were not big enough for the gas permeation test. The dispersion of ZIF-8 nanoparticles using the method of direct mixing of as-synthesized nanoparticles in this study considerably improved the observed mixing and dispersion in polymer matrix, compared to previous work on such mixed matrix systems [17].

![Figure 4.4: SEM images.](image)

**Figure 4.4: SEM images.** (A) ZIF-8 nanocrystals and (B-D) cross-sections of Matrimid®/ZIF-8 composite membranes. (B) example of poor dispersion using dried ZIF-8 nanoparticles (20 wt% loading), (C) example of good dispersion (20 wt% ZIF-8) using as synthesised ZIF-8 nanoparticles, and (D) high loading of ZIF-8 (30wt%). All samples were annealed at 230°C for 18 h under vacuum. Scale bars are 500 nm.

Wide-angle X-ray diffraction patterns of pure polymer and composite membranes are
presented in Figure 4.5. The pure Matrimid® polymer membrane is completely amorphous. For all the Matrimid®/ZIF-8 composite membranes with different loadings, the crystalline structures of ZIF-8 nanoparticles are clearly the same as that of pure ZIF-8. The crystallite thickness or diameter of the ZIF-8 nanocrystals in the composite membrane were quantitatively obtained by the Scherrer equation[27], giving average crystallite sizes in the range of 50-60 nm as summarized in Table 4.1.

![X-ray diffraction patterns](image)

**Figure 4.5: X-ray diffraction patterns.** (a) pure Matrimid® 5218, (b-e) composite membrane containing ZIF-8 nanoparticles with loading of (b) 5 wt%, (c) 10 wt%, (d) 20 wt%, (e) 30 wt%, and (f) ZIF-8 nanocrystals annealed at 230°C under vacuum, and (g) ZIF-8 nanocrystals dried at 60°C under vacuum. Note: patterns are not to scale.

FTIR spectra of pure ZIF-8, pure polymer, and composite membranes are shown in Figure 4.6. The spectrum of pure ZIF-8 matches well the pattern reported in the literature[21]. The absorption bands at 421 cm\(^{-1}\) is due to the Zn-N stretching. The peaks in the range of 900-1400 cm\(^{-1}\) are associated with the absorption of C-N bonds. The absorption bands at 2928 cm\(^{-1}\) and 3134 cm\(^{-1}\) are associated with the aromatic C-H stretching and the aliphatic C-H stretch of the imidazole. The peaks of pure Matrimid® also match the literature well[28]. For the Matrimid®/ZIF-8 composite membranes, OH stretching vibration (typically a broad peak centred between 3600-3000 cm\(^{-1}\)) was not observed. The peak in the pure ZIF-8 sample could be possibly due to the adsorption of moisture during preparation of the KBr platelet. All the peaks of Matrimid®/ZIF8 composite film could be assigned to ZIF-8 and Matrimid®, respectively. However, weak intermolecular interactions (e.g. hydrogen bonding)
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may be formed between the imidazole groups and the carbonyl groups of the polymer chains that will be discussed later.

Figure 4.6: FTIR analysis of pure Matrimid® and Matrimid®/ZIF-8 mixed matrix membranes. All samples were annealed at 230°C for 18 h under vacuum.

Figure 4.7: Gas sorption isotherms of Matrimid®/ZIF-8 nanocomposite membrane with 20 wt% loading of ZIF-8 nanoparticles. The membrane was annealed at 230°C for 18 h and tested in pure gas permeation. Prior to gas adsorption measurement, the membranes were degassed at 110°C for 4 h.
Figure 4.7 shows the gas sorption data of H₂ (77 K), N₂ (77 K) and CO₂ (288 K) of a representative polymer/ZIF-8 composite membrane with 20 wt% loading of ZIF-8. The adsorption of H₂ and N₂ was found to be quite low compared to the pure ZIF-8 sample, further verifying the defect-free interface between ZIF-8 and polymer. The BET surface area as measured was found to be only about 0.9 m² g⁻¹, which is mainly due to the adsorption of N₂ on the bulk surface of the membrane. This finding provides direct evidence that the ZIF-8 nanoparticles were indeed in excellent adhesion with the polymer matrix and with minimal defects at the interfaces (which would give high adsorption). In contrast, the CO₂ uptake at 288 K is appreciably higher than that of N₂ and H₂; this is accounted for by the high solubility of CO₂ in the composite membrane.

The glass transition temperature (T_g) of the pure polymer and nanocomposite membrane was analyzed by DMA as presented in Figure 4.8. Pure Matrimid® polymer shows T_g at 330°C, in the range reported in the literature (generally 300-340°C depending on the method of measurement) [26, 29]. With higher loading of ZIF-8 in the composite, the T_g increases from 330°C to around 349°C at 30 wt% loading. Similar observations were reported for mixed matrix membranes of Matrimid® with carbon molecular sieves (CMS) [26].

![Figure 4.8: Dynamic mechanical thermal analyses of membranes.](image)

The ratio of storage modulus to the loss modulus, or tan (δ) as a function of temperature, for (a) pure Matrimid® membrane and (b-e) Matrimid®/ZIF-8 nanocomposite membrane with loading of 5-30wt% measured by DMA.
Table 4.1 Physical and chemical characteristics of Matrimid®/ZIF-8 nanocomposite membranes and pure ZIF-8 nanocrystals. All samples were annealed at 230°C for 18 h under vacuum.

<table>
<thead>
<tr>
<th>$R_{ZIF-8}$ (wt%)</th>
<th>$\phi_{ZIF-8}^{a}$ (vol.%)</th>
<th>$\rho_{t}^{b}$ (g cm$^{-3}$)</th>
<th>$\rho_{b}^{c}$ (g cm$^{-3}$)</th>
<th>$T_{g}$ (°C)</th>
<th>$L_{ZIF-8}^{d}$ (nm)</th>
<th>$S_{BET}^{e}$ (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1.20</td>
<td>1.23±0.03</td>
<td>330</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>6.2</td>
<td>1.19</td>
<td>1.15±0.04</td>
<td>336</td>
<td>57±2</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>12.3</td>
<td>1.18</td>
<td>1.13±0.04</td>
<td>346</td>
<td>45±1</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>24.0</td>
<td>1.15</td>
<td>1.10±0.03</td>
<td>343</td>
<td>59±1</td>
<td>~0.9</td>
</tr>
<tr>
<td>30</td>
<td>35.1</td>
<td>1.13</td>
<td>1.12±0.04</td>
<td>349</td>
<td>46±1</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>45.7</td>
<td>1.10</td>
<td>-</td>
<td>60±2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.95</td>
<td>-</td>
<td>69±2</td>
<td>1358</td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$ Volume fraction of ZIF-8.

$^{b}$ Theoretical (bulk, not skeleton) density of the composite membrane calculated by the mass ratio of ZIF-8 and polymer. The density of Matrimid® 5218 polymer is 1.2 g cm$^{-3}$ and the theoretical density of ZIF-8 is about 0.95 g cm$^{-3}$.[20]

$^{c}$ Bulk density as quantified by measurement of weight and volume of the membranes, error was mainly subject to the uncertainty of thickness.

$^{d}$ Crystal size calculated from XRD data by the Scherrer equation.

$^{e}$ BET surface area measured by N$_2$ adsorption.

4.3.3 Effect of annealing temperature on gas transport properties

The residual solvent and interfacial defects between nanoparticles and polymer could have significant impact on the packing of polymer chains and gas permeation properties. Particularly, since we used the as-synthesized ZIF-8 colloidal nanoparticles for the membrane preparation in this study, residual solvent or reactant molecules could be trapped in the nanocrystals during synthesis and post-treatment, hence blocking the pores and channels of the ZIFs. To completely remove these solvents and guest molecules, we performed annealing under vacuum. In the meantime, annealing could also change the properties of the composite membranes, for example, allowing the relaxation of polymer chains towards densely packed state, and the removal of voids between the polymer and ZIF nanocrystals.

With the increase in annealing temperature, the membranes became more selective. For the pure polymer membranes (Figure 4.9), with the annealing temperature increased to around 200°C, the permeability of H$_2$ increased to around 30 Barrer, while the permeability of CO$_2$, O$_2$, N$_2$ and CH$_4$ decreased slightly and stabilized when the temperature was above 200°C. Furthermore, the selectivity of corresponding gas pairs increased and stabilized. The gas permeability follows the order of kinetic diameter of gas molecules: H$_2$ (2.89 Å) > CO$_2$ (3.3 Å) > O$_2$ (3.46 Å) > N$_2$ (3.6 Å) > CH$_4$ (3.8 Å). Similar to the pure polymer membrane, the composite membranes dried at temperature above 150°C became more selective, as shown in Table 4.2.
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Figure 4.9: Effect of annealing temperature on the pure gas permeation properties of pure Matrimid® 5218 membrane. (A) Permeability and (B) selectivity.

At higher annealing temperature under vacuum (around 300°C, below the degradation temperature), the Matrimid® polymer is still quite stable. In contrast, the degradation of ZIF-8 nanocrystals resulted in interfacial defects, which is especially pronounced for membranes containing high loadings of ZIF-8. For the composite membrane with ZIF-8 loading of 30 wt% annealed at temperature of 300°C, the permeability of H₂ and CO₂ increased to 144.5 and 29.2 Barrer, respectively, while the ideal selectivity of all gas pairs decreased, i.e. the selectivity of H₂/CH₄ and CO₂/CH₄ significantly decreased to 31.4 and 6.3, respectively.

Table 4.2 Gas permeation properties of Matrimid®/ZIF-8 nanocomposite membranes with 20 wt% loading of ZIF-8 nanoparticles. Membrane samples were annealed at various temperatures for 18 h under vacuum.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>60°C</td>
<td>28.89</td>
<td>19.75</td>
</tr>
<tr>
<td>150°C</td>
<td>36.38</td>
<td>8.78</td>
</tr>
<tr>
<td>180°C</td>
<td>48.23</td>
<td>12.96</td>
</tr>
<tr>
<td>200°C</td>
<td>56.52</td>
<td>12.92</td>
</tr>
<tr>
<td>230°C</td>
<td>63.53</td>
<td>16.63</td>
</tr>
</tbody>
</table>

4.3.4 Effect of ZIF-8 loading on gas transport properties

4.3.4.1 Gas permeability and selectivity

Table 4.3 and Figure 4.10 present the gas transport data of membranes with various loadings of ZIF-8, annealed at 230°C. For all the membranes, the gas permeability correlates
well with the kinetic diameter of gas molecules: H₂ (2.89 Å) > CO₂ (3.3 Å) > O₂ (3.46 Å) > N₂ (3.64 Å) > CH₄ (3.8 Å). As the ZIF-8 loading increases up to 20 wt%, the permeability of H₂ and CO₂ increased to twice that of pure polymer while the permeability of O₂, N₂ and CH₄ only showed moderate increase. Consequently the selectivity maintained similar to that of pure polymer. At high loadings, i.e. 30 wt%, the permeability increased to three times that of pure polymer, however, the selectivity of typical gas pairs decreased.

Table 4.3 Pure gas permeation properties of Matrimid® and Matrimid®/ZIF-8 composite membranes. All membrane samples were annealed under vacuum at 230°C for 18 h.

<table>
<thead>
<tr>
<th>Loading of ZIF-8</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>0</td>
<td>32.68</td>
<td>8.07</td>
</tr>
<tr>
<td>5 wt%</td>
<td>38.05</td>
<td>10.05</td>
</tr>
<tr>
<td>10 wt%</td>
<td>52.56</td>
<td>13.67</td>
</tr>
<tr>
<td>20 wt%</td>
<td>63.53</td>
<td>16.63</td>
</tr>
<tr>
<td>30 wt%</td>
<td>112.06</td>
<td>28.72</td>
</tr>
</tbody>
</table>

Figure 4.10: Representative (A-B) gas permeability and (C) selectivity as a function of volume fraction of ZIF-8 in the Matrimid®/ZIF-8 nanocomposite membranes. Symbols: experimental data; Lines: Maxwell model prediction rather than fitting. The lines are predicted data from Maxwell model (Equation 2-3) based on the gas permeability of pure polymer (this work), and ZIF-8 reported by Bux et al [3,4]. The gas flux of H₂, CO₂, O₂, N₂, and CH₄ through the ZIF-8 membrane (thickness of 30 µm) are 6.04, 1.33, 1.04, 0.52, 0.48×10⁻⁸ mol·m⁻²·s⁻¹·Pa⁻¹, corresponding to intrinsic gas permeability of 5411, 1192, 932, 466, 430 Barrer, respectively.

4.3.4.2 Solubility and diffusion coefficient

The gas permeation data were further analyzed and the diffusion coefficient and solubility of gases in the membrane could be derived; representative data are shown in Figure 4.11. The uncertainty of diffusion coefficient was within ±12%, although in the case
of H₂ it is slightly higher (maximum ±20%) because of the experimental error associated with time lag. Again, the diffusion coefficient of various gases are approximately correlated to the kinetic diameter, while the solubility of gases in the polymer is strongly dependent on the critical temperature of the gas molecules, following the order of CO₂ (304.19 K) >> CH₄ (190.9 K) > O₂ (154.6 K) > N₂ (126.3 K) > H₂ (33.20 K). These data are in agreement with the literature on Matrimid® polymer [26, 29]. As the loading of ZIF-8 increases, both diffusion coefficient and solubility of H₂ increased to several times that of the pure polymer, which could be attributed to the high capacity of adsorption and diffusion of H₂ in ZIF-8 [20]. The major contribution to the increase in CO₂ permeability originates from the diffusion coefficient while the solubility of CO₂ is relatively constant. The crystallographic pore aperture of ZIF-8 crystals is ~3.4 Å, ideally, it would allow the transport of gas molecules with smaller kinetic diameter, such as H₂ (2.89 Å) and CO₂ (3.3 Å), and block the large molecules, such as N₂ (3.64 Å) or CH₄ (3.8 Å). However, an increase of both solubility and diffusion coefficients of N₂ and CH₄ were observed accompanied with a moderate increase of permeability. These data suggest the interaction between these gas molecules and ZIF-8 crystals [30], and the flexible pore structure of ZIF-8 cages (via gate-opening, see Figure 4.2) permits the diffusion of molecules with larger kinetic diameters, as suggested in the literature [4, 31-32]. The increased free volume of the polymer also contributes to the overall diffusion of N₂ and CH₄ as indicated by PALS analysis.

![Fig. 4.11](image)

**Fig. 4.11** Apparent (A) diffusion coefficients and (B) solubility of gases in Matrimid®/ZIF-8 mixed matrix membrane with various loadings of ZIF-8. Membranes were annealed at 230°C for 18 h under vacuum.

### 4.3.5 Measurement of local free volume by PALS

In PALS experiments, a positron is injected into the material being tested and the length of time until that positron annihilates with one of the material’s electrons is measured.
When a positron enters a molecular material, it thermalizes within a few picoseconds, after which, it may diffuse through the material over a mean free path of a few nanometer, either as a free particle and self annihilate directly, or capture an electron to form a positronium-atom [33-34]. Positronium (Ps) is an electron-positron bound state with two spin states: \textit{para}-positronium (\textit{p}-Ps), a singlet state with zero spin angular momentum (the electron and positron have anti-parallel spins); and \textit{ortho}-positronium (\textit{o}-Ps), a triplet state of unit spin angular momentum (the electron and positron have parallel spins). In vacuum, due to the relative number of states available, the population of the two Ps spin states is \textit{o}-Ps: \textit{p}-Ps = 3:1 and \textit{p}-Ps and \textit{o}-Ps annihilate intrinsically with mean lifetimes of 0.125 ns and 142 ns, respectively [33-34]. In molecular materials, Ps localises in the free volume holes between the molecules, where it remains throughout its lifetime. When confined in a local free volume hole, \textit{o}-Ps undergoes numerous collisions with the molecules of the medium, therefore, there is a finite probability that the positron of the \textit{o}-Ps bound state may annihilate with a molecular electron with an opposite spin. This process is known as “pick-off annihilation” and it results in a reduction of the \textit{o}-Ps lifetime with hole size, from 142 ns in an infinitely sized hole (\textit{o}-Ps self-annihilation in vacuum) to 1 - 4 ns for sub-nanometer sized holes [33-34]. The lifetime of \textit{o}-Ps is, therefore, environment dependent and it delivers information pertaining to the size of the local free volume hole in which it resides.

Four discrete lifetimes were resolved in the PALS spectra measured for all Matrimid® based membranes at 25 °C but here we only discuss the two longer components attributed to \textit{o}-Ps annihilation. It is worth mentioning that the two shorter lifetimes, \(\tau_{\text{p-Ps}} \sim 0.20\) ns and \(\tau_{\text{e+}} \sim 0.40\) ns, attributed to annihilation from \textit{p}-Ps and free positron states, respectively (lifetimes are in agreement with the values reported for common polymers [33-34]) were found to be independent of the ZIF-8 loading level.

Table 4.4 PALS parameters measured for Matrimid® membranes with different loadings of ZIF-8 at 25 °C. All membranes were annealed under vacuum at 230°C for 18 h prior to the PALS measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_{\text{p-Ps},1}) (ns)</th>
<th>(\tau_{\text{e+},1}) (Å)</th>
<th>(\tau_{\text{p-Ps},2}) (ns)</th>
<th>(\tau_{\text{e+},2}) (Å)</th>
<th>(\tau_{\text{p-Ps},1}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrimid®</td>
<td>1.19±0.06</td>
<td>1.95±0.08</td>
<td>4.62±0.08</td>
<td>4.57±0.04</td>
<td>2.3±0.1</td>
</tr>
<tr>
<td>Matrimid®/ZIF-8-5wt%</td>
<td>1.53±0.10</td>
<td>2.37±0.12</td>
<td>4.99±0.20</td>
<td>4.74±0.08</td>
<td>2.4±0.1</td>
</tr>
<tr>
<td>Matrimid®/ZIF-8-10wt%</td>
<td>1.43±0.07</td>
<td>2.26±0.08</td>
<td>4.77±0.18</td>
<td>4.64±0.09</td>
<td>2.7±0.1</td>
</tr>
<tr>
<td>Matrimid®/ZIF-8-20wt%</td>
<td>1.54±0.05</td>
<td>2.39±0.05</td>
<td>4.75±0.23</td>
<td>4.63±0.11</td>
<td>3.0±0.2</td>
</tr>
<tr>
<td>Matrimid®/ZIF-8-30wt%</td>
<td>1.67±0.09</td>
<td>2.53±0.08</td>
<td>5.24±0.12</td>
<td>4.86±0.05</td>
<td>4.4±0.2</td>
</tr>
</tbody>
</table>
In Table 4.4, we report the two $o$-Ps lifetimes (and their respective intensities) and the average radii of the free volume elements measured for Matrimid® membranes with different ZIF-8 loading levels. The presence of two distinct $o$-Ps lifetimes in the pure Matrimid® membrane suggests that the distribution of free volume is bimodal [35]. Structurally, the ZIF-8 inclusions possess large pores, 11.6 Å in diameter, which are connected through by small apertures, 3.4 Å in diameter [20]. The lifetimes of $o$-Ps annihilating within such pores would be of the order of 5 ns and 1 ns for the larger and smaller pores, respectively. These lifetimes are too similar to the two $o$-Ps lifetimes measured in the pure Matrimid® membrane, meaning that they cannot be reliably resolved as separate lifetime components in the spectra of the composite membranes. Therefore, the PALS measurements reflect the changes in molecular packing of the base Matrimid® polymer.

