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Advances in Polymeric Membranes for CO₂ Separation

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Abstract

Global CO₂ emissions have increased steadily in tandem with the use of fossil fuels. A paradigm shift is needed in developing new ways that energy is supplied and utilized, together with the mitigation of climate change through CO₂ reduction technologies. There is an almost universal acceptance of the link between rising anthropogenic CO₂ levels due to fossil fuel combustion and global warming accompanied by unpredictable climate change. Therefore, renewable energy, non-fossil fuels and CO₂ capture and storage (CCS) must be deployed on a massive scale. CCS technologies provide a mean for reducing greenhouse gas emissions, in addition to the current strategies of improving energy efficiency. Coal-fired power plants are among the main large-scale CO₂ emitters, and capture of the CO₂ emissions can be achieved with conventional technologies such as amine absorption. However, this energy-consuming process, calculated at approximately 30% of the power plant capacity, would result in unacceptable increases in power generation costs. Membrane processes offer a potentially viable energy-saving alternative for CO₂ capture because they do not require any phase transformation. However, typical gas separation membranes that are currently available have insufficiently high permeability to be able to process the massive volumes of flue gas, which would result in a high CO₂ capture. Polymer membranes highly permeable to CO₂ and having good selectivity should be developed for the membrane process to be viable. This perspective review summarizes recent noteworthy advances in highly permeable, selective polymer membranes, particularly focusing on highly CO₂ permeable polymers that largely surpass the separation performance of conventional polymer membranes. Important classes of polymer membrane materials are highlighted, which provides an insight into polymer designs suitable for CO₂ separation from, for example, the post-combustion processes in coal-fired power plants.

1. Introduction

The emission of greenhouse gases (GHGs) mainly from fossil fuel combustion and other human economic and social activities has been escalating notably over the last century. The atmospheric concentration of CO₂ has been increasing since the mid-19th century, and the annual rate is greater than ever, which is believed to be largely associated with current global warming^[1]. To mitigate energy generation-related CO₂ emissions, the Intergovernmental Panel on Climate Change (IPCC) states in its third assessment report that the CO₂ emissions must be substantially reduced to achieve stabilization of the atmospheric CO₂ concentration during the 21st century^[2]. Today, a large number of carbon sources such as fossil fuels, biomass energy facilities, chemical industries, natural gas processing, synthetic fuel plants, and fossil fuel-based hydrogen production plants result in the emission of megatons of CO₂ per day. Recent data shows that fossil fuel-based power generation and industries, the main contributors to anthropogenic CO₂, cumulatively released about 30.8 billion tons in 2009, which represents a reduction of only 1.3% compared with 2008, a record year. In addition, it is estimated that CO₂ emissions will increase by more than 3% in 2010^[3]. This urgent situation is increasing the demand for more energy-efficient, cost-effective strategies for a massive reduction in CO₂ emissions. In the positive scenario, the use of carbon capture and storage (CCS) technologies in industry, fuel transformation and the power-generation sectors, which accounts for 14%-19% of the emissions, would result in a total of 5.1 Gt to 10.4 Gt of CO₂ being captured^[4].

In the post-combustion process, CO₂ can be captured from flue gases that contain 4% to 8% of CO₂ by volume for natural gas-fired power plants, and 12% to 15% by volume for coal-fired power plants^[4]. Typically the CO₂ is captured through the use of solvents and

subsequent solvent regeneration, sometimes in combination with membrane separation. Conventional absorption technology using amine-based solvents has been in use on an industrial scale for decades, but the challenge is to recover the CO₂ with a minimum energy penalty and at an acceptable cost (DOE target <\$20/ton CO₂)^[5]. Amine based CO₂ capture has been estimated to consume approximately 30% of the power plant capacity, with corresponding power generation cost increases of 50-90%^[6]. In the membrane-based separation process, there are challenges for treating the large volume of flue gases. The low CO₂ partial pressure gives rise to low driving forces for both permeation and separation. A combination of mild flue gas pressurization (<2 atm) and vacuum (0.2 atm) on the permeate side minimizes the energy requirements for flue gas pressurization and provides a feed/permeate pressure ratio sufficient for the desired separation. Energy savings are realized by using a slight vacuum on the permeate, because energy is expended on the CO₂-rich permeate rather than on the feed composed primarily of N₂^[7]. In order to reduce the large membrane area required, membranes with very high CO₂ throughput (or flux) are necessary to compensate for the reduced driving force for permeation. Operation at low pressure also has the benefit of capital cost reductions for membrane housings^[6]. An additional consideration is that polymer membranes should have tolerance to potentially harmful contaminants such as fly ash, SO₂, NO_x, water and trace metals that could reduce effectiveness and membrane lifetime.

In the past decades, membrane-based gas separations have been rapidly adopted industrially, because they offer advantages over conventional separation processes such as reduced environmental impact and lower capital and operating costs. The concept of membrane-based gas separation was originally proposed by Graham in 1866^[8], and was

realized as a result of Loeb and Sourirajan's practical fabrication of asymmetric membranes in 1961^[9, 10]. The first membrane gas separation process was hydrogen recovery, commercialized in 1977^[11]. The success inspired more awareness in this area, and led to different gas separation processes becoming commercially competitive with existing conventional technologies. Currently, membrane gas separation is utilized worldwide on an industrial scale for air separation (>99.5% nitrogen production and oxygen-enrichment), hydrogen recovery from ammonia purge stream, hydrocarbon/light gases separation, and CO₂ removal from natural gas^[12, 13].

In the membrane separation process, a feed gas mixture is driven by a pressure difference across the membrane. A feed mixture is separated into one or more gases, thus generating a specific gas-enriched permeate or retentate. For gases, membranes are generally used in the form of thin-film composite flat sheet spiral wound modules or hollow fibre membranes. The latter are typically utilized for industrial applications because of their high surface area per unit volume^[14]. To compete with well-established conventional separation processes and extend their applications further, however, polymer membranes with ultrahigh permeability and good selectivity must be developed. This need has been reflected in recent research efforts to make high permeance membranes targeted for CO₂ capture from flue gases in coal-fired power plants^[15]. The first CO₂ selective membranes, based on cellulose acetate and derivatives^[16], were demonstrated as early as the 1960s and the first industrial plants for CO₂ separation, using cellulose acetate membranes were installed in the 1980s. At the present time, there is much effort to develop CO₂ permeable, selective membrane materials and processes for applications such as natural gas sweetening and biogas refinery (CO₂/CH₄), CO₂ separation from post-combustion processes (CO₂/N₂) in coal-fired power plants^[17].

