Chapter 8

Polymeric Membranes for H₂ and N₂ Separation

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Abstract

H₂ and N₂ separations are of paramount importance to the global development of clean energy and environment. While the traditional thermal-driven processes are often deemed overly energy-intensive, the polymeric membrane technology presents an energy-efficient and potentially cost-effective alternative that comes with many operational and environmental advantages to offer. However, a variety of key challenges revolving around the membrane performance and stability issues require new material innovations in order to be eventually overcome. This chapter provides the background for polymeric gas separation membranes and also a detailed evaluation on state-of-the-art polymeric membrane materials for H₂ and N₂ separations. Performance enhancement strategies will also be discussed in the later parts.

Keywords

Membrane Gas Separation, Polymeric Membranes, Glassy Polymers, Hydrogen Recovery, CO₂ Capture, N₂/CH₄ Separation, Polymers of Intrinsic Microporosity, Mixed-Matrix Membranes

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1. Introduction

1.1 Overview of membranes for H₂ and N₂ separations

As the world increasingly recognizes the threats of rising carbon dioxide (CO₂) emissions, the transition away from fossil-fuel-based power sources is now fast becoming a global endeavor, which sparks the prospect of an economy based on clean and more efficient fuel alternatives, especially hydrogen (H₂) [1, 2]. Not only is hydrogen considered as a zero-emission fuel because its sole combustion product is water which is perfectly nonpolluting, hydrogen also offers a higher energy density than most hydrocarbon fuels [3]. However, the separation of hydrogen from a gas mixture is theoretically an entropy-decreasing, non-spontaneous process that requires an external energy input to occur. As such, the development of efficient hydrogen separation technologies is of critical importance to the production of high-purity, cost-effective hydrogen fuels. On the other hand, the significant role of nitrogen (N₂) separation for

environmental development lies not particularly in the utilization or production of N₂ gas, but rather, it lies in the efficient capture of environmentally problematic gas components, such as CO₂ and methane (CH₄). The N₂ separation process is also being increasingly demanded in the recovery and purification of valuable gas components, for instance, methane (CH₄), from refinery and petrochemical gas streams that usually contain considerable amounts of nitrogen [4-6].

Traditional thermal-driven technologies for H₂ and N₂ separations, such as pressure swing adsorption (PSA), fractional/cryogenic distillation or amine absorption, involve extremely energy-intensive processes and are generally deemed cost-ineffective, even though they are still dominating the gas separation (GS) industry [7]. In comparison, membrane GS, driven only by an applied transmembrane pressure, has no requirement for phase change, thermal regeneration, or any active moving parts during its operation, enabling a much smaller energy and maintenance input than the traditional methods [8]. This key advantage of energy efficiency, along with its other attractive features, such as small footprint, modular design, and simple and continuous operation, renders membrane GS the most promising technology for realizing energy-saving and potentially more cost-effective H₂ and N₂ separations. It also fits nicely with the process design principles delineated by the process intensification strategy which is central to all current chemical engineering developments [8]. Among various membrane materials including metals, inorganics, porous carbons and purely organic polymers, organic polymers are by far the most developed and the most commercially feasible choice of material for GS owing to their easy solution-processability, wide functioning temperature range as well as a balanced combination of cost, performance, mechanical and chemical properties [2].

1.2 History and key applications of polymer membranes for H₂ and N₂ separations

Modern polymeric membrane technology for gas separation was actually first developed upon the asymmetric cellulose acetate (CA) membrane developed by Loeb and Sourirajan for reverse osmosis (RO) seawater desalination in the early 1960s, which they later applied to gas separation [9]. However, the existence of only sub-Angstrom-level size difference between common industrial gas molecules renders the design of GS membranes technically much more challenging, because any defects formed during the membrane fabrication, though as small as at a nanometer-scale, could significantly compromise the membrane performance [10]. For example, as shown in Table 1, the differences between the kinetic diameters of H₂, N₂, CH₄ and CO₂, which are 2.89, 3.64, 3.80 and 3.30 Å respectively, are all smaller than 1.0 Å [11].

Table 1. Kinetic diameters of gas species of interest to gas separation

Gas Species	H ₂	CO ₂	O ₂	N ₂	CH ₄
Kinetic Diameter (Å)	2.89	3.30	3.46	3.64	3.80
Critical Temperature, T _c (K)	33.2	304.2	154.8	126.2	190.6

In the mid- to late-1970s, DuPont pioneered the first generation of small-diameter hollow fiber membranes (HFM) for GS which was groundbreaking, but the low manufacturing efficiency and gas permeance limited their economic viability for industrial applications [12, 13]. The key breakthrough occurred in 1980 when Monsanto first developed and commercialized the asymmetric polysulfone (PSF) HFMs coated by a thin silicone rubber layer that plugged the defects for separating H₂ from ammonia plant purge gases [14]. Inspired by Monsanto's success, Separex and Cynara soon applied similar design concepts to develop the spiral-wound CA membranes for H₂ and natural gas separations [15, 16], and Ube from Japan later introduced and commercialized the polyimide (PI) GS membranes which demonstrated one of the best thermal properties and solvent resistance at that time [17]. A brief timeline of the key developments in polymeric GS membranes is shown in Fig. 1.

Figure 1. Timeline of polymeric gas separation membranes

Thereafter, membrane GS technology underwent rapid growth and had spanned a great variety of commercial applications, such as H_2/N_2 and H_2/CH_4 separations for hydrogen recovery from ammonia purge gases, H_2/CO ratio adjustment in synthesis gas (syngas) production, and H_2 /light HCs separation in refineries or petrochemical processes (e.g. off-gases from hydrotreaters and hydrocrackers) [8]. Relatively new applications involving H_2 and N_2 separations also emerged, which included H_2/CO_2 separation for both pre-combustion CO_2 capture and syngas production, CO_2/N_2 separation for CO_2 capture from flue gas of power plants [18], N_2/CH_4 separation for N_2 rejection to enhance the heat value of natural gas [5], and also the recovery of organic vapors, like light olefins (e.g. C_2H_4 , C_3H_6), from N_2 -containing off-gases [6]. After a significant expansion over the past three decades, the current global membrane GS market reaches an estimated total sales value of around 1.0 to 1.5 billion US dollars each year [7]. Some subsidiary H_2 and N_2 separation markets, such as hydrogen recovery and organic vapor recovery as mentioned above, are now worth about US\$200 and US\$100 million per year, respectively. Table 2 provided a summary of the target applications and the common choices of polymer materials for some industrially important membrane-based H_2 and N_2 separations.

1.3 Performance and Mechanism of Polymeric Gas Separation Membranes

Evaluating the gas separation performance of a polymeric membrane is based on its two critical gas transport characteristics – permeability and selectivity. Permeability (P) is a thickness- and pressure-normalized measure of the flux of a particular gas permeant, which determines the throughput or productivity of the membrane gas separation process [2]. It is an intrinsic property of the polymer material and is generally expressed in units of *Barrer* ($1 \text{ Barrer} = 1 \times 10^{-10} \text{ cm}^3(STP) \text{ cm/cm}^2 \text{ s cmHg}$). When the membrane thickness is factored in the measurement of gas flux, permeance is used instead, which is calculated as the permeability divided by the thickness of the membrane (P/l) and is typically expressed in gas permeance units (*GPU*, $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3(STP)/\text{cm}^2 \text{ s cmHg}$). Selectivity, on the other hand, measures the effectiveness of the membrane in preferentially permeating one particular gas over the other, which determines the purity of the target gas after separation. The ideal selectivity ($\alpha_{i/j}$) is typically used for assessing the pure-gas separation efficiency of a membrane, which is expressed as a ratio between the pure-gas permeabilities of the membrane for two different gas species ($\alpha_{i/j} = P_i/P_j$) [2, 19].

Table 2. Common applications of H₂ and N₂ separation and their corresponding polymer materials [30]

Application	Separation	Traditional Technology	Membrane Materials
Hydrogen recovery from ammonia plants	H ₂ /N ₂ , H ₂ /CH ₄	PSA	polysulfone, polyimide
Adjustment of H ₂ /CO ratio in syngas plants	H ₂ /CO	PSA	polysulfone, polyimide
Hydrogen purification and CO ₂ capture from syngas production	H ₂ /CO ₂	Amine absorption	polybenzimidazole (PBI)
Hydrogen recovery in refineries (e.g. hydrocrackers)	H ₂ /hydrocarbons	Cryogenic distillation	silicon rubber, polyimide
CO ₂ capture from flue gas	CO ₂ /N ₂	Amine absorption	polyimide
Nitrogen removal from natural gas	N ₂ /CH ₄	Cryogenic distillation	silicon rubber
Vapor recovery	C ₂ H ₄ /N ₂ , C ₃ H ₈ /N ₂	Condensation	silicon rubber

Polymeric membranes are generally dense and nonporous such that the gas transport through them follows a well-established solution-diffusion mechanism that comprises three major processes: 1) gas molecules adsorb onto the membrane surface on the high-pressure upstream side, 2) then they diffuse into and through the polymer matrix, 3) and eventually desorb away from the low-pressure downstream side [3]. More specifically, from a microscopic point of view, process 2) actually does not occur as a continuous passage. Instead, it takes place by permeants making ‘jumps’, in the direction of the applied pressure gradient, from one transient gap to another, which is formed by the thermally agitated segment motions of the polymer backbone. An illustrative schematic of the solution-diffusion transport mechanism is shown in Fig. 2. As such, the permeability of polymeric membranes for a particular gas permeant can be expressed as the product of its solubility (S) and diffusivity (D) coefficients as shown in Eq. 1 below:

$$P = S \times D \quad (1)$$

Therefore, the ideal selectivity can be expressed as shown in Eq. 2:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \times \frac{D_i}{D_j} \quad (2)$$

There are some key distinctions between solubility and diffusivity. The former is associated with the thermodynamic phenomenon of gas adsorption onto the membrane and thus demonstrates a strong correlation to the condensability of gas permeants as well as the chemical interaction and affinity between the permeants and polymer matrix [20]. The latter, in contrast, is essentially a kinetic factor strongly influenced by the spatial extents of polymer chain random motions and is found closely related to the size of gas permeants, the polymer chain mobility and also the amount of free volume in the membrane (defined as the space unoccupied by the entangled polymer chains due to conformational constraints). As processes requiring an activation energy, both the solution and diffusion of gas permeants are usually temperature-dependent. Therefore, a successful polymeric GS membrane design must carefully consider both these gas transport parameters.

Figure 2. The membrane gas separation process and the solution-diffusion mechanism of gas transport in dense polymeric membranes

1.4 Difference between Glassy and Rubbery Polymers

Polymeric membranes can be categorized as glassy or rubbery depending on the operation temperature. When the operation temperature is below the glass transition temperature, T_g , of the polymer, the polymer exhibits behaviors of rigid glass and typically possesses a stiffened polymer backbone with a small amount of free volume that restricts large-scale cooperative chain movements [3]. When the operation temperature is kept above its T_g , the polymer displays rubbery characteristics and obtains a relatively larger amount of free volume owing to the motion of flexible polymer chains that gives

rise to greater transient voids. As a result, glassy polymers generally tend to exhibit a lower gas permeability, higher selectivity and also better mechanical properties than rubbery polymers [8]. Moreover, glassy polymers often produce GS membranes that are diffusivity-selective (i.e., the overall selectivity (permselectivity) is dominantly influenced by the diffusivity selectivity, D_i/D_j) while membranes fabricated from rubbery polymers are usually solubility-selective (i.e., the permselectivity is dominantly influenced by the solubility selectivity, S_i/S_j) [21, 22]. Therefore, glassy polymers demonstrate a stronger size-selective effect towards the separation of gas molecules by preferentially permeating the smaller ones, like H_2 and CO_2 , over the larger ones, like N_2 and CH_4 . In contrast, rubbery polymers tend to preferentially permeate the more condensable gases that possess higher solubility in the membranes [23]. This often results in a reverse-selective system whereby larger but more soluble gas molecules transport faster through the membrane than smaller, non-condensable ones. Examples of reverse-selective membranes include those that can enable high CO_2/H_2 or light HCs/(H_2 or N_2) selectivities. Industrially speaking, glassy polymers, including CA, PSF and PI, have achieved the widest commercial implementation over the past few decades in the GS industry, especially for H_2 separation, because of their good size-selectivity and mechanical robustness. On the other hand, rubbery polymers, such as poly(dimethyl siloxane) (PDMS) and poly(ethylene oxide) (PEO), have gained increasing attention recently for the reverse-selective H_2 and N_2 separations, including CO_2/H_2 and CO_2/N_2 separations for CO_2 capture as well as HCs/ H_2 and HCs/ N_2 separations for organic vapor recovery, because of their preferential affinity, solubility, and hence permeability for condensable gases.

1.5 Challenges in Polymeric Gas Separation Membrane Design

Despite the early commercial success, the ongoing growth and advancement of polymeric GS membranes are not without challenges. Firstly, by analyzing the huge pool of performance data from the available polymeric GS membrane materials, Robeson discovered in 1991 that there existed a characteristic trade-off relationship between the permeability and selectivity of polymeric GS membranes such that a high permeability was typically accompanied by a low selectivity and vice versa [24]. Based on the transition state theory, a simultaneous increase in both polymer chain stiffness (i.e., lower intrasegmental mobility) and interchain spacing (i.e., larger free volume) could systematically improve either permeability or selectivity without sacrificing the other, or in some occasions, improve both [25]. However, such improvement would quickly hit a limit when the interchain spacing becomes so large that the motion of thermally agitated polymer chains is no longer governing the diffusion process of gas permeants. Under such circumstances, without a substantial enhancement in solubility selectivity, this limit

would become the asymptotic end-point for the separation performance of polymeric membranes whose gas transport properties are ruled by the solution-diffusion mechanism. For example, certain glassy polymers can achieve an unprecedentedly high gas permeability (in the order of $\sim 10^4$ Barrer) due to their possession of an extraordinary amount of free volume arising from their microporous polymer structures, such as poly(trimethylsilyl propyne) (PTMSP) [26]. However, their extremely low selectivity renders them unfit for any large-scale commercial GS applications. This well-defined trade-off limit on the polymeric GS membranes is famously known as the upper bound (first proposed by Robeson) and has been widely used as the ‘gold standard’ for the comparison of membrane performance for several important H_2 and N_2 separations, including H_2/N_2 , H_2/CH_4 , H_2/CO_2 , CO_2/N_2 separations and so on [24]. A huge part of polymeric GS membrane research has been focused on overcoming this inherent performance limit, and detailed discussions on the material breakthroughs that have accelerated this cause will be given in later sections. A simplified illustration of the upper bound was shown in Fig. 3.

Figure 3. Illustrative diagram of the Robeson upper bound

Besides the challenge of intrinsic performance, the critical issues of plasticization and physical aging also put the operation durability of glassy polymers to the test. Plasticization occurs when the sorption of highly condensable gas components, like CO_2 and HCs, significantly swells the membrane, increases the free volume, and subsequently results in substantial losses of size-selectivity, especially under high operating pressures when the amount of irreversibly dissolved condensable gases in the membrane becomes significant [3]. In some occasions, the mechanical stability could also be compromised

due to swelling. Physical aging is the decrease of gas permeability with time caused by the gradual relaxation and subsequent collapse of non-equilibrium excess free volume elements in glassy polymers [7]. Its effect is more significant for highly permeable polymers like PTMSP and PIMs because the amount of thermodynamically unstable free volume in these polymers is particularly large. These critical durability problems, plus other stability issues (e.g. chemical, thermal or mechanical) and the challenge of large-scale fabrication of defect-free thin-film membranes, are the key impeding forces against the progress of the commercialization of new membrane materials. Consequently, current commercial membrane-based H_2 and N_2 separations are still relying heavily on the few polymers developed about 30 years ago. New polymeric membrane materials with not only better performance but also promising stability against plasticization, aging, harsh operating and fabrication conditions are what the industry needs to eventually break this stagnation.

The following sections will cover the key properties and performances of a variety of conventional and advanced polymeric membrane materials for H_2 and N_2 separation. The focus is primarily on glassy polymers because of the size-selective nature in these separations, but some rubbery polymers will also be discussed for solubility-selectivity-dominated separations, such as CO_2/H_2 , light HCs/ H_2 and CO_2/N_2 . Some discussions on the various material strategies for gas transport enhancement and the importance of membrane configuration will also be included in later parts of this chapter.

2. Polymeric Membranes for H_2 Separation

Hydrogen is highly permeable owing to its small molecular size so that it transports through size-selective membranes much faster than other larger gases that do not have high condensability, such as nitrogen (N_2), methane (CH_4) and carbon monoxide (CO). Therefore, the separation of hydrogen from these gases is relatively straightforward and was enabled as the first set of commercial applications [3]. For example, the earliest successful industrial-scale GS application based on polymeric membranes was the recovery of hydrogen from ammonia purge gases that contained nitrogen and methane (i.e., H_2/N_2 and H_2/CH_4 separations). These purge streams have been produced at high pressures and are ‘clean’ from condensable gas molecules, which make them ideal target mixtures to be separated by polymeric membranes. Similarly, the separation of hydrogen from carbon monoxide for the adjustment of syngas ratio (i.e., H_2/CO separation) was also among the first few commercially successful GS processes because CO has a similar size and non-condensability to N_2 . Glassy polymers are naturally preferred for these size-discrimination-based separations because of the dominance of diffusivity selectivity in their gas transport properties (Table 3). For example, the earliest commercial polymeric

membrane systems, installed for the hydrogen recovery in ammonia plants or for the syngas ratio adjustment, were developed based on asymmetric glassy polysulfone (PSF) hollow fiber membranes (HFMs) by Monsanto under the trade name of Prism® membrane. These PSF HFMs were coated by silicone rubbers to plug the ‘leaky’ defects formed during fabrication.

It is also of rising industrial interest and environmental importance to recover hydrogen from refineries to meet the increasing demand of hydrogen as a feedstock for hydrotreating, hydrocracking or other processes [27]. The target separations are H₂/CH₄ and H₂/light HCs separations in the purge or off gases from the refinery processes, and size-selective glassy polymers, such as PSFs (Prism®) and PIs, have been used industrially as the membrane materials. Now, hydrogen separation by polymeric membranes in ammonia plants, syngas production, and refineries and petrochemical processes is considered as a tried and true technology, and many plants have been installed and in operation since more than 30 years ago [7].

A major source of hydrogen for refineries, power production or chemical synthesis comes from the syngas produced primarily from the steam-methane reforming (SMR) reaction or coal gasification as a mixture of mainly H₂, CO and CO₂. An additional water-gas shift (WGS) reaction can convert CO into more hydrogen and CO₂, and the target separation becomes essentially the H₂/CO₂ separation for fulfilling both the recovery of high purity hydrogen and the capture of greenhouse gas, CO₂ [2]. The reaction equations were shown below as reaction 1 to 3.

Initial steam reforming (reaction 1): $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$

Water-gas shift (reaction 2): $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$

Overall SMR reaction (reaction 3): $\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2$

As an easily condensable gas with a high solubility in polymers, CO₂ is also very permeable in polymeric membranes due to its large solubility coefficient. Therefore, the success of using glassy polymers for the H₂/CO₂ separation is relatively limited due to the competition between the diffusivity selectivity-favored H₂ permeation and the solubility selectivity-favored CO₂ permeation as well as the CO₂-induced plasticization effect, especially under high operating pressures. On the other hand, gas transport in flexible rubbery polymers, like PDMS and PEO, or glassy polymers with an extremely high free volume, like PTMSP, is dominated by the solubility selectivity, which enables the reverse-selective separation whereby larger but more condensable gases could permeate faster than smaller, non-condensable gases [23]. One of the key process advantages offered by reverse-selective separations is that the desirable gases can be retained at the high-pressure feed side, avoiding or reducing the need for their recompression and hence

additional energy consumption. Also, the recovery of hydrogen from light hydrocarbons in refineries and petrochemical processes generally involves high-throughput separations so that the use of reverse-selective membranes with an extremely high permeability for the condensable hydrocarbons can minimize the required membrane areas, lowering the capital cost. Meanwhile, the adverse effect of plasticization on the diffusivity selectivity of polymeric membranes is arguably less detrimental to reverse-selective separations because these separations actually become more efficient when the solubility selectivity gains more dominance. Nevertheless, plasticization is still undesirable because it could compromise mechanical stability.

Table 3. Difference of gas transport characteristic between size-selective and reverse-selective membranes

Type of Selectivity	H ₂ -selective (size-selective)	H ₂ -rejective (reverse-selective)
$\frac{D_{H_2}}{D_{other\ gas}}$	>>> 1	>> 1
$\frac{S_{H_2}}{S_{other\ gas}}$	< 1	<<< 1
$\frac{P_{H_2}}{P_{other\ gas}}$	>> 1	< 1

In this section, a variety of glassy polymeric membrane materials used commercially or under research for H₂/N₂, H₂/CH₄ and H₂/CO₂ separations will be discussed and evaluated, followed by other polymers that are applicable to the reverse-selective separations, including CO₂/H₂ and light HCs/H₂ separations.

2.1 Polymers for H₂/N₂ and H₂/CH₄ Separations

2.1.1 Conventional Polymers

Early studies on the structure-property relationship based on polysulfone (PSF), polycarbonate (PC) and polyimide (PI) polymers revealed a key design principle for the concomitant enhancements in both permeability and selectivity for light gases over bulkier gases, which is to hinder the intersegmental/interchain packing while simultaneously restricting the intra-segmental mobility (equivalent to maximizing the polymer backbone rigidity) [28]. The chain packing efficiency is often reflected by the fractional free volume (FFV) in the membrane, while the large-scale segmental motions and the local sub-segmental mobility can be measured by the glass transition temperature

(T_g) and the sub- T_g s. Both the T_g and sub- T_g s can also serve as indications of the extent of steric effects among the polymer chains. It is important to note that the extent of condensability-dependent solubility selectivity is relatively much smaller than the size-dependent diffusivity selectivity in the overall gas transport of H_2/N_2 and H_2/CH_4 separations because the three involved gases; namely, H_2 , N_2 and CH_4 , all have low to less than moderate condensabilities in dense polymeric membranes. Therefore, the membranes designed for H_2/N_2 and H_2/CH_4 separations primarily target the size-selective effect.

2.1.1.1 Polysulfone

Polysulfones (PSF) are chemically and thermally stable engineering thermoplastics with attractive physical and chemical properties, including good mechanical strength, wide operating temperature range, high chemical resistance and facile processability [29]. Monsanto's PSF-based Prism® membranes were the first polymeric material being successfully commercialized for industrial gas separations. The structure of PSF is characterized by the diphenylene sulfone repeating units which effectively impart the polymer backbones with a certain degree of rigidity owing to their hindrance to the intra-segmental rotations. This bestows PSF with a high T_g of around 186 °C and a satisfactory combination of a H_2 permeability of 14 *Barrer* and H_2/N_2 and H_2/CH_4 selectivities of both 56 at 35 °C, which was fairly acceptable during the early stage of development for GS membranes [30]. The iconic structure of PSF, which is also a commercial product under the trade name of Ultrason® S, is shown in Fig. 4. There are generally two key structural modifications on PSFs that could manipulate their gas transport properties: changing the bridging moieties between the phenylene rings or changing the substitutions on the phenylene rings [29]. For example, PSF polymers can be made much more permeable by substituting the isopropylidene bridging group ($-C(CH_3)_2-$) with the bulkier hexafluoro bridging group ($-C(CF_3)_2-$) because the later significantly hinders interchain packing and enhances the FFV of polymer [31]. Also, symmetrical bulky methyl substitutions on the phenylene rings could result in a significant improvement of permeability as compared to the unsubstituted polymer because of the upset chain packing [32].