From Table 4.4 we can see that there is a systematic increase in the shorter $o$-Ps lifetime as a function of the increasing ZIF-8 loading (with the exception of the membranes containing 5 wt% of ZIF-8), while the changes in the longer $o$-Ps are significantly less pronounced. Our PALS measurements, therefore, illustrate that the ZIF-8 nanoparticles alter the molecular packing of the polyimide polymer chains, leading to an increase in the average sizes of the free volume elements. The effect of the ZIF-8 inclusions on the permeation properties of the membranes is, therefore, two-fold: they reduce the efficiency of the molecular packing of the base Matrimid® polymer, while gas molecules can freely diffuse though the pores of the ZIF-8 cages, both of which lead to an increase in the permeability of the composite membranes.

In Table 4.4 we also present the $o$-Ps intensities measured for the Matrimid® based membranes, which represent the relative number of positrons annihilating from each of the two $o$-Ps states. These parameters reflect the probability of $o$-Ps formation, which in molecular materials is related to the number of sites (free volume elements) available for Ps formation, as well as the chemical parameters governing the mechanism of Ps formation. The individual $o$-Ps intensities (as well as their sum which reflects the total relative number of positrons annihilating from an $o$-Ps state) measured for the Matrimid® based membranes are significantly lower than the $o$-Ps intensities measured for common polymers. Similar observations have been previously reported for a number of polyimide based materials, for which $o$-Ps intensities in the range of 0.5 -17 % have been measured and in some cases the long-lived $o$-Ps component was absent all together [36-38]. In general, polyimides are known to strongly suppress (inhibit) the formation of Ps and the inhibition effect is principally governed by the chemistry of the di-anhydride. Taking this into consideration, it must be noted that the $o$-Ps intensities measured do not directly correspond to the concentration of
free volume elements in the Matrimid® based membranes.

4.3.6 Modelling of gas transport properties

The gas permeation data of pure ZIF-8 membrane is re-calculated from the pure gas permeation data reported by Bux et al [4]. The gas flux of H₂, CO₂, O₂, N₂, and CH₄ through the 30 µm thickness membrane are 6.04, 1.33, 1.04, 0.52, 0.48×10⁻⁸ mol·m⁻²·s⁻¹·Pa⁻¹, corresponding to intrinsic gas permeability of 5411, 1192, 932, 466, 430 Barrer, respectively [3, 30]. With the gas transport properties of pure polymer and ZIF-8, the permeability of composite membranes could be estimated with the Maxwell model (Equation 2-3), as shown in Figure 4.10 and Figure 4.12. Model predictions suggest that gas permeability of the composite membrane is enhanced while the selectivity of the composite membrane remains constant if the fillers are far more porous than the polymer matrix. The model predictions match well with the experimental data, although there appears to be a systematic under-prediction of permeability for all the gases. This correlates well with the PALS observation of an enhanced polymer free volume (and hence larger contribution to permeability) with ZIF-8 loading, since this consideration and detailed dispersion characteristics are not included in the idealized Maxwell model.

![Figure 4.12: Plots of selectivity versus the permeability for industrially important gas pairs (A) CO₂/CH₄, (B) H₂/CH₄. The upper bound lines refer to Robeson’s upper bound in 1991 and 2008, respectively [39-40]. The apparent gas transport properties of ZIFs membrane are included: ZIF-7 [9, 11], ZIF-8 [3-4, 30], ZIF-90 [6-7]. The polyimide 6FDA-DAM and 6FDA-DAM/ZIF-90 mixed matrix membranes were reported by Bae et al [18]. Grey circles refer to Matrimid®/MOFs in the literature. Red balls refer to Matrimid®/ZIF-8 mixed matrix membranes in terms of the volume fraction of ZIF-8 (red). Dashed lines (red) indicate the Maxwell model prediction (Equation 2-3) using the gas permeation data of pure Matrimid® (this study) and permeability converted from the flux data of pure ZIF-8 membrane reported by Bux et al[4].](image-url)
4.3.7 Comparison with upper bound of polymeric membranes

The pure gas permeation properties are also compared with the Robeson’s upper bound as shown in Figure 4.12. The gas permeation properties of some other types of ZIFs, such as ZIF-7 and ZIF-90, are also included. The upper bound plot shows clearly that the gas permeability of composite membranes are enhanced, however, the enhancement is very limited although the ZIFs are highly permeable. Clearly, the polymer phase determines the baseline of separation performance of mixed matrix membranes.

4.4 Discussion

Compared to conventional inorganic molecular sieves, MOFs are expected to have better interfacial properties owing to the organic nature that would enable intermolecular forces between the functional groups of polymers and MOFs at the interface. In addition, when the size of fillers become smaller to nanometre scale, that is at the same length scale of polymer chains, the fillers would disrupt the packing of polymer chains and result in the change of free volume in the polymer phase, which is especially prominent for rigid polymers [41], which would also result in increase in permeability of light gas molecules.

The incorporation of nanocrystals into polymer matrix results in heterogeneous materials that present random distribution of nanocrystals, interfacial defects, and free volume elements in the glassy polymer phase. The complexity of the composite materials are subject to so many parameters that affect the physical properties of the mixed matrix membranes, and consequently the gas permeation mechanisms could be very complex. For example, Bae et al.[18] observed that both the permeability and selectivity were enhanced when ZIF-90 crystals at sub-nanometer size were incorporated into a rigid 6FDA-DAM polyimide, while for dense polyimides (e.g. polyetherimide and Matrimid) the enhancement is very limited. The authors did not analyze in detail on the mechanism. Yang et al.[23] also reported that addition of ZIF-7 nanoparticles into a polybenzimidazole (PBI) matrix enhanced the permeability of H₂ and selectivity over CO₂, which was also higher than that predicted by the Maxwell model. They attributed the increase of selectivity to the interaction of ZIF-7 with PBI.

Combined with various characterization analyses, we could conclude that the enhancement of gas permeability in our Matrimid® polyimide/ZIFs composite membranes could be attributed to several factors: (1) poor packing of polymer chains and increase in free volume according to the PALS analysis, (2) rapid diffusion of porous ZIF-8 crystals, and (3) better interface between ZIF-8 and polyimide polymer. In particular, the third factor is
probably owing to the interfacial interactions, such as hydrogen bonding between the imidazole group at the boundary of ZIFs crystals and the carbonyl groups in polyimide polymer chains, as schematically shown in Figure 4.13.

![Polyimide segments](ZIF-8-crystal.png)

**Figure 4.13: Possible hydrogen bonding between imidazole group at the boundary of ZIFs crystals and the carbonyl groups in polyimide polymer chains.**

Nevertheless, it is possible to achieve high gas separation performance by adopting the right combination of a highly selective MOF with a highly permeable polymer and tuning the interactions at interface. Recently, significant progress has been achieved on highly permeable polymers, such as PIMs [42-44]. Using a similar method of dispersing the ZIF nanoparticles established in this Chapter, further work on the combination of the highly permeable PIMs and ZIFs to achieve high performance of gas separation will be reported in Chapter 6.

### 4.5 Conclusion

In summary, we report the preparation of nanocomposite membranes composed of a polymer matrix which features good dispersion and adhesion of ZIF-8 nanoparticles within the polymer. We show that annealing the polymer nanocomposite membranes under vacuum has a positive impact on their gas permeation properties, as a consequence of residual solvent removal from the matrices coupled with the activation of ZIF-8 nanocrystals. Upon increasing the loading of ZIF-8 nanoparticles in the mixed matrix membranes, the gas permeability increases substantially while the selectivity remains largely unchanged in comparison with the pure polymer membrane. Gas adsorption studies further confirmed that the selective gas transport is dominated by the polymeric phase. Additionally, the PALS analyses indicated that incorporation of ZIF-8 reduces the efficiency of the molecular packing
of the polymer, while gas molecules can rapidly diffuse though the pores of the ZIF-8 cages, both of which lead to an increase in the permeability of the composite membranes. The experimental data are essentially predicted by the Maxwell model, but with deviations that can be associated with corrections for a small non-ideal distributions of nanoparticles and the influence of ZIF-8 loading on the packing of polymer chains.

4.6 References


Chapter 5 Photo-oxidation of polymer of intrinsic microporosity

5.1 Introduction

Ultraviolet (UV) light irradiation is a widely-used technique for processing of polymer materials [1-5], e.g. polymerization of novel gas-separation membranes[5], creating nanostructures from block copolymer[4], or surface modification of polymeric films and photolithography[1-4]. UV light irradiation has been used for modification of separation membranes since the early start of polymer membrane industry in the 1980s [6], for example, in crosslinking polyimide membranes containing benzophenone units [7-8] or degradation of siloxane-containing polymers [9]. However, the gas permeability of conventional polymers is considerably low, as summarized in a comprehensive review [10].

Figure 5.1: Photoluminescence phenomenon of PIM-1 polymer under (A) visible light and (B) UV light (λ=254 nm) in ambient conditions.

PIM-1 polymer is fluorescent and emits green light under excitation of light (Figure 5.1) or electrons. This phenomenon is unusual because PIM-1 is not a conjugated polymer, however, the mechanism of photoluminescence or electroluminescence is still not fully understood and further study is necessary. The photoluminescence inspires us to study the photo-oxidation process and its impact on the physical properties of polymer films, and particularly the packing of polymer chains and molecular sieving properties after the photochemical modification. Understanding of the photo-oxidation phenomenon and stability of microporous PIMs polymers is of broad interest to their wide range of applications, for example, gas separation, catalysis, optoelectronics and sensor technology.

In this study, using PIM-1 as a prototype of microporous polymers, we demonstrate that oxidative chain scission of PIM-1 polymer occurs upon short-wavelength UV irradiation in the presence of oxygen. Due to the limited penetration of UV light and diffusion of ozone in the polymer matrix, the oxidative chain-scission is restricted to the surface and leads to a
novel near-surface collapse and densification, which is especially pronounced in such open microporous polymeric materials. The resulting asymmetric membranes exhibit a superior selectivity in gas separation whilst maintaining an apparent permeability that is two orders of magnitude greater than commercially available polymeric membranes. The rapid transformation of the near surface physical and chemical properties via this photo-oxidative technique suggests further applications in other thin film technologies.

5.2 Experimental methods

The fresh PIM-1 polymer has an average molecular weight of $M_n = 100,000$ dalton and a polydispersity (PDI) of 1.8. Dense membranes were exposed to UV irradiation ($\lambda = 254$ nm, incident intensity of 8.0 mW cm$^{-2}$) in a commercial UV box (UVP model CX-2000, Cambridge, UK). The membranes were exposed in air for exposure time-studies. Alternatively, we controlled the atmosphere of UV irradiation using a temperature controlled, quartz-windowed, stainless steel reactor with constant flow (100 mL min$^{-1}$, STP) of different gases controlled by a mass flow controller (Bronkhost, EL-flow).

Thin films were prepared by spin coating or dip coating with diluted PIM-1 solution in chloroform. PIM-1 polymer solution (0.8 wt%) was dip-coated on glass substrate (effective area, $\sim 15\times 15$ cm) forming thin film with thickness of about 300 nm. The intensity of UV was relatively uniform over the irradiation area of films, as measured by a radiometer. Based on the SEM observation, we could assume the thin film was degraded through the membrane though a gradient exists through the film. After the UV irradiation in air, the film was removed and dried in vacuum oven for overnight. For each sample, about 20 pieces of PIM-1 thin film were prepared to collect enough sample for characterization analyses (density, TGA, and gas adsorption).

Pure gas permeation tests were carried out at a feed pressure of 4 bar and at temperature of 22°C. Mixed gas permeation was performed using the constant flow method, with certified gas mixtures of $\text{CO}_2/\text{N}_2$ (50/50 vol.%.) and $\text{CO}_2/\text{CH}_4$ (50/50 vol.%.) at feed pressure up to 35 bar at 22°C. The stagecut, defined by permeate flow rate to feed rate (1500 mL min$^{-1}$) was less than 1 %. The gas compositions were analyzed by a gas chromatograph as described in Chapter 3.

5.3 Results

5.3.1 Morphology of polymer membranes

The short-wavelength UV irradiation ($\lambda = 254$ nm) of PIM-1 membranes in the presence of oxygen resulted in the asymmetric changes of membrane morphology. Cross-
sectional SEM images (Figure 5.2) show the asymmetric physical changes at the surface of a 50 µm thick membrane upon UV irradiation, where a dense skin layer was formed above a mesoporous intermediate layer (pore size 2-20 nm, thickness about 0.1-2 µm). This intermediate layer was formed due to the stress induced from densification of the skin layer; the remainder of the film was pristine PIM-1. The dense skin layer, forming quickly to a thickness of 300 nm within 10 minutes of UV exposure, densified to 400 nm at longer exposure time (up to 60 min) (Figures 5.3 and 5.4), for both dense membranes and thin films.

![Figure 5.2: Cross-sectional morphologies of membranes.](image)

(A-B) Schematic diagram of UV irradiation of polymer membranes and formation of heterogeneous materials consisting of a thin modified layer at the surface. (C) Cross-sectional SEM of polymer of intrinsic microporosity (PIM-1) membrane (~50 µm thickness) after exposure to UV irradiation in air for 60 min, showing the formation of composite layers consisting of a denser skin layer and an intermediate mesoporous layer over the pristine dense PIM-1 layer. (D) Enlargement of cross-sectional SEM of surface layer. (E) Cross-sectional SEM of PIM-1 thin film. Inset shows the profile of UV light transmission as a function of depth. (F) Cross-sectional SEM of a fractured UV/ozone treated PIM-1 membrane.
Figure 5.3: Cross-sectional morphology of thin films. (A) Cross-sectional SEM images of PIM-1 films after exposure to UV irradiation in air over 10-60 min. (a-f) Membranes were exposed in air, (g-l) membranes sandwiched in two pieces of flat quartz glass. (m) Cross-section showing uniform thickness of sample exposed to UV irradiation in air for 20 min. (B) Average thickness of composite layer and dense skin layer (as showed in the inset) as a function of time of UV/ozone treatment. The membranes were spun-coated on silicon wafers.

Figure 5.4: Cross-sectional morphology of dense membranes. (A) Dense PIM-1 membrane (~50 µm), (B) UV irradiated in air for 10 min, (C) UV irradiated in air for 60 min, (D) UV irradiated in air for 10 min, (E) 30 min, and (F) 60 min. (B-C) membranes were exposed in air, (D-F) UV irradiation experiments were performed in air, with the membranes sandwiched in two pieces of flat quartz glass. Scale bars in all panels: 500 nm.
5.3.2 UV light transmission and optical properties

Figure 5.5 presents the plot of the transmitted intensity of UV light, $I(x)$, through the depth, $x$, of the film. Described by a Beer-Lambert expression as $I(x) = I_0 e^{x/L_0}$ [11], the incident intensity decreased significantly from 8 mW/cm$^2$ to 40 µW/cm$^2$ at the depth of 500 nm, reflecting a characteristic penetration depth ($L_0$) of ~105 nm for fresh PIM-1. Such exponentially decaying UV intensity correlates well with the significant structural changes of surface layer, as shown in Figure 5.2E. This large attenuation in UV intensity originates from the aromatic nature of PIM-1 which has high absorption of UV light. The significant loss of photoluminescence and PLQY of UV/ozone treated PIM-1 thin film indicates the degradation of polymer.

Figure 5.5: Optical properties. (A) Profile of normalized intensity of UV irradiation as a function of the depth of membrane. The intensity with depth of membrane was calibrated by stacking of PIM-1 thin films (100 nm of each) spin-coated on thin quartz plate, or dense membrane with different thickness (~10 µm and 50 µm). The incident intensity ($I_0$) was 8.0 mw cm$^2$. The intensity below the stack was measured by a radiometer (UVX-25, UVP Ltd, UK). The absorbance of UV light by quartz is negligible. Symbols: experimental data; Lines: model prediction with a Lambert-Beer law as $I(x) = I_0 e^{x/L_0}$, giving a characteristic penetration depth ($L_0$) of ~105 nm. (B) Evolution of the UV-visible absorption at 230 nm, absorbance at 254 nm (normalized by the maximum absorption of pristine PIM-1 at 230 nm), photoluminescence intensity at 490 nm, and photoluminescence quantum yield (PLQY) of PIM-1 thin films as a function of UV irradiation time. (C) UV-vis absorption spectra and (D) photoluminescence (PL) spectra of pure PIM-1 and UV/ozone treated PIM-1 thin film (~100 nm), excited at 420 nm.
5.3.3 Mechanical properties

During preparation of cross-section of membranes, very occasionally poorly-fractured edges (Figure 5.2F) indicated the contrast in mechanical properties of the skin and pristine regions. Nanoindentation measurements of the elastic modulus ($E$) and the hardness ($H$) were obtained on membranes using a sharp Berkovich tip in the continuous stiffness measurement (CSM) mode. The representative load-displacement profiles are shown in Figure 5.6. The pristine PIM-1 film with thickness of ~1 µm gave an overall Young’s modulus of 6.94 GPa and an average hardness of 0.23 GPa. After UV irradiation for 60 min in air, we found ~35% and ~50% increases of both Young’s modulus (9.00-9.33 GPa) and hardness (0.34-0.35 GPa) respectively. These measurements are subject to the influence of substrate and deviate from the true value; nevertheless, the comparison qualitatively confirms that the UV/ozone modified surface became hard and brittle owing to densification and enhanced rigidity.