From a materials standpoint, polymers for gas separation membranes should meet the following requirements: good mechanical properties, thermal/chemical resistance, plasticization resistance and physical aging tolerance, which helps ensure adequate robustness and membrane lifetime under the challenging conditions encountered in practical usage^[18,19]. A benefit of low pressure operation is that CO₂-induced plasticization will not affect mixed gas selectivity. Other considerations for large scale industrial applications are important such as cost-effectiveness and whether the membranes can be readily manufactured into membrane modules. For membrane gas separation in general, to achieve sufficient separation performance in a unit module, high permeability and high selectivity for a specific species in a mixture is required. However, in glassy or rubbery polymers, a well-known trade-off relationship is empirically observed between permeability (P) and selectivity (α) for useful gas mixtures, i.e., higher permeability is gained at the cost of lower selectivity and vice versa. This trade-off relationship can be represented by a double logarithmic plot of gas pair selectivity against the gas permeability of the fastest species. Robeson demonstrated the empirical upper bounds in such plots in 1991^[20] and revised the upper bounds in 2008 by incorporating new data^[21]. Although many polymers have been investigated for gas separation membranes, only a few have been successfully commercialized, which compete with existing separation technologies, partly due to this observed trade-off behavior. Therefore, it is highly desirable to expand the spectrum of high performance polymers having much higher gas permeability, while retaining adequate selectivity and fulfilling other requirements such as processability and long-term stability.

In this perspective review, some essential background knowledge on membrane gas separation and the importance of free volume in polymer design is first provided, and then

recent advances in highly CO₂ permeable polymers with good selectivity will be discussed.

2. General Principles of Membrane Gas Separation

In gas phase membrane applications, permeance and permeability are usually used as a measure of the gas transport rate. The permeance (Q) is the pressure and area normalized parameter quantifying the productivity of an asymmetric membrane or thin film composite. The permeability (P) is typically used with dense films where the thickness (δ) is well defined and is the permeance normalized by the thickness $P=Q/\delta$. Units for the permeance are $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ or, more conveniently Gas Permeation Units, (GPU) where $1 \text{ GPU}=10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2\cdot\text{sec}\cdot\text{cmHg}$. Units for permeability are $\text{mol}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ or Barrer, where $1 \text{ Barrer} = 10^{-10} \text{ cm}^3(\text{STP})\cdot\text{cm}/\text{cm}^2\cdot\text{sec}\cdot\text{cmHg}$. Hence a polymer with a permeability of 1 Barrer will have a permeance of 1 GPU if the thickness is 1 micron. When mixed gases are used, the partial pressure difference of a gas is used^[22]. The permeability of a polymer membrane for gases is dependent on the membrane properties (e.g., physical and chemical structures), the nature of the permeant species (e.g., size, shape, and polarity), and the interaction between the membrane and permeant species. Generally, the size and shape of a gas molecule determine its diffusional (kinetic) characteristics through a given polymer membrane, where the kinetic diameter, rather than the collision diameter, is the relevant property^[23,24]. Recently, revised values for the kinetic diameters have been proposed^[25,26]. The last factor is the interaction between membrane and permeant, which is a thermodynamic characteristic related to the solubility of the gas in the polymeric membrane. As such, gas permeation behavior through polymer membranes is generally well-explained by the solution-diffusion mechanism^[27,28]. That is, separation of gas pairs can be achieved not only by their diffusion through the dense polymeric matrix but also by the solubility of specific gases within the

membrane, which relies on the physiochemical interactions between the gas species and the polymers. The permeability coefficient (or permeability), P of a penetrant is the product of the diffusion coefficient or diffusivity (kinetic parameter), D , and the solubility coefficient or solubility (thermodynamic parameter), S :

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

In a membrane gas separation process, the permeant species are sorbed in the membrane at the higher pressure upstream side, diffuse through the membrane driven by the concentration gradient (measured by the partial pressure or fugacity difference), and then they desorb at the lower pressure downstream side. The solubility ($\text{cm}^3(\text{STP}) \text{cmHg}^{-1}$) is a measurement of the amount of gas sorbed by the membrane when equilibrated at a given gas pressure and temperature. Generally, penetrant solubility increases with increasing gas condensability (i.e., higher critical temperature or high normal boiling point) and more favorable interactions with the polymer. The diffusivity ($\text{cm}^2 \cdot \text{s}^{-1}$) is a concentration independent kinetic measure of penetrant transport rate through the membrane. Gas diffusivity can be enhanced by decreasing penetrant size, increasing polymer fractional free volume elements, and increasing polymer chain flexibility^[17]. Membranes utilized in separations ideally need to possess both high selectivity and high permeability. The selectivity of the membrane to specific gas or liquid molecules is subject to the ability of the molecules to diffuse through the membrane. The permselectivity (or ideal separation factor, determined from the permeation of individual pure gases), α , is simply the ratio of two gases, A and B , being separated:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B} \right] \times \left[\frac{S_A}{S_B} \right] \quad (2)$$

The permselectivity is also the product of the diffusivity selectivity and the solubility

selectivity as shown in equation (2). Robeson's empirically observed upper bounds were quantitatively predicted by Freeman^[29] by using theoretical relationships for gas diffusivity and solubility based on the gas diameters, in Eq 1. The slope of the upper bounds was proven to be predicted by $\lambda_{AB}=(d_A/d_B)^2-1$, where d_A and d_B are the kinetic diameters^[23,24], or the revised diameters^[25,26].

Membranes are broadly classified as derived from rubbery or glassy polymers, depending on the polymer glass transition temperature^[27]. For permanent gases (those having low gas-polymer interactions) in conventional glassy polymers, diffusivity selectivity dominates the permselectivity, with smaller gas molecules diffusing faster than larger ones. Improvements in the gas separation performance of polymeric membrane can be achieved by two different approaches^[29, 30]; by increasing the solubility of faster gas in the membrane through changes in polymer molecular structure or by increasing the diffusion of faster gas. For organic vapors and hydrocarbon gases in rubbery polymers, solubility selectivity generally dominates and the gas solubility in the polymer matrix follows Henry's law and is linearly proportional to the partial pressure, or fugacity f .

$$C_D = K_D \cdot f \quad (3)$$

where C_D is the concentration of gas in the polymer matrix and is proportional through the Henry's constant (K_D). On the other hand, glassy polymers generally exhibit more complex behavior. Below the glass transition temperature, glassy polymers do not reach thermodynamic equilibrium, which leads to inefficient chain packing and excess free volume in the polymeric matrix. In this case, Langmuir sorption also occurs, increasing the gas solubility. Therefore, the total concentration of sorbed gas C within glassy membranes in the dual-mode sorption model can be elucidated by a combination of Henry's law behavior, C_D

and Langmuir type behavior, C_H .

$$C = C_D + C_H = K_D \cdot f + C'_H \frac{bf}{1+bf} \quad (4)$$

where C_H is the standard Langmuir relationship and C'_H is the maximum sorption capacity, b is the ratio of rate coefficients of adsorption and desorption.

The maximum sorption capacity related to gas transport capacity in a glassy polymer can be also linked to the proportion and distribution of free volume elements. Free volume refers to the fraction of volume not occupied by the polymer molecular chain. When molecules are packed in a condensed phase, there is a limit to the packing density that can be achieved, so each molecule actually requires more space than its molecular volume. Typically the occupied volume is taken to include the van der Waals volume multiplied by a factor of 1.3, based on the packing density of a molecular crystal at 0 K. According to this concept, the disruption in chain packing is quantified by FFV and is calculated using the following relationship:

$$V_f = (V_{sp} - 1.3V_w) \quad (5)$$

$$FFV = (V_f / V_{sp}) \quad (6)$$

where V_f is the free volume, V_{sp} is the specific volume, and V_w is the specific van der Waals volume calculated using the group contribution method of Bondi^[31, 32, 33]. For a variety of glassy polymers, this approach gives values of V_f in the range of 0.11-0.23^[34]. It indicates that glassy polymers contain a certain amount of FFV . If the proportion of free volume is increased to a large extent and it is effectively interconnected, the polymer is likely to exhibit high sorption capacity similar to that of microporous materials with high surface areas^[35]. The free volume elements of glassy polymers may also be influenced by the solvent, casting

and annealing conditions.