2.1.1.2 Polycarbonate

Polycarbonates (PC) are widely used engineering thermoplastics with outstanding strength and toughness. They are characterized as the polyesters of carbonic acid that are typically derived from either diphenyl carbonate or phosgene [29]. Commercial PCs that contain structural units based on the bisphenol A groups (BPA) are the most commonly used type of PCs. Shown in Fig. 2.1 is the archetypical BPA-type PC structure which

possesses a reasonably high T_g of 150 °C and a comparable H_2 permeability of 13 *Barrer* and a lower H_2/CH_4 selectivity of 36 as compared to the analogous PSF [33]. Gas transport properties of PC membranes can be tuned via similar structural modifications as those for PSFs, including bridging moiety and/or aromatic ring substitutions. For example, substitution of bulkier hexafluoro bridging groups could similarly enhance the permeability, while symmetrical tetrabromo-substitution on the biphenyl rings of PC tends to reduce the diffusivity coefficient but enhances the diffusivity selectivity due to the higher interchain interaction by polar halogen groups [33, 34].

Figure 4. Structures of several well-established commercial polymers for gas separation

2.1.1.3 Cellulose Acetate

Cellulose Acetates (CA) are produced from the acetylation of cellulose using acetate esters, which make them relatively inexpensive given the abundance and the renewable nature of these raw materials [35]. The development of integrally skinned asymmetric membrane configuration, which enabled a higher process productivity by tremendously increasing the membrane area per unit volume, was initially based on CA that first targeted desalination applications and gave rise to the early commercialization of CA

membranes [9]. As the technology of membrane module production that stemmed from the development of asymmetric membranes quickly developed, CA membranes were soon found promising for GS applications, too. They became one of the earliest first-generation commercial GS polymers [15, 16]. CA membranes have been reported to demonstrate a lower H_2 permeability but much higher H_2/N_2 and H_2/CH_4 selectivities than PSFs [36, 37], and the overall separation performances of CA are similar to PSF in terms of their respective distance to the upper bound lines. The gas transport properties of CA membranes are strongly influenced by the degree of acetylation of the hydroxyl groups on cellulose [29]. The greater number of hydroxyl groups being substituted by the acetyl groups, the larger the degree of acetylation and the higher the gas permeability (accompanied by lower selectivity) are to be obtained, because the polymer structure is opened up by the bulky acetyl groups. One of the most common CA structures is the cellulose triacetate (CTA, Fig. 4), which is formed when the three hydroxyl groups in each glucose unit have all been acetylated.

2.1.1.4 Poly(phenylene oxide)

Poly(phenylene oxide) (PPO) is characterized by the aromatic ether linkage (-Ar-O-Ar-) which assumes a kinked conformation. The structure of its most iconic member, the symmetrically dimethyl-substituted poly(2,6-dimethyl-1,4-phenylene oxide), is shown in Fig. 4, which possesses a T_g of 220 °C [29, 38]. Being mechanically stable while having excellent thermo-oxidative resistance owing to its high T_g , PPO became one of the earliest high-performance (i.e., high-temperature) commercial engineering thermoplastics. In fact, PPO was introduced as early as in the 1960s by General Electric as the first commercially available polyether in the market, which later gained much interest as a membrane material for industrial gas separations [38, 39]. PPO demonstrates a much higher gas permeability than most other commercial glassy polymers, such as PSF, PC, CA and various polyimides (PI), but its selectivity is much lower due to its relatively open polymer structure [28]. The kinked ether linkages, in the absence of any polar groups substituted on the phenylene rings, could prevent efficient chain packing and induce a high free volume in the membrane. Also, there is high freedom of ring rotation about the ether bonds that could give PPO high intra-segmental mobility. The iconic dimethyl PPO is able to obtain a H_2 permeability of 113 *Barrer* and H_2/N_2 and H_2/CH_4 selectivities of around 24 and 18 respectively [40]. Structural modifications on the PPO polymers can take place by substituting the aromatic hydrogens with large polar atoms or substituting the existing methyl groups with other functionalities that could tune the free volume [41].

2.1.1.5 Polyamide

Aromatic polyamides are often abbreviated as aramids and are generally the polycondensation products of aromatic diamines and aromatic diacyl chlorides via a two-phase process known as interfacial polymerization, which has been one of the most common methods for the synthesis of aramids [29]. Nomex® and Kevlar® are two very representative examples of commercial aramids and they are actually the *meta*- and *para*-isomers of the same polyamide; namely, poly(*m*-phenylene isophthalamide) (PMPI) and poly(*p*-phenylene terephthalamide) (PPPT) (Fig. 4) [42]. Aramids typically possess excellent mechanical strength and thermal stability owing to their high cohesive energy and the extremely efficient polymer packing that both arise in a large part from the interchain hydrogen bonding between amide linkages. Such a tight packing imparts aramids with a very low gas permeability but a high size-selectivity [43]. Typical structural modifications on aramids involve bulky substitutions on aromatic rings that could act as spacers to reduce the extent of interchain hydrogen bonding such that the free volume and hence gas permeability could be increased [29]. Meanwhile, the weakened interchain interactions also help enhance aramids' processability in common solvents. For example, DuPont produced ring-substituted high-performance aramids for commercial hydrogen purification in refinery feed streams and they demonstrated a H₂ permeability from 4 to 40 *Barrer* and a H₂/CH₄ selectivity of 75 to 600 for separating equimolar H₂/CH₄ mixtures at a moderately high temperature of 90 °C [44].

2.1.1.6 Polyimide

Aromatic polyimides (PI) used as GS membrane materials are generally polycondensation products of aromatic dianhydrides and aromatic diamines [28]. PIs are by far the most studied and also the most rapidly growing family of gas separation polymers owing to their broad monomer choices, attractive gas transport properties, high processability in common organic solvents as well as one of the best mechanical and thermal properties among most glassy polymers [29]. The highly rigid polymer backbones of PIs impart them with very high T_g and hence superior thermo-oxidative resistance. A well-known example of commercial PIs is Matrimid® (Fig. 4) which is synthesized from 3,3'-3,3'-benzophenone tetracarboxylic dianhydride (BTDA) and diaminophenylindane (DAPI) [45]. The bent indane structure and the bulky methyl and phenyl groups that extend outside the plane could significantly hinder the intra-segmental mobility, effectively stiffening the polymer backbone and subsequently giving rise to a high T_g of above 300 °C for Matrimid®. Meanwhile, the efficient interchain packing is also impeded by these rigid and odd-shaped backbones, leading to the higher H₂ permeability and comparable or even better H₂/N₂ and H₂/CH₄ selectivities of Matrimid®

as compared to PC, PSF and CA [29]. As a result, Matrimid®'s H₂/N₂ and H₂/CH₄ separation performances were placed much closer to the 1991 upper bounds than most other first-generation commercial glassy polymers. Another good example of commercial PIs is BPDA-based (biphenyl tetracarboxylic dianhydride) polyimides that were developed and first commercialized by Ube Industries [46]. Upilex® (Fig. 4), synthesized from BPDA and 4,4'-oxydianiline (ODA) monomers, is one representative member of the Ube polyimide family and it has demonstrated outstanding hydrogen separation performance with a H₂ permeability of 50 *Barrer* and H₂/N₂ and H₂/CH₄ selectivities of 83 and 125, respectively [30].

One key reason why PIs have attracted such broad attention is that there exists a huge number of structural variants depending on the choice of dianhydride and diamine monomers, which offer a versatile opportunity to tailor their gas transport properties via a relatively easy polycondensation synthesis scheme. For example, the dianhydride structure can vary from being single-ring to double-ring and the choice of bridging moieties for the latter is also numerous [28]. The diamine structure can also vary in similar manners. Fig. 5 illustrates some common choices of dianhydride and diamine structures constituting the corresponding PI backbones. The general trend is that the permeability tends to increase and the selectivity tends to decrease as the dianhydride and/or diamine units become bulkier. Among the various dianhydride choices, those containing the hexafluoro bridging moieties, for example, hexafluoro isopropylidene diphthalic anhydride (6FDA), are highly popular because the bulky hexafluoro group could effectively hinder the intra-segmental mobility, stiffen the polymer backbone, and inhibit polymer packing and interchain interaction as spacers, resulting in not only a significant increase in permeability, but also sometimes a simultaneous enhancement in selectivity [29]. These favorable gas transport properties observed on hexafluoro dianhydrides allowed the 6FDA-based PIs to be among the earliest researched PIs and are often referred to as the first-generation PIs.

Figure 5. Some common choices of dianhydride and diamine for building polyimides. Reproduced with permission [28]. Copyright 1994, Elsevier Ltd.

2.1.1.7 Other Glassy Polymers for H₂/N₂ and H₂/CH₄ Separations

Besides the above six early commercial examples which have been relatively more extensively studied, there are many other glassy polymer choices available that have demonstrated viable H₂/N₂ and H₂/CH₄ separation performances. As discussed before, these two separations rely primarily on the high diffusivity selectivity of membranes, which is a common feature of most glassy polymers. They also involve no condensable species that tend to deteriorate the membrane performance and subsequently complicate the polymer choice and structural design. The chemical structures of additional representatives, either commercial or research glassy polymers, including polyetherimide (PEI), polyethersulfone (PES), polyetherketone (PEK), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyaniline, polyamide imide (PAI), polypyrrolone (PP), polytriazole (PT) and polynorbornene (PN), are summarized in Fig. 6.

Figure 6. Structures of various other glassy polymers for gas separation

Cardo-type polymers that are based on conventional polymer backbones but modified with the fluorene structure are an interesting class of glassy polymers. They demonstrate excellent thermal stability for operations up to 200 °C and could be made from many different choices of conventional polymers, such as polyimides, polyamides, polyesters, polysulfones, polycarbonates and polyetherketones, by incorporating the fluorene structure into the repeating unit of their polymer backbones [47]. The structure of a fluorene-based cardo-polycarbonate is shown in Fig. 6. It has been reported that the cardo-type PSF and PC exhibit higher H₂ permeabilities than their respective unmodified polymers while their H₂/CH₄ selectivities remain somewhat similar [48].

Teflon AF2400 ($x = 87$)

Hyflon AD60X ($x = 60$)

Figure 7. Structures of representative commercial perfluoropolymers for gas separation

Perfluoropolymers are a special class of glassy polymers whose hydrogen atoms have all been replaced with fluorine atoms. Besides having very good mechanical properties, perfluoropolymers generally possess extremely high chemical stability and thermal resistance owing to the high C-F bond energy [8]. One unique property of perfluoropolymers is their unusual sorption behavior which results in a very low solubility of condensable species in them. This gives rise to the high resistance of perfluoropolymers against the swelling and plasticization induced by highly condensable gases, like CO₂ and light HCs, even at high pressures. Because of that, perfluoropolymers have been actually developed initially for tackling challenging separations that involve hydrocarbons or for natural gas treatment. As the energy barrier for rotation is much higher when there are all fluorine atoms on the backbone, the rigidity of polymer chains is greatly enhanced and the tendency of efficient packing is reduced [49]. As a result, perfluoropolymers generally display very high H₂ permeabilities while maintaining good H₂/N₂ and H₂/CH₄ selectivities that allow their overall separation performances to be superior to most conventional commercial polymers discussed in previous sections. For example, Teflon AF2400 developed by DuPont has an unusually high H₂ permeability of 3300 *Barrer* and a sufficient H₂/CH₄ selectivity of 5.5 [50]. Hyflon AD60X developed by Solvay Solexis has a much lower H₂ permeability of 187 *Barrer*, which is still higher than most other conventional glassy polymers, and an excellent H₂/CH₄ selectivity of around 62 [51]. Such separation performances place these two commercial perfluoropolymers well beyond the 1991 upper bound, and in fact, the update on the upper bounds in 2008 was in part promoted by the high performance of perfluoropolymers [52]. Both the structures of Teflon AF2400 and Hyflon AD60X are shown in Fig. 7. It is interesting to note that unlike other highly permeable glassy polymers, most perfluoropolymers experience minimal physical aging. Fig. 8 summarizes the H₂/N₂ and H₂/CH₄ separation performances of most glassy polymers discussed so far on the respective 1991 and 2008 upper bounds.

Figure 8. Hydrogen separation performance of representative glassy polymers on 1991 and 2008 Robeson upper bounds.

The separation of H_2 from N_2 and CH_4 by their size differences is a straightforward membrane separation process and its mechanism is also relatively simple to understand as the gas transport is primarily governed by the diffusivity selectivity while the solubility selectivity plays a little role in that. Virtually all glassy polymers that can be fabricated into dense membranes could provide some selectivities for H_2 over N_2 and CH_4 because of their sufficiently large size differences (still on a sub-angstrom level though) as evidenced in this section by many examples viable for these two separations. The direction for new design is then shifted to enhancing H_2 permeability via creating a microporous polymer structure with an average pore size < 2 nm in the dense membranes for faster diffusion of gases. While most literatures, including this chapter, refer to such new polymer structures that are of interest to highly permeable gas separations as ‘microporous’, it is important to understand that the dimension of pores within these structures are, in fact, in the nano- or sub-nano range rather than the micron range.

2.1.2 Microporous polymers

2.1.2.1 Polyacetylene

Polyacetylenes are characterized by the alternating double bonds and are synthetic glassy polymers with the highest intrinsic permeabilities for small gas molecules, which is even higher than most rubbery polymers including PDMS [49, 53]. In 1983, Masuda et al. successfully synthesized the most representative member of disubstituted polyacetylene,

poly(trimethylsilyl)propyne (PTMSP), which possessed a high T_g of above 200 °C. It soon became the most widely known polyacetylene for GS and is now generally considered as the first generation of intrinsically microporous polymers [54]. The structure of PTMSP is shown in Fig. 9. The extraordinarily high gas permeability of PTMSP altered the common perception that only rubbery polymers could possess an extremely high permeability at that time.

PTMSP has very high chain stiffness due to both the alternating double bonds that rigidify the polymer backbone as well as the bulky trimethylsilyl side groups that further hinder the intra-segmental rotation and mobility [55]. The latter also serves as bulky spacers that induce looser packing among polymers and enlarge the interchain spacing. These effects collectively result in the extremely high FFV of PTMSP (up to 30%) with an average free volume size of around 0.68 nm which is more than twice as big as that of conventional glassy polymer [7, 8]. These free volume elements or nanopores also appear to be interconnected, forming a so-called interconnected microporous structure inside the PTMSP membranes. This special structure imparts PTMSP with diffusivities of several orders of magnitude higher for small gas molecules, like H₂ and CO₂, than other glassy polymers, and its H₂ permeability is in the range of $\sim 10^4$ Barrer [26]. However, the size-selectivity of PTMSP is among the lowest due to its extra-large FFV, which renders its commercial hydrogen separation unpreferable. The physical aging problem caused by the gradual relaxation of thermodynamically unstable excess free volumes with time further compromises its separation efficiency and attractiveness for commercial use [8]. Crosslinking the PTMSP polymers to reduce aging has been attempted in the literatures, but only limited success has been obtained so far. An extremely high H₂ permeability of 16,160 Barrer, coupled with very low H₂/N₂ and H₂/CH₄ selectivities of 2.4 and 1.01 respectively, has placed PTMSP at the high permeability end of the 1991 upper bounds [24].

Figure 9. The chemical structure of PTMSP.

Despite being unsuitable for the diffusivity-selectivity-governed H_2/N_2 and H_2/CH_4 separations, PTMSP have actually found promising applicability for the reverse-selective H_2 and N_2 separations, such as the HCs/H_2 and HCs/N_2 separations, which primarily rely on the high solubility selectivity of PTMSP for condensable gases over light gases [56]. The large free volume of PTMSP could act as spacious sorption sites for these condensable gases, giving them very high solubility in PTMSP and allowing them to effectively compete for passage through the polymers with small, non-condensable gases like H_2 [8]. PTMSP has thus been often compared with as an industrial benchmark for vapor/gas separation, and a more detailed discussion on polymers for reverse-selective H_2 and N_2 separations will be given in a later section.

2.1.2.2 Polymers of intrinsic microporosity

Polymers of intrinsic microporosity (PIM) are a new class of microporous glassy polymers with good solution processability, film-forming ability as well as high functional tunability. They were first developed by Budd and McKeown in 2004 and have revealed a novel polymer structure comprising interconnected micropores of less than 2 nm (20 Å) owing to the presence of bulky contortion sites on their rigid backbones that prevent efficient chain packing [57, 58]. Such microporosity is considered intrinsic because it arises from the inherent polymer structure instead of the processing protocol. The possession of intrinsic microporosity imparts PIMs with a large FFV and also higher gas and vapor solubility than the traditional glassy polymers, including even the most permeable PTMSP [49]. Shown in Fig. 10 is the archetypical ladder-type PIM-1 structure, which could obtain gas permeabilities about hundred times higher than traditional glassy polymers due to both high diffusivity and solubility coefficients arising from its large FFV [7]. The gas permeabilities of PIMs are generally in a decreasing order from CO_2 , H_2 , O_2 , CH_4 to N_2 [8]. At the same time, the diffusivity selectivity of PIM-1 is not completely compromised because of the high rigidity of polymer chains such that the permselectivity of PIM-1 remains within reasonable ranges even with such high permeabilities. As a result, the H_2/N_2 and H_2/CH_4 separation performances of early PIMs were typically between the 1991 and 2008 upper bounds or, in some cases, even surpassed the 2008 upper bounds [7]. In fact, the outstanding performance demonstrated by PIM membranes has promoted the redefinition of the upper bounds for these two hydrogen separations twice, once in 2008 and the other time in 2015, and have been attracting huge research attention among the membrane community ever since the advent of PIM-1 [37, 52]. One interesting key feature of PIM membranes is that they tend to swell reversibly in non-solvents like methanol or ethanol, which makes their gas permeation properties fairly sensitive to the film-forming protocol [8]. For example, a

certain duration of treatment in a non-solvent can result in a few times higher gas permeabilities of the PIM membranes as shown in Table 4.

Figure 10. The polymer structure of PIM-1. Reproduced with permission [59]. Copyright 2016, Springer Publishing Group.

In terms of the nature of their polymer backbone, PIMs can be classified into two general types: ladder PIMs and polyimides of intrinsic microporosity (PIM-PIs). Ladder PIMs usually contain a characteristic sterically hindered building block in their repeating units. These building blocks provide the sites of contortion for creating the kinked ladder conformation which gives rise to the rigid and contorted PIM backbones that significantly upset the efficient chain packing. For example, ladder-type monomers consisting of two aromatic rings linked by a single tetrahedral carbon atom (also known as the spiro-carbon center), such as the spirobisindane-based monomer used in PIM-1, are classic examples for constructing early ladder PIM structures. Ladder PIMs can be also sub-categorized according to the types of their sterically hindered building blocks, including but not limited to, spirobisindane (SBI), phenazine, ethanoanthracene (EA), triptycene (Trip), spirobifluorene (SBF), Troger's base (TB), and tetraphenylethylene (TPE) [10].

PIM-PIs are polyimides with rigid and contorted PIM segments that contain the sterically hindered contortion sites. The first series of PIM-PIs, ranging from PIM-PI-1 to 8, were reported by Ghanem et al. in 2008 [60]. The structural design of PIM-PIs generally depends on the target location of contortion sites, whether in the dianhydride unit or in the diamine unit, or both. A diagram illustrating the detailed classification of PIMs according to their structures is shown in Fig. 11. It is important to note that physical aging has been a notorious problem associated with highly permeable glassy polymers including PIMs, but the focus of this section is on PIM structural designs targeting superior intrinsic gas permeation properties so that the detailed discussions on aging behavior is outside the scope here [61].

(a) Ladder PIMs

As shown in Fig. 11, the structure of ladder PIMs is generally characterized by three types of linkage groups that integrate the sterically hindered building blocks into the backbone; namely, the benzodioxane-, phenazine-, and TB-based linkers. Given the highly rigid and/or contorted nature of the phenazine- and TB-based linkers, they can also be considered as the sterically hindered building blocks themselves. In the design of PIM structures, the key to generating the intrinsic microporosity is to use at least one monomer with a rigid and contorted structure that can effectively disrupt efficient chain packing while keeping sufficient chain stiffness for good diffusivity selectivity [10]. Common choices of monomers with bulky contortion sites (i.e., the sterically hindered building blocks) include those with the spiro-carbon center (e.g. SBI and SBF), a single covalent bond with highly restricted rotation (e.g. TPE), or non-planar rigid bulky 3D structures (e.g. EA and Trip), which in combination with the three types of linkers can produce a huge variety of ladder PIM structures.

Figure 11. Classification of polymers of intrinsic microporosity. Reproduced with permission [10]. Copyright 2018, Elsevier Ltd.

(b) Ladder PIMs with Benzodioxane Linker

The archetypal PIMs, also widely recognized as the first-generation PIMs, were synthesized by the aromatic nucleophilic substitution reaction that formed the benzodioxane linkers in the resultant polymers [57, 58]. Such reactions typically occur between a spirocyclic bis-catechol monomer (e.g. spirobisindane-based) and a tetrahalo monomer (often a tetrafluoro monomer) and will give rise to a fused-ring polymer structure. For example, PIM-1 is the earliest benzoedioxane-type ladder PIM which was synthesized from equimolar 5,5',6,6'-tetrahydroxy-3,3,3,3'-tetramethyl-1,1'-spirobisindane (TTSBI) and 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN), and has been by far the most extensively studied ladder PIM member for gas separation owing to its simple structure, promising performance and physical properties as well as excellent solution-processability [10]. McKeown's group recently reported a unique and interesting 2D ladder PIM structure, named PIM-TMN-Trip (TMN = tetramethyltetrahydronaphthalene), which is solution-processable and ultra-permeable [62]. In the PIM-TMN-Trip structure, two phenyl rings of the rigid Trip unit were used to construct the benzodioxane linkers in the ribbon-like, shape-persistent 2D backbones, while the third ring was fused to a TMN group to maintain the high 2D aspect ratio for obtaining the ultra-permeability by significantly impeding the efficient chain packing. The PIM-TMN-Trip membranes demonstrated an extraordinarily high H₂ permeability while keeping sufficient H₂/N₂ and H₂/CH₄ selectivities for easily surpassing the 2008 upper bounds. Various representative benzodioxane-based ladder PIM structures are shown in Fig. 12.

(c) Ladder PIMs with Phenazine Linker

Phenazine-based linkers are more rigid than the benzodioxane-based ones. Examples of phenazine-containing ladder PIMs include PIM-7, PSBI-AB and TPIMs whose structures are shown in Fig. 13 [63-65]. Among these examples, TPIM-1 developed by Pinnau's group in 2014, which comprised both phenazine linkers and Trip building blocks in its rigid, fused-ring structure, demonstrated superior hydrogen separation performances owing to its strong molecular-sieving characteristic [64]. TPIM-1 was actually one of the top-performance PIMs that was used to establish the 2015 H₂/N₂ and H₂/CH₄ upper bounds [37].