![Figure 5.6: Nanoindentation.](image)

(A) SEM images of cross-section of pristine and UV/ozone treated PIM-1 films. (B) Representative $P$–$h$ curve for membranes at different conditions of UV irradiation. (C) Elastic modulus and (D) Hardness properties of membranes at different conditions of UV irradiation as a function of indentation depth, wherein each error bar represents the standard derivation of 25 indents. Sample (a): pristine PIM-1 film; sample (b): UV/ozone treated PIM-1 film, UV irradiation in air for 60 min; sample (c): UV/ozone treated PIM-1 film, which was sandwiched between two pieces of flat quartz glass and exposed to UV irradiation in air for 60 min.
Table 5.1 Mechanical properties derived from nanoindentation measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Young’s Modulus, $E$ (Gpa)</th>
<th>Average Hardness, $H$ (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh PIM-1 film $^a$</td>
<td>6.94</td>
<td>0.23</td>
</tr>
<tr>
<td>PIM-1 UV/ozone 60 min $^b$</td>
<td>9.33</td>
<td>0.35</td>
</tr>
<tr>
<td>PIM-1 UV/ozone 60 min $^c$</td>
<td>9.00</td>
<td>0.34</td>
</tr>
</tbody>
</table>

$a$ fresh PIM-1 film casted on silicon wafer,
$b$ PIM-1 film casted on silicon wafer, exposed to UV irradiation in air for 60 min,
$c$ PIM-1 film casted on silicon wafer, sandwiched between two quartz plates and exposed to UV irradiation in air for 60 min.

5.3.4 Molecular weight and solubility

Post-UV treated membranes (~50 µm thick) and thin films (100-1000 nm) remained soluble in solvents (e.g. chloroform or tetrahydrofuran), confirming that UV treatment did not result in covalent crosslinking of polymer. Instead, gel permeation chromatography (GPC) measurements with PIM-1 thin film (~300 nm) showed that the average molecular weight decreased significantly (Figure 5.7), when samples were irradiated in air directly or through quartz glass. The pristine PIM-1 polymer has an average molecular weight of $M_n$=100 kdalton with a polydispersity index (PDI=$M_w/M_n$) of 1.8. After UV irradiation in air, the mean molecular weight decreased sharply indicating a broad range of fragmented polymer chains. However the high PDI (~20) of the irradiated material limits the accuracy of characterizing the material with a single average molecular weight. This is to be expected from the attenuated UV irradiation with the depth of the thin film sample. The degraded fractions also became soluble in polar solvents, i.e. dimethylformamide (DMF), acetone or methanol.

Figure 5.7: Molecular weight distribution. (A) PIM-1 thin films (about 300 nm) exposed in air directly, (B) PIM-1 thin films sandwiched in quartz glass. UV irradiation was performed in air.
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It should be noted that these measurements were based on PIM-1 thin films. The broad distribution indicates the nonlinear degradation through the film owing to the exponentially decaying of UV light field.

5.3.5 Density measurement

The bulk density of the UV-modified membranes was measured by quantification of the mass and volume of dense polymer films. The bulk density remained the same as that of PIM-1 membrane, in the range of 1.06-1.1 g cm\(^{-3}\). The skeletal density of polymers was measured by helium pycnometric method. The average skeletal density of the UV/Ozone treated PIM-1 thin film (~300 nm) is 1.418(16) g cm\(^{-3}\), which is higher than that of the pristine PIM-1 film, 1.277(11) g cm\(^{-3}\). The increase in skeletal density confirms the denser packing of polymer chains and loss of excess (hole) free volume.

5.3.6 Chemical changes

The photochemical modification of polymers usually involves complicated chemical reaction pathways, therefore we only tracked the \textit{ex situ} FTIR spectra of polymer films after exposure to UV/ozone, as shown in Figure 5.8.

![Fourier-transform infrared (FTIR) spectra](image)

**Figure 5.8:** Fourier-transform infrared (FTIR) spectra. PIM-1 thin films (about 300 nm) dip-coated on salt plate (Aldrich), were exposed to UV irradiation in air for 5-60 min.
Upon UV/ozone treatment, the PIM-1 thin films (~300 nm) show the carbonyl group (C=O) stretching at about 1730, 1630, and 1600 cm\(^{-1}\) and hydroxyl (O-H) groups around 3300 cm\(^{-1}\) simultaneously, and the intensities increased with time. The observation of the carbonyl groups clearly indicates that the polymer was oxidized by oxidants (ozone or atomic oxygen) induced by UV irradiation in air; however, the broad peaks indicate they may exist in several different forms such as aldehydes, ketones, or carboxylic acids. The absorbance of other groups were quite stable, such as aromatic C-H stretching at 3055 cm\(^{-1}\), C-H stretching within the methyl (C-CH\(_3\)) groups and methylene (CH\(_2\)) groups (initially on the spiro ring) at around 2955, 2930 and 2840 cm\(^{-1}\), C-H bending vibrations within methyl and methylene groups (1455 cm\(^{-1}\)), nitrile groups (-CN) at 2238 cm\(^{-1}\), aromatic bending (C=C) at 1607 cm\(^{-1}\), C-O stretching over 1300-1000 cm\(^{-1}\), and the long wavelength bands corresponding to aromatic bending. The sites for initial oxidation and chain cleavage is not clear, a possible site of initiation may be the benzodioxan linkages or spiro-carbon centres, though hydrogen abstraction of the methyl groups was more feasible initial reaction sites. Further studies are needed in the future. Another FTIR-ATR was used in reflection mode giving identical spectra, confirming the oxidation at the surface of membranes.

**5.3.7 Proposed mechanism of photo-oxidation.**

It is well known that under short wavelength UV irradiation, O\(_2\) can absorb photons generating strongly oxidizing agents, including singlet oxygen and ozone. Equally, the high free volume and permeability of PIM-1 should lead to a local abundance of O\(_2\). With an activation energy from heat or light, the PIMs materials behave as nanoreactors that are attacked by the oxidants generated within them, especially in the region of shallowly penetrating UV irradiation. We performed control experiments of UV irradiation of PIM-1 films in air, with films sandwiched between quartz glasses which limited extent of oxygen exposure at the interface and carried out extensive characterization analyses. This is supported by FTIR analysis indicating formation of carbonyl and hydroxyl groups in the surface of UV/ozone treated membranes. The conclusion of photo-oxidation and chain scission was essentially the same as those tests performed in air, or under gas flow with varied O\(_2\) concentration. Oxidative chain scission occurred as schematically shown in Figure 5.9. Nevertheless, the initial reaction site is still not clear and detailed mechanism merits further study.

For molecular modelling, energy minimization and molecular dynamics were performed with the Materials Studio software package (Version 4.3, Accelrys Inc, CA, USA).
In one amorphous cell, four PIM-1 polymer chains with 10 repeating units were constructed. To mimic the chain scission, 20 short chains containing two repeating units of PIM-1 with oxidized groups were constructed in another amorphous cell as well. The fragmented polymer segments pack more efficiently leading to loss of accessible free volume. This assumption was explored in molecular simulations of both PIM-1 (Figure 5.9B) and the degraded polymer (Figure 5.9C). The shorter polymer segments allow stronger intermolecular interactions (e.g. van der Waals forces and chain entanglement). The accessible free volume, as probed by CO₂ molecules with a kinetic diameter of 3.3 Å at 298 K was diminished in the simulation of densely-packed matrix of shorter polymer chains.

Figure 5.9: Molecular structure and simulation. (A) Schematic illustration of oxidative chain scission of PIM-1 upon exposure to UV irradiation in the presence of O₂, showing transformation of long contorted polymer chains to shorter chains after oxidation and scission. (B) Three-dimensional view of computer simulation of an amorphous cell with PIM-1 polymer chains (four polymer chains inside, each containing of 10 repeating units). Cell size: 31.8×31.8×31.8 Å, density of 1.05 g cm⁻³. (C) Three-dimensional view of computer simulation of an amorphous cell with degraded PIM-1, 20 polymer chains with two repeating PIM-1 units with oxidized groups, to mimic the shorter polymer chains after oxidative chain scission. Cell size: 29.5×29.5×29.5 Å, bulk density of 1.257 g cm⁻³. The grey surface indicates the van der Walls surface, green surface is the Connolly surface with probe radius of 1.65Å.

It should be noted that the chemical structures of degraded oligomers are not clear. It is also possible that the formation of hydroxyl-containing groups may introduce
intermolecular or intramolecular interactions via hydrogen bonding between ether linkages of the backbone and hydroxyl-containing groups (e.g. carboxylic acid) of oxidized polymer segments, as shown in Figure 5.10. The hydrogen bonding would form physical crosslinking and tighten the cleaved short chains. Though the hydrogen bonds have relatively weak energy, the collective effect enables that the network remain mechanically stable and selective for gas separation at high pressure.

Figure 5.10: Hydrogen-bonded polymer networks. (A) Three-dimensional molecular simulation of an amorphous cell containing 20 short polymer chain segments with each segment consisting of two PIM-1 repeating units capped with –COOH groups, to mimic the shorter polymer chains due to oxidative chain scission. Cell size: 31.7×31.7×31.7 Å, density: 1.174 g cm\(^{-3}\). (B) Enlargement to show the possible intermolecular interactions via hydrogen bonding (blue dotted line) between ether linkages of the backbone and hydroxyl-containing groups (carboxylic acid) of oxidized polymer segments. Carbon: black; Oxygen: red; Hydrogen: grey; Nitrogen: blue.

5.3.8 Gas sorption properties

\( \text{N}_2 \) adsorption was performed with pristine PIM-1 thin films (~300 nm) and modified films after exposure to UV irradiation in air for 20 min. As shown in Figure 5.11A, both pristine PIM-1 thin film and UV/ozone treated PIM-1 thin film exhibited high sorption of nitrogen molecules in the interconnected free volume elements. However, the UV/ozone modified polymer films showed relatively lower sorption. Similarly, we also observed slight loss of \( \text{CO}_2 \) solubility in the UV/ozone treated PIM-1 films (Figure 5.11B). Both samples show broad distributions of pore size as derived from the non-local density functional theory (NLDFT) method (Figure 5.11C). However, the UV/ozone treated sample shows reduced
pore volume in the ultramicropore range (<0.6 nm). This loss of microporosity resulted in the decrease of BET surface area from 779 m² g⁻¹ to 573 m² g⁻¹ and the micropore volume drops from 0.136 to 0.105 cm³ g⁻¹. The gas sorption measurements corroborate the prediction of local dense packing of polymer chains and loss in free volume by the molecular dynamics simulation.

**Figure 5.11: Gas sorption properties.** (A) N₂ adsorption isotherms at 77 K, (B) CO₂ sorption isotherms at 293 K, and (C) micropore size distribution derived from N₂ adsorption isotherms at 77 K by the NLDFT model. UV/ozone modified PIM-1 was prepared by UV irradiation of PIM-1 thin film (~300 nm) in air for 20 min. Solid and open symbols represent the adsorption and desorption branch, respectively.

### 5.3.9 Gas transport properties

The gas transport properties in terms of permeability and selectivity were measured with pure gas permeation using thick dense membranes. For homogeneous PIM-1 polymer membranes, the as-measured gas transport properties are the intrinsic properties of the materials. In contrast, the UV/ozone treated membranes became asymmetric after surface modification, the measured permeability and selectivity are an apparent overall property of the heterogeneous membranes.

We demonstrate that the oxygen has significant effect on the photo-oxidation process and the gas transport properties of the resulting membranes. We varied the concentration of O₂ in the UV irradiation atmosphere at a fixed exposure time (20 min) and found significant differences in pure gas permeation properties, as shown in **Figure 5.12**. Pristine PIM-1 membrane presents a CO₂ permeability of ~4500 Barrer with the CO₂/N₂ selectivity at ~20, and the CO₂/CH₄ selectivity at ~13, which are in agreement with the literature data[12]. Control experiments of UV exposure in pure N₂ showed no discernible difference in properties to that of pristine polymer. In contrast, increasing the concentration of O₂ (from 20.9 vol.% in air to pure O₂) enhanced the apparent selectivity of various gas pairs (e.g.
CO₂/N₂ and CO₂/CH₄ increased up to ~30) at the slight expense of permeability, corroborating the idea that UV-induced ozone within the open polymer framework is responsible for subsequent structural densification. From the viewpoint of chemical reaction engineering, as visualized in Figure 5.12(C-E), the photo-oxidation could be tuned by the concentration of O₂ in the porous polymer framework.

Figure 5.12: Effect of oxygen on the photo-oxidation and gas transport properties. (A) Apparent permeability and (B) selectivity of pristine and UV irradiated (20 min, 20°C) PIM-1 membranes (~50 μm) under different gas atmospheres. (C-E) Amorphous cells containing 4 PIM-1 polymer segments with each segment consisting of 10 repeating units, and gas molecules with different compositions: (C) N₂, (D) O₂/N₂, and (E) O₂, which visualize the tuneable atmosphere of photo-oxidation. N₂: blue; O₂: Red.

We examined the dynamic change of gas transport properties of membranes exposed to UV irradiation in ambient conditions for varied time of 5-60 min. Whether the membranes were exposed to air directly or sandwiched in quartz glass, we always observed the formation of denser skin layer and the decrease in molecular weight of the exposed PIM-1, confirming that the oxygen adsorbed within the polymer matrix was sufficient to induce the oxidation. However sandwiching the membranes limited the source of O₂ at the interface and consequently slightly affected the reaction kinetics and resulting gas transport properties.
without altering the general trend of lower permeability/higher selectivity for extended UV exposure.

Here we present the gas transport data of membranes exposed to UV irradiation in air, with the membranes exposed in air directly or sandwiched in quartz glass, as shown in Table 5.2 and Figure 5.13. Upon exposure to UV irradiation, the apparent permeability of CO₂ showed a slight increase (up to 7000 Barrer) after short exposure for 5-10 min, but then decreased with extended exposure for 20-60 min, while the selectivity evidently increased. The slight increase of permeability after short exposure (5-10 min) of UV irradiation was within the error of measurement and subject to plasticization and physical aging during the history of measurement (multiple cycles of vacuum and permeation of several gases). It can effectively be considered a transient effect that becomes less significant when considered over the overall trends of permeability-selectivity performance. The apparent selectivity of H₂ over each of N₂ and CH₄ increased up to ~60 with moderate decrease of permeability of H₂ (~2000 Barrer). The apparent permeability of O₂ decreased to 600 Barrer with an O₂/N₂ selectivity of ~6. The overall membranes have apparent selectivity of commonly used gas separation membrane materials whilst retaining orders-of-magnitude higher permeability.

Table 5.2 Apparent gas transport properties. PIM-1 membranes were exposed to UV/ozone treatment and tested at feed pressure of 4 bar at 22°C. 1 Barrer=1×10⁻¹⁰ cm³(STP)cm⁻²s⁻¹cmHg⁻¹.

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<th>Sample</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
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<tr>
<td></td>
<td>H₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>PIM-1 blank</td>
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<tr>
<td>Exposure to UV irradiation in air</td>
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</table>
Figure 5.13: Dynamic change of gas transport properties. Experimental data and model prediction of overall apparent gas permeability and selectivity of dense PIM-1 membrane (~50 µm) exposed to UV irradiation in air for a range of times. Symbols: experimental data; lines: model predictions with Equations 5-3 and parameters in Table 5.3. (A-B) membranes were exposed to UV irradiation in air, (C-D) membranes were sandwiched in two pieces of quartz glass, and exposed to UV irradiation in air.

The apparent gas transport properties of UV/ozone modified membranes exceed the limitations defined by Robeson’s 2008 upper bound (Figure 5.14). However, it should be noted that since the membranes became asymmetric after modification, these measured permeability and selectivity are an overall property of the heterogeneous membrane. The Robeson’s upper bound construction, on the other hand, reflects the intrinsic permeability and selectivity of homogeneous dense polymer membranes. Thus, in a strict sense, one should be cautious about making a comparison of the performance of our UV/ozone modified membranes to the upper bound. However in a field where it is becoming more common to generate composite materials for gas separation, whether through a bulk mixed matrix membranes, or as thin film composites, the comparison is still instructive. This is effectively illustrated in modeling our observed results below, where we illustrate that the permeability and selectivity of the surface modified PIM-1 can be predicted through a multi-layered model of varied intrinsic gas permeability so that the apparent ‘bulk’ values surpass the empirical upper bound limitation of a homogeneous material, as shown in Figure 5.14 and Figure 5.15.
Figure 5.14: Apparent gas transport properties of CO$_2$/CH$_4$ gas pair. Apparent CO$_2$/CH$_4$ selectivity versus apparent CO$_2$ permeability for PIM-1 (solid square) and UV/ozone modified PIM-1 membranes (solid circles). The dense membranes (~50 µm) were exposed to UV irradiation in air for varied time (5-60 min), with the membranes sandwiched in quartz glass. Open squares: literature data of PIM-1; Solid triangles: literature data of other PIMs [12-14]. The upper bounds were summarized by Robeson in 1991[15] and 2008[16], respectively. The dashed line corresponds to model prediction.
5.3.9.4. Mixed gas separation

Apparent selectivity of CO\(_2/\)CH\(_4\) of PIM-1 membrane (solid squares) and UV/ozone treated (30 min) PIM-1 membrane (solid circles) as a function of fugacity of CO\(_2\) in the mixed gas (CO\(_2/\)CH\(_4\), 50/50 vol.%). The fugacity was calculated from the Peng-Robinson equation of state [17], see Appendix C. Since practical applications of such membranes in separations involve mixtures of gases, the mixed gas selectivity of important gas pairs (such as CO\(_2/\)CH\(_4\), CO\(_2/\)N\(_2\)) was determined from equimolar gas mixtures indicating a significant enhancement in separation efficiency in UV treated membrane (Figure 5.16). Moreover,
these tests performed with clean cylinder mixed gas, indicated the physical stability of the modified membranes at high pressure.

**Figure 5.16: Mixed gas separation.** Apparent permeability and apparent selectivity of separation of gas mixture of (A-B) CO$_2$/N$_2$ and (C-D) CO$_2$/CH$_4$ for pristine and UV/ozone treated PIM-1 membranes. PIM-1 dense membrane was exposed to UV irradiation for 30 min in air. Feed gases were standard gas mixtures of CO$_2$/N$_2$ (50/50 vol.%) and CO$_2$/CH$_4$ (50/50 vol.%) at room temperature of 22°C.

### 5.4 Discussion

The observed trends in selectivity and permeability as a function of UV irradiation time can be understood given that the exponentially decaying UV field generates a concentration gradient of ozone within the surface layer of the polymer. Making the broad assumption that ozone (and singlet oxygen) is responsible for the collapse of the PIM-1 framework, and hence the increase in local density and decrease in local permeability, allows a determination of the overall and intrinsic permeability and selectivity of the membranes for different UV dosages. The intrinsic gas transport properties could be derived from a multiple-layered model as described in **Figure 5.17**.
Figure 5.17: Modelling of gas permeation. The overall permeability of a homogeneous membrane is calculated over a thickness $L$ as in (A). However, for asymmetric UV modified PIM-1 membranes, phenomenologically there is a difference in the density and hence permeability of the material at the skin layer as in (B). Expressing the overall permeability as analogous to a series circuit resistance across a potential as in (C), but substituting the pressure drop for potential and resistance for permeability as in (D), the overall permeability can be determined. For a continuous change in permeability, this calculation can be differentiated as in (E).