3. Recent Advances in Highly Permeable Polymers for CO₂ Separation

Polymeric membrane-based separation processes provide several advantages over other conventional separation techniques. First, the membrane process is a viable energy-saving alternate for CO₂ separation, since it does not require a phase change of the gases. Second, the necessary process equipment is relatively simple with only a few moving parts such as compressors or vacuum pumps, compact, relatively easy to operate and control, and amenable to scale-up. It is envisioned that polymeric membranes can be effectively used to separate CO₂ from the gases of power generation point sources, if the polymeric membranes have high CO₂ permeance (>1000 GPU, where 1 GPU = $1 \times 10^{-6} \text{ cm}^3(\text{STP}) \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} \cdot \text{cmHg}^{-1}$) and moderately good CO₂/N₂ selectivity (>30)^[6]. Although many classes of polymers may be applied to membrane technology for CO₂ separation applications, such as polyamides^[36], polyimides^[37], polyacetylenes^[38], polycarbonates^[39], polyarylates^[40], poly(phenylene oxide)s^[41], poly(ethylene oxides)^[42], polyanilines^[43], polysulfones^[44] and polypyrrolones^[45], only a few have high CO₂ permeability (> 100 Barrer). Moreover, consideration must also be given to the ability to prepare membranes with a thin gas separating layer, comprising either the skin layer of an asymmetric membrane or the coating of a thin-film composite. A polymer separating layer with a 100 nm effective thickness and a permeability coefficient of 100 Barrer will have a permeance of 1000 GPU, while a 1000 Barrer polymer with a layer thickness of 4 microns will have a permeance of only 250 GPU.

In this perspective review, we highlight highly permeable polymeric materials such as polyimides, thermally-rearranged polymers (TR polymers), substituted polyacetylenes,

polymers with intrinsic microporosity (PIMs) and poly(ethylene oxide) (PEO)-based polymers, because the majority of these polymers exhibit excellent characteristics for CO₂ separation applications (Figure 1).

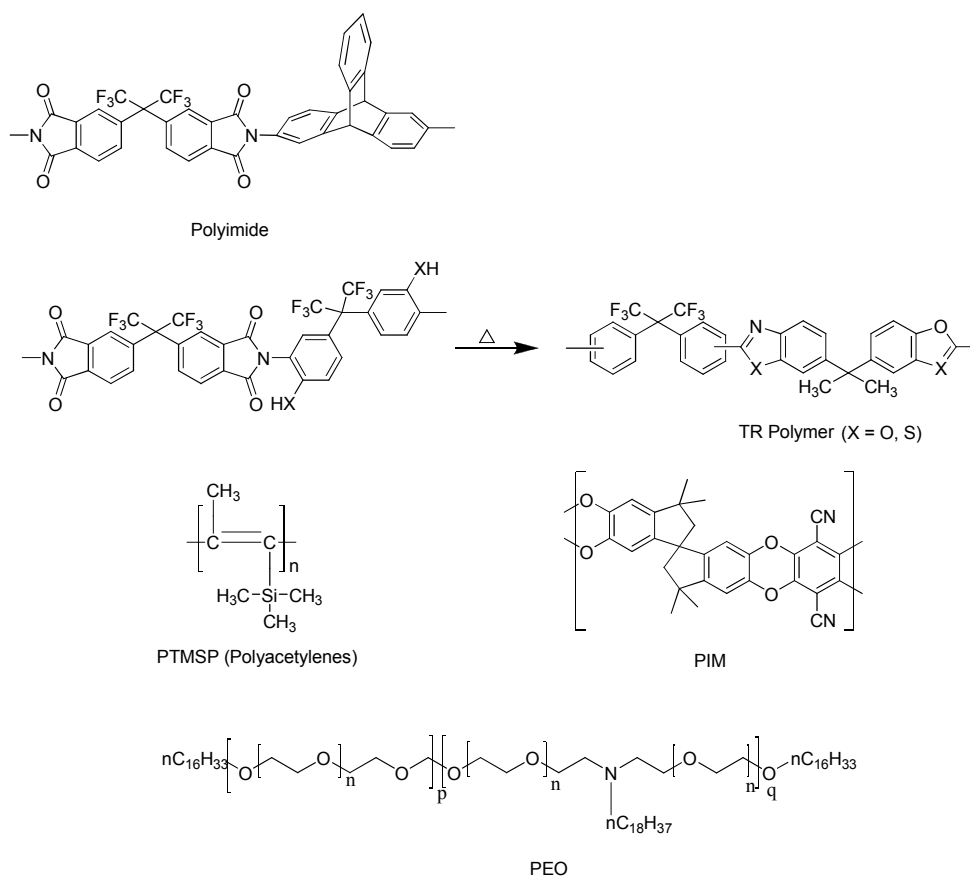


Figure 1. Representative chemical structures of highly CO₂ permeable polymers

3.1. High Permeability Polyimides

Polyimides are attractive materials for gas separation owing to their excellent gas separation and physical properties, such as high thermal stability, chemical tolerance, and mechanical strength^[46]. They are commonly prepared by step polymerization involving a

thermal or chemical imidization between a bis(carboxylic anhydride) and a diamine. The variation in structure-property relationships of polyimide membranes have been studied, relative to molar volume, density, free volume, and gas permeabilities by means of group contribution theory^[47,48]. Generally, polymer chain rigidity determines the diffusivity-selectivity while inter-chain spacing and chain mobility governs the diffusion rate. The main factors affecting the gas transport properties in polyimide membranes are (1) spatial linkage configurations, (2) type of bridging groups, and (3) bulky and polar groups incorporated into the structures^[49].

In the molecular design of polyimides for gas separation of commercially important gas pairs such as CO₂/CH₄, previous research suggests that the selectivity in polyimide membranes can be enhanced by incorporating (1) meta-linkages, (2) swivel linkages comprising bulky groups, and (3) polar and bulky pendant groups^[49]. For instance, asymmetric polyimides with meta-linkages show higher chain packing efficiency and restricted rotational freedom compared to the corresponding symmetric para-linked isomers^[50,51]. As a result, the meta-isomers show moderately lower fractional free volume (*FFV*) and gas permeability, but higher gas selectivity. Also, polyimides with bulky bridging groups reduce inter-chain rotation, resulting in less chain mobility and higher *FFV*. For example, polyimides derived from 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) with diamines such as 2,3,5,6-tetramethyl-1,4-phenyldiamine (4MPDA)^[52,53] and 3,3'-dimethylnaphthidine (DMN)^[54, 55] have increased chain stiffness due to the introduction of $-\text{C}(\text{CF}_3)_2-$ linkage groups. This linkage is believed to serve as a molecular spacer and chain stiffener; it reduces the intra-segmental mobility and limits the degree of chain packing thereby increasing the *FFV*. As a result, aromatic polyimides incorporating $-\text{C}(\text{CF}_3)_2-$

linkages tend to have both high CO₂ permeability and high CO₂/CH₄ selectivity.