Figure 12. Structures of some representative benzodioxane-based ladder PIMs

Figure 13. Structures of some representative phenazine-based ladder PIMs

(d) Ladder PIMs with Troger's Base Linker

Troger's base (TB) is a bulky and V-shape linker first introduced into PIMs and PIM-PIs in 2013 by Carta et al. [66]. They developed the novel PIM-EA-TB polymer that combined two highly rigid, bicyclic and shape-persistent groups; namely, ethanoanthracene (EA) and TB, into the same compact, fused-ring ladder structure with no spiro-carbon centers or dioxane linkers. Such an advanced polymer structure displayed a strong nature of intrinsic ultramicroporosity and also outstanding hydrogen separation performances. Various novel TB-based ladder PIM structures are shown in Fig. 14, and the hydrogen separation performances of several representative ladder PIMs are summarized in Table 4.

Figure 14. Structures of some representative TB-based ladder PIMs

(e) Polyimides of Intrinsic Microporosity

Highly rigid and sterically hindered bulky sites of contortion can be introduced into polyimide backbones to create polyimides of intrinsic microporosity (PIM-PI), which like conventional polyimides are typically synthesized via the polycondensation between an aromatic dianhydride and an aromatic diamine. Depending on where the introduced contortion site is (i.e., in the dianhydride monomer or the diamine monomer), the structure of PIM-PIs can be sub-categorized into those that contain dianhydride contortion sites, those that contain diamine contortion sites, or both.

Table 4. Summary of hydrogen separation performance of representative ladder PIMs[10, 37, 67]

Ladder PIMs	Permeability (Barrer)			Selectivity	
	H ₂	N ₂	CH ₄	H ₂ /N ₂	H ₂ /CH ₄
Benzodioxane-based					
PIM-1 ^a	1300	92	125	14.1	10.4
PIM-1 ^b	5010	823	1360	6.1	3.7
SBF-PIM-1 ^b	6320	786	1100	8	5.7
PIM-HPB ^b	1413	190	361	7.4	3.9
TPE-PIM ^c	604	33.4	41	18.1	14.7
PIM-TMN-Trip ^b	16900	2230	3420	7.6	4.9
Phenazine-based					
PIM-7 ^a	860	42	62	20.5	13.9
PSBI-AB ^c	1630	141	257	11.5	6.3
TPIM-1 ^e	2666	54	50	49.4	53.3
TB-base					
PIM-EA-TB ^b	7760	525	699	14.8	11.1
PIM-Trip-TB ^b	8039	629	905	12.8	8.9
PIM-TMN-Trip-TB ^b	6100	396	710	15.4	8.6
TB-Ad-Me ^b	1800	121	162	14.8	11.1
PIM-BTrip-TB ^b	9980	926	1440	10.8	6.9
PIM-MP-TB ^b	4050	200	264	20.3	15.3

^a As-cast membranes tested at 30 °C and 200 – 300 mbar

^b Methanol treated and air-dried before testing at 25 °C and 1 bar

^c Methanol treated, air-dried and then 120 °C dried under vacuum overnight before testing at 35 °C and 2 bar

^d Methanol treated before testing at 22 °C and 4.4 bar

^e Exactly same as ^b except that testing temperature was 35 °C

(f) Contortion Sites in the Dianhydride

The first series of PIM-PIs were invented by McKeown's group in 2008 which utilized the classic SBI unit as the contortion site in its dianhydride monomer [60]. The choice of diamine was varied to form PIM-PI-1 to PIM-PI-8. Compared with most conventional PIs, these early PIM-PIs exhibited a much higher FFV, larger Brunauer-Emmett-Teller (BET) surface area and lower density due to inefficient packing arising from the rigid and contorted PIM-type segments [68, 69]. As a result, they could achieve much higher H₂ permeabilities but lower H₂/N₂ and H₂/CH₄ selectivities than conventional PIs. Nevertheless, as compared to ladder PIMs, especially those with superior gas transport properties, the hydrogen separation performances of early PIM-PIs were not as attractive. The structures of some representative PIM-PIs built by SBI- or SBF-containing dianhydrides are shown in Fig. 15.

Figure 15. Structures of representative PIM-PIs built by SBI- or SBF-containing dianhydrides

The same principle in designing novel ladder PIMs, which utilized the bridged bicyclic building blocks with high rigidity and contortedness, such as TB, EA and Trip, to increase the chain rigidity and internal free volume of polymers, could be also applied to the design of advanced PIM-PI structures. For example, structures like PIM-PI-EA (also known as PIM-PI-12) and CTB-DMN (a PIM-PI based on EA and carbocyclic pseudo TB (CTB) building blocks) delivered much better H_2/N_2 and H_2/CH_4 separation performances than early PIM-PIs that utilized the comparatively less rigid SBI and SBF units. [70, 71]. Fig. 16 provides the structures of some representative PIM-PI structures with EA and TB-containing dianhydrides. One of the real breakthroughs took place when Ghanem et al. and Swaidan et al. developed a series of novel, top-performance PIM-PIs, called KAUST-PI-1 to KAUST-PI-7, using a rigid, 3D paddlewheel-structured Trip-containing dianhydride (Fig. 17) [72, 73]. With 2,3,5,6-tetramethyl-1,4-phenylene (TMPD or durene) being used as the diamine, the KAUST-PI-1 polymer reported by Ghanem et al. in 2014 achieved extraordinary H_2/N_2 and H_2/CH_4 separation performances that sit very close to or on the respective 2015 upper bounds [37, 72]. This innovative PIM-PI structure prompted the realization of an efficient strategy for designing high-performance PIM-PIs. It created a tightened bimodal interconnected microporous structure in the polymers with a unique combination of large micropores ($> 10 \text{ \AA}$) that not

only facilitated a high permeability and the formation of ultrafine micropores ($< 7 \text{ \AA}$) but also maintained a good size-selectivity. As a result, KAUST-PI-1 displayed far superior performance than early ladder PIMs and PIM-PIs. The hydrogen separation performances of several representative PIM-PIs containing contorted dianhydrides are summarized in Table 5.

Figure 16. Structures of representative PIM-PIs built by EA- or CTB-containing dianhydrides

Figure 17. Structures of representative PIM-PIs built by Trip-containing dianhydrides

Table 5. Summary of hydrogen separation performance of PIM-PIs with contorted dianhydrides[10, 37, 73]

PIM-PIs with Contorted Dianhydride	Permeability (Barrer)			Selectivity	
	H ₂	N ₂	CH ₄	H ₂ /N ₂	H ₂ /CH ₄
PIM-PI-1 ^a	530	47	77	11.3	6.9
PIM-PI-2 ^a	220	9	9	24.4	24.4
PIM-PI-3 ^a	360	23	27	15.7	13.3
PIM-PI-4 ^a	300	16	20	18.8	15
PIM-PI-7 ^a	350	19	27	18.4	13
PIM-PI-8 ^a	1600	160	260	10	6.2
PIM-PI-9 ^b	840	94	170	8.9	4.9
PIM-PI-10 ^b	670	84	168	8	4
PIM-PI-11 ^b	624	65	129	9.6	4.8
PIM-PI-12 ^d (PIM-PI-EA)	4230	369	457	11.5	9.3
SBFDA-DMN ^c	2966	226	326	13.1	9.1
EAD-DMN ^e	4703	480	707	9.8	6.7
CTB1-DMN ^c	1295	76.2	95.7	17	13.5
CTB2-DMN ^c	1150	39.9	40.4	28.8	28.5
KAUST-PI-1 ^c	3983	107	105	37.2	37.9
KAUST-PI-2 ^c	2368	98	101	24.2	23.4
KAUST-PI-3 ^c	1625	43	43	37.8	37.8
KAUST-PI-4 ^c	302	10.6	10.7	28.5	28.2
KAUST-PI-5 ^c	1558	87	77	17.9	20.2
KAUST-PI-6 ^c	409	14.4	11	28.4	37.2
KAUST-PI-7 ^c	3198	225	354	14.2	9

^a Air-dried before testing at 30 °C and 200–500 mbar

^b Methanol treated and air-dried before testing at 25 °C and 1 bar

^c Methanol treated, air-dried and then 120 °C dried under vacuum overnight before testing at 35 °C and 2 bar

^d Methanol treated for 8 hours and air-dried before testing at 25 °C and 1 bar

^e Methanol treated for 24 hours, air-dried for another 24 hours and then degassed under vacuum for 24 hours before testing at 35 °C and 2 bar

(g) Contortion Sites in the Diamine

Many choices of sterically hindered building blocks have been also explored on the diamines in PIM-PIs, including SBF, SBI, TB and Trip units [74-82]. The structures of various PIM-PIs containing contorted diamines or both contorted dianhydrides and diamines are shown in Fig. 18, 19 and 20. Generally, the gas separation performance of PIM-PIs with contorted diamines depended strongly on the type of dianhydride used, their overall separation performance fell below those containing the contorted dianhydrides mentioned before. The hydrogen separation performances of several representative PIM-PIs containing sterically contorted diamines are summarized in Table 6.

Figure 18. Structures of representative PIM-PIs containing SBF diamines

Figure 19. Structures of representative PIM-PIs containing Trip diamines

Figure 20. Structures of representative PIM-PIs containing TB diamines. Reproduced with permission [10]. Copyright 2018, Elsevier Ltd.

Table 6. Summary of hydrogen separation performance of PIM-PIs with contorted diamines[10, 75-82]

PIM-PIs with Contorted Diamine	Permeability (Barrer)			Selectivity	
	H ₂	N ₂	CH ₄	H ₂ /N ₂	H ₂ /CH ₄
6FDA-SBF ^a	234	7.8	6.4	30	36.6
PMDA-SBF ^a	230	8.5	9.1	27.1	25.3
SPDA-SBF ^a	501	28.6	41.1	17.5	12.2
6FDA-BSBF ^a	531	27	24.9	19.7	21.3
PMDA-BSBF ^a	560	28.8	36.5	19.4	15.3
SPDA-BSBF ^a	919	69	102	13.3	9
PI-TB-1 ^b	607	31	27	19.6	22.5
PI-TB-2 ^b	134	2.5	2.1	53.6	63.8
PI-TB-3 ^b	299	9.5	6.7	31.5	44.6
PI-TB-4 ^b	40	1.3	1	30.8	40
PI-TB-5 ^b	53.8	1.9	1.7	28.3	31.6
TBDA1-SBI-PI ^d	915	35	45	26.1	20.3
TBDA2-SBI-PI ^d	1155	49	65	23.6	17.8
PIM-PI-TB-1 ^a	612	42	44	14.6	13.9
PIM-PI-TB-2 ^a	582	34	31	17.1	18.8
4MTBDA-SBIDA ^c	3200	372	591	8.6	5.4
4MTBDA-SBFDA ^c	2901	264	371	11	7.8
6FDA-DAT1 ^a	198	4.7	3.2	42.1	61.9
6FDA-DAT2 ^a	281	9	7.1	31.2	39.6
6FDA-1,4-Trip ^e	49	0.66	0.37	74.2	132
6FDA-PPDA ^f	131	3.2	2.5	40.9	52.4

^a Methanol treated and then 120 °C dried under vacuum for 24 hours before testing at 35 °C and 2 bar^b Methanol treated, 120 °C dried under vacuum for 2 hours and then stored under ambient condition before testing at 35 °C and 1 bar^c Methanol treated and air-dried overnight before testing at 25 °C and 1 bar^d Dried under high vacuum for 24 hours, methanol treated, and then 120 °C dried again under vacuum for 24 hours before testing at 35 °C and 1 bar^e Dried at 200 °C for 24 hours, methanol treated, and then dried again at 200 °C for another 24 hours before testing^f Methanol treated for 24 hours and then 140 °C dried for another 24 hours before testing at 35 °C

(h) Functionalized PIMs

While ladder PIMs have successfully realized attractive performances and good processability for hydrogen separation, most of them still lack the competitiveness for more challenging separations that involve condensable species, like CO₂/N₂ separation for CO₂ capture from flue gas. Therefore, proper functionalization on PIM structures to optimize their affinity is a facile and effective design strategy to enhance the solubility of condensable gases like CO₂ [10]. While more details will be given in a later section where polymer chain-functionalization is to be discussed, the structures of some representative functionalized ladder PIMs are shown here in Fig. 21, which includes amidoxime-functionalized PIM-1 (AOPIM-1), tetrazole-functionalized PIMs (TZPIMs),

thioamide-functionalized PIM-1 (ThioPIM-1) and carboxylated PIM-1 (PIM-1-COOH) [83-86]. Some of these functionalized ladder PIMs also demonstrated improved H_2/N_2 and H_2/CH_4 separations due to the increased intersegmental hydrogen bonding between the introduced functional groups. For example, AOPIM-1 exhibited a lower H_2 permeability but much higher H_2/N_2 and H_2/CH_4 selectivities than PIM-1, which allowed AOPIM-1's overall separation performance to be placed on the 2008 upper bounds. The hydrogen separation performances of some representative functionalized ladder PIMs are summarized in Table 7. Similarly, the development of functionalized PIM-PIs, for example, the hydroxyl-functionalized ones, also targets gas separations that involve condensable gases [87].

Figure 21. Structures of representative functionalized ladder PIMs.

Table 7. Summary of hydrogen separation performance of functionalized ladder PIMs[83, 84, 86]

Functionalized ladder PIMs	Permeability (Barrer)			Selectivity	
	H_2	N_2	CH_4	H_2/N_2	H_2/CH_4
AOPIM-1 ^a	912	33	34	27.6	26.8
Thio-PIM-1 ^b	610	37	56	16.5	10.9
PIM-1-COOH ^c	408	24	-	17	-

^a Methanol treated and then 120 °C dried under vacuum for 24 hours before testing at 35 °C and 2 bar

^b Ethanol treated before testing at 25 °C and 1 bar

^c Hydrolyzed at 120 °C for 5 hours before testing at 35 °C and 4.4 bar

(i) Updated Separation Performance

The discovery of PIM structure simply opens a new realm of material research on polymeric GS membranes, which has been accelerating the update on the state-of-the-art performance upper bounds. While 17 years lapsed before the 1991 upper bound was first renewed in 2008 by the advent of ladder PIMs like PIM-1 and PIM-7, it only took another 7 years for the 2015 upper bounds for H_2/N_2 and H_2/CH_4 separations to be proposed by Swaiden et al. based on the extraordinary performance of the groundbreaking TPIMs and KAUST-PIs [24, 37, 52]. The 2019 upper bound for CO_2/N_2 performance was also recently published by McKeown's group using a large series of Trip-based ladder PIMs [88]. Most of the novel PIM structures were placed between the 2008 and 2015 upper bounds. As the design principles become more refined with an increasing number of relevant studies, the pool of high-performance PIMs will be further widened. The hydrogen separation performance of numerous representative ladder PIMs and PIM-PIs is compared with the three established upper bounds in Fig. 22. One general design principle widely recognized is to use rigid contorted bicyclic units, such as EA, TB and Trip for achieving superior separation performance [10]. Also, from studies on PIM-PIs, it has been discovered that the gas separation performance tends to follow the order of increasing rigidity of the contortion sites, from SBI, SBF, TB, EA to Trip, in both dianhydride and diamine moieties. However, the best separation performance achieved so far was by having contortion sites in the dianhydride moiety, whereas the performance enhancement was generally less prominent when placing contortion sites in the diamine moiety.

Figure 22. Hydrogen separation performance of representative ladder PIMs and PIM-PIs on 1991, 2008 and 2015 upper bounds

2.2 Polymers for H₂/CO₂ Separation

Compared with H₂/N₂ and H₂/CH₄ separations which only involve gases of low to less than moderate condensabilities, the H₂-selective separation of H₂ and CO₂ is much more challenging because CO₂ tends to exhibit a similar fast permeation rate as H₂ through polymeric membranes, owing to its high solubility in dense polymers, especially those having large free volume that could act as CO₂-favored sorption sites or those that could form polar interactions with CO₂ [49]. Besides, the size difference between H₂ and CO₂ gas molecules is much smaller than that between H₂ and N₂ or CH₄. In order to achieve a high selectivity for H₂ over CO₂, the solubility selectivity which favors the more condensable species needs to be suppressed such that the diffusivity selectivity and hence the size-sieving effect could be the governing factor for the overall gas transport, subsequently leading to the desired high H₂/CO₂ permselectivity [1]. Glassy polymers with relatively more rigid polymer chains, smaller free volume and higher diffusivity selectivity are attractive materials for enabling highly H₂-selective separation of H₂ and CO₂.

In terms of the operation conditions, the H₂/CO₂ separation is favored at high temperatures because the diffusivity of H₂ could be enhanced while the solubility of CO₂ could be suppressed [7, 8]. Operating at elevated temperatures also makes direct industrial sense because the syngas streams containing H₂ and CO₂ are processed or produced at temperatures typically from 150 °C to 300 °C [7]; therefore, no additional heat exchange processes would be required for cooling or heating these gas streams before separation. As such, it is of great industrial interest to find polymeric membrane materials that exhibit superior thermal and mechanical properties to withstand the harsh environments encountered in the H₂/CO₂ separation which aims at the efficient pre-combustion CO₂ capture from syngas. This operation constraint limits the polymer choice to only a few classes of high-performance, heat-resistant glassy polymers, such as polybenzazoles (e.g. polybenzimidazole (PBI) and polybenzoxazoles (PBO)), polyimides, polysulfones, polyamides and polyphosphazenes [89]. Among which, PBI has been showing the greatest promises for efficient membrane H₂/CO₂ separation.

2.2.1 Polybenzimidazole

Polybenzimidazoles (PBI) are a class of heterocyclic glassy polymers from the polybenzazole family and are one of the most widely recognized and studied polymeric material for H₂/CO₂ separation because of their extraordinary thermal stability and attractive separation performance, especially at high temperatures [3, 89]. The structure of the earliest and also the most representative PBI, *m*-PBI, which has been commercialized by Celanese under the trade name of Celazole®, is shown in Fig. 23

[90]. The *m*-PBI was synthesized from the polycondensation reaction between 3,3-diaminobenzidine and isophthalic acid and it possessed a very high T_g of 425 to 435 °C [91]. Besides its outstanding thermal properties and heat-resistance (decomposition temperature as high as 550 °C), PBI also exhibits high mechanical strength and superior chemical resistance that is uncommon to find in most glassy polymers owing to its rigid aromatic backbone as well as the extensive inter-segmental hydrogen bonding between the imidazole groups [92]. The highly rigid polymer chain also provides higher resistance against CO₂-induced plasticization that could severely deteriorate the size-selectivity of the polymer, which is another advantage of PBI for H₂/CO₂ separation [93]. However, their extremely high chemical resistance results in the low solubility and hence poor solution-processability of bulk PBI polymers in most organic solvents, which limits the use of standard solution-casting method to fabricate thin PBI films [94]. In fact, the poor processability problem is encountered by most thermally and chemically resistant polymers because their extreme stability leads to their low solubility in common organic solvents, rendering their membrane fabrication via the common solution-casting method very difficult. Structural modifications, such as substituting the rigid 3,3-diamine monomer with the 3,3',4,4'-tetraaminodiphenylsulfone (TADPS) monomer that contains a flexible and kinked sulfonyl linkage, are recently found capable of enhancing the solubility of PBI by inhibiting the chain packing and interchain interactions [94].

Figure 23. The chemical structures of m-PBI and TADPS-PBI

Many research efforts have also been devoted, since the early 2000s, to the fabrication of 3,3-diamine-based PBIs into flat and fibrous membranes for studying their gas transport properties. Their success has revealed very attractive H₂/CO₂ separation performances. For example, *m*-PBI at 43 °C exhibited a H₂ permeability of around 4 *Barrer* and a H₂/CO₂ selectivity of around 15 which placed its overall performance very close to the 2008 upper bound [95], as shown in Fig. 24. While the H₂ permeability of PBI

membranes is small at low temperatures due to the strong π - π stacking effect arising from its rigid, rod-like aromatic chains and strong intermolecular hydrogen bonding, their separation performances in terms of permeability and selectivity could be tremendously enhanced at high operating temperatures. In addition, their H_2 permeability tends to experience a much larger increase than their CO_2 permeability due to the suppressed solubility coefficient of CO_2 at high temperatures [3, 7]. For example, at 250 °C, *m*-PBI could achieve a pure-gas H_2 permeability of around 77 Barrer and a H_2/CO_2 selectivity of around 23 which allowed its overall performance to be placed far beyond the 2008 upper bound (Fig. 24) [95]. Structural modifications, such as bulky substitutions on the diacid monomer or using more flexible diacid structures, could also effectively improve the H_2 permeability by hindering the interchain packing and interactions to create a more opened-up pore structure or by increasing the intra-segmental mobility, respectively [92, 95]. As for now, the poor processability of PBI has already been deemed much less of an issue after more than a decade of research efforts, especially after the asymmetric PBI hollow fiber membranes (HFMs) have been successfully fabricated, which marked its fulfilment of the important prerequisite – spinnability – for becoming a commercially practical polymer [96]. Recently, Zhu et al. prepared polyprotic acid-crosslinked PBI membranes via a simple acid doping method, which demonstrated unprecedented size-sieving nature due to their much tightened pore structure after crosslinking (Fig. 25) [97]. The resultant membranes obtained an extraordinarily high H_2/CO_2 selectivity of around 140 at 150 °C which was comparable to some state-of-the-art 2D materials.

Figure 24. H_2/CO_2 separation performance of *m*-PBI at low and high temperatures. Reproduced with permission [95]. Copyright 2014, Elsevier Ltd.

Figure 25. The illustrative schematic and H_2/CO_2 separation performance of acid-crosslinked PBI. Reproduced with permission [97]. Copyright 2018, The Royal Society of Chemistry.

2.2.2 Polyimide

The VTEC™ Polyimide (PI) developed and commercialized by RBI during the mid to late 2000s is also an advanced membrane material for efficient H_2/CO_2 separation [98]. Like PBI, the VTEC™ PI also demonstrated superior thermal stability that is able to withstand > 250 °C operating temperatures [89]. Its chemical resistance and mechanical strength at high temperatures are also impressive. The exact chemical structure of VTEC™ PI is not disclosed given proprietary information, but studies found that it possessed very good film-forming property. The precursor polyamic acid solution could be easily cast into films, and after a high temperature treatment process that initiated the condensation reaction, these polyamic acid prepolymer films then turned into the final VTEC™ PI membranes. This is a similar procedure as the production of Kapton® PI films shown in Fig. 26. Nevertheless, despite the facile precursor-facilitated film-forming protocol, the final VTEC™ PI polymers themselves have poor solubility in organic solvents and hence lack solution-processability, which is typical of all chemically and heat-resistant glassy polymers. The H_2/CO_2 separation performance of VTEC™ PI at high temperatures is very attractive. It demonstrates a mixed-gas H_2 permeability of 83

Barrer and a H_2/CO_2 selectivity of around 9 at 250 °C, which in combination well surpasses the 2008 upper bound and is comparable to the *m*-PBI membranes [89].

Figure 26. Film-forming process of Kapton® PI. Reproduced with permission [89].
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2.3 Polymers for Reverse-selective Hydrogen Separations

Given the high intra-segmental mobility and large free volume of rubbery polymers, condensable gases, such as CO_2 and hydrocarbons (HCs), tend to exhibit preferential sorption in them over the light gases [23]. This results in rubbery polymers typically possessing a very high solubility selectivity for CO_2 and HCs that significantly outweighs their diffusivity selectivity for light gases like H_2 . Subsequently, rubbery polymers are often intrinsically more permeable to CO_2 and HCs than H_2 , leading to the reverse-selective membranes, which are also known as H_2 -rejective membranes [2]. Fig. 27 illustrates the difference between size-selective and reverse-selective membrane separations. In addition, the high solubility of CO_2 in rubbery polymers allows CO_2 to occupy the sorption sites in the dense membranes at a faster rate than H_2 via a phenomenon known as competitive sorption, which tends to further enhance the preferential permeation and hence the selectivity of CO_2 under mixed-gas conditions [99]. Despite having rigid backbones, high-free-volume glassy polymers, such as polyacetylenes and PIMs, can be also reverse-selective owing to their possession of large amounts of free volume that acts as sorption sites for condensable gases. For example, PTMSP demonstrates fairly good HCs over H_2 (HCs/ H_2) selectivities [100].