Analogous to the generation of current under potential through series circuits, a series resistance model can be used to describe the gas flux ($N$) under the driving force of pressure ($\Delta p$) through the membrane with resistance ($L/P$) can be described as:

$$N = \frac{\Delta p}{L} P = \frac{\Delta p}{\sum_{i=1}^{n} \frac{L_i}{P_i}}$$  \hspace{1cm} (5-1)

Therefore, the overall resistance is defined as the integration of resistance of multiple layers, as following equation:

$$\left( \frac{L}{P} \right)_{\text{overall}} = \frac{L_{\text{total}}}{P_{\text{apparent}}} = \sum_{i=1}^{n} \left( \frac{L_i}{P_i} \right) = \int_{0}^{L_{\text{total}}} \frac{1}{P} \, dx$$  \hspace{1cm} (5-2)

where $L_{\text{total}}$ is the total thickness of the membrane, $P_{\text{apparent}}$ is the apparent overall permeability as calculated from the gas flux, pressure driving force and total thickness. For a homogeneous PIM-1 polymer membrane, $P$ is equal to the intrinsic permeability, $P_{\text{PIM-1}}$. For a UV/ozone surface modified PIM-1 membrane, we must estimate the permeability $P(x)$ in order to determine the overall membrane permeability.

We can assume that the loss in permeability of the open sponge-like network is directly related to the collapse of this network under ozone degradation. Therefore $P(x,t) \sim C(x,t)$ where $C(x,t)$ describes the temporal local non-degraded PIM-1 concentration. Since polymer degradation is often considered to be a first order reaction process, $C(x,t)$ can be described as $C(t) = C_0 \exp(-kt)$ where the local rate of degradation $k(x)$ could be described as $k(x) = k_0 \exp(-x/L_0)$. $k(x)$ itself is defined by the local concentration of ozone, and hence its
generation by the local UV field which is experimentally derived as \( P(x,t) = P(x=0,t=\infty) + \left[ P(x=L,t=\infty) - P(x=0,t=\infty) \right] \exp(-k_0 \exp(-x/L_0)t) \) (5-3)

where \( P(x=0,t=\infty) \) expresses the limiting permeability of the material after prolonged UV/ozone treatment. \( P(x=L,t=\infty) \) is the permeability at the base of the membrane after prolonged UV/ozone treatment (and is effectively \( P_{PM-1} \)).

Substituting (Equation 5-3) into (Equation 5-2), yields an expression that can be fit against the experimental data of \( (L/P)_{overall} \) to determine the permeability profile in the material as a function of time for different gases (Figure 5.18) and numerically correlate selectivity versus permeability predictions (see Figure 5.14 and Figure 5.15).

### Table 5.3 Kinetics parameters derived from modeling.

<table>
<thead>
<tr>
<th>UV irradiation in air</th>
<th>Gas species</th>
<th>( P(x=L,t=\infty) ) (Barrer)</th>
<th>( P(x=0,t=\infty) ) (Barrer)</th>
<th>( k_0 ) (min(^{-1}))</th>
<th>( L_0 ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membranes exposed directly in air</td>
<td>H(_2)</td>
<td>3195</td>
<td>6.76</td>
<td>0.450</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
<td>5622</td>
<td>2.27</td>
<td>0.354</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>O(_2)</td>
<td>1089</td>
<td>0.686</td>
<td>0.396</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>N(_2)</td>
<td>325</td>
<td>0.0774</td>
<td>0.396</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>CH(_4)</td>
<td>418</td>
<td>0.0772</td>
<td>0.410</td>
<td>105</td>
</tr>
<tr>
<td>Membranes sandwiched in quartz glass</td>
<td>H(_2)</td>
<td>3195</td>
<td>7.42</td>
<td>0.354</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
<td>5622</td>
<td>3.081</td>
<td>0.376</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>O(_2)</td>
<td>1089</td>
<td>0.621</td>
<td>0.350</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>N(_2)</td>
<td>325</td>
<td>0.073</td>
<td>0.400</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>CH(_4)</td>
<td>418</td>
<td>0.066</td>
<td>0.420</td>
<td>105</td>
</tr>
</tbody>
</table>

An encouraging result of this model is the step-like depth dependent permeability front that moves into the thin film over prolonged UV exposure time (Figure 5.18) over similar time and length scales to the observed skin-layer structures. The model also allows prediction of overall permeability and selectivity of other important gas pairs, as shown Figure 5.15. Though the model is too basic to describe the complex photo-oxidation process, e.g. the generation of oxidants and diffusion of ozone in the matrix, time-dependent effect of structural collapse, and more accurate definition of boundary conditions should be considered.

In the case of possible hydrogen bonding, a second order reaction kinetic equation may give better fitting of the gas transport properties (not shown here). However, the current model captures the essence of the observed structural changes at the surface. This explains why the model predicts a continuous densification of skin layer into the bulk of the sample whereas in fact this slows down experimentally as the framework above it collapses.
In this study, the key contribution to the observed enhanced material properties arise from the role of UV induced, internally generated oxidant, in producing a dense selective surface-skin to an high-permeability and porous material. The resulting asymmetric membrane geometry is analogous to thin film composite (TFC) membranes. Nevertheless, from a chemical reaction viewpoint, the kinetics of photo-oxidation in PIM-1 could be tuned, i.e. by controlling the intensity of UV irradiation, exposure time, and oxygen concentration \([O_2]\) within the polymer framework. These parameters determine the concentration of intermediate species of ozone \([O_3]\), singlet oxygen \([\cdot O]\) and radicals within the polymer matrix. To verify the effect of ozone, we performed control experiments by exposing membranes to constant flow of ozone. The ozone was produced by an ozone generator, concentration of 2500 ppmv in air, with total flow rate of 2 L min\(^{-1}\) (atmospheric pressure and temperature). Permeability and selectivity of PIM-1 membrane as a function of time of exposure to ozone were tracked, showing similar trend as the UV/ozone treated membranes, due to the surface densification. Of course, the ozone treatment and UV induced ozone would be different because of the diffusion effect, energy provided by UV light, and the presence of UV gradient. As a method of surface modification, it might be possible to scale down the asymmetric pore structure on thin film composite membranes, to achieve higher selectivity while maintaining high permeance. As a rapid and simple processing technique, this implied modification of PIM-1 can be applied to various geometries of separation unit (e.g. flat-sheet, spiral wound or hollow fiber configurations). However, understanding the materials science is more important at the moment prior to any further technical development.

Though the system has immediate application in dry gas atmosphere, the instability to condensable polar vapours and solvents may initially limit its use in some industrial gas
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processing systems. For example, the membranes recovered the high permeability and low selectivity of fresh PIM-1 membranes after the UV/ozone-modified membrane had been immersed in polar solvents. Actually, such a disadvantage in membrane separation field can become useful for applications in thin film technology. With a strong resonance to techniques used in photolithography, the UV-generated rapid structural phase change should also make the material amenable to wet- and dry-etch photoresist and pattern development techniques. As a simple demonstration, PIM-1 films were exposed to UV light through a rudimentary edge-mask. A relatively clean, but unoptimized, topographical step profile was obtained after wet-etching of the film with DMF (Figure 5.19).

![Figure 5.19: Photoresist development. Optical microscopy image and SEM image (inset) of PIM-1 polymer thin film exposed to UV irradiation and wet etching with polar solvent. The PIM-1 polymer film (initial thickness of 300 nm) was exposed to UV irradiation in air for 10 min with the right half of the film protected by an overlying cleaved silicon wafer used as a basic mask; followed with wet-etching in a polar solvent, dimethylformamide (DMF), the UV-exposed area was dissolved away in DMF as indicated by the interface shown in the inset SEM image.](image)

![Figure 5.20: Thermal analyses of pristine PIM-1 thin film and UV/ozone treated PIM-1 thin films. PIM-1 thin films with an initial thickness of 300 nm were exposed to UV irradiation in air for different time.](image)
The instability in accelerated solvent test confirms the surface degradation of the polymer chains after UV irradiation. The degraded oligomers would also be thermally evaporated as examined by thermal analysis in TGA (Figure 5.20). If we heat those UV-irradiated membranes at temperature of 300-400°C for 1 h under vacuum, the surface layer would evaporate and the membranes recover the high permeability and low selectivity close to that of pristine PIM-1 membrane. The lower solvent-resistance and thermal stability indeed limits the applicability and endurance of the material. However, this would suggest that if we only locally oxidize the polymer chains in the polymer matrix and introduce carbonyl and hydroxyl groups that can be used to induce crosslinking upon thermal treatment, for example, via decarboxylation-induced crosslinking [18], or thermal rearrangement [19].

A previous patent by the UOP company found that UV irradiation of PIM-1 polymer resulted in higher selectivity and compromised permeability and attributed this performance, without any scientific proof, to UV crosslinking of PIM-1 [20]. During the writing of a paper produced from our study, Chung and co-workers reported similar phenomenon of PIM-1 polymer membranes sandwiched between quartz plates and exposed to UV irradiation; they proposed a rearrangement mechanism at the spiro-centre[21], which clearly is wrong, and they did not find the critical role of oxygen. There are no significant differences in the measured gas permeability reported in such work and this paper. However, the attribution of the performance to cross-linking (in the UOP patent) or chain rearrangement by Chung and co-workers is clearly in error. Here we proposed a photo-oxidative surface modification mechanism based on the evidence of our physical and chemical characterizations. Specifically we observed the evident loss of PIM-1 molecular weight upon UV irradiation (in air or quartz-sandwiched samples), the limited UV transmission within the polymer and formation of surface densified layers. These observations deny the possibility of a bulk material transformation. In ruling out these other explanations, and by revealing the true physical transformation at work, we can describe a simple reaction controlled model of a surface limited densification of the material. The robustness of such a model is reinforced through its good predictions of apparent permeability in UV transformed PIM-1 over a wide range of industrially important gas pairs.

Most important of all, this study raises an interesting question on the chemical modification of PIMs polymers. Even very mild chemical reactions induce significant changes of physical properties of the polymer. This inspires us to modify the polymer by thermal oxidative crosslinking in Chapter 6.
5.5 Conclusion

In summary, photo-oxidation can be a simple and powerful method to enhance the gas-separation performance of high free volume polymeric molecular sieve membranes. These materials, and indeed other microporous materials, have an intrinsically greater potential for structural collapse than conventional dense polymers. The tight surface attenuation, due in part to the strong photo-absorbance in PIM-1, allows the generation of a sharp near-surface structural transformation within the first few hundred nanometers of the material in an eminently tuneable fashion. Such controlled surface modification should be available through other analogous chemistry and can be used beyond the discussed separation application, for example, in microfabrication and coating technologies.

5.6 References

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Chapter 6 Thermal oxidative crosslinking of polymer of intrinsic microporosity

6.1 Introduction

Thermal treatment is a commonly used method for processing of polymeric materials. However, thermal treatment at excessive high temperature could induce chemical reactions or degradation of the polymers depending on the thermal stability of functional groups and atmosphere. Degradation of polymers is defined as the deterioration of the properties, such as hardening, reduced ductility and brittleness, softening, cracking, colour changes, and reduction in other desirable physical properties. Thermal degradation of conventional polymers typically begins around 150-200°C. At higher temperature, the rate of degradation increases. Thermal degradation can be divided into three types: depolymerisation, random chain scission, and substituent reactions. The former two types of degradation usually involve the scission of backbone and change of molecular weight (and distribution). Significant degree of chemical reactions involved in thermal degradation at high temperature could lead to not only the deterioration of physical and chemical properties, but also transformation to carbon materials or complete combustion to gaseous products depending on the atmosphere.

On the other hand, controlled thermal treatment could also be useful for modifying the physical and chemical properties of polymer to achieve specific purpose. For example, thermal pre-oxidation of polyacrylonitrile (PAN) is an important step prior to carbonization in inert atmosphere to produce carbon fibers. As introduced in Chapter 2, the thermal treatment of polymers has been used for transforming conventional dense polyimides to microporous materials, known as thermally rearranged (TR) polymers.

In amorphous polymer matrix, the flexibility of polymer chains results in a broad size distribution of free volume elements that compromises their selectivity in separating molecules. For high-free-volume polymers such as PIMs, tailoring the structure of free volume elements is critical to enhancing the molecular sieving performance. In particular, for industrially and environmentally important gases, such as CO₂/CH₄ separation in natural gas industry, both of which have high solubility in glassy polymers, tailoring the distribution and sizes of free volume elements is crucial for substantial increase of diffusivity selectivity via molecular sieving function. In previous chapter, we have demonstrated that it is possible to selectively oxidize the polymer with oxidizing agents.

Here we demonstrate a simple thermal treatment method for the transformation of independent rigid polymer chains to covalently crosslinked polymer networks with
significantly enhanced molecular-sieving selectivity. From a microscopic point of view, the interconnected micropores in PIMs polymer matrix behave as a series of nano-reactors, which allow sorption and fast diffusion of oxygen molecules between the interconnected chambers (Figure 6.1E). Upon heating in the presence of oxygen at suitable temperature (350-450°C), oxidation and crosslinking of polymer chains occur following a free-radical degradation mechanism and in situ decarboxylation reaction. Thermodynamically, the O₂ molecules in motion migrate between interconnected microcavities through gates. Because there is a broad size distribution of channels, the O₂ molecules should migrate preferentially through the largest channels with the least resistance. Therefore, we hypothesize that crosslinking reactions occur at the largest gates. As visualized in Figure 6.1E and 1F, we expect that local oxidative crosslinking at the larger gates results in narrower (or closed) gates, which have better molecular-sieving function or shape-selectivity, while the overall free volume, statistically, is still sufficiently high allowing high solubility and fast diffusion of light gas molecules.

Figure 6.1: Schematic visualizations of polymer molecular sieve membranes. (A) An ideal molecular model of a PIM-1 polymer chain segment. (B) Three-dimensional view of an amorphous cell of PIM-1 polymer (four polymer segments inside, each containing 10 repeating units). Cell size: 31.8×31.8×31.8 Å, apparent bulk density of 1.050 g cm⁻³. The grey surface indicates the van der Waals surface, green surface is the Connolly surface with probe radius of 1.65 Å (kinetic radius of a CO₂ molecule). (C) Two-dimensional schematic illustration of transformation of independent PIM-1 polymer chains (black contorted lines) to (D) covalently crosslinked polymer network via thermal oxidation in the presence of trace amount of oxygen molecules. (E) Two-dimensional schematic illustration of the interconnected free volume elements in PIM-1 polymer membranes and (F) thermal oxidative crosslinked polymer membranes with narrower or closed gate (indicated by dashed circles) between interconnected cavities. White regions indicate the accessible free volume, grey regions indicates the inaccessible pore walls (polymer chains).
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6.2 Experimental

The molecular weight was determined from gel permeation chromatography (GPC), giving an average molecular weight of $M_n = 80,000$ dalton and a polydispersity (PDI) of 2.0. The membranes were exposed to thermal treatment in a high-temperature vacuum oven (Hereaus, 20-400°C) with controlled atmosphere. The vacuum oven was modified allowing operation in vacuum or purging mode. The pressure was monitored continuously by vacuum pressure transmitters (Keller Ltd, UK). It should be noted that this high temperature vacuum oven does not give ultra-high vacuum; however, the presence of trace amount of oxygen in the oven leads to thermal oxidative crosslinking of polymers. Under high temperature annealing, the polymer films experience complicated physical and chemical changes owing to heat transfer (conduction and convection), mass transfer (diffusion of oxygen and products in polymer matrix), and reactions (oxidative chain scission and crosslinking, and also probably decomposition). In order to have better understandings of the mechanism of thermal treatment of these microporous polymer membranes, we changed the protocols of thermal treatment using a reaction engineering approach by varying the parameters such as reaction temperature, atmosphere (concentration of oxygen), and reaction time.

A series of experiments were performed by heating the polymer at different temperature under continuous vacuum (1 mbar). Flat polymer films were placed on the plate in the vacuum oven and heated under vacuum at 120°C for 3 h, then heated to final temperature (300, 350, and 385°C) at 10°C min$^{-1}$. Then the samples were maintained at the temperature for extended time up to 24 h. In order to achieve suitable degree of crosslinking while maintaining reasonable mechanical strength, slow thermal oxidation for prolonged exposure time is necessary, which is operable compared to more delicate treatment of inorganic molecular sieves (zeolites, etc).

Another series of experiments were carried out by heating PIM-1 membranes in the vacuum oven at 385°C, with the vacuum pressure controlled at 1, 10, 20, 50, 100, 200 mbar, to confirm the critical role of oxygen in thermal oxidative crosslinking of the polymer.

In extreme cases, the polymer films were baked in air. In one series of experiment, the polymer films were heated from 120°C to 385°C at 10°C min$^{-1}$. Rapid change of colour from fluorescent yellow to brownish and partially black was observed when the temperature was above 350°C. During this heating stage, the polymer films were turned over frequently, manually with a tweezers. When the temperature reached to 385°C, the thermally oxidized brown polymer films were removed from the oven to avoid excessive degree of degradation (too brittle for gas permeation tests), and cooled down naturally to ambient temperature.
Alternatively, the oven was switched to vacuum mode. In the mean time, the power of the oven was turned off allowing the films to cool down to room temperature under vacuum. In another series of isothermal experiment, fresh membranes were moved from ambient condition to the preheated oven (385°C) and baked for 10 min, and removed from the oven immediately. The two methods gave similar degree of degradation of polymer, with weight loss up to ~2.5 wt%. Caution should be taken to control the extent of weight loss and avoid over degradation due to the fast reaction rate.

Alternatively, we controlled the atmosphere of heat treatment by purging different gases, including high purity argon (B.I.P. grade, O<sub>2</sub> <10 ppb, Air products), and O<sub>2</sub> balanced with argon (BOC), with nominal O<sub>2</sub> concentration at 10(9.2), 50(55), 100(104), 200(215) ppm, where the value in parentheses are the calibrated concentration. The flow rate was controlled by a metering valve and confirmed by a soap bubble flow meter. The polymer films were placed on the heating plate in the oven, and exposed to vacuum at 120°C under vacuum for 1 h, then purging gas was introduced to the oven to pressurize the oven close to 1000 mbar, then vacuum was switched on again to reduce the pressure to 1 mbar. After at least five cycles of vacuum-pressurization, the samples were exposed to continuous flow of purging gas.