The incorporation of spatial bridging groups into polyimides increases the free volume elements significantly. Polyimides containing spiro-centers^[56,57,58,59], bulky bis-phenylfluorenyl^[60] and three-dimensional rigid triptycene frameworks^[61] have been reported, which exhibit some of the highest permeability and selectivity data so far for polyimides, even exceeding the empirical upper bound performance limit. Polyimides with high free volume and appropriate cavity size to separate gas molecules of similar kinetic diameter, as well as those with polar or bulky groups were also reported, such as silica pendant groups^[62], hydroxyl, carboxylic acid, and sulfonic acids, or other bulky groups^[63]. The presence of bulky and polar pendant groups increases inter-chain spacing and reduces the packing efficiency of polymer chains, hence significantly improving permeability. Furthermore, gas transport properties in polyimides is influenced by hydrogen bonding and intermolecular interactions^[64,65].

However, problems related to the swelling and plasticization of polyimides by CO₂ with mixed gases has hindered their adoption in CO₂ gas separation applications. In general, glassy polymers, including polyimides, swell by sorption of CO₂ that is present in a mixed gas, thereby increasing the permeation of other species (e.g., CH₄ and N₂) in the mixed gas. Hence, the increased permeability of the 'slower' gas in the mixture results in losses in selectivity, in mixed gas separations. Since plasticization and physical aging originate from chain flexibility and the non-equilibrium state of glassy polymers, several approaches can mitigate these undesirable phenomena by increasing polymer chain rigidity or by inter-chain crosslinking. For example, plasticization-resistant membranes were prepared by cross-linking of carboxyl-containing polyimides with aliphatic diamines (C2 – C4) or propanediol or by a

thermal decarboxylation cross-linking reaction^[66]. Cross-linking not only offers the potential to improve the mechanical and thermal properties of a membrane, but also improve gas transport properties. Polyimide networks in conjunction with pseudo-interpenetrating networks (IPN) also restrict the mobility of the polymer chains and suppress CO₂-induced plasticization^[67]. In addition, polycondensation of dianhydride and tetraamine monomers provide polypyrrones, which are structurally similar to polyimides. However, they have considerably more rigid chains due to the ladder structures, with higher thermal and chemical resistance, and behave similarly to organic molecular sieves^[68, 69, 70]. Pure gas permeability and selectivity of highly permeable polyimide membranes are shown in Table 1.

<Table 1> ^[71,72,73,74]

More recently, a new triptycene polyimide design was reported^[61], which has high internal free volume elements derived from three-dimensional rigid triptycene units, simultaneously having high permeability and selectivity. These triptycene polyimides are readily soluble in common organic solvents; thus they are processable for membrane fabrication. The triptycene-based polyimide exhibits very good tolerance to CO₂ plasticization in mixed gas separation^[61], e.g., CO₂/CH₄, while many glassy polymers having high *FFV* suffer from a large reduction in mixed gas selectivity. It is believed that this behavior arises from a physical hindrance effect due to the interlocking of the triptycene phenyl rings perpendicular to the polymer backbone, providing the spatial orientation for π - π interactions to occur between phenyl rings. The triptycene-based polyimide membranes can impact emerging CO₂ gas separation applications such as natural gas purification and biogas

purification for clean energy resources.

3.2. Thermally Rearranged (TR) Polymers

Membrane-based separation systems need to achieve both high gas throughput and high selectivity. For polymer membranes, separations depend on the size of the cavities that lead to porosity on the sub-nano scale. These cavities, so called free volume elements, generally exhibit a broad scale distribution. Recently, rod-like polymers derived from functionalized polyimides by a thermal post-membrane conversion process, i.e., thermally rearranged (TR) polymers. These appear to have more uniform cavity sizes that create tailored free volume elements with well-connected morphology in amorphous polymers. The TR membranes have outstanding transport and separation properties for small gas molecules and ions. The TR membrane concept was proposed by Park and Lee^[75,76], which adopts a post-membrane fabrication polymer-modifying reaction and to obtain dense polybenzoxazole (PBO) and polybenzothiazole (PBT) membranes by the thermal rearrangement of soluble aromatic polyimides containing ortho-linkage positioned functional groups (e.g., –OH and –SH). The TR polymers exhibit excellent separation performance, particularly for CO₂/CH₄ mixtures, with high selectivity and permeability due to an unusual microstructure whose cavity size and distribution could be further controlled by the proper selection of template molecules and heat treatment protocols. The unexpected physical phenomena in TR polymers are of great importance in that the random chain conformations that occur in the condensed polymer phase lead to tuned microvoids, which contribute to performance enhancement in the selective molecular transport. One of the strongest benefits of the thermal rearrangement concept is the relatively easy degree of control over the average interchain spacing and free

volume elements that directly lead to molecular sieving effects. Thermal rearrangement is a potential method for producing polymeric membranes with high permeability and selectivity suitable for gas separations.

One of the attractive features of TR membranes is their strong tolerance to plasticization in mixed-gas permeation experiments at 35 °C for CO₂ partial pressures ^[75] reaching 20 atm. The same group reported a series of TR polymer membranes with ultrahigh gas selectivity derived from structurally different copolymer precursors, and hypothesized that the use of copolymers is desirable to generate desired polymeric properties to enable them to be processed into fibre or flat sheet form ^[77]. The polymeric precursors are composed of polyimide (PI) and hydroxyl-containing polyimide (HPI), the latter of which can be thermally converted to TR polybenzoxazole (PBO) units. As a result, surface area and pore volume varied significantly relative to the ratio of PBO and PI domains. Gas permeation and separation performance (e.g., O₂/N₂ and CO₂/CH₄) was linearly dependent on the ratio of PBO, surpassing the empirical upper bounds of conventional polymeric membranes. In addition, poly(benzoxazole-co-pyrrolone) (PBO-co-PPL) copolymers having various compositions were prepared by thermal rearrangements from the respective polyimide precursors containing hydroxyl or amino groups ^[78]. These copolymers also showed higher CO₂ permeabilities than their precursors, as well as higher gas selectivity than the individual PBO or PPL homopolymers. Indeed, thermally rearranged copolymers of rigid-chain and selective pyrrolones with highly permeable benzoxazoles having high free volume elements, is a novel route to enhance gas selectivity without significant loss in gas permeability. Using a similar concept, microporous polybenzimidazole (TR-PBI) membranes were reported by thermal rearrangement ^[79]. The membranes showed exceptionally high permeability to small

gas molecules as well as excellent molecular sieving properties. In general, typically-structured PBI membranes have very rigid, well-packed chains due to their strong intermolecular interactions, resulting in very low gas permeation properties unsuitable for gas separation. However, alkaline hydrolysis of PPL followed by thermal rearrangement led to highly permeable TR-PBI membranes having microporous character (i.e., high fractional free volume).