Figure 27. Difference between (a) size-selective and (b) reverse-selective membrane gas separation. Reproduced with permission [23]. Copyright 2013, Elsevier Ltd.

In general, reverse-selective gas separations like CO_2/H_2 and H_2/CO_2 favor low operating temperatures because the solubility of CO_2 could be further enhanced, which is opposite to the H_2/CO_2 separation where a high temperature is desired to reduce the solubility of CO_2 and to enlarge the size-sieving effect [2, 7]. As shown in Fig. 28, the CO_2/H_2 upper bound established based on data from the 2008 Robeson's paper displays an upward-sloping line due to its reverse-(size)-selective nature. In contrast, all other separations that preferentially permeate the smaller gas molecules by either the diffusivity selectivity (e.g. H_2/N_2 , H_2/CH_4) or by the solubility selectivity (e.g. CO_2/N_2 , CO_2/CH_4), have downward-sloping upper bounds. In this case, an upward-sloping line no longer indicates a trade-off relationship between the permeability and selectivity, so the interpretation of CO_2/H_2 separation performance could be made by directly comparing the respective magnitudes of permeability and selectivity between polymers.

Figure 28. H_2/CO_2 and CO_2/H_2 upper bounds. Reproduced with permission [7]. Copyright 2017, American Chemical Society.

2.3.1 Poly(ethylene oxide) for CO₂/H₂ Separation

Poly(ethylene oxides) (PEO), also known as poly(ethylene glycols) (PEG), are the simplest structured member from the rubbery polyether family, which have been widely used for membrane CO₂/H₂ and CO₂/N₂ separations. The general structure of PEO is shown in Fig. 29. The ether moieties form the characteristic structure of PEO and have high affinity for the CO₂ molecules due to their polar interactions [23]. As compared to other interactive moieties including acetates, nitriles and carbonates, polymers containing ether oxygen (EO) atoms were found by Lin and Freeman to exhibit the highest CO₂ solubility and could provide an attractive combination of a CO₂ permeability of 13 *Barrer* and a CO₂/H₂ selectivity of 7.4 when being tested as semi-crystalline pure PEO membranes [101]. Although polar groups in the polymer matrix generally tend to enhance packing due to the stronger interchain interactions which subsequently promote chain crystallization, EO units actually tend to impede the efficient chain packing due to their bent structure and could actually increase the free volume of polymers and the gas diffusivity when they are in an amorphous state [23].

Figure 29. The chemical and matrix structure of PEO. Reproduced with permission [102]. Copyright 2018, Elsevier Ltd.

Nevertheless, despite that a high concentration of EO in the polymer could theoretically improve the permeability for CO₂ by possibly enhancing both its diffusivity and solubility, the high tendency of EO-containing segments to crystallize among themselves

remains a challenge for utilizing pure PEO polymers for practical membrane CO₂/H₂ separation. The polymer matrix of semi-crystalline PEO polymers assumes a structure of impermeable, barrier-like crystals being embedded or dispersed in an amorphous phase that is highly permeable to gases (Fig. 29) [102]. As such, the overall gas permeation through PEO membranes is governed by both the volume of amorphous phase and the tortuosity of transport pathways through the amorphous phase which is strongly influenced by the content of PEO crystallites. Reducing the PEO crystallinity to a hypothetical fully amorphous state could significantly enhance the CO₂ permeability, it is the key to design a highly CO₂-permeable PEO membrane. This has been commonly and effectively achieved by branching and/or crosslinking the PEO chains such that the crystallization tendency could be suppressed. Followed by increasing the EO content in the branched or crosslinked chains, both the diffusivity and solubility of CO₂ could then be enhanced [103]. For example, crosslinked polyether polymers based on a mixture of diacrylate terminated PEG monomers could obtain very attractive CO₂/H₂ separation performance with a CO₂ permeability of 100 *Barrer* and a CO₂/H₂ selectivity of 9.5 obtained at 23 °C and 6.8 bar [104]. Lin et al. developed another crosslinked copolymer network based on a poly(ethylene glycol) methyl ether acrylate (PEGMEA) monomer and a PEG-diacrylate crosslinker, which was entirely amorphous and exhibited an outstanding separation performance with a CO₂ permeability of 420 *Barrer* and a CO₂/H₂ selectivity of 10 [105].

While it is known that the solubility of CO₂ could be enhanced at low temperatures, the crystallization tendency of EO-containing segments also favors low operating temperatures. By suppressing the crystallization tendency of PEOs via crosslinking, the operating temperatures could be reduced to improve the CO₂/H₂ separation performance. The increased sorption and solubility of CO₂ at low temperatures could also result in higher plasticization of polymers by the sorbed CO₂, which swells the interchain spacing, increases the chain mobility and FFV, and eventually enhances the CO₂ diffusivity as well [106]. On top of that, this enhanced plasticization also significantly hampers the diffusivity selectivity of H₂ [107]. Therefore, the combined effect of crosslinking PEOs and operating them at lower temperatures could lead to a tremendous enhancement in CO₂/H₂ separation performance. For example, an extraordinary CO₂/H₂ selectivity of 37 could be achieved by PEGMEA membranes at -20 °C [106].

Despite their promising CO₂/H₂ separation performances, pure PEO or polyether membranes are in general mechanically unstable. A common approach to overcome this weakness is to utilize the versatile chemistry of PEO to copolymerize it with mechanically strong glassy polymers like polyimides and polyamides [108, 109]. Their mechanical properties could be significantly enhanced by the harder and stronger glassy

segments/micro-domains, while the efficient CO₂/H₂ separation still takes place primarily in the CO₂-favored PEO phase.

2.3.2 PTMSP and PDMS for HCs/H₂ or HCs/N₂ Separation

The separation of organic vapors, mainly light paraffins and olefins like C₂₋₄, from hydrogen- or nitrogen-containing streams is important to the refinery industry because of the high value of these minor components. While such separations share similar gas transport characteristics with the separation of H₂ and CO₂ when using polymeric membranes, both of them can proceed via the diffusivity- or solubility-selective mode. The particularly high condensability of light HCs and the high throughput nature of refinery processes suggest that the use of solubility-selective polymers, especially those with a high free volume, is much preferable and could deliver better separation efficiencies. This is because the high-free-volume polymers have ability to achieve more effective preferential sorption of the large and highly condensable HCs over light gases. Common choice of polymers for HCs/H₂ and HCs/N₂ separations include organosilane-based rubbery polymers like PDMS and ultra-high-free-volume glassy polyacetylenes like PTMSP.

Figure 30. The chemical structure of PDMS.

PDMS is among the most permeable rubbery polymers owing to its highly flexible siloxane linkage and the bulky dimethyl siloxane (DMS) side groups (Fig. 30) such that its permeability for C₂₋₄ HCs could be extremely high which is in the order of about 10³ to 10⁴ *Barrer* with good C₂₋₄/H₂ or C₂₋₄/N₂ selectivity [107, 110]. For example, Pinnau et al. reported a C₂H₆ permeability of 3900 *Barrer* and a C₂H₆/H₂ selectivity of 4, and a C₃H₈ permeability of 7400 *Barrer* and a C₃H₈/H₂ selectivity of 7.5 demonstrated by PDMS membranes at 35 °C, which could be further tremendously improved at lower temperatures [107]. Substituting bulkier groups on the side chain or directly on the backbone of PDMS was a common method to alter its transport properties. However, such modifications interestingly tended to decrease the permeability of HCs and increase the size-selectivity of PDMS for H₂ possibly due to the hindered intra-segmental mobility

and enhanced chain rigidity from bulky moieties on the polymer chains, which has been reflected in some studies by the increased T_g of polymers when the bulkiness of substitution increased [28]. Apparently, the HCs/light gas separations do not favor such a structural change.

PTMSP, as a rigid-chain, ultra-high-free-volume glassy polymer, possesses even better C_2+ / H_2 separation performances than PDMS in both the permeability and selectivity for HCs, especially for the relatively larger ones like n-butane [100]. However, the practical use of PTMSP is strongly limited by its weak chemical resistance against aliphatic or aromatic hydrocarbon contaminants in the refinery processes. On the other hand, easily crosslinkable rubbery PDMS exhibits less impressive but still attractive enough performance, while having much more practical chemical resistance against the harsh vapor environments than PTMSP [107].

3. Polymeric Membranes for N_2 Separation

Among the light gases, nitrogen (N_2) is considered as a slow permeating gas due to its relatively large size and low condensability. However, N_2 is one of the most abundant gases encountered in industrial processes which will be commonly mixed with other valuable gases. Therefore, as put forward in the beginning of this chapter, the industrial meaning of N_2 separation, apart from its utilization as pure N_2 gas, lies in the efficient capture of other components in the gas mixture, such as (1) the capture of CO_2 from flue gas of power plants and (2) the recovery of methane (CH_4) from gas streams in petrochemical or refinery processes for natural gas production and purification. Moreover, both CO_2 and CH_4 are greenhouse gases which need to be reduced or captured before releasing the constituting gas streams into the atmosphere. Several polymers which have been vigorously researched for these applications will be discussed in the following sections.

3.1 CO_2/N_2 Separation

The majority of CO_2 emissions are generated by combusting fossil fuels, such as coal and natural gas, to generate electricity in power plants or petrol engines, and the combustion gas products typically contain a moderate to major amount of N_2 at the atmospheric pressure. Therefore, it is of critical importance to capture CO_2 from these gas products to curb the anthropogenic climate change. Both rubbery and glassy membranes can be utilized for CO_2/N_2 separation depending on the transport characteristics required for the separation. Rubbery polymers favor solubility selectivity for CO_2/N_2 separation due to their flexible chains that selectively permeate condensable gas species more easily while glassy polymers are contingent on the diffusivity selectivity due to their more rigid chains

that selectively permeate gas species by size-discrimination. It is also important to note that because of the atmospheric operating pressure which is typically below the onset pressure for CO₂-induced plasticization, the plasticization phenomenon is not a particular issue for glassy polymers when being used for membrane CO₂/N₂ separation. The main challenge for CO₂/N₂ separation is, however, its enormous volume requirement. For example, a typical 600 MWe coal-fired power plant emits 460 tons of CO₂ per hour. It requires not only the use of highly permeable and selective membrane materials but also the fabrication of these materials into useful configurations with a large membrane area at an economically competitive cost [111].

3.1.1 Rubbery Polymers

Considering the differences in the kinetic diameter and condensability which both favor the permeation of CO₂ over N₂ through polymeric membranes, rubbery-type polymers have been widely investigated for the CO₂/N₂ separation targeting CO₂ capture from flue gas. In particular, PEO-based polymers have been regarded as one of the most suitable rubbery membrane materials for this separation owing to the excellent affinity of CO₂ with polyether moieties which increases the solubility of CO₂ and in turn further enhances the permeability of CO₂ and the throughput of the process [111]. Most of the PEO or PEO-containing polymers discussed in Section 2.3.1, which demonstrated promising CO₂/H₂ separation performances, also possessed very attractive CO₂/N₂ separation efficiencies. The chemical structures and CO₂/N₂ separation performances of a number of representative PEO-containing polymeric membranes are shown in Table 8.

To date, the best performing PEO-based membrane was developed by Jiang et al. via the construction of a semi-interpenetrating network (SIPN) by embedding PEGDME into a crosslinked backbone of either PEGMEA, PEGDA or a mixture of both PEGMEA and PEGDA, as provided in Fig. 31 [112]. The SIPN crosslinked PEO-based membranes retained their amorphous structures which thereby enhanced their gas separation performance. Without PEGDME, the crosslinked PEGMEA/PEGDA (7:3) membrane only possessed a CO₂ permeability of 405.7 *Barrer* and a CO₂/N₂ selectivity of 49.8. However, when PEGDME was embedded into the crosslinked PEGMEA/PEGDA (7:3) membranes with the weight percentage of PEGDME being equal to the total weight percentages of PEGMEA and PEGDA, the CO₂ permeability was enhanced to 2980 *Barrer* while the CO₂/N₂ selectivity slightly decreased to 45.7. These unprecedented results further pushed the separation performance of crosslinked PEO membranes to go beyond even the recently updated 2019 upper bound for CO₂/N₂ separation, which will be discussed in a later section.

Table 8. Chemical structures, CO₂ permeability and CO₂/N₂ selectivity of representative PEO-based membranes [111]. Copyright 2016, John Wiley and Sons.

Polymer/monomer	Chemical structure	CO ₂ permeability [Barrer]	CO ₂ /N ₂ selectivity
PEO		12	48
Pebax 1074		120	51
PEO-co-PBT (Polyactive 1000)		71	44
Pebax+PEG-DME (50 wt %)		606	44
Crosslinked poly(ethylene glycol) diacrylate (XLPEGDA)		110	50
Crosslinked poly(ethylene glycol) methyl ether acrylate (XLPEGMEA)		570	41

Figure 31. A schematic illustration and reaction of the fabrication of SIPN crosslinked PEO-based membrane. Reproduced with permission [112]. Copyright 2017, The Royal Society of Chemistry.

3.1.2 Glassy Polymers

The separation of CO₂ from N₂ by glassy polymers, such as polyacetylenes, poly(arylene ether)s, polyimides, and polysulfones, which benefit from the smaller kinetic diameter of CO₂ over N₂, has also been extensively investigated [4]. The main advantage of utilizing glassy polymers instead of rubbery polymers stems from the relatively higher thermal and mechanical stability. However, prior to the invention of PIMs and the introduction of any modifications to the polymer chains, traditional glassy polymers have relatively average separation performance because of their relatively small free volume and often their lack of sufficient CO₂ affinity. For example, 6FDA-durene, a widely studied research polyimide, displays a CO₂ permeability of 456 *Barrer* and a CO₂/N₂ selectivity of 12.8, which translate to an overall CO₂/N₂ separation performance point that falls far below the 2008 upper bound [113]. In order to boost the efficiency of glassy polymers for CO₂/N₂ separation, the CO₂ diffusivity has to be increased by introducing more fractional free volume (FFV) while maintaining or improving the chain stiffness of the polymer backbones so that the CO₂/N₂ selectivity will not be compromised. As a result, both PIMs and thermally rearranged (TR) polymers were invented and extensively explored for CO₂ capture from flue gas [57, 63, 114].

3.1.2.1 Polymers of Intrinsic Microporosity (PIMs)

As discussed in Section 2.1.2.2, PIMs were originally synthesized via the polycondensation reactions of aromatic tetrahydroxy- and tetrafluoro-containing monomers resulting in benzodioxane-bridged ladder structures that are sterically contorted by a spiro-carbon center like the spirobisindane (SBI) unit [58]. As a result of their rigid and contorted backbone structures, PIMs pack their chains highly inefficiently, which gives rise to their high FFV and BET surface area that in turn endow their membranes with a high gas diffusivity and a moderate CO₂/N₂ selectivity (e.g. ~ 25 for PIM-1) [63]. However, extending the contorted spiro-carbon centers by substituting tetrafluoroterephthalonitrile (TFTPN) in PIM-1 with phenazine-containing tetrachlorospirobisindane monomers in PIM-7 lowers the BET surface area of PIM-7 and results in a lower CO₂ diffusivity but a higher CO₂/N₂ diffusivity selectivity [63, 115]. Nevertheless, given their intrinsic microporosity granted by the frustrated chain packing in PIMs, these early PIMs still possess much more attractive CO₂/N₂ separation performance than the traditional glassy polymers. It is important to note that their relatively higher CO₂/N₂ permselectivity stems from their high solubility selectivity for CO₂ over N₂ instead of their diffusivity selectivity [111]. Besides, PIMs possess one of the largest free volumes among known glassy polymers, which allows them to

demonstrate a high CO₂ solubility which, coupled with their high diffusivity, translates to an unusually high CO₂ permeability (in the range of 10³ to 10⁴ *Barrer*).

The high backbone rigidity of PIMs that arises from the presence of a variety of sites of contortion also helps them retain a sufficient size-sieving effect. As a result, numerous ladder PIMs and PIM-PIs have been developed that exhibit promising CO₂/N₂ separation performances, which include many that have been discussed before in Section 2.1.2.2. Recent development of PIMs was concentrated at increasing the chain rigidity to improve the diffusivity selectivity without compromising their CO₂/N₂ selectivity by substituting the SBI contorted structure into the more rigid bridged-bicyclic-ring system, such as the ethanoanthracene (EA), Troger's base (TB) and triptycene (Trip) moieties. Carta et al. demonstrated via molecular modelling that the SBI structure was more flexible than EA and TB [66]. Instead of a direct combination of Trip and TB structures that aims at maximizing the structural contortedness by having as many contortion sites as possible in the backbone, a more distinct innovation was created via the benzodioxane linkage of benzotriptycene (BTrip) moieties, which resulted in unique solution-processable, ribbon-shaped porous 2D polymers, such as PIM-TMN-Trip and PIM-BTrip as shown in Fig. 32 [62, 88]. Because of the highly stiffened BTrip structures and the 2D co-planar arrangement of each BTrip group in the polymer chains, a freshly methanol treated PIM-TMN-Trip membrane could obtain an ultra-high CO₂ permeability of 52,800 *Barrer* which is on par with the most permeable polyacetylene-based membranes, such as PTMSP. Meanwhile, the CO₂/N₂ selectivity of PIM-TMN-Trip (14.9) is also higher than that of PTMSP (10.7) [88]. As a result of this new innovation in PIM design, the upper bound of CO₂/N₂ separation was recently revised by the gas separation performances of several series of BTrip-based PIMs as shown in Fig. 32.

Figure 32. (a) PIM-TMN-Trip chemical structure, (b) two 3D conformational views of PIM-TMN-Trip fragment, and (c) the upper-bound relationships for the CO_2/N_2 gas pair with the recently proposed upper bound shown in a red dotted line and the 2008 upper bound shown in solid blue line. The CO_2/N_2 gas separation performance of BTrip-based PIMs are provided in solid symbols and open symbols indicate the data of other PIMs and non-PIM polymers. (a) and (b) are reproduced with permission [62]. Copyright 2017, Nature Publishing Group. (c) is reproduced with permission [88]. Copyright 2019, The Royal Society of Chemistry.

3.1.2.2 Thermally Rearranged (TR) Polymers

TR polymers are generally derived from *ortho*-functionalized polyimides (*o*-PIs) or polyamides (*o*-PAs) via a solid-state thermal post-treatment process that can generate a rigid and microporous polymer/membrane structure by releasing CO_2 or H_2O depending on the polymer/membrane precursor [114, 116]. As a result, higher free volume membranes can be fabricated with narrowly distributed micropores that are interconnected, which are beneficial to induce rapid diffusion of small gases while maintaining good size-sieving properties [117]. However, conventional TR polymers, which are obtained from *o*-PIs, face serious energy penalty because of their high temperature requirement ($> 400^\circ\text{C}$) for initiating the thermal conversion. On the other hand, *o*-PAs require a lower energy for their thermal conversion which can be attributed to the more flexible secondary amine in the polyamide backbones as compared to the more rigid tertiary amine in polyimides. However, the gas separation performance of *o*-PAs and their corresponding TR polymers are generally lower than that of *o*-PIs and their corresponding TR polymers. Therefore, reducing the energy penalty whilst improving their gas separation performance has become one of the key foci for TR polymer

research. Reducing the glass transition temperature (T_g) of the polymer precursor which subsequently decreases the thermal conversion temperature has been achieved by introducing more flexible macromolecular chains onto the *ortho*-hydroxyl groups, such as acetate, pivalate or allyl ether groups [118, 119]. As compared to the pristine 6FDA-HAB polymers which were also thermally treated at the same temperature (e.g., 350°C), the allyl-functionalized 6FDA-HAB polymers demonstrated a much higher CO₂ permeability at the expense of a slightly lowered CO₂/N₂ selectivity, because of their higher TR conversion ratio at a lower temperature. Similarly, a reduced thermal conversion temperature has also been observed via allylation of *ortho*-hydroxyl polyamides [120].

Figure 33. Thermal rearrangement of (a) *ortho*-functionalized polyimide and (b) *ortho*-functionalized polyamide to generate TR polymers. Reproduced with permission [116]. Copyright 2015, Elsevier Ltd

3.2 N₂/CH₄ Separation

Nitrogen removal from methane in refineries for natural gas purification to meet pipeline specifications is a huge industrial process due to the high nitrogen content in natural gas reserves [121, 122]. However, nitrogen removal from methane has been considered one of the most challenging separation processes by membrane technology owing to the almost similar kinetic diameters and condensability between N₂ and CH₄ (Table 1). In

light of this challenge, there are limited polymer materials that could demonstrate promising separation performance for N₂/CH₄ separation.

Perfluoropolymers are currently the best known material for this application, which have defined the N₂/CH₄ separation upper bound in 2008 and are commercially available under the trade names of Teflon AF, Hyflon AD and Cytop [52, 123, 124]. Among these commercial perfluoropolymers, both Teflon AF and Hyflon AD, which are based on perfluorodioxolane structures, display the best N₂/CH₄ separation performance. Therefore, numerous dioxolane-based perfluoropolymers and copolymers have been recently synthesized, studied and reported to possess N₂/CH₄ separation performance located above the corresponding 2008 upper bound. Yavari et al. reported that poly(perfluoro-2-methylene-4-methyl-1,3-dioxolane) (poly(PFMMD)) membranes obtained an N₂ permeability of 7.7 *Barrer* and a N₂/CH₄ selectivity of 3.85 [125]. Fang et al. copolymerized PFMMD with perfluoro-(2-methylene-1,3-dioxolane) (PFMD) and showed that the 50/50 PFMMD-co-PFMD membranes displayed an extraordinary N₂/CH₄ selectivity of 6 [126]. In addition to the perfluorodioxolane-based polymers, Belov et al. discovered that poly(hexafluoropropylene) (poly(HFP)) membranes could achieve better N₂/CH₄ separation properties than the commercial Hyflon AD80 membranes, although they were still located below the 2008 upper bound [127]. In accordance with these new developments, Wu et al. proposed that there existed a so-called perfluoropolymer upper bound for N₂/CH₄ separation which emphasized the outstanding diffusivity selectivity for N₂ over CH₄ of dioxolane-based perfluoropolymers [128].