Thermal analyses of polymer films were also performed in a thermogravimetric analyser (TGA) Q500 and Q600 (simultaneous TGA-DSC) to study the thermal stability and simulate the thermal oxidative crosslinking reaction with well-controlled atmosphere. The gas species evolved from the TGA was analyzed by a FTIR. The gas atmosphere includes Argon (Air products), Air (zero grade, air products), and O<sub>2</sub>/Argon mixture (200 ppm O<sub>2</sub>, balance argon, BOC).

In one series of experiments, polymer films were dynamically heated from room temperature to 1000°C at 10°C min<sup>-1</sup> in inert atmosphere or in air.

Another series of experiments were carried out using O<sub>2</sub>/Argon mixture (200 ppm O<sub>2</sub>, balance argon, BOC) to simulate slow thermal degradation. A batch of dense polymer films (~5 mg, dimension of 3x3 mm) were heated at 120°C for 1 h under continuous flow of purging gas to remove moisture or residual solvents, then heated at 10°C min<sup>-1</sup> to set-point temperature (300-450°C), then kept at the set-point temperature for 2 h. The films recovered from the TGA were further analyzed with FTIR-ATR to confirm the presence and intensity of oxidized groups (particularly the carbonyl and hydroxyl groups).
6.3 Results

6.3.1 Thermal analyses of PIM-1 polymer membranes

A critical issue for the thermal transformation of PIM-1 polymer is that the chemical reactions could be divided into three categories depending on the atmosphere: oxidative degradation, decomposition, and controlled oxidation, as clearly showed in Figure 6.2A. PIM-1 polymer is thermally stable in inert atmosphere, with evident decomposition occurring at temperature above 450°C in pure argon (Figure 6.2A). In situ FTIR spectra of gaseous products evolved during pyrolysis in TGA (Figure 6.2C) indicates that the scission of ether linkages in the backbone is the major step of decomposition since only dioxane linkages are the oxygen-containing groups, followed by decarboxylation reaction generating, primarily, CO₂ as gaseous product (2260 cm⁻¹). At higher temperature, the resulting fragments undergo further chemical reactions including crosslinking, cyclization, and finally become carbonaceous materials. In contrast, thermal oxidative degradation of polymer is accelerated by increasing the O₂ concentration, with evident oxidation starting at 350°C in air and generating CO₂ as major gaseous product (Figure 6.2B). Such oxidative degradation is confirmed by baking the polymer membranes to high temperature in air at atmospheric pressure. Alternatively, exposing the membranes in air in the temperature range of 300-450°C for prolonged period could result different degree of degradation (Figure 6.2D-F). While the high degree of degradation is not favoured for the application of membranes, these accelerated experiments confirm the mechanism of oxidative degradation in the presence of oxygen. These thermal analyse also confirm that the oxidation reactions could occur through the film rather than surface oxidation, owing to the high permeability of oxygen in the matrix.

We confirmed the critical role of oxygen in thermal oxidative crosslinking of the polymer membranes. The rate of thermal oxidation of PIM-1 polymer could be significantly slowed down in inert purging gas with low concentration of O₂ (Figure 6.2A and Figure 6.3A). For example, the polymer heated in argon containing 200 ppm O₂ at 450°C underwent pyrolysis (Figure 6.3A), rather than complete degradation in air (Figure 6.2D). As the reaction temperature increase, the films after thermal degradation changed from fluorescent yellow to dark brown and black (Figure 6.3C). FTIR spectra of the polymer films after isothermal TG experiments correspond to the degree of degradation of the polymer. Similarly, the thermal oxidative degradation could also occur for ZIFs nanocrystals and PIM-based composite membranes (Figure 6.4). These accelerated experiments clearly demonstrate that we are able to control the extent of oxidation and crosslinking, and stop the reaction at the suitable point rather than significant degradation or carbonization.
Figure 6.2: Thermogravimetric analyses of PIM-1 polymer membranes. (A) Thermogravimetric analysis of PIM-1 polymer membranes in argon (black), 200 ppm O$_2$ in argon (blue), and air (red). Samples were heated to 1000°C at 10°C min$^{-1}$, and corresponding in situ FTIR spectra of evolved gaseous products under purging gas of air (B) and argon (C). (D) Isothermal degradation over 300-450°C. (E) Isothermal degradation at 385°C and (F) In situ FTIR spectra of evolved gaseous products. For dynamic thermal analysis (A-C), the polymer films were heated from room temperature to 1000°C at 10°C min$^{-1}$. For isothermal analysis (D-F), the polymer films were heated from room temperature to set-point temperature at 10°C min$^{-1}$, and then maintained for 120 min. The major peaks in FTIR spectra (B-F) at 2260 cm$^{-1}$ corresponds to the absorption of CO$_2$ as primary gaseous product during thermal processing.
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Figure 6.3: Thermal analysis of dense PIM-1 polymer films. (A) Isothermal TGA analyses of PIM-1 membranes over 300-450°C (see Appendix D). (B) FTIR-ATR spectra of after isothermal TGA analyses. (C) Photographs of resulting polymer films with temperature marked above. Note: the sample at 385°C was still transparent. The samples were stabilized at 120°C for 1 h under 200 ppm O₂ in argon, then heat up to 385°C at 10°C min⁻¹, then maintained at 385°C for 120 min.

Figure 6.4: Thermal oxidative degradation of polymer nanocomposite membranes. (A) PIM-1/ZIF-8 nanocomposite membranes, (B) PIM-1/SiO₂ nanocomposite membranes. The samples were stabilized at 120°C for 1 h under 200 ppm O₂ in argon, then heat up to 385°C at 10°C min⁻¹, then maintained at 385°C for 60 min.

From the perspective of chemical reaction engineering, the thermal crosslinking or degradation of PIM-1 polymer could be subject to a variety of parameters, such as external mass transfer, chemical reaction, and internal diffusion. In this study, the reaction rate was not limited by external mass transfer given sufficient gas flow rate. Owing to the high O₂ permeability (~1000 Barrer) and particularly high diffusion coefficient of oxygen, internal diffusion is not limiting the reactions as proved by samples with different thickness. Over the reaction temperature range (<450°C), thermal decomposition could be assumed as not so significant compared to oxidation. Therefore, the thermal degradation of PIM-1 polymer film
is likely to be kinetically controlled by chemical reactions of polymer with oxygen, and can be described as the following equation:

\[
\frac{dw}{dt} = r = k_0 \exp(-\frac{E_a}{RT})(C_{O_2,b} - C_{O_2,e})^n
\]  

where \( \frac{dw}{dt} \) and \( r \) is the rate of reaction, \( k_0 \) is the coefficient of rate constant, \( E_a \) is the apparent activation energy, \( R \) is gas constant, \( T \) is temperature, \( C_{O_2,e} \) is the equilibrium concentration of \( O_2 \) in the polymer matrix, \( C_{O_2,b} \) is the bulk concentration. Therefore, the degree of oxidation and crosslinking of polymer could be tuned by controlling the parameters, such as the temperature, oxygen concentration, and time.

The equilibrium oxygen concentration is subject to chemisorption at the reaction temperature and unknown in this study:

\[
C_{O_2,e} = k_b P_{O_2} + \frac{c_{b,P_{O_2}}^b}{1 + bP_{O_2}}
\]

Assuming the difference between the equilibrium and the bulk concentration as constant, the apparent activation energy \( (E_a) \) could be derived as shown in Figure 6.5. The activation energy of polymer degradation in air and 200 ppm O\(_2\) is 73±2 and 122±10 kJ mol\(^{-1}\), respectively. Alternatively, the TGA was operated in modulated mode and the activation energy derived from high-resolution dynamic heating protocol gave similar values of activation energy. Currently, it is still not clear how to correlate this activation energy with the bond dissociation energy, e.g. hydrogen abstraction from the polymer chain.

**Figure 6.5: Arrhenius plot of rates of polymer degradation.** Squares: 200 ppm O\(_2\)/Argon, Circles: 20.9 % O\(_2\)/N\(_2\). The reactions rates were derived from linear fitting of the isothermal weight loss stage in Figure 6.2D and Figure 6.3A.

### 6.3.2 Solubility and molecular weight evolution

For dense PIM-1 membranes or thin films, after thermal treatment at 385°C for 24 h under vacuum, the transparent membranes changed from fluorescent yellow to dark brown as
visually observed (Figure 6.6) while remaining transparent. The thermally crosslinked PIM-1 (termed as TXL-PIM-1 hereafter) polymer membranes became largely insoluble (gel content >95%) in solvents that readily dissolve the PIM-1 polymer, such as chloroform, tetrahydrofuran, or dichloromethane. These thermally treated membranes showed slight solubility in polar solvents releasing oxidized fragments.


Table 6.1 Gel fractions of crosslinked PIM-1 membranes in common solvents.

<table>
<thead>
<tr>
<th>No</th>
<th>Solvents</th>
<th>Density</th>
<th>Gel fraction (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chloroform</td>
<td>1.498</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Chloroform</td>
<td>1.498</td>
<td>94.1</td>
</tr>
<tr>
<td>3</td>
<td>Tetrahydrofuran (THF)</td>
<td>0.886</td>
<td>92.6</td>
</tr>
<tr>
<td>4</td>
<td>Dichloromethane (DCM)</td>
<td>1.3266</td>
<td>95.1</td>
</tr>
<tr>
<td>5</td>
<td>Chlorobenzene</td>
<td>1.1066</td>
<td>98.9</td>
</tr>
<tr>
<td>6</td>
<td>1,2 Dichlorobenzene</td>
<td>1.306</td>
<td>99.4</td>
</tr>
<tr>
<td>7</td>
<td>N-Methyl-2-pyrrolidone (NMP)</td>
<td>1.030</td>
<td>96.9</td>
</tr>
<tr>
<td>8</td>
<td>Dimethylformamide (DMF)</td>
<td>0.944</td>
<td>97.6</td>
</tr>
<tr>
<td>9</td>
<td>1,4 Dioxane</td>
<td>1.033</td>
<td>98.8</td>
</tr>
<tr>
<td>10</td>
<td>Acetone</td>
<td>0.786</td>
<td>99.0</td>
</tr>
<tr>
<td>11</td>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>1.092</td>
<td>99.0</td>
</tr>
<tr>
<td>12</td>
<td>Toluene</td>
<td>0.867</td>
<td>100</td>
</tr>
<tr>
<td>13</td>
<td>Hexane</td>
<td>0.655</td>
<td>100</td>
</tr>
<tr>
<td>14</td>
<td>Cyclohexane</td>
<td>0.779</td>
<td>100</td>
</tr>
<tr>
<td>15</td>
<td>Acetic acid</td>
<td>1.049</td>
<td>100</td>
</tr>
<tr>
<td>16</td>
<td>Isopropanol</td>
<td>0.785</td>
<td>100</td>
</tr>
<tr>
<td>17</td>
<td>Ethanol</td>
<td>0.789</td>
<td>100</td>
</tr>
<tr>
<td>18</td>
<td>Methanol</td>
<td>0.791</td>
<td>100</td>
</tr>
<tr>
<td>19</td>
<td>HCl in water</td>
<td>~1.0</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>NaOH in water</td>
<td>~1.0</td>
<td>100</td>
</tr>
</tbody>
</table>

For those membranes cured at 385°C for up to 24 h under vacuum, the weight as measured before and after heat treatment showed a loss up to 2-3 wt%. Compared to those delicately controlled experiments operated in TGA (Figure 6.3A), these values were interfered by the gas and moisture. Yet, the extent of degradation and corresponding weight loss do agree well with the accelerated experiments in TGA. The skeleton density of
crosslinked membranes slightly increased from 1.335±0.006 g cm⁻³ to 1.365±0.007 g cm⁻³ according to measurement by helium pycnometer. Also there is no substantial change in apparent bulk density (1.060-1.100 g cm⁻³).

We further tuned the degree of thermal crosslinking of PIM-1 polymer by controlling the chemical reaction kinetics, via changing the O₂ concentration, temperature, and reaction time. The evolution of molecular weight distribution indicates the oxidative chain scission occurred under these thermal treatment conditions, while the gel content increased simultaneously indicating that in situ covalent crosslinking occurred. The FTIR spectra of thermally treated polymer films under low vacuum confirmed the presence of carbonyl groups and hydroxyl groups (Figure 6.8), particularly for samples treated at intermediate temperature (300-350°C), a clear evidence of oxidation. To summarize, these characterization analyses suggest a thermal degradation mechanism following pathways of free-radical induced oxidative chain scission, and in situ covalent crosslinking upon combination of adjacent radical sites via the decarboxylation reactions.

![Figure 6.7](image)

**Figure 6.7:** Molecular weight distribution and gel content. (A-B) Effect of temperature and (C-D) effect of reaction time. (A) and (C) Molecular weight distributions of soluble fractions of polymer membranes after exposure to thermal treatment. (B) and (D) Gel content analysis and peak molecular weight of soluble fractions of PIM-1 polymer membranes. The polymer membranes were heated at 385°C under continuous vacuum (1 mbar) up to 24 h.
Figure 6.8: Ex situ FTIR spectra of polymer membranes. (A) thermally treated PIM-1 membranes. (B) thermally treated PIM-1/ZIF-8 nanocomposite membranes. All samples were annealed under vacuum for 24 h, except that the samples at 300°C were annealed for 48 h.

6.3.3 Optical properties

Thin films were prepared by spin-coating of diluted PIM-1 polymer solution in chloroform (0.8 wt%) on thin quartz glass substrate, at speed of 2000 rpm with an acceleration speed of 1500 rpm. The thermal treatment was performed in the high-temperature vacuum oven, the same batch as the thermal treatment of dense polymer
membranes. Though the mechanism of fluorescence remains to be studied in detail, the loss of photoluminescence as shown in Figure 6.9 clearly indicates the degradation of polymer.

Figure 6.9: Optical properties. UV-vis absorption (A) and photoluminescence (B) spectra of PIM-1 thin films thermally treated at different conditions.

6.3.4 Morphology of polymer membranes

Cross-sectional SEM images (Figure 6.10) show that TXL-PIM-1 films are dense without defects, and crosslinking is also effective for nanocomposite membranes, either with porous fillers (e.g. ZIF-8) or nonporous inorganic nanoparticles (e.g. silica). The poor interface observed in the unmodified nanocomposites could be improved after thermal treatment.

Figure 6.10: Cross-sectional SEM images. (A-B) pure PIM-1, and (C) TXL-PIM-1. (D-E) PIM-1/ZIF-8 nanocomposite membranes, and (F) TXL-PIM-1/ZIF-8. (G-H) PIM-1/SiO₂ nanocomposite membranes, and (I) TXL-PIM-1/SiO₂. (C), (F), and (I) were thermally oxidative crosslinked at 385°C for 24 h under vacuum (1 mbar).
The crosslinking is also effective for thin films coated on different substrates, including glass or silicon wafer (Figure 6.11). The thin films after crosslinking became insoluble in chloroform. These characterization analyses indicate that it is feasible to fabricate thermally crosslinked polymer thin films, for example, by coating the polymer on porous thermally stable inorganic membrane substrates forming thin film composite (TFC) membranes. The fabrication of TFC membranes, which we believe would become an engineering issue, so was not covered in this study.

Figure 6.11: Cross-sectional SEM images of fresh and thermally crosslinked PIM-1 thin films. (A) Fresh as casted PIM-1 film. (B) Thermally oxidative crosslinked at 385°C for 24 h under continuous purging gas of 10 ppm O2 in argon, and (C) soaked in chloroform for 24 h. (D) Thermally oxidative crosslinked PIM-1 thin film at 385°C for 24 h under continuous purging gas of 100 ppm O2 in argon, (E) further soaked in chloroform for 24 h, and (F) surface. Thermal oxidative crosslinked PIM-1 thin films (G-I) at 385°C for 24 h under vacuum of 1 mbar, and soaked in chloroform for 24 h. Polymer thin films were formed by spin-coating diluted solution on (A-G) glass substrate and (H-I) silicon wafer. Scale bar in all panels: 200 nm. (A-F) Films were spin-coated with 2wt% polymer solution in chloroform at 2000 rpm with an acceleration speed of 1500 rpm, giving an initial thickness of ~250 nm. (G-I) Films were spin-coated with 0.8 wt% polymer solution in chloroform at 2000 rpm with an acceleration speed of 1500 rpm, giving an initial thickness of ~100 nm.

6.3.5 Thermal stability

Thermogravimetric analysis indicated that the TXL-PIM-1 remain stable up to ~450°C in an inert argon atmosphere (Figure 6.12). The heat flow measured by differential scanning calorimetry (DSC) reflects the difference in the amount of heat required to increase
the temperature of a sample and reference are measured as a function of temperature. Here, we observed the weak endothermic peaks at temperature of 500°C, which is likely due to the rapid endothermic decomposition of polymer. These peaks correspond to the maximum rate of decomposition of polymer. There is no obvious glass transition in these DSC curves. For the glassy PIM-1 polymer with rigid and contorted macromolecular structure consisting of aromatic rings, the glass transition temperature is not meaningful because the polymer decomposes to carbon at such high temperature rather than transit to liquid state. Instead, the initial degradation temperature became a critical parameter to evaluate the thermal stability.

![TGA/DSC analysis](image)

**Figure 6.12: Thermal stability.** TGA/DSC analyses of fresh PIM-1 and thermally crosslinked (TXL) PIM-1 polymer membranes in argon, at a heating rate of 10°C/min. The thermally crosslinked membrane was annealed at 385°C for 24 h under vacuum of 1 mbar.

### 6.3.6 Mechanical properties

The thermally crosslinked polymer membranes in low concentration of oxygen, either under vacuum or purging gas, were still mechanically flexible. A typical plot of stress-strain curve (Figure 6.13) shows that TXL-PIM-1 polymer networks become stiff but are still mechanically robust in terms of tensile strength (50-60 MPa), elongation strain at break (in the range of 4-8 %), and Young’s modulus (1.2 to 1.7 Gpa). The TXL-PIM-1 membranes have the mechanical properties comparable to TR polymers initially reported by Park et al [1], but certainly are far more flexible than carbon molecular sieve membranes (Table 6.2). The carbon membranes prepared from PIM-1 polymer at temperature higher than 450°C also became very brittle because the polymer backbone has been excessively broken. In contrast, for the thermally crosslinked PIM-1 polymer, we expect that thermal oxidative chain scission
Chapter 6  

Thermal oxidative crosslinking of polymers of intrinsic microporosity  

and crosslinking occur locally at the gates of micropores while the most part of the polymer chains maintained intact. For those nanocomposite membranes, the mechanical properties deteriorate with the loading of fillers increase.