3.3. Highly Permeable Substituted Polyacetylenes

Highly permeable substituted polyacetylenes generally have many molecular scale voids, which are formed by the presence of bulky pendant groups. They are prepared by polymerization of acetylenic monomers using transition metal catalysts^[80]. It is known that various metal catalysts yield polymers with different geometric structures and properties. For example, NbCl₅ gives a more *cis*-rich poly(1-trimethylsilyl-1-propyne) than TaCl₅^[81]. The pendant groups inhibit rotation of the rigid backbone^[82], which leads to inefficient chain packing (Table 2). The large free volume distribution includes both small disconnected elements and larger continuous microvoids. However, the large free volume elements collapse with time owing to vapour sorption, contamination⁸³ and/or relaxation phenomenon, resulting in significant decreases in gas permeability.

Poly(1-trimethylsilyl-1-propyne) (PTMSP) and related polymers in the class are among the most permeable polymers to any gases, having almost ten times higher permeability than the rubbery polymer poly(dimethylsiloxane). Hence, its gas transport properties have been extensively studied^[84, 85, 86]. Although glassy PTMSP exhibits some properties that are similar to rubbers, gas transport through polyacetylenes is described in

terms of the dual-mode sorption mechanism^[87].

The molecular design for highly permeable polyacetylenes is usually focused on incorporating different substituent groups. It has been deduced that the steric shape of the substituents attached to poly(diphenylacetylenes) plays a very important role in gas permeability^[88,89]. Polyacetylenes with *t*-butyl substituents provide higher permeability. In 2008, Hu et al. reported an indan-containing poly(diphenylacetylene) derivative, which exceeded the oxygen permeability of even PTMSP, which previously had the highest permeability^[90]. In some substituted polyacetylenes, especially those with very high *P* values, which were based on both high diffusivity and solubility contributions, long-chain *n*-alkyl substituents had relatively high diffusivity, while those with phenyl substituents had relatively high solubility^[80]. It is believed that large microvoids give rise to high diffusion coefficients compared to other glassy polymers and also lead to high apparent solubility coefficients.

<Table 2> ^[38,90]

Although substituted polyacetylenes have characteristically high permeabilities, their selectivities are low, in accordance with performance trade-off behavior. Furthermore, significant aging problems in polyacetylenes impede their application in industrial membranes. Although polyacetylene-based membranes have high CO₂ permeability, they have not been considered for CO₂ separations because of low selectivity and strong physical aging. However, there are opportunities for improving the properties of substituted polyacetylenes through macromolecular structural design. For example, approaches include

grafting CO₂-philic groups onto the PTMSP backbone, in order to enhance the solubility selectivity^[91], reversing ageing by methanol treatment^[92], or reducing ageing effects by cross-linking the membrane^[93].

3.4. Polymers with Intrinsic Microporosity

High free volume polymers can be achieved through rigid ladder backbone structures, instead of linear chains formed by single bonds with rotational freedom. Ladder polymers have traditionally been considered to be generally dense, intractable materials with poor mechanical properties. The basis for this is founded on the premise that linear ladder polymers are unable to form highly entangled chain matrices. However, in 2002, pioneering work on new ladder polymers incorporating ‘sites of contortion’ was reported by Budd and McKeown. Originally, the concept developed out of work aimed at producing high surface area cross-linked polymer networks incorporating catalytic centers^[94,95]. Subsequently it was found that readily soluble, membrane-forming rigid ladder polymers with good mechanical properties could be prepared^[96,97]. This class of materials is obtained by polycondensation reaction of tetrahydroxy-monomers containing spiro- or contorted centers with tetrafluoro-monomers^[98,99]. The resulting ladder polymer backbones have no degrees of conformational freedom, but are sufficiently contorted to prevent effective packing in the solid state as well as to provide some mechanical strength through entanglement^[100]. Furthermore, the microporous structures of these polymers are not as highly dependent on process and thermal treatment history as previous materials, and hence the term ‘polymers of intrinsic microporosity’ (PIMs) was coined by the inventors. Compared with conventional molecular sieves, they represent a new class of microporous material with interconnected pores less than

2 nm in size. Unlike inorganic microporous materials, such as zeolites and activated carbon, they generally have very good solubility and are thus readily processable.

The term 'PIM-1' was designated for a fluorescent yellow high molecular weight polymer with one of the simplest structures in the PIM class of materials, prepared by polycondensation reaction of commercial monomers 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethylspiro-bisindane with tetrafluorophthalonitrile. PIM-1 is soluble in a number of solvents such as chloroform, toluene or tetrahydrofuran, and can be cast from solution to form robust membranes. Low-temperature N₂ adsorption–desorption analysis indicates that PIM-1 in powder or membrane form has a high apparent surface area ($S_{\text{BET}} = \sim 800 \text{ m}^2/\text{g}$) and exhibits microporous character. PIMs are considered as amorphous materials, since there is no evidence of crystallinity or a glass transition below the decomposition temperature. The latter observation may be expected, since there is no degree of chain rotational mobility, at least over short length scales. Initial data for PIM-1 membranes exhibited gas permeabilities exceeded only by very high free volume polymers such as PTMSP and Teflon AF2400. Combined with selectivities, the performance trade-off is typically located between the 1991 and the 2008 Robeson upper bounds for gas pairs, such as O₂/N₂ and CO₂/CH₄ and it is an upper bound material for CO₂/N₂^[101]. In the majority of glassy polymers, the typical order of permeability is He > CO₂. However, PIM-1 has an unusually high CO₂ permeability, with the order of decreasing permeability being CO₂ > H₂ > He > O₂ > CH₄ > N₂. This is because CO₂ selectivity for PIM-1 is dominated by high solubility selectivity, and less so by diffusivity selectivity. Subsequent studies showed that permeability could be substantially enhanced by a methanol treatment, which helps to remove residual bound casting solvent^[102].

Although many PIMs could be theoretically prepared by double aromatic

nucleophilic substitution (S_NAr) polycondensation, only a few PIMs structures having high molecular weight have been reported. This can be attributed to (1) a limited choice of available monomers, (2) reactivity of available monomers in producing sufficiently high molecular weight polymers, (3) poor solubility of the growing chain during polycondensation and (4) side reactions and cross-linking. Solvent processable materials with high molecular weight are crucial for fabricating gas separation membranes in the form of thin film composites, free-standing asymmetric membranes, or isotropic films^[103]. Therefore, an important step in the evolution of PIMs for CO_2 selective separations is to expand the spectrum of high molecular weight materials having new structures, derived either from monomers or by modification, for the purpose of determining the structure – gas transport properties of this unique class of materials. From the solution-diffusion model, an improvement in CO_2 selectivity can be achieved by a combination of greater gas diffusivity selectivity or by an increase in the solubility of the faster gas (i.e. CO_2) in the polymer matrix.