4. Material Strategies for Performance and Properties Enhancement

4.1 Grafting

In order to allow a larger degree of control over the gas separation performance of the fabricated membranes, the grafting technique has been widely investigated whereby a specific functional moiety is chemically transferred onto the polymer backbones. Suzuki et al. grafted amine-terminated dimethylsiloxane (DMS) onto poly(styrene-co-maleic anhydride) (poly(St-co-MAH)), which increased the CO₂ permeability tremendously (more than 100-fold), although the CO₂/N₂ selectivity decreased by 44% [129]. This phenomenon was attributed to the larger free volume of the poly(St-co-MAH-graft-DMS) as compared to the pristine poly(St-co-MAH). An increase in free volume of the membranes was also observed when thermally labile macromolecules, for example, cyclodextrins (CDs) and saccharides, were grafted onto 3,5-diaminobenzoic acid (DABA) containing 6FDA-durene-DABA copolyimide backbones [130-132]. The

additional free volume insignificantly altered the CO₂/N₂ separation performance of the fabricated 6FDA-durene/DABA(9:1)-g-CD membranes when the membranes were annealed at 200°C, as provided in Table 9. When the membranes were annealed at 400°C, the CO₂ permeability could be improved by 79% by grafting γ -CD onto the 6FDA-durene/DABA(9:1) copolyimide at the expense of only a 13% reduction in the CO₂/N₂ selectivity, which was ascribed to the formation of micropores because of the decomposed CDs [132]. A similar micropore formation was also observed by thermally decomposing the grafted saccharides (such as glucose, sucrose and raffinose) in the 6FDA-durene/DABA(1:1)-g-saccharide membranes [131]. Therefore, both lower increment in CO₂ permeability and lower reduction in CO₂/N₂ selectivity can be achieved by varying the size of grafted CDs and saccharides in the 6FDA-durene/DABA copolyimides.

Table 9. Summary of the CO₂/N₂ separation performance of grafted polyimide membranes [113, 114]

Membrane	Annealing Temperature (°C)	Permeability (Barrer)		CO ₂ /N ₂ Selectivity
		CO ₂	N ₂	
6FDA-durene-DABA (9:1)	200	235	13.4	17.6
6FDA-durene-DABA (9:1)-g- α CD	200	241	14.5	16.6
6FDA-durene-DABA (9:1)-g- β CD	200	239	14.4	16.6
6FDA-durene-DABA (9:1)-g- γ CD	200	251	15.5	16.3
6FDA-durene-DABA (9:1)	400	520	38.0	13.7
6FDA-durene-DABA (9:1)-g- α CD	400	569	48.5	11.7
6FDA-durene-DABA (9:1)-g- β CD	400	772	62.9	12.3
6FDA-durene-DABA (9:1)-g- γ CD	400	930	77.8	11.9
6FDA-durene-DABA (5:5)	400	366	23.0	16.0
6FDA-durene-DABA (5:5)-g-glucose	400	533	33.7	15.8
6FDA-durene-DABA (5:5)-g-sucrose	400	370	21.7	17.0
6FDA-durene-DABA (5:5)-g-raffinose	400	407	27.8	14.7

4.2 Polymer Chain-Functionalization

Polymer chain-functionalization is commonly utilized to modify the polymer chains prior to the membrane fabrication. For both hydrogen and nitrogen separation, PIM-1 is the most widely functionalized polymer owing to its nitrile (–CN) groups. These reactive nitrile groups can be easily converted into a variety of polar functional groups, including the N- and S- containing ones, such as those in AOPIM-1, TZPIMs and ThioPIM-1, or the hydroxyl or carboxyl groups, such as those in PIM-1-COOH, which all are capable of modifying the polar interaction between the polymers and the permeating CO₂ gases [83-

86]. These polar functional groups are capable of not only inducing higher affinity of CO₂ with the polymers, but also altering the packing density of the polymer chains in the membranes, which can consequently tune the gas separation performance. Mason et al. showed that reducing the nitrile groups into amine groups enhanced both CO₂ sorption uptake and the ideal CO₂/N₂ sorption/solubility selectivity [133]. However, the amine groups also introduced the formation of inter- and intra-chain hydrogen bonds which imparted additional chain stiffness to the polymer network in the membrane. As a result, amine-PIM-1 was H₂-selective instead of CO₂-selective as compared to other functionalized PIM-1, and the ethanol-treated membrane demonstrated H₂/CO₂ separation performance above the Robeson 2008 upper bound. On the other hand, TZPIM-1 exhibited the highest CO₂ permeability, while AOPIM-1 displayed the highest ideal CO₂/N₂ selectivity among the functionalized PIM-1 membranes [83]. Further methylation of TZPIM-1 (referred to as MTZ100PIM-1) had also been investigated by Du et al. [134]. It improved the processability, solubility in polar protic and aprotic solvents and thermal stability of TZPIM-1, and the resultant MTZ100PIM-1 had lower CO₂ permeability and CO₂/N₂ selectivity than TZPIM-1.

4.3 Crosslinking

Crosslinking is considered as a common post-treatment on polymeric membranes to enhance their gas separation performance, particularly to improve their diffusivity selectivity or molecular-sieving properties. In addition, crosslinking is also widely employed as a method to improve the stability of the membranes, especially to mitigate the plasticization phenomenon often observed in separations involving highly condensable gases at high operating pressures. Generally, there are three crosslinking methods which vary by the source for bond formation or cleavage during the crosslinking reaction; namely, chemical, thermal and UV (also known as photo-oxidative) crosslinking.

4.3.1 Chemical Crosslinking

Diamine crosslinking is a very popular chemical crosslinking method which was originally patented by Hayes in 1989 to improve the O₂/N₂ separation performance of polyimide membranes [135]. About a decade later in 2001, Liu et al. cross-linked the 6FDA-durene membranes with *p*-xylenediamine (*p*XDA) in methanol solutions to enhance He/N₂ selectivity by more than 8-fold, which was the first reported literature of diamine crosslinking with polyimide membranes [136]. A wide variety of diamine molecules has thereafter been utilized to tune the molecular-sieving properties of polyimide membranes, particularly for H₂/CO₂, H₂/N₂, H₂/CH₄ and, in certain cases, CO₂/N₂ and CO₂/H₂ separation [137]. Yong et al. showed that by changing the molecular

structures of the diamine molecules, the gas separation performance of PIM-1/Matrimid (90:10) polymeric blending membranes could be tuned from CO₂-selective into H₂-selective, which depended on not only the reactivity but also the spatial structure of the diamine molecules [138]. Meanwhile, Zhao et al. demonstrated that H₂-selective Matrimid® membranes could be modified into CO₂-selective membranes by crosslinking Matrimid® with diamino-based polymers, such as Jeffamine® or O,O'-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol [139]. On one hand, diamine crosslinking generally enhanced the gas separation performance by decreasing the diffusivity of gases and increasing the molecular-sieving properties because of the tightened interchain spacing of the membranes. On the other hand, when being crosslinked with Jeffamine, the Matrimid® membranes exhibited both higher CO₂ permeability and CO₂/N₂ and CO₂/H₂ selectivities despite their tightened interchain spacing. This was ascribed to the rubbery nature of Jeffamine or the PEO-containing phase that commonly exhibits small *d*-spacings [140] but possesses mobile polymer chains to allow easy gas passages.

Although diamine crosslinking has been proven effective in enhancing the gas transport properties of polyimide membranes, the polyamide network generated by the crosslinking process could possibly revert back to its corresponding polyimide network at elevated temperatures depending on the combination of the polymer and the diamine molecule [141]. The release of diamine molecules and the polymer chain scission have also been observed when the reverse-imidization of the polyamide network occurred [142, 143]. Besides, the polymer chain scission issue could also occur in the conventional solution-phase diamine crosslinking [144], which consequently inspired the development of vapor-phase crosslinking method by Shao et al. to minimize such issue [145]. The advantages of vapor-phase crosslinking were further reported by Wang et al. when they crosslinked 6FDA-durene membranes with diethylenetriamine (DETA) [146]. The vapor-phase crosslinked membrane exhibited a much higher increment of H₂/CO₂ selectivity (130-fold) than the solution-phase one (13-fold) albeit its lower gel content. Japip et al. demonstrated that the vapor-phase crosslinking of 6FDA-durene-ZIF71 mixed matrix membranes (MMMs) by tris(2-aminoethyl)amine (TAEA) could significantly improve the H₂/CO₂ separation performance as compared to the TAEA-crosslinked pristine 6FDA-durene membrane because of the additional crosslinked network formed at the interface between the polyimide matrix and ZIF-71 nanoparticles [147]. Meanwhile, the *in-situ* free volume, gas permeability and diffusivity measurements of the crosslinked membranes at 150 °C revealed the thermal motion of the crosslinked network and also its dependency on the molecular structure of the di/triamine crosslinkers [148]. A larger tri-podal crosslinker (TAEA) displayed superior H₂/CO₂ separation performance at lower

temperatures (e.g. 35 °C), while a shorter di-podal crosslinker (EDA) presented superior H₂/CO₂ separation performance at higher temperatures (150 °C) because of the restricted thermal motion owing to its shorter chain length.

Diol crosslinking is an alternative chemical crosslinking strategy, but is limited to polymers containing carboxylic acid or sulfonic acid groups only [137]. As opposed to diamine crosslinking, diol crosslinking has been generally reported not to reduce the gas permeability. Instead, gas permeabilities generally tend to increase on polyimide membranes after diol crosslinking. Staudt-Bickel and Koros showed that 6FDA-mPD/DABA copolyimide crosslinked with ethylene glycol displayed higher CO₂ permeability and CO₂/N₂ selectivity by 45% and 35%, respectively, owing to the increased free volume because of the insertion of ethylene glycol [149]. However, if the uncrosslinked polymer membrane has a particularly large free volume because of its loose packing structure, the gas permeabilities would still decrease notwithstanding the improved selectivity. Zhang et al. demonstrated that crosslinking PIM-TB copolymers that contained carboxylic acid groups (CoPIM-TB) with glycidol could reduce the permeability of all light gases due to the tightened *d*-spacing. As a result, the selectivity for a number of gas pairs, such as CO₂/N₂ and H₂/N₂, was greatly enhanced [150].

4.3.2 Thermal Crosslinking

Thermal crosslinking can be considered as one of the oldest methods to improve gas separation performance and the stability of polymeric membranes. Diacetylene and benzenecyclobutane groups are two of the earliest molecular structures utilized to generate thermally crosslinked membranes with improved gas separation performance [151-153]. In 2008, Kratochvil and Koros presented a new thermal crosslinking technique for carboxylic acid containing polyimides by decarboxylation of the acid pendant groups at high temperatures [154]. Similar to the diol crosslinking, the decarboxylation-induced thermal crosslinking increased the *d*-spacing which consequently enhanced the gas permeability [155-157]. More specifically, the increased *d*-spacing originated from the breaking of hydrogen bonding and the subsequent formation of anhydride intermediate during the thermal annealing process. However, during the decarboxylation step which formed phenyl radicals, the resultant *d*-spacing would be determined by the original polymer structure and free volume. Zhang et al. demonstrated that 6FDA-CADA1 (CADA1 refers to 2-(3,6-bis(4-amino-2-(trifluoromethyl) phenoxy)-9H-xanthen-9-yl) benzoic acid) polymers displayed an increasing *d*-spacing trend upon thermal crosslinking even after the temperature (425 °C) was above their *T_g* [156]. In contrast, both Askari et al. and Xiao et al. reported that the *d*-spacing of 6FDA-Durene/DABA polymers esterified with CDs increased as a function of

annealing temperature up to 400 °C, but the *d*-spacing decreased when the membranes were heated at 425 °C, as schematically drawn in **Error! Reference source not found.** [130, 132]. A similar decarboxylation-induced thermal crosslinking modification was also observed for DC-PIM-1 (DC refers to decarboxylated) to increase CO₂ permeability and CO₂/N₂ selectivity when being compared to its non-thermally-crosslinked counterpart cPIM-1 [84, 158].

Figure 34. Schematic evolution of polyimides bearing pendant carboxylic acid groups through grafting with CDs and thermal crosslinking process. Reproduced with permission [130]. Copyright 2011, The Royal Society of Chemistry.

During the thermal crosslinking process, an inert environment (i.e., vacuum or nitrogen atmosphere) is typically used to minimize the effect of oxygen which may accelerate the degradation of polymer chains. Nonetheless, Song et al. introduced thermal oxidative crosslinking on PIM-1 membranes (TOX-PIM-1) with improved molecular-sieving properties at the expense of gas permeability [159]. The reduced gas permeability was attributed to the reduced ultramicroporosity upon thermal oxidative crosslinking due to the narrower bottleneck of the interconnected micropores. In contrast to the high free volume PIM-1, Zhang et al. demonstrated that it was possible to enhance both gas permeability and selectivity of a lower free volume cardo-polyimide containing the phenolphthalein structure via thermal oxidative crosslinking [160]. The *d*-spacing was increased as a function of the crosslinking temperature.

4.3.3 UV Crosslinking

UV/photo-induced crosslinking of polymers containing benzophenone units is the most well-known classic organic photochemistry reaction which takes place via radical coupling after the hydrogen removal from benzylic hydrogen donor groups by an excited benzophenone unit [161]. One of the first reports on UV crosslinking which could enhance the gas separation performance of polyimide membranes was found in the patent

by R.A. Hayes [162]. Afterwards, Kita et al. demonstrated the enhanced selectivity with a reduced gas permeability as a function of UV irradiation time on polyimide membranes based on benzophenone tetracarboxylic dianhydride (BTDA) and 2,4-diaminomesitylene (DAM) [163]. Because of the radical coupling that results in a bond formation, UV crosslinking reduces the diffusivity coefficients of the permeating gases and is more effective in improving the selectivity for gas pairs that features a relatively big size difference such as the H_2/CH_4 separation. Besides polyimide, polyarylate and polyaryletherketone, which both possess benzophenone groups, can also be crosslinked via UV irradiation [164-166]. However, polyarylate polymers that contain aromatic esters and a free *ortho* or *para* position next to the ester moiety may undergo the photo-Fries rearrangement instead of crosslinking. Meanwhile, polyimide membranes, which do not contain benzophenone groups, will not undergo UV crosslinking. Rather, they experience densification as a result of photo-oxidative chain scission of the polymers [167-169]. Nevertheless, the photo-oxidative effect is generally not as significant for polymers with low free volumes as for those with high free volumes such as PIMs.

4.4 Thin-film Composite (TFC) Membranes

Practical membrane configurations usually consist of a thin selective layer on top of a porous mechanically stable support to improve the throughput (flux) of membranes for gas separation. There are in general two different practical membrane configurations, i.e., integrally skinned asymmetric membranes made from a single polymer and thin film composite (TFC) membranes made from a combination of different polymers [170]. Because of the additional polymeric materials used in TFC membranes, they provide a higher degree of control over the gas separation performance. In addition, it becomes now possible to utilize a highly crosslinked polymer which may not be soluble after its polymerization reaction, via a bottom-up approach, thereby broadening the material selection. In contrast, a more general top-down approach uses the soluble or solution-processable polymers which are coated onto a porous substrate to create the desired TFC membranes. While the gas separation properties of TFC membranes are mostly constrained by the polymers chosen as the selective layer, the presence of an intermediate gutter layer and/or a sealing layer and the structural properties of the porous support will also inadvertently influence the overall separation properties [171].

One of the bottom-up methods to fabricate TFC membranes is based on the interfacial polymerization (IP) technique which takes place on the interface of two immiscible liquids such as water and oil. Jimenez-Solomon et al. reported the synthesis of highly crosslinked polyarylates (PAR) TFC membranes via the interfacial reaction between aqueous phenoxide and trimesoylchloride (TMC) in the hexane solution, as illustrated in

Fig. 35 [172]. Because of the ultra-thinness of the highly crosslinked PAR nanofilms, the permeation of small gas molecules such as He and H₂ was not affected by the contorted molecular structures. In contrast, the degree of contortion in PAR nanofilms exerts a greater effect on the permeation of larger gas molecules such as N₂ and CH₄. Thus, the molecular-sieving properties for hydrogen purification could be enhanced by increasing the degree of contortion as observed in PAR-RES (resorcinol) nanofilms. In addition to PAR, TFC membranes made of polyamide (PA) or hybrid inorganic-organic PI have demonstrated outstanding hydrogen purification performances [173, 174].

Figure 35. The fabrication method of PAR TFC membranes (a) chemical reaction and monomers, (b) schematic interfacial polymerization, and (c) SEM image of a representative PAR-RES TFC membrane. Reproduced with permission [172]. Copyright 2016, Nature Publishing Group.

4.5 Mixed Matrix Membranes (MMMs)

Among the many advanced membrane modification methods, incorporating inorganic, organic or hybrid nanoparticles/nanomaterials (NPs/NMs) into the polymer matrix gains phenomenal popularity among the membrane community, especially for gas separation [175]. Such strategy utilizes the unique topologies, sub-nanometer molecular-sieving pores (targeting the diffusivity selectivity) or special functionalities (targeting the

solubility selectivity) of the incorporated NPs/NMs to potentially enhance the overall gas transport properties of the composite membrane materials. This membrane design is widely known as the mixed matrix membranes (MMMs) which are capable of simultaneously harnessing the polymer processability and tapping the superior gas separation properties of nano-fillers for overcoming the inherent trade-off limitation on polymeric membranes [7].

Figure 36. Illustration of MMM structure

As shown in the illustrative diagram in Fig. 36, the MMM structure is characterized by the discrete nano-filler phase dispersed within a continuous polymer phase/matrix. Ever since the pioneering work on the first MMM fabricated by silicone rubbers being incorporated with zeolite 5A in the 1970s by Paul and Kemp et al., there have been a substantial number of filler choices being extensively studied during the following few decades, such as zeolites, activated carbons, carbon molecular sieves, metal oxides, mesoporous silica, carbon nanotubes and polyhedral oligomeric silsesquioxane (POSS), which are generally considered as the early conventional fillers [175, 176].

The central challenge encountered in designing MMMs is the formation of nano-defects at the polymer-filler interface, which could significantly shoot up the permeability but deteriorate the selectivity to an unusable level, due to the poor compatibility or interaction between polymers and fillers [8]. Common strategies deployed to solve this issue are to strengthen the interfacial interaction between the filler and polymer by modifying the polymer functionalities or the filler surface in order to improve their adhesion [7, 177, 178]. The success of MMM design also depends on the choice of polymer as well as the particle size and dispersion because both the intrinsic gas transport properties of the polymer and the size-dependent dispersibility of fillers can play a critical role in determining the resultant composite properties [179].

4.5.1 Advanced Filler Choices

The poor interfacial problem in early MMMs arose from the strong inorganic nature of early fillers as well as their limited tunability in size, shape, morphology or functionality. A variety of new hybrid or organic nanomaterials with intrinsic porosity, tunable 2D/3D architect and better polymer interactions, such as metal organic frameworks (MOFs), covalent organic frameworks (COFs), porous organic cages (POCs) and organic macrocyclic molecules (OMMs), have been substantially explored as more advanced fillers for MMM designs and have created MMMs with much better gas transport characteristics that could surpass the trade-off limitations.

4.5.1.1 Metal Organic Frameworks (MOFs)

MOFs were first incorporated into polymeric membranes for gas separation in 2004 and have since gained explosive popularity because the highly tunable properties, outstanding gas transport characteristics as well as much improved interfacial interactions demonstrated by MOF-incorporated membranes simply presented a major breakthrough in the MMM research. MOFs are porous hybrid materials possessing three- or two-dimensional (3D or 2D) porous networks of transition metal complexes [180]. Owing to the abundance of transition metal nodes and the functionalizability of the polytopic organic linkers, MOFs are considered a powerful toolbox to design MMMs with improved polymer-fillers compatibility and ultimately gas separation performance. Among thousands of MOFs synthesized to date, zeolitic imidazolate frameworks (ZIFs), Cu-based MOFs, MOF-74, Materials Institute Lavoisier (MIL), and University of Oslo-66 (UiO-66) series are the most typical series of MOFs utilized for fabricating MMMs for gas separation. Depending on the applications or types of gases to be separated, a judicious selection of MOFs is required mainly based on their aperture size, functional groups of the polytopic organic linkers and the transition metal nodes. This would lead to MMM designs with either enhanced diffusivity or solubility in addition to having better dispersion of fillers with superior polymer-filler interactions [181, 182].

Spatial distribution of the embedded MOFs with micro-, 3D nano- or 2D nano-crystals/sheets inside the polymer matrices is another important aspect to fabricate MMMs with an enhanced separation performance. Rodenas et al. utilized a tomographic focused-ion-beam scanning electron microscope (FIB-SEM) to prove the better spatial occupancy of 2D nano-sheets Cu-based MOFs (CuBDC) inside the Matrimid® matrix than their 3D nano- and micro-crystals, as shown in Fig. 37 [183]. Subsequently, MMMs embedded with 2D nano-sheets demonstrated a superior selectivity owing to the improved interaction of gas molecules with CuBDC nano-sheets that resulted in an enhanced molecular-sieving capability. Meanwhile, Kang et al. verified this observation

using another Cu-based MOF ($[\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n$) and discovered that MMMs containing 2D nano-sheets showed the best H_2/CO_2 separation performance among all of their prepared MMMs including those containing 3D micro- and nano-crystals [184].

Figure 37. Spatial occupancy of 8 wt% CuBDC (a) 2D nano-sheets, (b) 3D nano-crystals, and (c) 3D sub-micrometer crystals in Matrimid® 5218 MMMs from 3D surface-rendered view of the segmented FIB-SEM tomograms. Reproduced with permission [183]. Copyright 2015, Nature Publishing Group.

4.5.1.2 Covalent Organic Frameworks (COFs)

COFs were first discovered in 2005 and only found its applicability as an MMM filler choice very recently [185]. They comprise purely organic building blocks joined together by covalent bonds and possess a rigid 2D or 3D extended structure with a high surface area, widely tunable chemistry and pore structure, and excellent affinity for organic polymers [181]. As an emerging filler choice, the first COF-incorporated MMM (Fig. 38) for gas separation application was developed in 2016 by Kang et al. using exfoliated water-stable, 2D COF-sheets, which obtained much higher H_2/CO_2 separation performance arising from the favorable gas transport characteristics of 2D COF and the good polymer-filler compatibility [186]. Following the success of Kang's work, Biswal et al. later also prepared two 2D-COF-incorporated MMMs based on a tert-butylpolybenzimidazole (PBI-BuI) polymer matrix which displayed good mechanical and gas transport properties [187].

Figure 38. Illustration of gas transport through 2D COF-sheets (NUS-2 and NUS-3) and their simulated crystal structures. Reproduced with permission [186]. Copyright 2016, American Chemical Society.

4.5.1.3 Porous Organic Cages (POCs)

POCs are a relatively new class of nanomaterials first created in 2009 [188]. Like COFs, POCs are also completely organically built, but instead of having an extended framework-type structure, POCs exhibit a confined, molecular structure that also has highly tunable pore architectures and diverse choices of functionalities [181]. POCs possess excellent solubility in a variety of common solvents, making them a versatile filler choice for fabricating MMMs via the standard solution-mixing procedure. The pioneering POC-based MMM work using the classic CC3 cage molecules (Fig. 39) was not successful in realizing superior gas separation performance due to the high crystallization tendency of the dissolved CC3 cages during and after solvent evaporation [188, 189]. Later, Zhu et al. synthesized a new POC structure, called ASPOC, that had less stronger inter-cage interactions and hence better solubility in solvents and interactions with polymers, such that more homogeneously blended Matrimid®-based MMMs were obtained with greatly enhanced CO₂/N₂ performance [190].

Figure 39. The molecular structure of CC3 cage used in GS MMMs. Reproduced with permission [189]. Copyright 2013, John Wiley & Sons.