![Figure 6.13: Stress-strain curves of PIM-1 and thermally crosslinked PIM-1 membranes.](image)

**Table 6.2 Mechanical properties.** The data were derived from stress-strain curves of PIM-1, thermally crosslinked PIM-1 films, and some representative membranes in the literature.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile strength at break (MPa)</th>
<th>Elongation Strain at break (%)</th>
<th>Young’s modulus (GPa)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1</td>
<td>47.5±2.3</td>
<td>14.3</td>
<td>1.43±0.15</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1 385°C 1 mbar 8h</td>
<td>56.5±2.8</td>
<td>7.1</td>
<td>1.28±0.37</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1 385°C 1 mbar 12h</td>
<td>60.0±3.0</td>
<td>5.8</td>
<td>1.45±0.05</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1 385°C 1 mbar 24h</td>
<td>54.8±2.7</td>
<td>4.4</td>
<td>1.72±0.05</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1 385°C 10 mbar 1h</td>
<td>36.4±1.8</td>
<td>2.3</td>
<td>1.80±0.02</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1 385°C air 10 min</td>
<td>14.0±0.7</td>
<td>0.7</td>
<td>1.96±0.03</td>
<td>This work</td>
</tr>
<tr>
<td>Crosslinked nanocomposite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIM-1/SiO$_2$ 1 wt% 385°C 1 mbar 24 h</td>
<td>38</td>
<td>2.4</td>
<td>1.90</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1/SiO$_2$ 2 wt% 385°C 1 mbar 24 h</td>
<td>35</td>
<td>2.3</td>
<td>1.60</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1/SiO$_2$ 5 wt% 385°C 1 mbar 24 h</td>
<td>21</td>
<td>1.4</td>
<td>1.55</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1/SiO$_2$ 10wt% 385°C 1 mbar 24 h</td>
<td>15</td>
<td>1.0</td>
<td>1.50</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1/ZIF-8 5 wt% 385°C 1 mbar 24 h</td>
<td>23</td>
<td>1.6</td>
<td>1.51</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1/ZIF-8 10 wt% 385°C 1 mbar 24 h</td>
<td>19</td>
<td>1.4</td>
<td>1.39</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1/ZIF-8 20 wt% 385°C 1 mbar 24 h</td>
<td>16</td>
<td>1.3</td>
<td>1.33</td>
<td>This work</td>
</tr>
<tr>
<td>Literature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIM-1</td>
<td>47.8</td>
<td>10.0</td>
<td>n.a.</td>
<td>[2]</td>
</tr>
<tr>
<td>PIM-EA-TB</td>
<td>-</td>
<td>-</td>
<td>0.80</td>
<td>[3]</td>
</tr>
<tr>
<td>spiroTR-PBO-6F</td>
<td>82.3±1.3</td>
<td>20.0±4.0</td>
<td>n.a.</td>
<td>[4]</td>
</tr>
<tr>
<td>spiroTR-PBO-PM</td>
<td>79.2±3.5</td>
<td>17.3±3.6</td>
<td>n.a.</td>
<td>[4]</td>
</tr>
<tr>
<td>spiroTR-PBO-BP</td>
<td>94.4±1.4</td>
<td>14.9±0.5</td>
<td>n.a.</td>
<td>[4]</td>
</tr>
<tr>
<td>spiroTR-PBO-BPA</td>
<td>69.9±4.4</td>
<td>19.7±0.2</td>
<td>n.a.</td>
<td>[4]</td>
</tr>
<tr>
<td>TR-PI-350</td>
<td>87</td>
<td>3.8</td>
<td>n.a.</td>
<td>[1]</td>
</tr>
<tr>
<td>TR-PI-400</td>
<td>95</td>
<td>3.5</td>
<td>n.a.</td>
<td>[1]</td>
</tr>
<tr>
<td>TR-PI-450</td>
<td>98</td>
<td>3.9</td>
<td>n.a.</td>
<td>[1]</td>
</tr>
<tr>
<td>CMS-Kapaton 600°C</td>
<td>42</td>
<td>0.4</td>
<td>n.a.</td>
<td>[1]</td>
</tr>
<tr>
<td>CMS-Kapaton 800°C</td>
<td>52</td>
<td>0.3</td>
<td>n.a.</td>
<td>[1]</td>
</tr>
<tr>
<td>CMS-PiOFG-1 600°C</td>
<td>34</td>
<td>0.6</td>
<td>n.a.</td>
<td>[1]</td>
</tr>
</tbody>
</table>

Nanoindentation measurements were performed on the surface of dense polymer membranes. Compared to the data obtained with thin film in previous chapter where
indentation of thin films was affected by the silicon wafer substrate, thick membranes gave more reasonable intrinsic values of mechanical properties. The Young’s modulus maintained at 1.9 GPa while the hardness increased from 150 to 190 MPa, corresponding to the formation of crosslinked polymer network.

![Nanoindentation](image)

**Figure 6.14: Nanoindentation profiles.** (A) Load-displacement curves of PIM-1 (black) and thermally crosslinked dense TXL-PIM-1 (red) membranes (~50 µm). (B) Hardness as a function of displacement (indentation depth).

**Table 6.3** Young’s modulus and Hardness derived from nanoindentation measurement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus $E$ (GPa)</th>
<th>Hardness $H$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1 120°C 24 h</td>
<td>1.876±0.029</td>
<td>149±4.0</td>
</tr>
<tr>
<td>TXL-PIM-1 385°C 24h</td>
<td>1.885±0.039</td>
<td>188±3.0</td>
</tr>
<tr>
<td>PIM-1/ZIF-8 20wt% 120°C 24 h</td>
<td>1.954±0.075</td>
<td>159±13.0</td>
</tr>
<tr>
<td>TXL-PIM-1/ZIF-8 20wt% 385°C 24h</td>
<td>1.732±0.027</td>
<td>158±4.0</td>
</tr>
</tbody>
</table>

6.3.7 Gas sorption properties

The porosity or free volume elements in the crosslinked PIM-1 network were probed with gas sorption measurements. Low temperature gas sorption/desorption is a widely used method to probe the pore structure of microporous materials. However it is not effective for PIMs polymer membranes. For PIM-1 thin films or open ZIF-8 framework, the sorption of nitrogen molecules was not limited by diffusion. Therefore, high adsorption occurred at low pressure, as shown in **Figure 6.15A**. The pore size distribution derived from NLDFT model indicates a bimodal shape. In contrast, the N$_2$ adsorption in thick polymer membranes or
thermally crosslinked membranes at 77 K showed an unexpected gate-opening effect, as presented in Figure 6.15C, which is related to the kinetic-limited diffusion of N\textsubscript{2} molecules through the dynamically open-and-shut gates connecting free volume elements. Crosslinked nanocomposite membranes also show similar kinetic-controlled sorption (Figure 6.15D).

These adsorption isotherms indicate that the nitrogen molecules are probably too big to probe the structure of free volume elements and channels which are at molecular dimensions.

Figure 6.15: N\textsubscript{2} adsorption-desorption isotherms at 77 K. (A) N\textsubscript{2} adsorption-desorption isotherms of PIM-1 polymer thin film and ZIF-8 nanoparticles at 77 K. (B) Pore size distribution derived from the non-local density functional theory (NLDFT) method. Both samples were degassed at 120°C under high vacuum prior to gas sorption measurements. (C) N\textsubscript{2} sorption of PIM-1 thin film and dense membranes at 77 K. Squares: PIM-1 thin film (300 nm) dried at 120°C under vacuum; Blue circles: Dense PIM-1 membranes annealed at 120°C under vacuum; Uptriangles: Dense PIM-1 membranes annealed at 300°C for 48 h under vacuum; Red circles: Thermally crosslinked PIM-1 membrane at 385°C for 24 h under vacuum (1 mbar). (D) PIM-1/ZIF-8 nanocomposite membranes. Squares: annealed at 120°C for 24 h; Uptriangles: annealed at 300°C for 48 h under vacuum; Circles: thermally crosslinked at 385°C for 24 h under vacuum. The loading of ZIF-8 nanocrystals was 20 wt%.

Gas sorption isotherms were also measured with CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} at 273 K and 295 K, as shown in Figure 6.16. In particular, the sorption of CO\textsubscript{2} at 273 K has been widely used to probe the porosity in microporous materials. Here, the TXL-PIM-1 polymer showed slightly lower CO\textsubscript{2} sorption as compared to PIM-1. However, the hysteresis phenomenon observed during CO\textsubscript{2} desorption indicate that the CO\textsubscript{2} molecules may induce structural
transformation or swelling of the polymer matrix. High-pressure gas sorption isotherms of TXL-PIM-1 show comparable high solubility to unmodified PIM-1 at room temperature (295 K), following the dual mode sorption mechanism without observable plasticization at high pressure (Figure 6.16B). The pore size distribution derived from the CO$_2$ sorption isotherms indicate the loss of porosity mainly occur in the size range smaller than 6 Å (in which gas probing becomes less reliable), which is in agreement with our hypothesis that thermal oxidative crosslinking occur at the gates and channels connecting free volume elements.

Figure 6.16: Gas sorption properties. (A) Gas sorption of unmodified PIM-1 and TXL-PIM-1 membranes, measured at 273 K. (B) High-pressure gas sorption of unmodified PIM-1 and thermally crosslinked TXL-PIM-1 membranes, measured at room temperature of 295 K. (C) CO$_2$ sorption of dense PIM-1 and PIM-1/ZIF-8 nanocomposite membranes, measured at 273 K. The samples were annealed at 300°C for 48 h under vacuum (1 mbar). (D) Gas sorption of PIM-1/ZIF-8 and thermally...
crosslinked TXL-PIM-1/ZIF-8 membranes, measured at 273 K. The crosslinked membrane was annealed at 385°C for 24 h under vacuum (1 mbar). (E-F) Pore size distribution derived from CO2 sorption isotherm at 273 K based on non-local density functional theory (NLDFT) method.

### 6.3.8 Gas transport properties

Single-gas permeations through polymer membranes were performed at 22°C with industrially-important gas molecules with different kinetic diameters, including H2 (2.89 Å), CO2 (3.3 Å), O2 (3.46 Å), N2 (3.64 Å), and CH4 (3.8 Å). As shown in Table 6.4 and Figure 6.17, the gas permeability of unmodified PIM-1 follows the sequence of CO2>H2>O2>CH4>N2, owing to the combined effects of preferable sorption (e.g condensable CO2 and CH4) and diffusion (gas molecules with smaller sizes). After slow thermal crosslinking at 385°C, the membrane showed significantly lower gas permeability for large molecules (N2 and CH4) by two magnitudes, while small gas molecules (H2, CO2, O2) maintained considerably high permeability, giving a more evident molecular sieving function. For TXL-PIM-1, the O2/N2 selectivity increased up to 8.1 with a high O2 permeability of 250 Barrer. The CO2/CH4 selectivity is as high as 70 with a CO2 permeability of 1100 Barrer. We derived the solubility and diffusion coefficient and confirmed that the significant increase of gas pair selectivity is attributed to the increase in diffusivity selectivity (DA/DB) while the solubility selectivity (SA/SB) is quite constant, in agreement with the expected structural modification of the gateways between the interconnected free volume elements.

#### Table 6.4 Gas permeability, solubility, and diffusion coefficient for PIM-1 and a representative thermally crosslinked TXL-PIM-1 membranes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pure gas</th>
<th>Gas pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H2</td>
<td>CO2</td>
</tr>
<tr>
<td>Critical temperature Tc (K)</td>
<td>33.2</td>
<td>304.2</td>
</tr>
<tr>
<td>Kinetic diameter (Å)</td>
<td>2.89</td>
<td>3.30</td>
</tr>
<tr>
<td>Effective diameter (Å)</td>
<td>2.14</td>
<td>3.02</td>
</tr>
<tr>
<td>DK (10^-5 cm² s⁻¹)</td>
<td>11.78</td>
<td>2.51</td>
</tr>
<tr>
<td>P (Barrer)</td>
<td>34088</td>
<td>5135</td>
</tr>
<tr>
<td>S [cm³ (STP) cm⁻³ bar⁻¹]</td>
<td>0.452</td>
<td>34.60</td>
</tr>
<tr>
<td>D (10⁻⁸ cm² s⁻¹)</td>
<td>4647</td>
<td>117</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pure gas</th>
<th>Gas pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TXL-PIM-1</td>
<td></td>
</tr>
<tr>
<td>Critical temperature Tc (K)</td>
<td>385</td>
<td>190.9</td>
</tr>
<tr>
<td>Kinetic diameter (Å)</td>
<td>2.89</td>
<td>3.8</td>
</tr>
<tr>
<td>Effective diameter (Å)</td>
<td>2.14</td>
<td>3.02</td>
</tr>
<tr>
<td>DK (10^-5 cm² s⁻¹)</td>
<td>11.78</td>
<td>2.51</td>
</tr>
<tr>
<td>P (Barrer)</td>
<td>34088</td>
<td>4647</td>
</tr>
<tr>
<td>S [cm³ (STP) cm⁻³ bar⁻¹]</td>
<td>0.452</td>
<td>4647</td>
</tr>
<tr>
<td>D (10⁻⁸ cm² s⁻¹)</td>
<td>3317</td>
<td>24.9</td>
</tr>
</tbody>
</table>

*reference [5].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pure gas</th>
<th>Gas pairs</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>TXL-PIM-1</td>
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</tr>
<tr>
<td>Critical temperature Tc (K)</td>
<td>385</td>
<td>190.9</td>
</tr>
<tr>
<td>Kinetic diameter (Å)</td>
<td>2.89</td>
<td>3.8</td>
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<tr>
<td>Effective diameter (Å)</td>
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<td>3.02</td>
</tr>
<tr>
<td>DK (10^-5 cm² s⁻¹)</td>
<td>11.78</td>
<td>2.51</td>
</tr>
<tr>
<td>P (Barrer)</td>
<td>34088</td>
<td>4647</td>
</tr>
<tr>
<td>S [cm³ (STP) cm⁻³ bar⁻¹]</td>
<td>0.452</td>
<td>4647</td>
</tr>
<tr>
<td>D (10⁻⁸ cm² s⁻¹)</td>
<td>3317</td>
<td>24.9</td>
</tr>
</tbody>
</table>

Knudsen diffusion coefficient, calculated from equation: $D = d_p^2RT/6M$, where $d_p$ is the pore diameter (m, here we assume the pore diameter as 2 nm), $R$ is the gas constant (J mol⁻¹ K⁻¹), $T$ is the temperature (K), $M$ is the molecular weight of gas molecules (g mol⁻¹).

gas solubility measured at 1 bar at 22°C
$d$ calculated from $D=P/S$, as the gas permeability is quite constant at low permeation pressure.

Figure 6.17: Permeability ($P$), solubility ($S$) and diffusion coefficients ($D$) for PIM-1 and a representative thermally crosslinked TXL-PIM-1 membranes. (A) Permeability versus kinetic diameter of gas molecules. (B) Solubility (1 bar, 295 K) as a function of critical temperature ($T_c$) of gas molecules. (C) Diffusion coefficients as a function of square of effective molecular diameter ($d_{\text{eff}}$) of gas molecules. Lines are added to guide eyes. The TXL-PIM-1 membrane was cured at 385°C for 24 h under vacuum (1 mbar).

From the viewpoint of chemical reaction engineering, we could tailor the degree of crosslinking and gas transport properties via controlling temperature, reaction time, and O$_2$ concentration in purging gas or vacuum pressure, consequently we are able to tune the gas transport properties. The detailed data are given in Figures 6.18, 6.19, and 6.20, and Tables 6.5 and 6.6.

To demonstrate the critical effect of oxygen in tuning the structure of free volume elements, we baked the polymer at 385°C in air. The selectivity was enhanced up to 70, while the CO$_2$ permeability maintained as high as ~500 Barrer, though the membrane became brittle due to the extensive oxidative chain scission.

Figure 6.18: Gas transport properties of thermally treated PIM-1 membranes at varied curing temperature under vacuum. All samples were thermally treated at set-point temperature for 24 h under vacuum of 1 mbar, except that the sample at 400°C was annealed for 12 h.
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Table 6.5 Gas transport properties of thermally crosslinked PIM (TXL-PIM) membranes. $1 \text{ Barrer} = 10^{-10}$ cm$^3$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
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<tbody>
<tr>
<td></td>
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<td>CO$_2$</td>
</tr>
<tr>
<td>PIM-1</td>
<td>3408</td>
<td>5135</td>
</tr>
<tr>
<td>TXL-PIM-1 385°C 1 h</td>
<td>2979</td>
<td>5101</td>
</tr>
<tr>
<td>TXL-PIM-1 385°C 2 h</td>
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<td>4532</td>
</tr>
<tr>
<td>TXL-PIM-1 385°C 4 h</td>
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<td>3876</td>
</tr>
<tr>
<td>TXL-PIM-1 385°C 8 h</td>
<td>2328</td>
<td>1956</td>
</tr>
<tr>
<td>TXL-PIM-1 385°C 12 h</td>
<td>2204</td>
<td>1680</td>
</tr>
<tr>
<td>TXL-PIM-1 385°C 24 h</td>
<td>1820</td>
<td>1100</td>
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</tbody>
</table>

Figure 6.19: Gas transport properties as a function of thermal crosslinking time. The membranes were thermally treated at 385°C under vacuum.

Table 6.6 Sensitivity of gas transport properties of thermally crosslinked PIM-1 polymer membranes to oxygen concentration during thermal treatment. $1 \text{ Barrer} = 10^{-10}$ cm$^3$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$.  