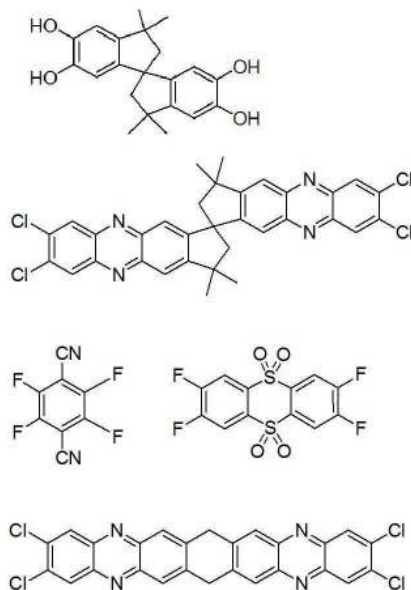


Figure 2. PIM monomers providing different unit lengths

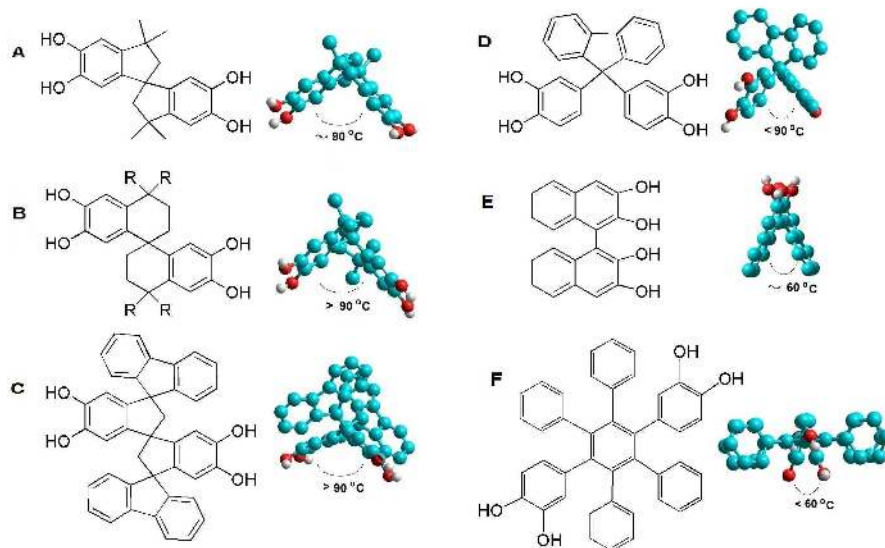


Figure 3. Visual models of PIM monomers with different angle of spiro or twist centers as simulated with energy minimization

In the majority of previous work, increased performance was achieved mainly by improving diffusivity-selectivity through an increase in the chain rigidity or by tuning cavity size. Three factors significantly affecting PIM diffusivity-selectivity appear to be (1) the molecular length of the quasi-linear ladder units between contorted centers (Figure 2), (2) the angle of the spiro- or contorted (twist) center (Figure 3), and (3) pendant groups on the polymer backbone (Figure 4).

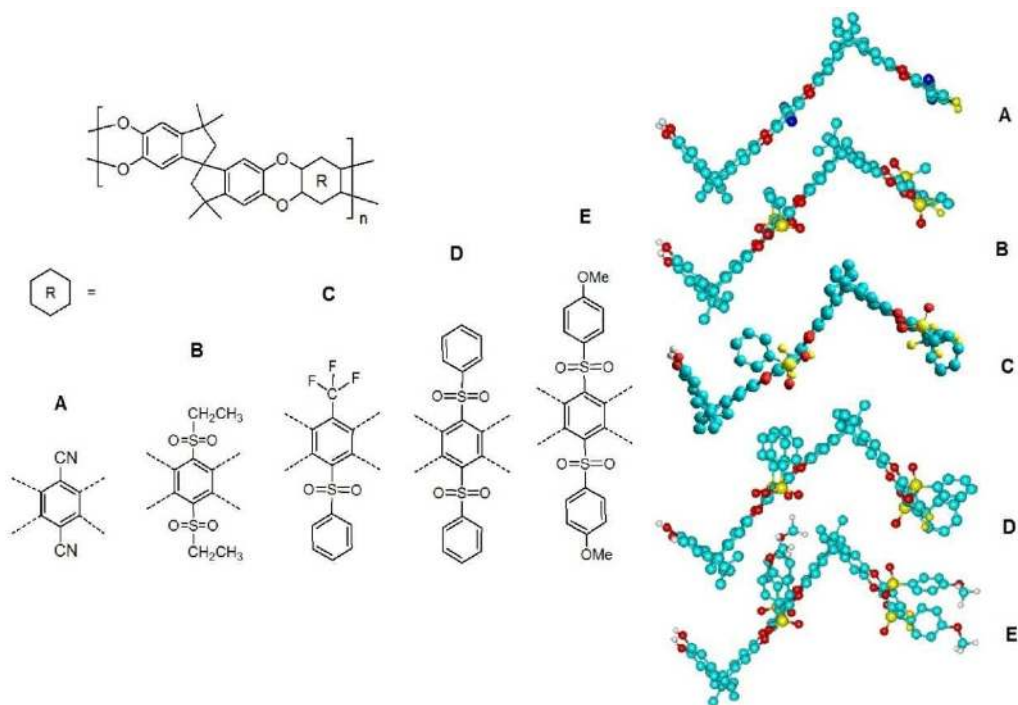


Figure 4. Visual models of PIM monomers with different pendent groups as simulated with energy minimization. Adapted from refs. [103 and 113].

The permeability / selectivity properties could be tuned by incorporating molecular units of different lengths between the spirocenters, such as thianthrene^[104], 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene^[105], ethanoanthracene^[106] and PIM-7 containing pyrazine^[107]. The angle of the spiro or twist centers also affects the permeability / selectivity properties^[108,109,110,111], for example, dinaphthyl^[108], spiro-fused fluorene-based monomers^[109], and 1,2- or 1,4-di(3',4'-dihydroxyphenyl)tetraphenylbenzene^[111]. Pendant substituents on the PIMs backbone may also increase chain rigidity, and act as interchain filling material, which effectively tunes the cavity shape and size, such as carboxylic acid groups^[112], sulfone-based groups^[103], and trifluoromethyl groups^[113].