4.5.1.4 Organic Macrocyclic Molecules (OMMs)

OMMs, such as cyclodextrins (CD) or calixarenes (CA), are an interesting class of supramolecules that have been discovered for a long time and have found many good applications in analytical chemistry, host-guest recognition, and biochemistry [191]. They generally possess a unique 3D molecular structure with a single open cavity that varies in size and rim functionalities. These cavities in OMMs could possibly act as either ultra-permeable or highly size-sieving gas transport channels for enhancing the separation performance, but such an idea is still quite underexplored at present. Despite showing interesting gas sorption properties, the application of OMMs in gas separation is relatively much rarer as compared to other fillers choices as mentioned before. Liu et al. incorporated β -CD into PIM-1 polymers via a copolymerization scheme to develop a series of PIM-CD membranes (Fig. 40) which achieved significantly enhanced H_2 and CO_2 permeabilities without sacrificing the selectivity, surpassing the 2008 upper bounds for H_2/N_2 , H_2/CH_4 and CO_2/N_2 separations at only small loadings of β -CD [192]. However, the β -CD pore size was too large to maintain the selectivity at higher loadings. Wu et al. later prepared a series of 4-tert-butylcalix[4]arene (CA)-incorporated PIM-1 membranes (PIM-CA) using a similar copolymerization scheme (Fig. 41). As the size of CA4 was much smaller than CD and fell within the range of gas molecule sizes, their PIM-CA membranes were able to achieve a much higher selectivity at higher loadings and hence demonstrated greatly enhanced gas separation performances, especially for CO_2/N_2 , which were well beyond the 2008 upper bounds [193]. CA molecules were also found capable of favorably tuning the polymer structure towards more efficient gas

transport due to their rigid cup-shape conformation and their possession of bulky t-butyl pendant groups.

Figure 40. Illustration of the synthesis and polymer structure of PIM-CD copolymers. Reproduced with permission [192]. Copyright 2017, Elsevier Ltd.

Figure 41. Illustration of the synthesis and polymer structure of PIM-CA copolymers. Reproduced with permission [193]. Copyright 2018, John Wiley & Sons.

In a very recent study by Wu et al., an unconventional post-fabrication infiltration method for incorporating OMMs into MMMs after the dense polymer films have been

formed was proposed. It enabled the infiltration of a water-soluble member of CA, 4-sulfocalix[4]arene (SCA4) into already fabricated dense membranes (Fig. 42) [194]. The post-fabrication infiltration method sidestepped the problem of interfacial nano-defects or filler agglomeration tendency, while the SCA4 molecules could also act as strongly size-sieving molecular gatekeepers that drastically boosted the H_2/N_2 and H_2/CH_4 separation performance of the membrane. Just like framework-type fillers, OMMs also possess high tunability on their cavity size, functionality and physical properties.

4.3.1.5 2D Nanosheets

2D nanosheets have also attracted growing attention as an efficient MMM filler. 2D nanomaterials, such as graphene oxide (GO) sheets, 2D MOFs, and 2D COFs, generally have large aspect ratios and exhibit outstanding size-sieving capability using their sub-nano-sized interlayer spacing [184, 186, 195, 196]. The presence of large aspect ratios results in 2D nanosheets in the polymer matrix with a higher tortuosity for gas transport. This favors the passage of smaller gas molecules over bulkier ones and further enhances the size-selectivity. In addition to the interlayer spacing, surface pores/defects can be created on the nanosheets that act as angstrom-level, size-sieving openings in connection with the interlayer spacing so as to further enhance the overall size-selective effect. For example, thermally reduced GO (rGO) nanosheets could possess size-sieving surface defects due to the removal of thermally labile O-containing functionalities on the nanosheets. Similarly, 2D COF-sheets could possess large and highly permeable intrinsic surface pores arising from their porous architectures [197, 198].

Figure 42. Illustration of SCA4 molecules acting as gatekeepers inside microporous membranes via the PFI method. Reproduced with permission [194]. Copyright 2020, The Royal Society of Chemistry.

4.5.2 Thin-film Nanocomposite (TFN) Membranes

The emergence of finely sized, highly polymer-compatible and easily dispersible organic or hybrid fillers prompts the advancement of TFC membranes into thin-film nanocomposite (TFN) membranes [199, 200]. The key characteristic of the TFN membranes is that their ultra-thin selective layer is incorporated with high-performance, functional nanofillers (i.e., the selective layer is an MMM) such that their gas separation could be greatly enhanced while only a small amount of nanomaterials is consumed due to the ultra-thinness of the selective layer. An illustrative diagram of TFN membranes was shown in Fig. 43. The size and interfacial chemistry of the nanofillers are critical to the successful design of TFN membranes because the minimal thinness as well as the mechanical stability are determined by these factors.

Figure 43. Illustration of TFN membrane structure. Reproduced with permission [175]. Copyright 2007, Elsevier Ltd.

5. Summary

H₂- and N₂-related gas separations are of paramount importance to the ongoing clean energy and environmental development. Great promises of practical applications have been found in polymeric membranes given their high energy-efficiency, small footprint and ease of operation. Since their first successful commercial implementation in the 1970s, polymeric membranes have been playing a growing role in the GS industry, especially when an increasing number of new gas pairs to be separated are being put on the table.

Early successes have been witnessed on relatively simpler separations that involved primarily a size-discrimination process, such as H₂/N₂ and H₂/CH₄ separations, and quite a number of commercially viable polymeric membrane products have been developed over the past several decades. Despite the inherent trade-off relationship between the permeability and selectivity of polymeric membranes, with the advent of the ultra-

efficient new generation of intrinsically microporous polymers, like PIMs and PIM-PIs, these limits have been constantly transcended or prompted for updates. As such, the use of polymeric membranes for these so-called straightforward separations is gaining a greater competitive edge over the traditional thermally driven, energy-intensive technologies. While these new-generation polymers indeed produce undeniably extraordinary performances for not only hydrogen separations but also other gas separations, the physical aging problem which gradually deteriorates the gas permeability with time remains a key challenge against their applicability for actual industrial processes. Nevertheless, with more studies and research efforts being devoted to overcome this constraint, the membrane community are accumulating more and more tools and strategies against the aging problem, including, but not limited to, controlled crosslinking, advanced thermal treatment, and the incorporation of functional nanomaterials

On the other hand, when dealing with the more challenging gas separations that involve condensable species, which present a fast-growing market of gas separation these days due to the rising industrial demand for CO₂ capture and hydrocarbon treatment/recycling/separation, the membrane design could be much more complicated and the gas transport properties and the commercial practicality of the resultant polymeric membranes are less predictable. For instance, in such separations, the final gas transport properties of membranes are often a result of the competition between the size-selectivity and the solubility selectivity of the polymers. Therefore, a good membrane design not only needs to consider the diffusivity-related factors, such as FFV and chain rigidity, but also solubility-related ones, such as affinities and polar functionalities. Besides, the plasticization effect induced by condensable gases which severely compromises the separation efficiency and possibly mechanical stability of polymeric membranes remains a critical issue yet to be satisfactorily addressed. This is especially true for very thin polymeric films (either in flat or HFM mode) which are the most preferred but also the most plasticization-affected membrane configuration. While in this chapter a variety of polymeric membrane materials have been extensively discussed largely on their gas separation performances, in the actual design of polymeric membranes involving condensable gases, their intrinsic separation performance needs to be always considered in conjunction with their durability against the strongly plasticizing environment. This multifaceted design principle is also the future direction for new polymer development that aims at delivering easily processable, high-performance, and aging- and plasticization-resistant membranes.

Apart from designing new polymer backbones, the advent of the mixed matrix membrane (MMM) concept also opens a new door to gas separation membrane design given its high

versatility and the virtually countless filler choices. Many of which have already demonstrated extraordinary composite properties previously unperceived in the neat polymers. With the development of thin film nanocomposite (TFN) membranes, the community has been one big step closer to the eventual commercial use of MMMs for actual industrial processes which could be another effective catalyst that will speed up the takeover of the gas separation industry by membrane technology.

References

- [1] J.D. Perry, K. Nagai, W.J. Koros, Polymer membranes for hydrogen separations, *MRS Bull.*, 31 (2006) 745-749. <https://doi.org/10.1557/mrs2006.187>
- [2] N.W. Ockwig, T.M. Nenoff, Membranes for hydrogen separation, *Chem. Rev.*, 107 (2007) 4078-4110. <https://doi.org/10.1021/cr0501792>
- [3] X. Huang, H. Yao, Z. Cheng, Hydrogen separation membranes of polymeric materials, in: Y.-P. Chen, S. Bashir, J.L. Liu (Eds.) *Nanostructured Materials for Next-Generation Energy Storage and Conversion: Hydrogen Production, Storage, and Utilization*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2017, pp. 85-116. https://doi.org/10.1007/978-3-662-53514-1_3
- [4] C.E. Powell, G.G. Qiao, Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases, *J. Membr. Sci.*, 279 (2006) 1-49. <https://doi.org/10.1016/j.memsci.2005.12.062>
- [5] M.A. Carreon, Molecular sieve membranes for N₂/CH₄ separation, *J. Mater. Res.*, 33 (2018) 32-43. <https://doi.org/10.1557/jmr.2017.297>
- [6] L. Liu, A. Chakma, X. Feng, D. Lawless, Separation of VOCs from N₂ using poly(ether block amide) membranes, *Can. J. Chem. Eng.*, 87 (2009) 456-465. <https://doi.org/10.1002/cjce.20181>
- [7] M. Galizia, W.S. Chi, Z.P. Smith, T.C. Merkel, R.W. Baker, B.D. Freeman, 50th anniversary perspective: Polymers and mixed matrix membranes for gas and vapor separation: A review and prospective opportunities, *Macromolecules*, 50 (2017) 7809-7843. <https://doi.org/10.1021/acs.macromol.7b01718>
- [8] P. Bernardo, E. Drioli, G. Golemme, Membrane gas separation: A review/state of the art, *Ind. Eng. Chem. Res.*, 48 (2009) 4638-4663. <https://doi.org/10.1021/ie8019032>
- [9] (a) S. Loeb, S. Sourirajan, Sea water demineralization by means of an osmotic membrane, in: R.F. Gould (Ed.) *Saline Water Conversion—II*, American Chemical Society, Washington, D.C., 1963, pp. 117-132; <https://doi.org/10.1021/ba-1963->

- 0038.ch009 (b) A. Giwa, M. Ahmed, S.W. Hasan, Polymers for membrane filtration in water purification, in: R. Das (Ed.), *Polymeric Materials for Clean Water*, Springer, Cham, 2019, pp. 167-190. https://doi.org/10.1007/978-3-030-00743-0_8
- [10] Y. Wang, X. Ma, B.S. Ghanem, F. Alghunaimi, I. Pinnau, Y. Han, Polymers of intrinsic microporosity for energy-intensive membrane-based gas separations, *Mater. Today Nano*, 3 (2018) 69-95. <https://doi.org/10.1016/j.mtnano.2018.11.003>
- [11] A.F. Ismail, K.C. Khulbe, T. Matsuura, Fundamentals of gas permeation through membranes, in: *Gas Separation Membranes: Polymeric and Inorganic*, Springer International Publishing, Cham, 2015, pp. 11-35. https://doi.org/10.1007/978-3-319-01095-3_2
- [12] R.J. Gardner, R.A. Crane, J.F. Hannan, Hollow fiber permeator for separating gases, *Chem. Eng. Prog.*, 73 (1977) 76-78.
- [13] R.R. Zolandz, G.K. Fleming, Gas permeation applications, in: W.S.W. Ho, K.K. Sirkar (Eds.) *Membrane Handbook*, Chapman and Hall, New York, 1992, pp. 78. https://doi.org/10.1007/978-1-4615-3548-5_5
- [14] J.M.S. Henis, M.K. Tripodi, Multicomponent membranes for gas separations, U.S. Patent 4,230,463A, 1980
- [15] W.J. Schell, C.D. Houston, Spiral-wound permeators for purifications and recovery, *Chem. Eng. Prog.*, 78 (1982).
- [16] B. Zornoza, C. Casado, A. Navajas, Advances in hydrogen separation and purification with membrane technology, in: L.M. Gandía, G. Arzamendi, P.M. Diéguez (Eds.) *Renewable Hydrogen Technologies*, Elsevier, Amsterdam, 2013, pp. 245-268. <https://doi.org/10.1016/B978-0-444-56352-1.00011-8>
- [17] H. Makino, Y. Kusuki, H. Yoshida, A. Nakamaura, Process for preparing aromatic polyimide semipermeable membranes, U.S. Patent 4,378,324, 1983
- [18] P. Luis, T. Van Gerven, B. Van der Bruggen, Recent developments in membrane-based technologies for CO₂ capture, *Prog. Energy Combust. Sci.*, 38 (2012) 419-448. <https://doi.org/10.1016/j.pecs.2012.01.004>
- [19] S. Adhikari, S. Fernando, Hydrogen membrane separation techniques, *Ind. Eng. Chem. Res.*, 45 (2006) 875-881. <https://doi.org/10.1021/ie050644l>
- [20] M. Mulder, Membrane processes, in: M. Mulder (Ed.) *Basic Principles of Membrane Technology*, Springer Netherlands, Dordrecht, 1991, pp. 198-280. https://doi.org/10.1007/978-94-017-0835-7_6

- [21] J.G. Wijmans, R.W. Baker, The solution-diffusion model: A review, *J. Membr. Sci.*, 107 (1995) 1-21. [https://doi.org/10.1016/0376-7388\(95\)00102-I](https://doi.org/10.1016/0376-7388(95)00102-I)
- [22] S. Matteucci, Y. Yampolskii, B.D. Freeman, I. Pinnau, Transport of gases and vapors in glassy and rubbery polymers, in: Y. Yampolskii, B.D. Freeman, I. Pinnau (Eds.) *Materials Science of Membranes for Gas and Vapor Separation*, John Wiley & Sons, Chichester, 2006, pp. 1-47. <https://doi.org/10.1002/047002903X.ch1>
- [23] C.H. Lau, P. Li, F.Y. Li, T.S. Chung, D.R. Paul, Reverse-selective polymeric membranes for gas separations, *Prog. Polym. Sci.*, 38 (2013) 740-766. <https://doi.org/10.1016/j.progpolymsci.2012.09.006>
- [24] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.*, 62 (1991) 165-185. [https://doi.org/10.1016/0376-7388\(91\)80060-J](https://doi.org/10.1016/0376-7388(91)80060-J)
- [25] B.D. Freeman, Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes, *Macromolecules*, 32 (1999) 375-380. <https://doi.org/10.1021/ma9814548>
- [26] C.F. Tien, A.C. Savoca, A.D. Surnamer, M. Langsam, Chemical structure/permeation relationship for polysilylpropynes, *Polym. Mater. Sci. Eng. Prepr.*, 61 (1989) 507-511.
- [27] Y. Alqaheem, A. Alomair, M. Vinoba, A. Pérez, Polymeric gas-separation membranes for petroleum refining, *Int. J. Polym. Sci.*, 2017 (2017). <https://doi.org/10.1155/2017/4250927>
- [28] S.A. Stern, Polymers for gas separations: The next decade, *J. Membr. Sci.*, 94 (1994) 1-65. [https://doi.org/10.1016/0376-7388\(94\)00141-3](https://doi.org/10.1016/0376-7388(94)00141-3)
- [29] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: A review, *Polymer*, 54 (2013) 4729-4761. <https://doi.org/10.1016/j.polymer.2013.05.075>
- [30] R.W. Baker, Gas separation, in: *Membrane Technology and Applications*, Third Edition, John Wiley & Sons, United Kingdom, 2012, pp. 325-378. <https://doi.org/10.1002/9781118359686.ch8>
- [31] C.L. Aitken, W.J. Koros, D.R. Paul, Gas transport properties of biphenol polysulfones, *Macromolecules*, 25 (1992) 3651-3658. <https://doi.org/10.1021/ma00040a008>

- [32] C.L. Aitken, W.J. Koros, D.R. Paul, Effect of structural symmetry on gas transport properties of polysulfones, *Macromolecules*, 25 (1992) 3424-3434.
<https://doi.org/10.1021/ma00039a018>
- [33] M.W. Hellums, W.J. Koros, J.C. Schmidhauser, Gas separation properties of spirobiindane polycarbonate, *J. Membr. Sci.*, 67 (1992) 75-81.
[https://doi.org/10.1016/0376-7388\(92\)87041-U](https://doi.org/10.1016/0376-7388(92)87041-U)
- [34] W.J. Koros, G.K. Fleming, Membrane-based gas separation, *J. Membr. Sci.*, 83 (1993) 1-80. [https://doi.org/10.1016/0376-7388\(93\)80013-N](https://doi.org/10.1016/0376-7388(93)80013-N)
- [35] T. Heinze, T. Liebert, Chemical characteristics of cellulose acetate, *Macromol. Symp.*, 208 (2004) 167-238. <https://doi.org/10.1002/masy.200450408>
- [36] A.C. Puleo, D.R. Paul, S.S. Kelley, The effect of degree of acetylation on gas sorption and transport behavior in cellulose acetate, *J. Membr. Sci.*, 47 (1989) 301-332. [https://doi.org/10.1016/S0376-7388\(00\)83083-5](https://doi.org/10.1016/S0376-7388(00)83083-5)
- [37] R. Swaidan, B. Ghanem, I. Pinnau, Fine-tuned intrinsically ultramicroporous polymers redefine the permeability/selectivity upper bounds of membrane-based air and hydrogen separations, *ACS Macro Lett.*, 4 (2015) 947-951.
<https://doi.org/10.1021/acsmacrolett.5b00512>
- [38] K. Toi, G. Morel, D.R. Paul, Gas sorption and transport in poly(phenylene oxide) and comparisons with other glassy polymers, *J. Appl. Polym. Sci.*, 27 (1982) 2997-3005. <https://doi.org/10.1002/app.1982.070270823>
- [39] A.S. Hay, Oxidation of phenols and resulting products, U.S. Patent 3,306,875A, 1967
- [40] G.A. Polotskaya, A.V. Penkova, A.M. Toikka, Z. Pientka, L. Brozova, M. Bleha, Transport of small molecules through polyphenylene oxide membranes modified by fullerene, *Sep. Sci. Technol.*, 42 (2007) 333-347.
<https://doi.org/10.1080/01496390600997963>
- [41] B.J. Story, W.J. Koros, Sorption and transport of CO₂ and CH₄ in chemically modified poly(phenylene oxide), *J. Membr. Sci.*, 67 (1992) 191-210.
[https://doi.org/10.1016/0376-7388\(92\)80025-F](https://doi.org/10.1016/0376-7388(92)80025-F)
- [42] O.M. Ekiner, G. Vassilatos, Polyaramide hollow fibers for H₂/CH₄ separation: II. Spinning and properties, *J. Membr. Sci.*, 186 (2001) 71-84.
[https://doi.org/10.1016/S0376-7388\(00\)00665-7](https://doi.org/10.1016/S0376-7388(00)00665-7)

- [43] J.M. García, F.C. García, F. Serna, J.L. de la Peña, High-performance aromatic polyamides, *Prog. Polym. Sci.*, 35 (2010) 623-686.
<https://doi.org/10.1016/j.progpolymsci.2009.09.002>
- [44] O.M. Ekiner, G. Vassilatos, Polyaramide hollow fibers for hydrogen/methane separation — spinning and properties, *J. Membr. Sci.*, 53 (1990) 259-273.
[https://doi.org/10.1016/0376-7388\(90\)80018-H](https://doi.org/10.1016/0376-7388(90)80018-H)
- [45] P. Falcigno, M. Masola, D. Williams, S. Jasne, Comparison of properties of polyimides containing DAPI isomers and various dianhydrides, in: C. Feger, M.M. Khohasteh, J.E. McGrath (Eds.) *Polyimides: Materials, Chemistry and Characterization*, Elsevier, New York, 1989, pp. 497-512.
- [46] Y. Sasaki, H. Inoue, H. Itatani, M. Kashima, Process for preparing polyimide solution, U.S. Patent 4,290,936A, 1981
- [47] Z. Xu, C. Dannenberg, J. Springer, S. Banerjee, G. Maier, Gas separation properties of polymers containing fluorene moieties, *Chem. Mater.*, 14 (2002) 3271-3276.
<https://doi.org/10.1021/cm0112789>
- [48] M. Aguilar-Vega, D.R. Paul, Gas transport properties of polycarbonates and polysulfones with aromatic substitutions on the bisphenol connector group, *J. Polym. Sci. Part B: Polym. Phys.*, 31 (1993) 1599-1610.
<https://doi.org/10.1002/polb.1993.090311116>
- [49] Y. Yampolskii, Polymeric gas separation membranes, *Macromolecules*, 45 (2012) 3298-3311. <https://doi.org/10.1021/ma300213b>
- [50] I. Pinnau, L.G. Toy, Gas and vapor transport properties of amorphous perfluorinated copolymer membranes based on 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole/tetrafluoroethylene, *J. Membr. Sci.*, 109 (1996) 125-133.
[https://doi.org/10.1016/0376-7388\(95\)00193-X](https://doi.org/10.1016/0376-7388(95)00193-X)
- [51] M. Macchione, J.C. Jansen, G. De Luca, E. Tocci, M. Longeri, E. Drioli, Experimental analysis and simulation of the gas transport in dense Hyflon® AD60X membranes: Influence of residual solvent, *Polymer*, 48 (2007) 2619-2635.
<https://doi.org/10.1016/j.polymer.2007.02.068>
- [52] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.*, 320 (2008) 390-400.
<https://doi.org/10.1016/j.memsci.2008.04.030>
- [53] K. Nagai, T. Masuda, T. Nakagawa, B.D. Freeman, I. Pinnau, Poly[1-(trimethylsilyl)-1-propyne] and related polymers: synthesis, properties and functions, *Prog. Polym. Sci.*, 26 (2001) 721-798. [https://doi.org/10.1016/S0079-6700\(01\)00008-9](https://doi.org/10.1016/S0079-6700(01)00008-9)

- [54] T. Masuda, E. Isobe, T. Higashimura, K. Takada, Poly[1-(trimethylsilyl)-1-propyne]: A new high polymer synthesized with transition-metal catalysts and characterized by extremely high gas permeability, *J. Am. Chem. Soc.*, 105 (1983) 7473-7474. <https://doi.org/10.1021/ja00363a061>
- [55] Y. Ichiraku, S.A. Stern, T. Nakagawa, An investigation of the high gas permeability of poly (1-trimethylsilyl-1-propyne), *J. Membr. Sci.*, 34 (1987) 5-18. [https://doi.org/10.1016/S0376-7388\(00\)80017-4](https://doi.org/10.1016/S0376-7388(00)80017-4)
- [56] I. Pinnau, L.G. Toy, Transport of organic vapors through poly(1-trimethylsilyl-1-propyne), *J. Membr. Sci.*, 116 (1996) 199-209. [https://doi.org/10.1016/0376-7388\(96\)00041-5](https://doi.org/10.1016/0376-7388(96)00041-5)
- [57] P.M. Budd, E.S. Elabas, B.S. Ghanem, S. Makhseed, N.B. McKeown, K.J. Msayib, C.E. Tattershall, D. Wang, Solution-processed, organophilic membrane derived from a polymer of intrinsic microporosity, *Adv. Mater.*, 16 (2004) 456-459. <https://doi.org/10.1002/adma.200306053>
- [58] P.M. Budd, B.S. Ghanem, S. Makhseed, N.B. McKeown, K.J. Msayib, C.E. Tattershall, Polymers of intrinsic microporosity (PIMs): Robust, solution-processable, organic nanoporous materials, *Chem. Commun.*, (2004) 230-231. <https://doi.org/10.1039/b311764b>
- [59] P.M. Budd, Polymer with intrinsic microporosity (PIM), in: E. Drioli, L. Giorno (Eds.) *Encyclopedia of Membranes*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2016, pp. 1606-1607.
- [60] B.S. Ghanem, N.B. McKeown, P.M. Budd, J.D. Selbie, D. Fritsch, High-performance membranes from polyimides with intrinsic microporosity, *Adv. Mater.*, 20 (2008) 2766-2771. <https://doi.org/10.1002/adma.200702400>
- [61] Z.X. Low, P.M. Budd, N.B. McKeown, D.A. Patterson, Gas permeation properties, physical aging, and its mitigation in high free volume glassy polymers, *Chem. Rev.*, 118 (2018) 5871-5911. <https://doi.org/10.1021/acs.chemrev.7b00629>
- [62] I. Rose, C.G. Bezzu, M. Carta, B. Comesaña-Gándara, E. Lasseuguette, M.C. Ferrari, P. Bernardo, G. Clarizia, A. Fuoco, J.C. Jansen, Kyle E. Hart, T.P. Liyana-Arachchi, C.M. Colina, N.B. McKeown, Polymer ultrapermeability from the inefficient packing of 2D chains, *Nat. Mater.*, 16 (2017) 932-937. <https://doi.org/10.1038/nmat4939>
- [63] P.M. Budd, K.J. Msayib, C.E. Tattershall, B.S. Ghanem, K.J. Reynolds, N.B. McKeown, D. Fritsch, Gas separation membranes from polymers of intrinsic