<table>
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<tr>
<th>Operation condition</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
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<td>CO$_2$</td>
</tr>
<tr>
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<tr>
<td>1 mbar 1 h</td>
<td>2979</td>
<td>5101</td>
</tr>
<tr>
<td>10 mbar 1 h</td>
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<tr>
<td>100 mbar 1 h</td>
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<td>100 mbar 2 h</td>
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<td>297</td>
</tr>
<tr>
<td>200 mbar 20 min</td>
<td>1828</td>
<td>1460</td>
</tr>
<tr>
<td>1 bar air 10 min</td>
<td>1547</td>
<td>518</td>
</tr>
<tr>
<td>1 bar air PIM-1/ZIF-8</td>
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<td>2011</td>
</tr>
<tr>
<td><strong>Batch 2, O$_2$ concentration</strong></td>
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<td></td>
</tr>
<tr>
<td>Argon (O$_2$&lt;10ppb) 1 h</td>
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<tr>
<td>10 ppm O$_2$/Ar 1 h</td>
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<td>50 ppm O$_2$/Ar 1 h</td>
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<td>5223</td>
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<tr>
<td>100 ppm O$_2$/Ar 1 h</td>
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<td>3781</td>
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<tr>
<td>200 ppm O$_2$/Ar 1 h</td>
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<td>2473</td>
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<tr>
<td><strong>Batch 3, O$_2$ concentration</strong></td>
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<tr>
<td>10 ppm O$_2$/Ar 24 h</td>
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<td>1540</td>
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Figure 6.20: Sensitivity of gas transport properties to oxygen during thermal oxidative crosslinking. (A) Permeability and (B) selectivity of membranes thermally treated at 385°C at for 1 h under varied vacuum pressure. (C) Permeability and (D) selectivity of membranes thermally treated at 385°C at for 1 h under continuous purge gas containing varied concentration of O₂. (E) Permeability and (F) selectivity of membranes thermally treated at 385°C for 24 h under continuous purge gas containing varied concentration of O₂ over extended time. Note: samples in (C-D) were based on a separate batch exposed to thermal treatment.
**Figure 6.21** shows a representative plot of selectivity *versus* permeability for an industrially important CO\textsubscript{2}/CH\textsubscript{4} gas pair along with the upper bound limit of polymer membranes. The high permeability of PIM-1 For a representative TXL-PIM-1 membrane (sample No. 6 in **Figure 6.21**), the CO\textsubscript{2}/CH\textsubscript{4} selectivity increased up to 70 with a high CO\textsubscript{2} permeability of 1100 Barrer. The significantly enhanced gas selectivity along with high permeability improves the overall gas transport properties, surpassing the upper bound that has been limiting the performance of polymer membranes for decades. To the best of our knowledge, the overall separation performance is better than all the existing soluble PIMs polymers, and comparable or superior to TR polymers [1, 6].

**Figure 6.21:** Plot of CO\textsubscript{2}/CH\textsubscript{4} selectivity *versus* CO\textsubscript{2} permeability. Commercial polymers are included for comparison: cellulose acetate (CA); ethyl cellulose (EC); polycarbonate (PC); Matrimid® 5218 polyimide (PI); polyetherimide (PEI); polyphenyleneoxide (PPO); polysulfone (PSF), cited from reference [7]. Red lines: upper bound of polymer membrane [8]. Open squares: PIM-1 in literature; solid triangles: other PIMs in literature [3, 9-10], TZ-PIM[11], PIM-SBF [10], PIM-EA-TB [3], and PIM-SBI-TB [3]; Open circles: TR polymers [1, 6, 12-14]; Solid squares (black): PIM-1; Solid squares (red): TXL-PIM-1 membranes; Conditions for samples (1-13): (1) 385°C for 24 h in argon (O\textsubscript{2} concentration < 10 ppb), (2) 385°C for 24 h in 10 ppm O\textsubscript{2} in argon, (3) 385°C for 24 h in 100 ppm O\textsubscript{2} in argon, (4) Baked in air at 385°C for 10 min, (5) 385°C for 8 h under vacuum (1 mbar), (6) 385°C for 24 h under vacuum (1 mbar), Samples (7-11): PIM-1/SiO\textsubscript{2} (blue circles) with silica nanoparticles loadings of 1, 2, 5, 10, 20 wt%, respectively; Samples (12-14): TXL-PIM-1/ZIF-8 (green circles) with ZIF-8 loading of 5, 10, 20 wt%, respectively. Samples (6-14) were thermally crosslinked at 385°C for 24 h under vacuum of 1 mbar.
The separation performance of other industrially important gas pairs, such as O$_2$/N$_2$, CO$_2$/N$_2$, H$_2$/N$_2$, and H$_2$/CH$_4$, are all above their respective upper bounds, as shown in Figure 6.22. For example, the O$_2$/N$_2$ selectivity could be as high as ~8.0 with a high O$_2$ permeability of 250 Barrer, which is very promising for air separation. The notable H$_2$ separation over N$_2$ and CH$_4$ are attractive for practical applications in H$_2$ recovery and natural gas purification.

Figure 6.22: Summary of representative gas transport properties. Selectivity versus permeability of PIM-1 and thermally crosslinked PIM-1 membranes for industrially important gas pairs. (A) H$_2$/CH$_4$, (B) H$_2$/N$_2$, (C) O$_2$/N$_2$, and (D) CO$_2$/N$_2$. Red lines: upper bound of polymer membrane[8]. Commercial polymers (grey regions) are included for comparison. Open squares: PIM-1 in literature; Solid triangles (yellow regions): other PIMs in the literature [3, 9-11]; Open circles: TR polymers [1, 6, 12-14]; Solid squares (black): PIM-1 membrane; Solid squares (red): TXL-PIM-1 membranes under different thermal treatment conditions.

We also demonstrate the excellent selectivity of the thermally crosslinked polymer membranes in separation of gas mixtures, such as CO$_2$/CH$_4$ (up to 60) and CO$_2$/N$_2$ (up to 40) (Figure 6.23). In a mixed gas atmosphere, both CO$_2$ and CH$_4$ molecules compete for sorption sites, particularly at high pressure. Therefore, we observed a decrease in the CO$_2$/CH$_4$ selectivity at high pressure, which nevertheless is still as high as 30 over CO$_2$ fugacity of 5-10 bar, a range of interest for industrial natural gas purification.
Figure 6.23: Mixed gas separation performance. Permeability and selectivity of PIM-1 and thermally crosslinked PIM-1 membranes for (A-B) CO$_2$/CH$_4$ mixture and (C-D) CO$_2$/N$_2$ mixture. (E-F) CO$_2$/CH$_4$ mixture separation for thermally crosslinked PIM-1/ZIF-8 and PIM-1/SiO$_2$ nanocomposite membranes. (G-H) CO$_2$/CH$_4$ mixture separation for PIM-1 and PIM-1/ZIF-8 nanocomposite membranes, annealed at 300°C for 48 h under vacuum.

Aging is a particular concern for the use of glassy polymeric materials as gas separation membranes because their performance drops over several years.
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Thermodynamically, the rigid polymer chains still tend to pack space efficiently due to relative freedom of conformation and rotation, and intermolecular noncovalent interactions (chain entanglements, hydrogen bonding, etc), showing loss of permeability as the system tends to reach equilibrium. Such physical aging is especially severe for high free volume polymers, such as poly(1-trimethylsilyl-1-propyne) (PTMSP) [15].

**Figure 6.24**: Pure gas transport properties as a function of aging time. (A-B) Unmodified PIM-1 membrane. (C-D) Thermally crosslinked dense PIM-1 membranes. (E-F) Thermally crosslinked PIM-1/ZIF-8 nanocomposite membranes. The thermal oxidative crosslinking was performed by annealing at 385°C for 24 h under vacuum (1 mbar). The membranes were kept under vacuum between gas permeation measurements.
The gas permeability of PIM-1 shows gradual loss whilst the selectivity shows a slight increase as the system tends to reach equilibrium. The rate of loss of permeability is much slower than PTMSP. Similarly, the thermally crosslinked PIM-1 membranes showed a decrease in permeability and increase in selectivity under vacuum-mode over initial 3-5 days, but then slowly stabilized and maintained over a subsequent month (Figures 6.24 and 6.25). It is not surprising that the thermally crosslinked membranes still experience aging because only mild oxidative chemical changes have taken place primarily at the gateways with minimal impact on the overall fractional free volume. On the other hand, the hydrogen bonding between the oxidized groups is also possible for the thermally treated polymers, which may also lead to dense packing of polymer matrix. Some representative data of aged membranes are shown for a representative CO₂/CH₄ gas pair in Figure 6.26, confirming that the gas transport properties of aged crosslinked polymer network remained at a significant level.

Figure 6.25: Pure gas transport properties of thermally crosslinked PIM-1 membranes as a function of aging time. (A-B) TXL-PIM-1 membrane heated at 385°C under 10 ppm O₂ in Argon for 24 h. (C-D) TXL-PIM-1 membrane heated at 385°C under 100 ppm O₂ in Argon for 24 h.
Figure 6.26: Aging of PIM-1 and TXL-PIM-1 membranes. Sample (2) was thermal treated at 385°C under 10 ppm O₂ in Argon for 24 h. Sample (3) was heated at 385°C under 100 ppm O₂ in Argon for 24 h. The unmodified dense PIM-1 polymer membrane was annealed at 120°C for 24 h under vacuum.

6.3.9 Nanocomposite membranes

Mixed matrix membrane, conventionally known as mixing ordered molecular sieves into polymer matrix, is a promising approach to enhance the gas separation performance [16]. We fabricated mixed matrix (or nanocomposite) membranes by adding microporous zeolitic imidazolate frameworks (ZIF-8) nanocrystals (primary size of 60 nm) [17], or nonporous inorganic nanoparticles (fumed silica, primary size of 12 nm) into the polymer matrix, following a previously established solution-mixing strategy [18].

Nanoparticles were dispersed as colloids and mixed with polymer solution. After casting and evaporation of solvents, self-standing, transparent and flexible nanocomposite membranes were obtained with well-dispersed nanoparticles in the polymer matrix. For the nanocomposite membranes containing ZIF-8, XRD analyses (Figure 6.27) confirmed the high crystallinity of ZIF-8 after annealing at moderate temperatures (<200°C). However, mesoporous cavities could always be observed in the polymer phase or around the nanoparticles by high magnification SEM (Figure 6.10). Similar mesoporous morphology were observed in other nonporous fillers, even in the case of pure PIM-1 polymer if non-dissolved particles (~100 nm) were not removed completely prior to casting. Such poor interface is attributed to the phase separation between the polymer phase and fillers.
packing in nanocomposite membranes is also reflected in their relatively lower thermal conductivity (see Appendix E).

In fact, the incorporation of nanoparticles into polymer matrix disrupts the packing of polymer chains, according to previous findings by Freeman and co-workers[19]. This is reflected in the significant difference in gas sorption isotherms (Figure 6.15). Compared to dense PIM-1 membranes, the nanocomposite membranes annealed at moderate temperatures (120°C) showed enhanced N₂ sorption at low pressure stage, and slightly higher than that of PIM-1 thin films (~300 nm), while the gate-opening behaviour was not observed in these nanocomposite films, because the gas sorption was not limited by kinetic control of diffusion owing to the disrupted packing of polymers behaving as thin films. In contrast, gas sorption isotherms of those crosslinked membranes showed gate-opening type sorption.

Figure 6.27: Wide angle X-ray scattering of thermally treated polymer membranes. (A) PIM-1 polymer films after exposure to thermal treatment under vacuum; (B) PIM-1/ZIF-8 nanocomposite with different loadings of ZIF-8 nanocrystals, samples annealed at 120°C for 24 h; (C) PIM-1/ZIF-8 nanocomposite with ZIF-8 loading of 20wt%, thermally treated at different temperatures under vacuum; (D) ZIF-8 nanocrystals after thermal treatment at various temperatures under vacuum.

Incorporation of nanofillers into polymer matrix could also alter the mobility and glass transition temperature of polymer chains surrounding the nanoparticles [20]. Here, we show that addition of nanoparticles speed up the oxidation of polymer chains, because the
packing of polymer chains became further inefficient and behave as thin films in isolated state. Therefore, the polymers become more accessible to external gas molecules (e.g. O$_2$) and prone to be oxidative cleaved as verified by the analysis of molecular weight distribution (Figure 6.7).

The thermal treatment also induce degradation of the ZIF-8 fillers, as indicated by the lower crystallinity observed in XRD patterns of nanocomposite membranes or ZIF-8 nanocrystals alone (Figure 6.27). TGA analyses of ZIF-8 show weight loss because the organic linkers are not stable at higher temperature. The ZIF-8 nanocrystals aggregated after exposure to thermal treatment at high temperature in low concentration of oxygen (Figure 6.28). In particular, the ZIF-8 nanocrystals heated at 300°C for prolonged period of 48 h under vacuum became irregular shaped (Figure 6.28C) and lose crystallinity completely (Figure 6.27D). These characterization analyses also raise an important concern of the stability of metal-organic frameworks as fillers for nanocomposite membranes.

At intermediate temperature (300-350°C), thermal oxidation of membranes occurred with negligible covalent crosslinking. For example, exposing nanocomposite membranes at
intermediate temperature of 300°C for prolonged exposure time of 48 h at low pressure (1 mbar) resulted in oxidative chain scission of polymer. The polymers were still completely soluble, however the average molecular weight ($M_n$) decreased from ~80 kdalton to 40 kdalton, while the dense PIM-1 membranes were stable. The thermal treatment also improved the polymer/filler interface (Figure 6.29), which is likely due to the intermolecular interactions and surrounding polymer chains that tightens the interface.

Figure 6.29: Cross-sectional SEM images of PIM-1/ZIF-8 nanocomposite membranes. (A-B) Cross-section of PIM-1/ZIF-8 membranes dried at 120°C, (C-D) thermally oxidized PIM-1/ZIF-8 membranes heated at 300°C for 48 h under vacuum. The membrane contains ZIF-8 loading of 20 wt%. Scale bars: (A), (B), and (D), 500 nm; (C), 1 µm.

We demonstrate that incorporation of nanoparticles as fillers into the polymer matrix could also alter the gas transport properties. Generally, after methanol treatment and heat treatment at moderate temperature (<200°C), the PIM-1/ZIF-8 composite membranes show higher permeability, while the selectivity remained constant or approximate to that of PIM-1 membranes. Similar phenomena were observed in recent studies on PIM-1/ZIF-8 composite membranes [21], or PIM-1/nanocages [22] with “as-casted” or “ethanol-treated” membranes without heat treatment. Treating PIM-1 polymer membrane in alcohols swells and relaxes the polymer chains [23], consequently, creating additional free volume elements. Although these alcohol-treated PIM-1-based nanocomposites have shown high permeability, their selectivity for various gas pairs is not satisfactory for practical applications.
The gas transport properties of nanocomposite membranes were significantly dependent on the degree of oxidation and crosslinking. For example, when the nanocomposite membranes were annealed at moderate temperature 300°C for 48 h at 1 mbar, the polymer was oxidized without covalent crosslinking. As shown in Table 6.7, the CO₂ permeability decreased significantly to ~1000 Barrer with selectivity of both CO₂/N₂ and CO₂/CH₄ as high as ~30. Gas sorption of this nanocomposite membrane (Figure 6.16C) showed that CO₂ and CH₄ solubility were about the same as pure PIM-1 polymer, however N₂ adsorption at 77 K (Figure 6.15D) indicated higher gate-opening pressure (0.3 bar). Oxidative chain scission results in shorter chain segments, smaller interchain spacing and more efficient packing of polymer. In addition, the oxidation could also introduce intermolecular interactions in the oxidized polymer matrix, e.g. between oxidized polymer chains, or hydrogen bonding between ZIF-8 (e.g. imidazole group at surface of crystals), which would enhance the local rigidity of polymer chains and selectivity.

Table 6.7 Gas transport properties of PIM-1/ZIF-8 nanocomposite membranes. The membranes were annealed under vacuum (1 mbar).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>PIM-1 120°C 24 h</td>
<td>3316</td>
<td>5152</td>
</tr>
<tr>
<td>PIM-1/ZIF-8 120°C 24 h</td>
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<td>6342</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>901</td>
</tr>
<tr>
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<td>1007</td>
</tr>
<tr>
<td>PIM-1/ZIF-8 300°C 48 h aged</td>
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<td>459</td>
</tr>
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</table>

* Samples were soaked in methanol prior to annealing.

Covalently crosslinked polymer nanocomposite membranes (>350°C) offer higher permeability. The enhancement of gas permeability of nanocomposite membranes containing silica and ZIF-8 could be correlated with the volume fraction of fillers, as shown in Figure 6.30 and listed in Table 6.8. The intrinsic permeability of small molecules through the pure ZIFs membrane is quite high (e.g. CO₂ ~1200 Barrer for ZIF-8) according to Caro and coworkers [24], while the selectivity is quite poor (e.g. CO₂/N₂ and CO₂/CH₄ at about 2-3). Such low selectivity is generally attributed to the flexible pore aperture of ZIF-8 giving high diffusion coefficient of light gas molecules, although the crystallography pore aperture size of 3.4 Å is expected to offer sharp molecular sieving effect. Ideally, addition of ZIF-8 into PIM-1 matrix would result in lower CO₂ permeability and lower selectivity of CO₂/N₂ and CO₂/CH₄ according to the predictions by Maxwell model [25]. However, these gas
permeation properties of composite membranes did not follow the model prediction. We proved that similar behaviour was observed using nonporous nanoparticles (e.g., nanosized silica and TiO$_2$) as fillers.

Table 6.8 Representative gas transport properties of PIM-based nanocomposite membranes. PIM-1 and nanocomposite membranes were dried at 120°C for 24 h. Thermally crosslinked membranes including TXL-PIM-1, TXL-PIM-1/SiO$_2$, TXL-PIM-1/ZIF-8 were cured at 385°C for 24 h under vacuum of 1 mbar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume fraction</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>5544</td>
<td>8505</td>
</tr>
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<td>TXL-PIM-1</td>
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<td>1820</td>
<td>1104</td>
</tr>
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<tr>
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</tr>
<tr>
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<td>3944</td>
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</table>

Table 6.9 Solubility and diffusion coefficient of thermally crosslinked PIM-1 and nanocomposite membranes. Membranes were cured at 385°C for 24 h under vacuum.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$D$ (10$^{-8}$ cm$^2$ s$^{-1}$)</th>
<th>$S$ (10$^{-2}$ cm$^3$ cmHg$^{-1}$ s$^{-1}$)</th>
<th>Diffusivity selectivity</th>
<th>Solubility selectivity</th>
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<td>49.0</td>
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<td>49.4</td>
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<td>11.4</td>
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<td>49.4</td>
</tr>
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<td>50.3</td>
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<td>50.6</td>
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<td>83.3</td>
<td>43.9</td>
<td>12.0</td>
<td>47.3</td>
</tr>
</tbody>
</table>

We also derived the gas solubility and diffusion coefficient of these nanocomposite membranes (Table 6.9 and Figure 6.30). The gas solubility of these nanocomposites is close
to that of pure polymers, so the increase of permeability is attributed to the increase in diffusion coefficients. The enhancement of diffusion is likely to be affected by the inefficient packing of polymer chains and defects at the polymer/filler interfaces. Nanofillers disrupt the packing of polymer chains and physically change the microstructure and free volume elements of polymer phase, as demonstrated previously by Freeman and co-workers [19]. These additional free volume elements and heterogeneous microstructure resulted in more complicated interface when the membranes were exposed to reaction and crosslinking.