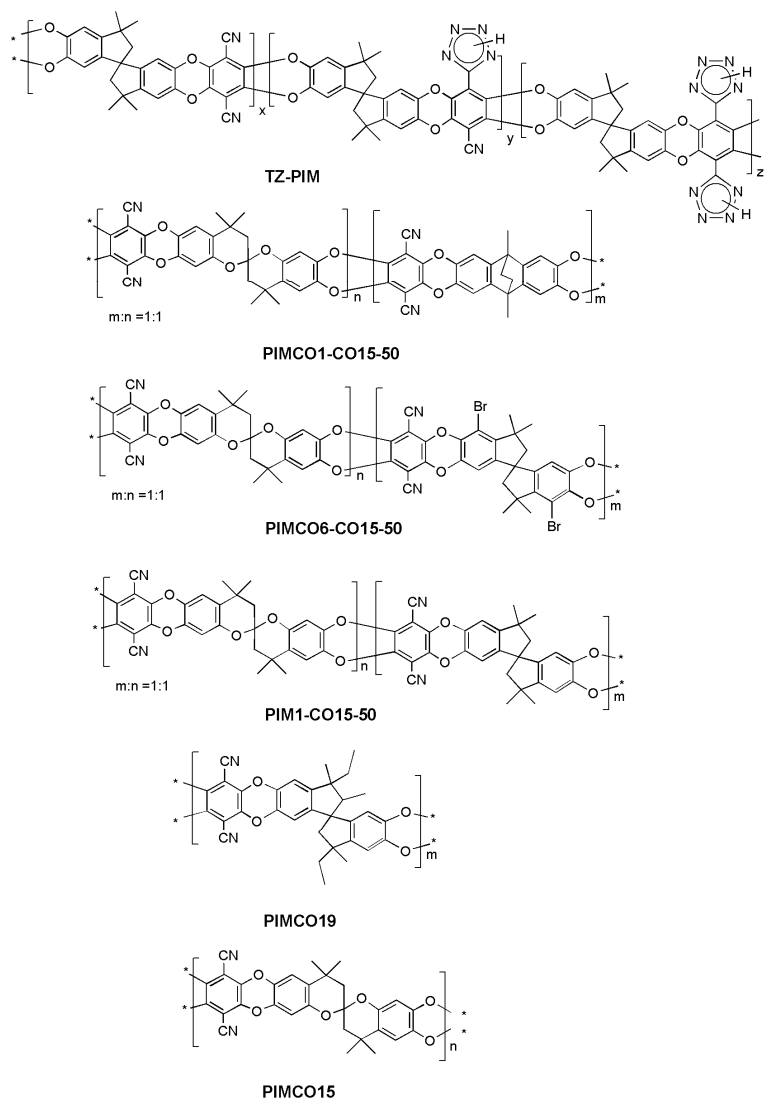


Figure 5. PIMs with high solubility coefficients

A different approach to enhancing CO₂ selectivity is by increasing the solubility-selectivity of the “faster gas”, since even modest increases in solubility-selectivity should lead to obvious improvements in overall selectivity. Fritsch et al. reported novel PIMs with spiro-bischromane structures, among which two polymers, PIMCO1-CO15-50 (a) and (b) showed remarkably high solubility coefficients for CO₂ even compared to the value for PIM-1

(Figure 5). Hence, although they may not provide a significant improvement over PIM-1 for separations involving permanent gases, these two polymers have good selectivity for separations involving condensable gases and vapors due to the enhanced solubility contribution to their overall permeability^[114].

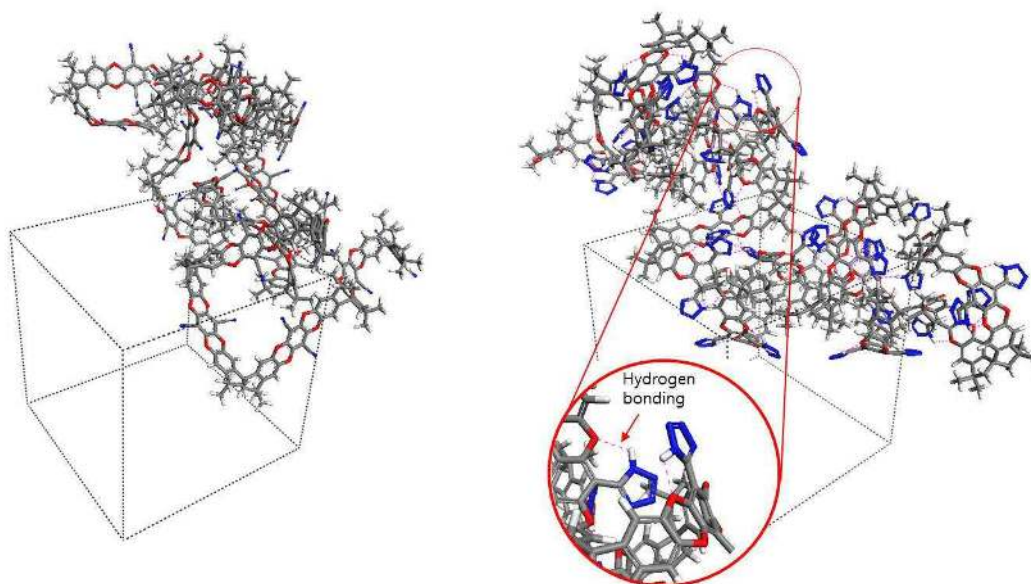


Figure 6. Three-dimensional view of PIM-1 in an amorphous periodic cell (the number of repeat units in PIM-1 is 20), and (c) three dimensional view of TZPIM-3 containing tetrazole in an amorphous periodic cell (the number of repeat units in TZPIM is 20; 100% full conversion from nitrile groups to tetrazole groups; the blue dotted lines indicate possible hydrogen bonding modes). Adapted from ref. [115]. Nature Publishing Group, Macmillan Publishers Ltd.

Recently, a new class of PIMs, incorporating tetrazoles into the microporous polymeric framework, was shown to have very high permeability for CO₂ and excellent CO₂/N₂ mixed gas separation, even under polymer plasticization conditions (Figure 6)^[115].

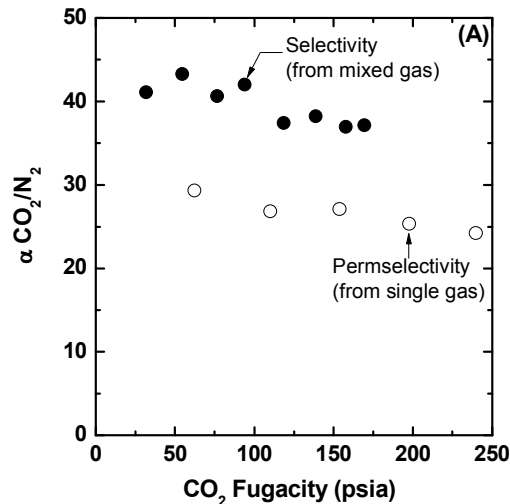


Figure 7. (a) Effect of CO₂ partial pressure on mixed-gas CO₂/N₂ selectivity in TZPIM-2 at 25 °C. Mixed gas composition (in mol% CO₂ : mol% N₂) was 50:50. (b) Effect of CO₂ partial pressure on mixed-gas CO₂/CH₄ selectivity in TZPIM-2 at 25 °C. Mixed gas compositions (in mol% CO₂ : mol% CH₄) were 50:50 and 80:20. Adapted from ref. [115]. Nature Publishing Group, Macmillan Publishers Ltd.

The presence of the tetrazole groups leads to favorable CO₂ sorption and selective pore blocking by presorbed CO₂ molecules, thus limiting access by other light gas molecules such as nitrogen (Figure 7). The introduction of tetrazoles into PIM is the first example of a [2+3] cycloaddition modification of a polymer containing aromatic nitrile groups with an azide. This strategy of incorporating nitrogen heterocycles into PIMs provides new directions in the design of other polymeric membrane materials for important CO₂ separation processes. Pure gas permeability and selectivity of a variety of structural PIM membranes are shown in Table 3. PIMs also undergo some degree of physical aging and plasticization. PIM-1 was cross-linked with diazides in order to reduce plasticization at high CO₂ partial pressures^[116].

<Table 3> [57, 96, 100, 103, 104, 106, 108, 112, 113, 114, 115, 116, 117]

3.5. Solubility-Selective Poly(ethylene oxide) (PEO) Based Membranes

PEO, or more generally, polyethers have been identified as outstanding CO₂-selective materials, due to their relatively easy fabrication^[118,119] and high performance, which has been attributed to the strong interaction between the high concentration of polar ether oxygen atoms and CO₂^[120]. However, PEO has a strong tendency to crystallize, due to the polar oxygen atoms in the matrix, bringing about efficient polymer chain packing that leads to significant reductions in gas permeability. There has been no systematic study of gas transport properties in pure PEO. Various strategies have been proposed to inhibit or depress crystallization by changing the content and molecular weight of the ethylene oxide segment or by tuning of the micro-domain morphology. Among the main techniques to reduce crystallinity in PEO, the design of purely polymer structures, such as block copolymers with short ethylene oxide (EO) segments that effectively prevent crystallization at room temperature, and highly branched, cross-linked PEO network, have attracted the most attention.