- microporosity, *J. Membr. Sci.*, 251 (2005) 263-269.
<https://doi.org/10.1016/j.memsci.2005.01.009>
- [64] B.S. Ghanem, R. Swaidan, X. Ma, E. Litwiller, I. Pinnau, Energy-efficient hydrogen separation by AB-type ladder-polymer molecular sieves, *Adv. Mater.*, 26 (2014) 6696-6700. <https://doi.org/10.1002/adma.201401328>
- [65] B. Ghanem, F. Alghunaimi, N. Alaslai, X. Ma, I. Pinnau, New phenazine-containing ladder polymer of intrinsic microporosity from a spirobisindane-based AB-type monomer, *RSC Adv.*, 6 (2016) 79625-79630. <https://doi.org/10.1039/C6RA16393A>
- [66] M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J.C. Jansen, P. Bernardo, F. Bazzarelli, N.B. McKeown, An efficient polymer molecular sieve for membrane gas separations, *Science*, 339 (2013) 303-307. <https://doi.org/10.1126/science.1228032>
- [67] C.G. Bezzu, M. Carta, A. Tonkins, J.C. Jansen, P. Bernardo, F. Bazzarelli, N.B. McKeown, A spirobifluorene-based polymer of intrinsic microporosity with improved performance for gas separation, *Adv. Mater.*, 24 (2012) 5930-5933.
<https://doi.org/10.1002/adma.201202393>
- [68] B.S. Ghanem, N.B. McKeown, P.M. Budd, N.M. Al-Harbi, D. Fritsch, K. Heinrich, L. Starannikova, A. Tokarev, Y. Yampolskii, Synthesis, characterization, and gas permeation properties of a novel group of polymers with intrinsic microporosity: PIM-polyimides, *Macromolecules*, 42 (2009) 7881-7888.
<https://doi.org/10.1021/ma901430q>
- [69] Y. Rogan, L. Starannikova, V. Ryzhikh, Y. Yampolskii, P. Bernardo, F. Bazzarelli, J.C. Jansen, N.B. McKeown, Synthesis and gas permeation properties of novel spirobisindane-based polyimides of intrinsic microporosity, *Polym. Chem.*, 4 (2013) 3813-3820. <https://doi.org/10.1039/c3py00451a>
- [70] Y. Rogan, R. Malpass-Evans, M. Carta, M. Lee, J.C. Jansen, P. Bernardo, G. Clarizia, E. Tocci, K. Friess, M. Lanč, N.B. McKeown, A highly permeable polyimide with enhanced selectivity for membrane gas separations, *J. Mater. Chem. A*, 2 (2014) 4874-4877. <https://doi.org/10.1039/C4TA00564C>
- [71] X. Ma, M.A. Abdulhamid, I. Pinnau, Design and synthesis of polyimides based on carbocyclic pseudo-Tröger's Base-derived dianhydrides for membrane gas separation applications, *Macromolecules*, 50 (2017) 5850-5857.
<https://doi.org/10.1021/acs.macromol.7b01054>

- [72] B.S. Ghanem, R. Swaidan, E. Litwiller, I. Pinnau, Ultra-microporous triptycene-based polyimide membranes for high-performance gas separation, *Adv. Mater.*, 26 (2014) 3688-3692. <https://doi.org/10.1002/adma.201306229>
- [73] R. Swaidan, M. Al-Saeedi, B. Ghanem, E. Litwiller, I. Pinnau, Rational design of intrinsically ultramicroporous polyimides containing bridgehead-substituted triptycene for highly selective and permeable gas separation membranes, *Macromolecules*, 47 (2014) 5104-5114. <https://doi.org/10.1021/ma5009226>
- [74] X. Ma, O. Salinas, E. Litwiller, I. Pinnau, Novel spirobifluorene- and dibromospirobifluorene-based polyimides of intrinsic microporosity for gas separation applications, *Macromolecules*, 46 (2013) 9618-9624. <https://doi.org/10.1021/ma402033z>
- [75] Y. Zhuang, J.G. Seong, Y.S. Do, H.J. Jo, Z. Cui, J. Lee, Y.M. Lee, M.D. Guiver, Intrinsically microporous soluble polyimides incorporating Tröger's base for membrane gas separation, *Macromolecules*, 47 (2014) 3254-3262. <https://doi.org/10.1021/ma5007073>
- [76] Y. Zhuang, J.G. Seong, Y.S. Do, W.H. Lee, M.J. Lee, M.D. Guiver, Y.M. Lee, High-strength, soluble polyimide membranes incorporating Tröger's Base for gas separation, *J. Membr. Sci.*, 504 (2016) 55-65. <https://doi.org/10.1016/j.memsci.2015.12.057>
- [77] B. Ghanem, N. Alaslai, X. Miao, I. Pinnau, Novel 6FDA-based polyimides derived from sterically hindered Tröger's base diamines: Synthesis and gas permeation properties, *Polymer*, 96 (2016) 13-19. <https://doi.org/10.1016/j.polymer.2016.04.068>
- [78] M. Lee, C.G. Bezzu, M. Carta, P. Bernardo, G. Clarizia, J.C. Jansen, N.B. McKeown, Enhancing the gas permeability of Tröger's Base derived polyimides of intrinsic microporosity, *Macromolecules*, 49 (2016) 4147-4154. <https://doi.org/10.1021/acs.macromol.6b00351>
- [79] Z. Wang, D. Wang, J. Jin, Microporous polyimides with rationally designed chain structure achieving high performance for gas separation, *Macromolecules*, 47 (2014) 7477-7483. <https://doi.org/10.1021/ma5017506>
- [80] F. Alghunaimi, B. Ghanem, N. Alaslai, R. Swaidan, E. Litwiller, I. Pinnau, Gas permeation and physical aging properties of triptycene diamine-based microporous polyimides, *J. Membr. Sci.*, 490 (2015) 321-327. <https://doi.org/10.1016/j.memsci.2015.05.010>

- [81] J.R. Wiegand, Z.P. Smith, Q. Liu, C.T. Patterson, B.D. Freeman, R. Guo, Synthesis and characterization of triptycene-based polyimides with tunable high fractional free volume for gas separation membranes, *J. Mater. Chem. A*, 2 (2014) 13309-13320. <https://doi.org/10.1039/C4TA02303J>
- [82] S. Luo, Q. Liu, B. Zhang, J.R. Wiegand, B.D. Freeman, R. Guo, Pentriptycene-based polyimides with hierarchically controlled molecular cavity architecture for efficient membrane gas separation, *J. Membr. Sci.*, 480 (2015) 20-30. <https://doi.org/10.1016/j.memsci.2015.01.043>
- [83] R. Swaidan, B.S. Ghanem, E. Litwiller, I. Pinnau, Pure- and mixed-gas CO₂/CH₄ separation properties of PIM-1 and an amidoxime-functionalized PIM-1, *J. Membr. Sci.*, 457 (2014) 95-102. <https://doi.org/10.1016/j.memsci.2014.01.055>
- [84] N. Du, G.P. Robertson, J. Song, I. Pinnau, M.D. Guiver, High-performance carboxylated polymers of intrinsic microporosity (PIMs) with tunable gas transport properties, *Macromolecules*, 42 (2009) 6038-6043. <https://doi.org/10.1021/ma9009017>
- [85] N. Du, H.B. Park, G.P. Robertson, M.M. Dal-Cin, T. Visser, L. Scoles, M.D. Guiver, Polymer nanosieve membranes for CO₂-capture applications, *Nat. Mater.*, 10 (2011) 372-375. <https://doi.org/10.1038/nmat2989>
- [86] C.R. Mason, L. Maynard-Atem, N.M. Al-Harbi, P.M. Budd, P. Bernardo, F. Bazzarelli, G. Clarizia, J.C. Jansen, Polymer of intrinsic microporosity incorporating thioamide functionality: Preparation and gas transport properties, *Macromolecules*, 44 (2011) 6471-6479. <https://doi.org/10.1021/ma200918h>
- [87] X. Ma, R. Swaidan, Y. Belmabkhout, Y. Zhu, E. Litwiller, M. Jouiad, I. Pinnau, Y. Han, Synthesis and gas transport properties of hydroxyl-functionalized polyimides with intrinsic microporosity, *Macromolecules*, 45 (2012) 3841-3849. <https://doi.org/10.1021/ma300549m>
- [88] B. Comesaña-Gándara, J. Chen, C.G. Bezzu, M. Carta, I. Rose, M.-C. Ferrari, E. Esposito, A. Fuoco, J.C. Jansen, N.B. McKeown, Redefining the Robeson upper bounds for CO₂/CH₄ and CO₂/N₂ separations using a series of ultrapermeable benzotriptycene-based polymers of intrinsic microporosity, *Energy Environ. Sci.*, 12 (2019) 2733-2740. <https://doi.org/10.1039/C9EE01384A>
- [89] J.R. Klaehn, C.J. Orme, E.S. Peterson, F.F. Stewart, J.M. Urban-Klaehn, High temperature gas separations using high performance polymers, in: S.T. Oyama, S.M. Stagg-Williams (Eds.) *Membrane Science and Technology*, Elsevier, Great Britain, 2011, pp. 295-307. <https://doi.org/10.1016/B978-0-444-53728-7.00013-6>

- [90] H. Vogel, C.S. Marvel, Polybenzimidazoles, new thermally stable polymers, J. Polym. Sci., 50 (1961) 511-539. <https://doi.org/10.1002/pol.1961.1205015419>
- [91] Y. Wang, T.X. Yang, K. Fishel, B. Benicewicz, T.S. Chung, Polybenzimidazoles, in: O. Olabisi, K. Adewale (Eds.) Handbook of Thermoplastics Second Edition, CRC Press, Boca Raton, 2015, pp. 617-667.
- [92] S.C. Kumbharkar, P.B. Karadkar, U.K. Kharul, Enhancement of gas permeation properties of polybenzimidazoles by systematic structure architecture, J. Membr. Sci., 286 (2006) 161-169. <https://doi.org/10.1016/j.memsci.2006.09.030>
- [93] S.D. Kenarsari, D. Yang, G. Jiang, S. Zhang, J. Wang, A.G. Russell, Q. Wei, M. Fan, Review of recent advances in carbon dioxide separation and capture, RSC Adv., 3 (2013) 22739-22773. <https://doi.org/10.1039/c3ra43965h>
- [94] H. Borjigin, K.A. Stevens, R. Liu, J.D. Moon, A.T. Shaver, S. Swinnea, B.D. Freeman, J.S. Riffle, J.E. McGrath, Synthesis and characterization of polybenzimidazoles derived from tetraaminodiphenylsulfone for high temperature gas separation membranes, Polymer, 71 (2015) 135-142. <https://doi.org/10.1016/j.polymer.2015.06.021>
- [95] X. Li, R.P. Singh, K.W. Dudeck, K.A. Berchtold, B.C. Benicewicz, Influence of polybenzimidazole main chain structure on H₂/CO₂ separation at elevated temperatures, J. Membr. Sci., 461 (2014) 59-68. <https://doi.org/10.1016/j.memsci.2014.03.008>
- [96] S.C. Kumbharkar, Y. Liu, K. Li, High performance polybenzimidazole based asymmetric hollow fibre membranes for H₂/CO₂ separation, J. Membr. Sci., 375 (2011) 231-240. <https://doi.org/10.1016/j.memsci.2011.03.049>
- [97] L. Zhu, M.T. Swihart, H. Lin, Unprecedented size-sieving ability in polybenzimidazole doped with polyprotic acids for membrane H₂/CO₂ separation, Energy Environ. Sci., 11 (2018) 94-100. <https://doi.org/10.1039/C7EE02865B>
- [98] J.R. Klaehn, C.J. Orme, E.S. Peterson, T.A. Luther, M.G. Jones, A.K. Wertsching, J.M. Urban-Klaehn: CO₂ separation using thermally optimized membranes: A comprehensive project report (2000 - 2007) (Idaho National Laboratory, Idaho 2008). <https://doi.org/10.2172/928082>
- [99] W.J. Koros, R.T. Chern, V. Stannett, H.B. Hopfenberg, A model for permeation of mixed gases and vapors in glassy polymers, J. Polym. Sci. Polym. Phys. Ed., 19 (1981) 1513-1530. <https://doi.org/10.1002/pol.1981.180191004>

- [100] I. Pinnau, C.G. Casillas, A. Morisato, B.D. Freeman, Hydrocarbon/hydrogen mixed gas permeation in poly(1-trimethylsilyl-1-propyne) (PTMSP), poly(1-phenyl-1-propyne) (PPP), and PTMSP/PPP blends, *J. Polym. Sci. Part B: Polym. Phys.*, **34** (1996) 2613-2621. [https://doi.org/10.1002/\(SICI\)1099-0488\(19961115\)34:15<2613::AID-POLB9>3.0.CO;2-T](https://doi.org/10.1002/(SICI)1099-0488(19961115)34:15<2613::AID-POLB9>3.0.CO;2-T)
- [101] H. Lin, B.D. Freeman, Gas solubility, diffusivity and permeability in poly(ethylene oxide), *J. Membr. Sci.*, **239** (2004) 105-117. <https://doi.org/10.1016/j.memsci.2003.08.031>
- [102] S.B. Aziz, R.M. Abdullah, Crystalline and amorphous phase identification from the $\tan\delta$ relaxation peaks and impedance plots in polymer blend electrolytes based on [CS:AgNt]_x:PEO(_x-1) ($10 \leq x \leq 50$), *Electrochim. Acta*, **285** (2018) 30-46. <https://doi.org/10.1016/j.electacta.2018.07.233>
- [103] Y. Hirayama, Y. Kase, N. Tanihara, Y. Sumiyama, Y. Kusuki, K. Haraya, Permeation properties to CO₂ and N₂ of poly(ethylene oxide)-containing and crosslinked polymer films, *J. Membr. Sci.*, **160** (1999) 87-99. [https://doi.org/10.1016/S0376-7388\(99\)00080-0](https://doi.org/10.1016/S0376-7388(99)00080-0)
- [104] N.P. Patel, A.C. Miller, R.J. Spontak, Highly CO₂-permeable and selective polymer nanocomposite membranes, *Adv. Mater.*, **15** (2003) 729-733. <https://doi.org/10.1002/adma.200304712>
- [105] H. Lin, E. Van Wagner, B.D. Freeman, L.G. Toy, R.P. Gupta, Plasticization-enhanced hydrogen purification using polymeric membranes, *Science*, **311** (2006) 639-642. <https://doi.org/10.1126/science.1118079>
- [106] M. Wessling, S. Schoeman, T. van der Boomgaard, C.A. Smolders, Plasticization of gas separation membranes, *Gas Sep. Purif.*, **5** (1991) 222-228. [https://doi.org/10.1016/0950-4214\(91\)80028-4](https://doi.org/10.1016/0950-4214(91)80028-4)
- [107] I. Pinnau, Z. He, Pure- and mixed-gas permeation properties of polydimethylsiloxane for hydrocarbon/methane and hydrocarbon/hydrogen separation, *J. Membr. Sci.*, **244** (2004) 227-233. <https://doi.org/10.1016/j.memsci.2004.06.055>
- [108] V.I. Bondar, B.D. Freeman, I. Pinnau, Gas sorption and characterization of poly(ether-b-amide) segmented block copolymers, *J. Polym. Sci. Part B: Polym. Phys.*, **37** (1999) 2463-2475. [https://doi.org/10.1002/\(SICI\)1099-0488\(19990901\)37:17<2463::AID-POLB18>3.0.CO;2-H](https://doi.org/10.1002/(SICI)1099-0488(19990901)37:17<2463::AID-POLB18>3.0.CO;2-H)

- [109] H.Z. Chen, Y.C. Xiao, T.S. Chung, Synthesis and characterization of poly (ethylene oxide) containing copolyimides for hydrogen purification, *Polymer*, 51 (2010) 4077-4086. <https://doi.org/10.1016/j.polymer.2010.06.046>
- [110] S.H. Choi, J.H. Kim, S.B. Lee, Sorption and permeation behaviors of a series of olefins and nitrogen through PDMS membranes, *J. Membr. Sci.*, 299 (2007) 54-62. <https://doi.org/10.1016/j.memsci.2007.04.022>
- [111] J. Liu, X. Hou, H.B. Park, H. Lin, High-performance polymers for membrane CO₂/N₂ Separation, *Chem. Eur. J.*, 22 (2016) 15980-15990. <https://doi.org/10.1002/chem.201603002>
- [112] X. Jiang, S. Li, L. Shao, Pushing CO₂-philic membrane performance to the limit by designing semi-interpenetrating networks (SIPN) for sustainable CO₂ separations, *Energy Environ. Sci.*, 10 (2017) 1339-1344. <https://doi.org/10.1039/C6EE03566C>
- [113] S.L. Liu, R. Wang, T.S. Chung, M.L. Chng, Y. Liu, R.H. Vora, Effect of diamine composition on the gas transport properties in 6FDA-durene/3,3'-diaminodiphenyl sulfone copolyimides, *J. Membr. Sci.*, 202 (2002) 165-176. [https://doi.org/10.1016/S0376-7388\(01\)00754-2](https://doi.org/10.1016/S0376-7388(01)00754-2)
- [114] H.B. Park, C.H. Jung, Y.M. Lee, A.J. Hill, S.J. Pas, S.T. Mudie, E. Van Wagner, B.D. Freeman, D.J. Cookson, Polymers with cavities tuned for fast selective transport of small molecules and ions, *Science*, 318 (2007) 254-258. <https://doi.org/10.1126/science.1146744>
- [115] N.B. McKeown, P.M. Budd, K.J. Msayib, B.S. Ghanem, H.J. Kingston, C.E. Tattershall, S. Makhseed, K.J. Reynolds, D. Fritsch, Polymers of intrinsic microporosity (PIMs): Bridging the void between microporous and polymeric materials, *Chem. Eur. J.*, 11 (2005) 2610-2620. <https://doi.org/10.1002/chem.200400860>
- [116] S. Kim, Y.M. Lee, Rigid and microporous polymers for gas separation membranes, *Prog. Polym. Sci.*, 43 (2015) 1-32. <https://doi.org/10.1016/j.progpolymsci.2014.10.005>
- [117] H.B. Park, S.H. Han, C.H. Jung, Y.M. Lee, A.J. Hill, Thermally rearranged (TR) polymer membranes for CO₂ separation, *J. Membr. Sci.*, 359 (2010) 11-24. <https://doi.org/10.1016/j.memsci.2009.09.037>
- [118] R. Guo, D.F. Sanders, Z.P. Smith, B.D. Freeman, D.R. Paul, J.E. McGrath, Synthesis and characterization of thermally rearranged (TR) polymers: Influence of ortho-positioned functional groups of polyimide precursors on TR process and gas

- transport properties, *J. Mater. Chem. A*, 1 (2013) 262-272.
<https://doi.org/10.1039/C2TA00799A>
- [119] A. Tena, S. Rangou, S. Shishatskiy, V. Filiz, V. Abetz, Claisen thermally rearranged (CTR) polymers, *Sci. Adv.*, 2 (2016) e1501859.
<https://doi.org/10.1126/sciadv.1501859>
- [120] M.R. de la Viuda, A. Tena, S. Neumann, S. Willruth, V. Filiz, V. Abetz, Novel functionalized polyamides prone to undergo thermal Claisen rearrangement in the solid state, *Polym. Chem.*, 9 (2018) 4007-4016. <https://doi.org/10.1039/C8PY00467F>
- [121] R.W. Baker, K. Lokhandwala, Natural gas processing with membranes: An overview, *Ind. Eng. Chem. Res.*, 47 (2008) 2109-2121.
<https://doi.org/10.1021/ie071083w>
- [122] A. Tena, A. Marcos-Fernández, A.E. Lozano, J.G. de la Campa, J. de Abajo, L. Palacio, P. Prádanos, A. Hernández, Thermally segregated copolymers with PPO blocks for nitrogen removal from natural gas, *Ind. Eng. Chem. Res.*, 52 (2013) 4312-4322. <https://doi.org/10.1021/ie303378k>
- [123] Z. Cui, E. Drioli, Y.M. Lee, Recent progress in fluoropolymers for membranes, *Prog. Polym. Sci.*, 39 (2014) 164-198.
<https://doi.org/10.1016/j.progpolymsci.2013.07.008>
- [124] Y. Yampolskii, N. Belov, A. Alentiev, Perfluorinated polymers as materials of membranes for gas and vapor separation, *J. Membr. Sci.*, 598 (2020) 117779.
<https://doi.org/10.1016/j.memsci.2019.117779>
- [125] M. Yavari, M. Fang, H. Nguyen, T.C. Merkel, H. Lin, Y. Okamoto, Dioxolane-based perfluoropolymers with superior membrane gas separation properties, *Macromolecules*, 51 (2018) 2489-2497.
<https://doi.org/10.1021/acs.macromol.8b00273>
- [126] M. Fang, Z. He, T.C. Merkel, Y. Okamoto, High-performance perfluorodioxolane copolymer membranes for gas separation with tailored selectivity enhancement, *J. Mater. Chem. A*, 6 (2018) 652-658. <https://doi.org/10.1039/C7TA09047A>
- [127] N.A. Belov, A.A. Zharov, A.V. Shashkin, M.Q. Shaikh, K. Raetzke, Y.P. Yampolskii, Gas transport and free volume in hexafluoropropylene polymers, *J. Membr. Sci.*, 383 (2011) 70-77. <https://doi.org/10.1016/j.memsci.2011.08.029>
- [128] A.X. Wu, J.A. Drayton, Z.P. Smith, The perfluoropolymer upper bound, *AIChE J.*, 65 (2019) e16700. <https://doi.org/10.1002/aic.16700>