Figure 6.30: Gas permeation properties of thermally crosslinked PIM-1 nanocomposite membranes. (A) Permeability, (B) selectivity, (C) Diffusion coefficient and (D) diffusivity selectivity, (E) solubility and (F) solubility selectivity. All membranes were cured at 385°C for 24 h under vacuum.
6.4 Discussion

Understanding the degradation mechanisms of PIMs is important for their applications and future improvements. Thermal degradation of polymer is generally not desired for polymeric membranes. Here we demonstrate controlled oxidative degradation and crosslinking could be useful for tailoring the microstructure of free volume elements. The concept of chemical crosslinking in microporous polymers is considered by other works, though less effectively than our approach reported here. A decarboxylation-induced crosslinking mechanism has been proposed by Koros and co-workers for carboxylic acid-containing polyimides [26], and carboxylated PIMs by Du and Guiver [27-28]. Notably, and quite non-intuitively, Chung and co-workers [29] described an uncontrolled thermal processing of PIM-1 at 300°C (described as being done within a vacuum oven with no information on the environment) and reported the simultaneous increase of both permeability and selectivity. However our own experience is that the work of Chung and coworkers is unrepeatable. We have shown that annealing membranes at 300°C under vacuum or inert atmosphere, the polymer remains stable, with our strong evidence of molecular weight distribution, IR spectra, and gas permeation data.

Taken as a whole, the data presented here confirms an overall change in the heterogeneity of the bulk material through the chemical tuning of relatively discrete points within it. The enhancement in selectivity and reduction in overall permeability is governed by the thermo-oxidative alteration of the gateways between high-free-volume domains. The novelty of our finding is the critical role of oxygen in tuning the microcavities of the PIM-1 polymer, involving oxidation and crosslinking, although the mechanism is still not fully understood in this study.

Compared to the complex science of combustion of hydrocarbons, the pyrolysis and oxidation of organic polymers is even more complicated requiring more detailed studies to understand the mechanism. Our initial thermal analyses indicate that the thermal decomposition in inert atmosphere at temperature above 450°C (Figure 6.31) involves the scission of dioxane linkages with the evidence of CO₂ gaseous product. As for the thermal treatment in oxidative atmosphere, we found that the polymer is less stable in the presence of oxygen, with evident degradation occurring at temperature above 350°C. However, we did not identify the exact crosslinking pathways involved with functional groups. The initiation (e.g. hydrogen abstraction), propagation, and termination (crosslinking) of free radicals are not clear. In the temperature window of 350-450°C, the possible reaction sites could involve the methyl groups, spiro-rings, and dioxane groups (Figure 6.31B), while the fused aromatic
rings should be more stable. It is well-known that the relative reactivity of C-H bonds in polymers follows the order of: allylic>tertiary>secondary>primary. The weaker methyl groups on the spiro-carbon centre are possibly the initial sites of abstraction of allylic hydrogen.

**Figure 6.31:** Possible initial reaction sites of (A) thermal decomposition and (B) oxidative degradation of PIM-1.

Mass balance obtained in TGA (Figure 6.3A) indicates that very little amount of weight loss is sufficient for the crosslinking reactions. The chemical formula for one repeating unit of PIM-1 is C_{29}H_{20}N_{2}O_{4}, corresponding a molecular weight of 460.5 g mol^{-1}. A weight loss of 1.5-2.5 wt% seems to be sufficient to achieve high degree of crosslinking with excellent molecular sieving properties. Such little amount of weight loss corresponds to 7-11.5 g for each repeating unit, ideally, abstraction of several hydrogen atoms from the four methyl groups (-CH_{3}, containing 12 H atoms) would be enough. Of course, these estimations are based on our limited characterization analysis, because the other functional groups were also involved in the random chain scission.

The free-radical degradation leads to crosslinking due to the combination of radical sites on adjacent chains. The evolution of molecular weight distribution as the function of extent of reaction indicates the disperse mixture of fragments of molecular weight from 100 kdalton down to several hundred Dalton, indicating a mechanism of random scission involving the backbone, rather than chain depolymerisation. The mechanism of covalent
crosslinking is not fully understood. On the other hand, physical crosslinking could possibly be formed by relatively weak hydrogen bonding between dangling bonds or oxidized groups.

Since this study is focused on the physical properties and particularly molecular sieving properties. Future work would be performed using advanced techniques. In this study, the thermal oxidation of polymer was investigated with TGA, in situ FTIR spectroscopy, gel-permeation chromatography (GPC). More advanced techniques, such as NMR spectroscopy, electron-spin resonance spectroscopy (ESR), gas chromatography (GC) and mass spectroscopy (MS) may be used to probe the fragments and gaseous products.

The controlled oxidation method is a widely-used method for modification of organic materials, for example, in gasification and activation of activated carbon. Koros and co-workers also found the critical role of oxygen in controlling the atmosphere of polymer pyrolysis to tailor the gas separation performance of CMS membranes [30]. For the first time, our work report the controlled oxidation of microporous polymer precursors to crosslinked polymer networks exhibiting excellent gas separation performance comparable to that of CMS membranes (see a summary of data in Appendix F), but with superior mechanical flexibility and low-cost processability. Furthermore, our understandings would be useful for modification of PIMs materials and other microporous polymers, fabrication of nanocomposites and carbon materials, and lead to improvements in the design of novel microporous polymers and polymer molecular sieves.

With both high permeability and selectivity, our thermally treated polymer is comparable to those thermally rearranged (TR) polymers derived from polyimides containing ortho-positioned functional groups (e.g. -OH and -SH) [1]. In those TR polyimides, thermal rearrangement transforms solution processable dense-packing polymers to high-performance microporous materials with rigid chain structure, i.e. polybenzoxazole (PBO) structure. The TR polymers have hour-glass shaped micropore structure. The TR polymers start from dense glassy polyimides through thermal transformation to porous polymers. The gas transport properties change from the region of high selectivity and low permeability to significantly higher permeability and slight loss in selectivity (Figure 6.32). In contrast, our approach starts from membranes fabricated from solution processable microporous polymer precursor and transformation to crosslinked polymer networks by irreversible thermal oxidative crosslinking reactions. The thermally crosslinked PIM-1 membranes showed remarkably enhanced selectivity while the gas permeability remained at a significant level that is two-to-three magnitude higher than commercial polymers. The loss in permeability in the PIM-1 material and its enhanced selectivity arises from closure of the necks without complete carbonization to a CMS material. The optimal temperature for our process appears to be
around 375-385°C (tunable depending on the O\textsubscript{2} concentration). At this temperature, the film is still transparent, flexible and mechanically flexible in comparison to the samples annealed at higher temperature for prolonged periods where the onset of carbonization has occurred. This is supported in simulated accelerated experiments in TGA, where we proved that a weight loss of 1.5-2.5 wt% due to thermal oxidation would be sufficient to crosslink the polymer without significant degradation or carbonization. Our correct understanding of the science of this process allowed us to control the degree of crosslinking and precisely tune the diffusion coefficients and consequently the gas separation performance.

We proposed the mechanism of thermal oxidative chain scission and crosslinking, though further studies are necessary to fully understand the mechanism. To some extent, the thermochemical crosslinking in this study is similar to well-known example of vulcanization.

**Figure 6.32: Comparison of gas transport properties.** Circles: TR polymers reported by Park et al [1], Triangles: thermally treated PIM-1 polymer by Li et al [29], Black squares: PIM-1, Red squares: TXL-PIM-1 reported in this work. Arrows are added to guide the eyes, showing the evolution of the gas transport properties as a function of the extent of transformation.
of rubber, in which the heat and sulphur play important role. Similar crosslinking techniques using other molecules and chemicals are under investigation.

In addition, our approach also works for crosslinking of nanocomposite membranes. It should be extendable to post-synthetic modification of a wide range of polymers and fillers, such as MOFs [31] and porous cages [32].

We expect that the thermally crosslinked membranes could be readily fabricated using established techniques and module designs of polymeric membranes (flat sheet, spiral wound, or hollow fibers), or coated on ceramic membranes, and then exposed to heat treatment at controlled atmosphere, analogous to the preparation of TR polymers. These highly permeable and selective membranes show great potential for large-scale gas separations, such as biogas and natural gas purification, air separation, hydrogen separation, capturing CO₂ from flue gas, separation of hydrocarbons (olefin/paraffin) in petrochemical industries. In addition, these membranes also show great potential for separation of liquid fuels and chemicals owing to their better stability to chemicals and solvents. With tailored porosity at sub-nanometer scale, these microporous network materials would find a wide range of applications beyond separation processes.

6.5 Conclusion

We demonstrate a simple thermal crosslinking method to tailor the architecture of free volume elements in amorphous polymers by heat treatment in the presence of trace amounts of oxygen molecules. The resulting covalently crosslinked polymer networks offer superior thermal stability, chemical stability, reasonable mechanical strength, enhanced rigidity, and drastic improvement of molecular-sieving function that yields significant selectivity and high gas permeability. These highly permeable and selective membranes are promising for industrial molecular separations including biogas and natural gas purification, carbon dioxide capture, and air separation. Our findings contribute to better understandings of the physical and chemical properties of the novel PIMs polymers.

6.6 References


Chapter 6  
Thermal oxidative crosslinking of polymers of intrinsic microporosity


Chapter 6  Thermal oxidative crosslinking of polymers of intrinsic microporosity


Chapter 7 Conclusions and outlook

7.1 Conclusions

Sustainable energy supply and environmental protection are the major global scientific challenges in the 21st century. Membrane separation technology offers attractive energy-efficient and environmental-friendly solutions to these challenges, in capture of greenhouse gas, natural gas purification, air separation, production of renewable hydrogen fuels, and desalination of seawater for clean water. Over the past decade, there has been an explosive growth in the number of novel microporous polymers with well defined molecular structure and porosity, all of which showing great potential for a wide range of applications. One of the most promising applications of these porous organic polymeric materials is molecular-level separations. This PhD thesis is focused on design and fabrication of membranes from novel molecularly defined polymers and understanding the physical properties and transport phenomena of gas molecules in the polymer membranes, which have important implications for membrane separation technology.

First, we demonstrate a simple approach of fabricating novel polymer nanocomposite gas-separation membranes using established colloidal science. Crystalline microporous zeolitic imidazolate frameworks (ZIFs) nanocrystals were incorporated into a polyimide polymer via solution mixing. The resulting nanocomposite membranes showed excellent dispersion of nanoparticles, good adhesion at the interface, and enhanced gas permeability while the selectivity remained at high level. Advanced characterization techniques indicate the increase of the free volume elements which correlates with the gas transport properties.

We then developed a new membrane material system based on polymers of intrinsic microporosity (PIMs). PIMs polymers have rigid and contorted macromolecular structure; consequently, the polymer chains cannot pack efficiently in the solid state, generating interconnected free volume elements. However, the flexibility and amorphous nature of the microporous polymers results in a broad size distribution of free volume elements and channels that compromises their selectivity in separating molecules. Using the PIM-1 polymer as a prototype, we discovered that ultraviolet irradiation of the PIM-1 membrane in the presence of oxygen induces oxidative chain scission at the surface, which results in dense packing of the shorter chains and local densification. Consequently, the membranes become asymmetric with a more gas-selective layer formed at the surface, while the overall
permeability maintains at a high level. Molecular dynamics simulation indicates that the entanglement and hydrogen bonding are possible reason for the densification. Based on the discovery of photo-oxidation, we have better understandings on the impact of chemical reactions and intermolecular interactions on the structure of free volume elements in the polymer matrix.

Finally, we invented a simple thermal oxidative crosslinking method to tailor the architecture of free volume elements in PIM-1 polymers by heat treatment in the presence of trace amounts of oxygen molecules. The resulting covalently crosslinked polymer networks offer superior thermal stability, chemical stability, reasonable mechanical strength, enhanced rigidity. Most important of all, the thermal crosslinking effectively narrows the gates or channels of interconnected free volume elements, mimicking the hour-glass-like microstructure of water and ion channels in natural biological membranes. The high free volume allows high sorption and rapid movement of gas molecules, while the narrow gates serve as effective sieves that allow small gas molecules to pass through while blocking large molecules. Such unique structure significantly improves the molecular-sieving function yielding significantly enhanced selectivity and high gas permeability that surpasses the upper bound limiting the polymer membranes for decades. We further demonstrated that the thermal crosslinking method is also effective for crosslinking of nanocomposite membranes with porous or nonporous fillers. These highly permeable and selective membranes have great potential for industrial molecular separations including separating CO₂ from flue gas, natural gas purification, air separation, separation of liquids, and separations of molecules in petrochemical industries.

In summary, this PhD dissertation demonstrates the design and fabrication of polymer molecular sieve membranes from novel molecularly defined microporous polymers. By adopting versatile processing methods, we are able to tune the physical properties and particularly the molecular sieving properties. The processing methods range from incorporation of nanocrystals into polymer matrix forming nanocomposite membranes, to transformation of molecular structure and packing by irradiation or heat treatment. The intermolecular interactions, including weak van der Waals forces, hydrogen bonding and strong covalent crosslinking, play important role in tuning the packing of polymer chains and architecture of free volume elements. The key findings of this thesis demonstrate that even very mild chemical changes of the polymer could have significant impacts on their physical properties, an important feature of soft matter.
7.2 Future work

The intermolecular interactions in polymer and polymer nanocomposites are critical to determining the physical and mechanical properties. More delicate experiments should be performed to prove the existence of hydrogen bonding between polymer chains, or between polymer and colloidal nanocrystals. For example, temperature-dependent properties can be measured to prove the thermal-reversible physical crosslinking induced by hydrogen bonding, and establishing the correlation with changes of free volume and microporosity. In addition, only one typical type of MOFs, ZIF-8, was used as filler in this thesis due to its ease of synthesis of nanocrystals and high thermal stability. There are thousands of MOFs candidates in the database, most of which can potentially be fabricated in the nanocrystal form and incorporated into polymer matrix. Understanding the potential physical and chemical interactions between the polymer chains and fillers are important for rational design of nanocomposite membranes.

The degradation of the novel microporous polymers under various conditions (heat, irradiation, etc) merits further study with advanced techniques, such as nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, electron-spin resonance spectroscopy (ESR), gas chromatography (GC) and mass spectroscopy (MS) may be used to probe the functional groups and their fragmentation products. Understanding the degradation reaction mechanisms would be useful for more rational design of functional polymers in the future.

In this study, we used existing polymers as model membrane materials for studying molecular sieving properties. In the future, new polymer chemistry and synthetic pathways should be developed in close collaboration with chemists. The future direction of polymer synthesis is design of rigid polymer chains with large intrachain spacing to achieve both high permeability and high selectivity. An alternative approach is chemical modification of existing polymers. The approach include introducing functional groups into the polymer chains to enhance the interactions of specific molecules with the polymer matrix and solubility selectivity, or tuning the free volume elements to tailor the diffusion selectivity. Novel means of crosslinking would be performed. The polymer membranes would be analyzed in detail with more advanced techniques, including PALS, grazing-incidence small-angle scattering (GISAXS) to understand the structure of free volume and chain packing.

The mechanisms of gas transport in polymers are incompletely understood, particularly the sorption, diffusion and interaction of gas molecules within the polymer matrix, which need to be considered on a molecular level. In this study, we derived the solubility and diffusion coefficients with the solution-diffusion model. However, we need
more theoretical models to describe the mechanism of gas diffusion in the polymers on a molecular level, with free-volume, statistical, quantum mechanical, energetic, structural and other considerations. A better understanding of the gas transport mechanisms in polymers would facilitate the development of high-performance polymers and their new applications. One possible approach is molecular dynamics simulations to build the molecular model of polymers, studying the packing of polymer chains and microstructure of free volume, sorption and dynamic diffusion of molecules within the polymers. In this study, we have performed some initial work to understand and visualize the packing of polymer chains. More molecular dynamics simulations will be necessary to estimate the diffusion coefficients and compare them with the experimental values.

Looking back at the history of polymers in the 20th century, we realize that the advance of polymer materials is always driven by their practical applications. The novel microporous polymers have great potential for a wide range of applications, for example, in molecular-level separations, gas storage, catalysis, optoelectronics and sensor. In particular, the molecular separations including membrane separation and adsorption are very promising and likely to be commercialized in the near future. In this study, we only studied the transport properties of light gas molecules. In fact, these molecular sieve membranes are also promising for separation of large molecules owing to their high solubility, separation of hydrocarbons (olefin/paraffin) in petrochemical industries, separation of liquid fuels (alcohols/water), and desalination of seawater for clean water production. Furthermore, the crosslinked membranes also show great potential for liquid or chemical separation owing to better stability to chemicals and solvents. Most of these applications focused on enhancing the flux and selectivity of molecules rather than the intrinsic permeability as shown in this study. This means that more practical modules should be developed with the selective layer as thin as possible, such as hollow fibres, asymmetric membranes with thin selective layers, or thin film composite membranes supported on other polymer or inorganic membrane substrates will be developed. Therefore, future work would be directed to explore these applications.
Appendices
Appendix A Chemical structure of conventional polymers

Figure A1. Chemical structure of conventional dense polymers.
Appendix B Chemical structure of monomers for PIMs

Figure A2. Synthetic pathway and monomers for non-network PIMs via dibenzodioxin formation reactions. Chemical structures are redrawn from references [1-9].
Figure A2. Synthetic pathway and monomers for non-network PIMs via dibenzodioxin formation reactions (continued). Chemical structures are redrawn from references [1-5, 10-14].
Figure A3. Monomers for network PIMs. Chemical structures are adapted from references [1-4]. Monomer B22 was used for synthesis of network PIMs but not included in this PhD thesis.
Appendix C Fugacity coefficient of non-ideal gas molecules

Figure A4. Fugacity coefficients of each component for CO$_2$/CH$_4$ gas mixture (50/50 vol.) at room temperature of 295 K. The fugacity coefficients were derived from the Peng-Robinson equation of state [15].
Appendix D Thermal analyses of PIM-1 membranes

Figure A5: Thermal analysis of dense PIM-1 polymer membranes. The polymer membranes were heated in 200 ppm O$_2$ in argon, from 120°C to set-point temperature (300-450°C) at 10°C min$^{-1}$ and maintain for 120 min.
Appendix E Thermal conductivity of membranes

Figure A6. Thermal conductivity of as prepared dense PIM-1 and PIM-1/ZIF-8 nanocomposite membranes.
Appendix F Gas transport properties of molecular sieve membranes

### Appendix Table A1. Representative gas transport properties of thermally crosslinked PIM-1 membranes, thermally rearranged (TR) polymers, and carbon molecular sieve (CMS) membranes.

1 Barrer = 10^-10 cm^3 (STP) cm cm^-2 s^-1 cmHg^-1.

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<th>Selectivity</th>
<th>Ref</th>
</tr>
</thead>
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<td>O₂</td>
</tr>
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Appendix references