- [129] F. Suzuki, K. Nakane, Y. Hata, Grafting of siloxane on poly (styrene-co-maleic acid) and application of this grafting technique to a porous membrane for gas separation, *J. Membr. Sci.*, 104 (1995) 283-290. [https://doi.org/10.1016/0376-7388\(95\)00043-C](https://doi.org/10.1016/0376-7388(95)00043-C)
- [130] Y.C. Xiao, T.S. Chung, Grafting thermally labile molecules on cross-linkable polyimide to design membrane materials for natural gas purification and CO₂ capture, *Energy Environ. Sci.*, 4 (2011) 201-208. <https://doi.org/10.1039/C0EE00278J>
- [131] M.L. Chua, Y.C. Xiao, T.S. Chung, Effects of thermally labile saccharide units on the gas separation performance of highly permeable polyimide membranes, *J. Membr. Sci.*, 415 (2012) 375-382. <https://doi.org/10.1016/j.memsci.2012.05.022>
- [132] M. Askari, Y.C. Xiao, P. Li, T.S. Chung, Natural gas purification and olefin/paraffin separation using cross-linkable 6FDA-Durene/DABA co-polyimides grafted with α , β , and γ -cyclodextrin, *J. Membr. Sci.*, 390–391 (2012) 141-151. <https://doi.org/10.1016/j.memsci.2011.11.030>
- [133] C.R. Mason, L. Maynard-Atem, K.W.J. Heard, B. Satilmis, P.M. Budd, K. Friess, M. Lanč, P. Bernardo, G. Clarizia, J.C. Jansen, Enhancement of CO₂ affinity in a polymer of intrinsic microporosity by amine modification, *Macromolecules*, 47 (2014) 1021-1029. <https://doi.org/10.1021/ma401869p>
- [134] N. Du, G.P. Robertson, M.M. Dal-Cin, L. Scoles, M.D. Guiver, Polymers of intrinsic microporosity (PIMs) substituted with methyl tetrazole, *Polymer*, 53 (2012) 4367-4372. <https://doi.org/10.1016/j.polymer.2012.07.055>
- [135] R.A. Hayes, Amine-modified polyimide membranes, U.S. Patent 4,981,497, 1991
- [136] Y. Liu, R. Wang, T.S. Chung, Chemical cross-linking modification of polyimide membranes for gas separation, *J. Membr. Sci.*, 189 (2001) 231-239. [https://doi.org/10.1016/S0376-7388\(01\)00415-X](https://doi.org/10.1016/S0376-7388(01)00415-X)
- [137] K. Vanherck, G. Koeckelberghs, I.F.J. Vankelecom, Crosslinking polyimides for membrane applications: A review, *Prog. Polym. Sci.*, 38 (2013) 874-896. <https://doi.org/10.1016/j.progpolymsci.2012.11.001>
- [138] W. F. Yong, F.Y. Li, T.S. Chung, Y.W. Tong, Highly permeable chemically modified PIM-1/Matrimid membranes for green hydrogen purification, *J. Mater. Chem. A*, 1 (2013) 139 14-13925. <https://doi.org/10.1039/c3ta13308g>
- [139] H.Y. Zhao, Y.M. Cao, X.L. Ding, M.Q. Zhou, J.H. Liu, Q. Yuan, Poly(ethylene oxide) induced cross-linking modification of Matrimid membranes for selective

- separation of CO₂, *J. Membr. Sci.*, 320 (2008) 179-184.
<https://doi.org/10.1016/j.memsci.2008.03.070>
- [140] H. Lin, T. Kai, B.D. Freeman, S. Kalakkunnath, D.S. Kalika, The effect of cross-linking on gas permeability in cross-linked poly(ethylene glycol diacrylate), *Macromolecules*, 38 (2005) 8381-8393. <https://doi.org/10.1021/ma0510136>
- [141] H.K. Yun, K. Cho, J.K. Kim, C.E. Park, S.M. Sim, S.Y. Oh, J.M. Park, Adhesion improvement of epoxy resin/polyimide joints by amine treatment of polyimide surface, *Polymer*, 38 (1997) 827-834. [https://doi.org/10.1016/S0032-3861\(96\)00592-7](https://doi.org/10.1016/S0032-3861(96)00592-7)
- [142] L. Shao, T.S. Chung, S.H. Goh, K.P. Pramoda, Polyimide modification by a linear aliphatic diamine to enhance transport performance and plasticization resistance, *J. Membr. Sci.*, 256 (2005) 46-56. <https://doi.org/10.1016/j.memsci.2005.02.030>
- [143] C.E. Powell, X.J. Duthie, S.E. Kentish, G.G. Qiao, G.W. Stevens, Reversible diamine cross-linking of polyimide membranes, *J. Membr. Sci.*, 291 (2007) 199-209. <https://doi.org/10.1016/j.memsci.2007.01.016>
- [144] B.T. Low, Y.C. Xiao, T.S. Chung, Y. Liu, Simultaneous occurrence of chemical grafting, cross-linking, and etching on the surface of polyimide membranes and their Impact on H₂/CO₂ separation, *Macromolecules*, 41 (2008) 1297-1309. <https://doi.org/10.1021/ma702360p>
- [145] L. Shao, B.T. Low, T.S. Chung, A.R. Greenberg, Polymeric membranes for the hydrogen economy: Contemporary approaches and prospects for the future, *J. Membr. Sci.*, 327 (2009) 18-31. <https://doi.org/10.1016/j.memsci.2008.11.019>
- [146] H. Wang, D.R. Paul, T.S. Chung, Surface modification of polyimide membranes by diethylenetriamine (DETA) vapor for H₂ purification and moisture effect on gas permeation, *J. Membr. Sci.*, 430 (2013) 223-233. <https://doi.org/10.1016/j.memsci.2012.12.008>
- [147] S. Japip, K.S. Liao, Y.C. Xiao, T.S. Chung, Enhancement of molecular-sieving properties by constructing surface nano-metric layer via vapor cross-linking, *J. Membr. Sci.*, 497 (2016) 248-258. <https://doi.org/10.1016/j.memsci.2015.09.045>
- [148] S. Japip, K.S. Liao, T.S. Chung, Molecularly tuned free volume of vapor cross-linked 6FDA-Durene/ZIF-71 MMMs for H₂/CO₂ separation at 150 °C, *Adv. Mater.*, 29 (2017) 1603833. <https://doi.org/10.1002/adma.201603833>
- [149] C. Staudt-Bickel, W. J. Koros, Improvement of CO₂/CH₄ separation characteristics of polyimides by chemical crosslinking, *J. Membr. Sci.*, 155 (1999) 145-154. [https://doi.org/10.1016/S0376-7388\(98\)00306-8](https://doi.org/10.1016/S0376-7388(98)00306-8)

- [150] C. Zhang, L. Fu, Z. Tian, B. Cao, P. Li, Post-crosslinking of triptycene-based Tröger's base polymers with enhanced natural gas separation performance, *J. Membr. Sci.*, 556 (2018) 277-284. <https://doi.org/10.1016/j.memsci.2018.04.013>
- [151] M.E. Rezac, E. Todd Sorensen, H.W. Beckham, Transport properties of crosslinkable polyimide blends, *J. Membr. Sci.*, 136 (1997) 249-259. [https://doi.org/10.1016/S0376-7388\(97\)00170-1](https://doi.org/10.1016/S0376-7388(97)00170-1)
- [152] A.C. Puleo, D.R. Paul, P.K. Wong, Gas sorption and transport in semicrystalline poly(4-methyl-1-pentene), *Polymer*, 30 (1989) 1357-1366. [https://doi.org/10.1016/0032-3861\(89\)90060-8](https://doi.org/10.1016/0032-3861(89)90060-8)
- [153] C.T. Wright, D.R. Paul, Feasibility of thermal crosslinking of polyarylate gas-separation membranes using benzocyclobutene-based monomers, *J. Membr. Sci.*, 129 (1997) 47-53. [https://doi.org/10.1016/S0376-7388\(96\)00327-4](https://doi.org/10.1016/S0376-7388(96)00327-4)
- [154] A.M. Kratochvil, W.J. Koros, Decarboxylation-induced cross-linking of a polyimide for enhanced CO₂ plasticization resistance, *Macromolecules*, 41 (2008) 7920-7927. <https://doi.org/10.1021/ma801586f>
- [155] W. Qiu, C.C. Chen, L. Xu, L. Cui, D.R. Paul, W.J. Koros, Sub-*T_g* cross-linking of a polyimide membrane for enhanced CO₂ plasticization resistance for natural gas separation, *Macromolecules*, 44 (2011) 6046-6056. <https://doi.org/10.1021/ma201033j>
- [156] C. Zhang, P. Li, B. Cao, Decarboxylation crosslinking of polyimides with high CO₂/CH₄ separation performance and plasticization resistance, *J. Membr. Sci.*, 528 (2017) 206-216. <https://doi.org/10.1016/j.memsci.2017.01.008>
- [157] R. Xu, L. Li, X. Jin, M. Hou, L. He, Y. Lu, C. Song, T. Wang, Thermal crosslinking of a novel membrane derived from phenolphthalein-based cardo poly(arylene ether ketone) to enhance CO₂/CH₄ separation performance and plasticization resistance, *J. Membr. Sci.*, 586 (2019) 306-317. <https://doi.org/10.1016/j.memsci.2019.05.084>
- [158] N. Du, M.M. Dal-Cin, G.P. Robertson, M.D. Guiver, Decarboxylation-induced cross-linking of polymers of intrinsic microporosity (PIMs) for membrane gas separation, *Macromolecules*, 45 (2012) 5134-5139. <https://doi.org/10.1021/ma300751s>
- [159] Q. Song, S. Cao, R.H. Pritchard, B. Ghalei, S.A. Al-Muhtaseb, E.M. Terentjev, A.K. Cheetham, E. Sivaniah, Controlled thermal oxidative crosslinking of polymers of intrinsic microporosity towards tunable molecular sieve membranes, *Nat. Commun.*, 5 (2014) 4813. <https://doi.org/10.1038/ncomms5813>

- [160] C. Zhang, B. Cao, P. Li, Thermal oxidative crosslinking of phenolphthalein-based cardo polyimides with enhanced gas permeability and selectivity, *J. Membr. Sci.*, 546 (2018) 90-99. <https://doi.org/10.1016/j.memsci.2017.10.015>
- [161] A.A. Lin, V.R. Sastri, G. Tesoro, A. Reiser, R. Eachus, On the crosslinking mechanism of benzophenone-containing polyimides, *Macromolecules*, 21 (1988) 1165-1169. <https://doi.org/10.1021/ma00182a052>
- [162] R.A. Hayes, Polyimide gas separation membranes, U.S. Patent 4,717,393, 1988
- [163] H. Kita, T. Inada, K. Tanaka, K.-i. Okamoto, Effect of photocrosslinking on permeability and permselectivity of gases through benzophenone- containing polyimide, *J. Membr. Sci.*, 87 (1994) 139-147. [https://doi.org/10.1016/0376-7388\(93\)E0098-X](https://doi.org/10.1016/0376-7388(93)E0098-X)
- [164] M.S. McCaig, D.R. Paul, Effect of UV crosslinking and physical aging on the gas permeability of thin glassy polyarylate films, *Polymer*, 40 (1999) 7209-7225. [https://doi.org/10.1016/S0032-3861\(99\)00125-1](https://doi.org/10.1016/S0032-3861(99)00125-1)
- [165] C.T. Wright, D.R. Paul, Gas sorption and transport in UV-irradiated polyarylate copolymers based on tetramethyl bisphenol-A and dihydroxybenzophenone, *J. Membr. Sci.*, 124 (1997) 161-174. [https://doi.org/10.1016/S0376-7388\(96\)00215-3](https://doi.org/10.1016/S0376-7388(96)00215-3)
- [166] J.R. Rowlett, Q. Liu, W. Zhang, J.D. Moon, M.E. Dose, J.S. Riffle, B.D. Freeman, J.E. McGrath, Gas transport properties and characterization of UV crosslinked poly(phenylene oxide-co-arylene ether ketone) copolymers, *J. Mater. Chem. A*, 4 (2016) 16047-16056. <https://doi.org/10.1039/C6TA05320C>
- [167] S. Matsui, T. Ishiguro, A. Higuchi, T. Nakagawa, Effect of ultraviolet light irradiation on gas permeability in polyimide membranes. 1. Irradiation with low pressure mercury lamp on photosensitive and nonphotosensitive membranes, *J. Polym. Sci. Part B: Polym. Phys.*, 35 (1997) 2259-2269. [https://doi.org/10.1002/\(SICI\)1099-0488\(199710\)35:14<2259::AID-POLB6>3.0.CO;2-R](https://doi.org/10.1002/(SICI)1099-0488(199710)35:14<2259::AID-POLB6>3.0.CO;2-R)
- [168] I.K. Meier, M. Langsam, H.C. Klotz, Selectivity enhancement via photooxidative surface modification of polyimide air separation membranes, *J. Membr. Sci.*, 94 (1994) 195-212. [https://doi.org/10.1016/0376-7388\(93\)E0174-I](https://doi.org/10.1016/0376-7388(93)E0174-I)
- [169] Q. Song, S. Cao, P. Zavala-Rivera, L. Ping Lu, W. Li, Y. Ji, S.A. Al-Muhtaseb, A.K. Cheetham, E. Sivaniah, Photo-oxidative enhancement of polymeric molecular sieve membranes, *Nat. Commun.*, 4 (2013) 1918. <https://doi.org/10.1038/ncomms2942>

- [170] C.Z. Liang, T.S. Chung, J.-Y. Lai, A review of polymeric composite membranes for gas separation and energy production, *Prog. Polym. Sci.*, 97 (2019) 101141. <https://doi.org/10.1016/j.progpolymsci.2019.06.001>
- [171] K. Xie, Q. Fu, G.G. Qiao, P.A. Webley, Recent progress on fabrication methods of polymeric thin film gas separation membranes for CO₂ capture, *J. Membr. Sci.*, 572 (2019) 38-60. <https://doi.org/10.1016/j.memsci.2018.10.049>
- [172] M.F. Jimenez-Solomon, Q. Song, K.E. Jelfs, M. Munoz-Ibanez, A.G. Livingston, Polymer nanofilms with enhanced microporosity by interfacial polymerization, *Nat. Mater.*, 15 (2016) 760-767. <https://doi.org/10.1038/nmat4638>
- [173] Z. Ali, F. Pacheco, E. Litwiller, Y. Wang, Y. Han, I. Pinnau, Ultra-selective defect-free interfacially polymerized molecular sieve thin-film composite membranes for H₂ purification, *J. Mater. Chem. A*, 6 (2018) 30-35. <https://doi.org/10.1039/C7TA07819F>
- [174] M.J.T. Raaijmakers, M.A. Hempenius, P.M. Schön, G.J. Vancso, A. Nijmeijer, M. Wessling, N.E. Benes, Sieving of hot gases by hyper-cross-linked nanoscale-hybrid membranes, *J. Am. Chem. Soc.*, 136 (2014) 330-335. <https://doi.org/10.1021/ja410047u>
- [175] (a) T. S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, *Prog. Polym. Sci.*, 32 (2007) 483-507; <https://doi.org/10.1016/j.progpolymsci.2007.01.008> (b) P. Banerjee, R. Das, P. Das, A. Mukhopadhyay, Membrane technology, in: R. Das (Ed.), *Carbon Nanotubes for Clean Water*, Springer, Cham, 2018, pp. 127-150. https://doi.org/10.1007/978-3-319-95603-9_6
- [176] Y.C. Xiao, K.Y. Wang, T.S. Chung, J. Tan, Evolution of nano-particle distribution during the fabrication of mixed matrix TiO₂-polyimide hollow fiber membranes, *Chem. Eng. Sci.*, 61 (2006) 6228-6233. <https://doi.org/10.1016/j.ces.2006.05.040>
- [177] M.D. Guiver, G.P. Robertson, Y. Dai, F. Bilodeau, Y.S. Kang, K.J. Lee, J.Y. Jho, J. Won, Structural characterization and gas-transport properties of brominated Matrimid polyimide, *J. Polym. Sci. A Polym. Chem.*, 40 (2002) 4193-4204.
- [178] R. Mahajan, R. Burns, M. Schaeffer, W.J. Koros, Challenges in forming successful mixed matrix membranes with rigid polymeric materials, *J. Appl. Polym. Sci.*, 86 (2002) 881-890.
- [179] R. Mahajan, W.J. Koros, Factors controlling successful formation of mixed-matrix gas separation materials, *Ind. Eng. Chem. Res.*, 39 (2000) 2692-2696.

- [180] J.L.C. Rowsell, O.M. Yaghi, Metal–organic frameworks: A new class of porous materials, *Microporous Mesoporous Mater.*, 73 (2004) 3-14.
<https://doi.org/10.1016/j.micromeso.2004.03.034>
- [181] Y. Cheng, Y. Ying, S. Japip, S.D. Jiang, T.S. Chung, S. Zhang, D. Zhao, Advanced porous materials in mixed matrix membranes, *Adv. Mater.*, 30 (2018) 1802401.
<https://doi.org/10.1002/adma.201802401>
- [182] B. Ghalei, K. Sakurai, Y. Kinoshita, K. Wakimoto, A.P. Isfahani, Q. Song, K. Doitomi, S. Furukawa, H. Hirao, H. Kusuda, S. Kitagawa, E. Sivaniah, Enhanced selectivity in mixed matrix membranes for CO₂ capture through efficient dispersion of amine-functionalized MOF nanoparticles, *Nat. Energy*, 2 (2017) 17086.
<https://doi.org/10.1038/nenergy.2017.86>
- [183] T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F.X. Llabrés i Xamena, J. Gascon, Metal–organic framework nanosheets in polymer composite materials for gas separation, *Nat. Mater.*, 14 (2015) 48-55.
<https://doi.org/10.1038/nmat4113>
- [184] (a) Z. Kang, Y. Peng, Z. Hu, Y. Qian, C. Chi, L.Y. Yeo, L. Tee, D. Zhao, Mixed matrix membranes composed of two-dimensional metal–organic framework nanosheets for pre-combustion CO₂ capture: A relationship study of filler morphology versus membrane performance, *J. Mater. Chem. A*, 3 (2015) 20801-20810;
<https://doi.org/10.1039/C5TA03739E> (b) G.R. Xu, J.M. Xu, H.C. Su, X.Y. Liu, L. Li, H.L. Zhao, H.J. Feng, R. Das, Two-dimensional (2D) nanoporous membranes with sub-nanopores in reverse osmosis desalination: Latest developments and future directions, *Desalination*, 451 (2019) 18-34. <https://doi.org/10.1016/j.desal.2017.09.024>
- [185] A.P. Côté, A.I. Benin, N.W. Ockwig, M. Keeffe, A.J. Matzger, O.M. Yaghi, Porous, crystalline, covalent organic frameworks, *Science*, 310 (2005) 1166.
<https://doi.org/10.1126/science.1120411>
- [186] Z. Kang, Y. Peng, Y. Qian, D. Yuan, M.A. Addicoat, T. Heine, Z. Hu, L. Tee, Z. Guo, D. Zhao, Mixed matrix membranes (MMMs) comprising exfoliated 2D covalent organic frameworks (COFs) for efficient CO₂ separation, *Chem. Mater.*, 28 (2016) 1277-1285. <https://doi.org/10.1021/acs.chemmater.5b02902>
- [187] B.P. Biswal, H.D. Chaudhari, R. Banerjee, U.K. Kharul, Chemically stable covalent organic framework (COF)-polybenzimidazole hybrid membranes: Enhanced gas separation through pore modulation, *Chem. Eur. J.*, 22 (2016) 4695-4699.
<https://doi.org/10.1002/chem.201504836>

- [188] T. Tozawa, J.T.A. Jones, S.I. Swamy, S. Jiang, D.J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S.Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsá, A.M.Z. Slawin, A. Steiner, A.I. Cooper, Porous organic cages, *Nat. Mater.*, 8 (2009) 973-978. <https://doi.org/10.1038/nmat2545>
- [189] A.F. Bushell, P.M. Budd, M.P. Attfield, J.T.A. Jones, T. Hasell, A.I. Cooper, P. Bernardo, F. Bazzarelli, G. Clarizia, J.C. Jansen, Nanoporous organic polymer/cage composite membranes, *Angew. Chem. Int. Ed.*, 52 (2013) 1253-1256. <https://doi.org/10.1002/anie.201206339>
- [190] G. Zhu, F. Zhang, M.P. Rivera, X. Hu, G. Zhang, C.W. Jones, R.P. Lively, Molecularly mixed composite membranes for advanced separation processes, *Angew. Chem. Int. Ed.*, 58 (2019) 2638-2643. <https://doi.org/10.1002/anie.201811341>
- [191] C.D. Gutsche, Using the baskets: Calixarenes in action, in: *Calixarenes: An Introduction*, Second Edition, The Royal Society of Chemistry, Cambridge, 2008, pp. 208-237. <https://doi.org/10.1039/9781847558190-00208>
- [192] J.T. Liu, Y.C. Xiao, K.S. Liao, T.S. Chung, Highly permeable and aging resistant 3D architecture from polymers of intrinsic microporosity incorporated with beta-cyclodextrin, *J. Membr. Sci.*, 523 (2017) 92-102. <https://doi.org/10.1016/j.memsci.2016.10.001>
- [193] J. Wu, J.T. Liu, T.S. Chung, Structural tuning of polymers of intrinsic microporosity via the copolymerization with macrocyclic 4-tert-butylcalix[4]arene for enhanced gas separation performance, *Adv. Sustainable Syst.*, 2 (2018) 1800044. <https://doi.org/10.1002/adsu.201800044>
- [194] J. Wu, S. Japip, T.S. Chung, Infiltrating molecular gatekeepers with coexisting molecular solubility and 3D-intrinsic porosity into a microporous polymer scaffold for gas separation, *J. Mater. Chem. A*, 8 (2020) 6196-6209. <https://doi.org/10.1039/C9TA12028A>
- [195] J. Shen, M. Zhang, G. Liu, K. Guan, W. Jin, Size effects of graphene oxide on mixed matrix membranes for CO₂ separation, *AIChE J.*, 62 (2016) 2843-2852. <https://doi.org/10.1002/aic.15260>
- [196] M. Chen, F. Soyekwo, Q. Zhang, C. Hu, A. Zhu, Q. Liu, Graphene oxide nanosheets to improve permeability and selectivity of PIM-1 membrane for carbon dioxide separation, *J. Ind. Eng. Chem.*, 63 (2018) 296-302. <https://doi.org/10.1016/j.jiec.2018.02.030>

- [197] G. Dong, J. Hou, J. Wang, Y. Zhang, V. Chen, J. Liu, Enhanced CO₂/N₂ separation by porous reduced graphene oxide/Pebax mixed matrix membranes, *J. Membr. Sci.*, 520 (2016) 860-868. <https://doi.org/10.1016/j.memsci.2016.08.059>
- [198] Y. Wang, X. Wang, J. Guan, L. Yang, Y. Ren, N. Nasir, H. Wu, Z. Chen, Z. Jiang, 110th anniversary: Mixed matrix membranes with fillers of intrinsic nanopores for gas separation, *Ind. Eng. Chem. Res.*, 58 (2019) 7706-7724. <https://doi.org/10.1021/acs.iecr.9b01568>
- [199] B.H. Jeong, E.M.V. Hoek, Y. Yan, A. Subramani, X. Huang, G. Hurwitz, A.K. Ghosh, A. Jawor, Interfacial polymerization of thin film nanocomposites: A new concept for reverse osmosis membranes, *J. Membr. Sci.*, 294 (2007) 1-7. <https://doi.org/10.1016/j.memsci.2007.02.025>
- [200] S. Yu, S. Li, S. Huang, Z. Zeng, S. Cui, Y. Liu, Covalently bonded zeolitic imidazolate frameworks and polymers with enhanced compatibility in thin film nanocomposite membranes for gas separation, *J. Membr. Sci.*, 540 (2017) 155-164. <https://doi.org/10.1016/j.memsci.2017.06.047>