The copolymers typically have microphase-separated structures containing soft PEO segments and hard segments such as polyamides^[121], (Pebax[®] polyether block amide), polyimides^[122] and polysulfone^[123]. The hard segments provide mechanical stability and inhibit crystallization of PEO. The PEO phase in these block copolymers is believed to be the continuous path for gas diffusion, because of the similar values of CO₂/N₂ selectivity in these copolymers. The morphology is believed to determine the gas permeability, such as the domain shape and spatial arrangement, which is influenced by the hard segment composition and the lengths of the PEO and hard segment blocks. The development of innovative PEO membranes, which are capable of efficiently and selectively permeating CO₂ from other gases while maintaining high permeability, is still a major challenge. Several PEO copolymers with

high CO₂ permeability were synthesized^[124]. Recently, Nijmeijer et al.^[125,126] reported a series of PEO membranes based on a highly permeable polyether-based segmented block copolymer. For example, a block copolymer system based on soft segments containing a random distribution of PEO and PPO and uniform tetra-amide (T6T6T) hard segments, referred to as PEO-*ran*-PPO-T6T6T, achieved CO₂ permeabilities as high as 470 Barrer with selectivity of 43 for the CO₂/N₂ gas pair^[127]. The PEO copolymer was further modified to give significantly higher CO₂ permeability and CO₂/light gas selectivity than block copolymers by introducing certain additives. When PEO-*ran*-PPO₅₀₀₀-T6T6T was blended with poly[dimethylsiloxaneco-methyl(3-hydroxypropyl)siloxane]-graft-poly(ethylene glycol) methyl ether — PDMS-PEG, CO₂ permeability of blends increased from 447 to 896 Barrer with a selectivity decrease from 42.5 to 36.0 for the CO₂/N₂ gas pair^[128]. Further development of highly permeable block copolymer systems for CO₂ separation based on the concept of combining soft and hard segments in PEO-based membranes is an active area of research.

Cross-linked polymers based on PEO, having less crystallinity, have been prepared by plasma irradiation^[129] or UV photo-polymerization^[130]. These materials may provide improved chemical resistance and suppressed plasticization by CO₂ (or other gas impurities). Hirayama^[131] reported that CO₂ solubility significantly increased with PEO content, while CO₂/N₂ selectivity changed slightly, in the range of 56-69 at 25 °C. Freeman et al.^[129] reported cross-linked PEO membranes with excellent gas separation performance (CO₂ permeability around 400 Barrer at 35 °C, 10 atm), using acrylate monomer and cross-linking.

4. Conclusions

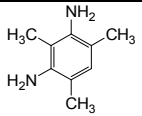
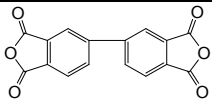
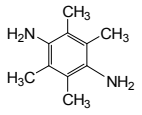
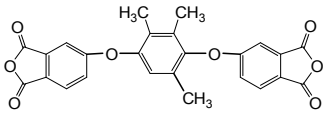
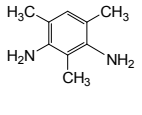
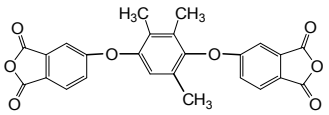
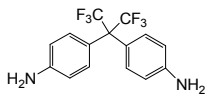
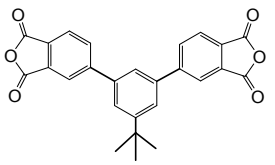
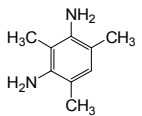
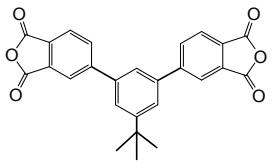
Membrane technology could play an important role in separating or capturing CO₂ from large point sources such as coal-fired power plants, cement and steel plants. Membranes compete with other separation processes on the basis of overall economics, safety, environmental and technical aspects. Thus, improving the separation performance of polymeric membranes for CO₂ capture from flue gas and other industrial sources is a very active area of research. In this perspective review, a number of different classes of polymers have been discussed as high permeability materials for gas separation membranes that are effective for separating CO₂. Useful CO₂ separation membranes should ideally possess a number of properties such as 1) high CO₂ permeability (more practically, high CO₂ flux), 2) high CO₂/gas selectivity (especially mixed gas selectivity, rather than pure gas permselectivity), 3) tolerance against CO₂ plasticization, 4) no severe physical aging, 5) low cost, 6) ability to be economically fabricated into different membrane modules (e.g., hollow fibre or spiral wound modules) and 7) thermal and chemical resistance. The direction of research for CO₂-selective polymer membrane materials in recent years is to achieve ultra-high CO₂ permeability in polymers via new concepts – cavity engineering in rigid or semi-rigid, amorphous glassy polymers for improving both fast CO₂ diffusion and CO₂ sorption capacity. PIMs and TR polymers are representative polymers belonging to this family. These polymers have rigid backbones, retaining high selectivity, and the free volume elements (cavity sizes and shapes) can also be further controlled via physical and chemical modification methods, which lead to high diffusion rates through cavities. Subtle changes in molecular architecture can result in profound effects on gas permeation and separation properties. That is, the diffusivity-selectivity can be enhanced by increasing free volume and tuning its distribution. The solubility can be enhanced by introducing CO₂-philic groups.

Additionally, it is also important to ensure that membranes are physically durable and resistant to both chemical attack and plasticization, while maintaining good processability. For this reason, research efforts must be directed towards designing readily processable polymers that have desirable combinations of permeability and selectivity, with long-term stability, in order to have immediate significant impact on scale-up and commercialization.

Acknowledgements

The research support of the WCU (World Class University) program, National Research Foundation (NRF) of the Korean Ministry of Science and Technology (No. R31-2008-000-10092-0), is gratefully acknowledged.

Table 1 Gas permeability and selectivity in selected polyimide dense films.

amine	anhydride	P (atm)	T (°C)	$P(\text{CO}_2)$ (Barrer)	$P(\text{N}_2)$ (Barrer)	$P(\text{CH}_4)$ (Barrer)	α CO_2/N_2	α CO_2/CH_4	Ref
		10/2	35	137	8.42	8.08	16.3	17	71
		1	30	200	8.1	7.6	24.7	26.3	72
		1	30	110	3.8	4.0	28.9	27.5	73
		3	/	114	5.8	5.0	19.6	22.9	73
		3	/	600	35.1	47.6	17.1	12.6	73

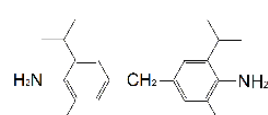
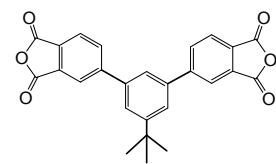
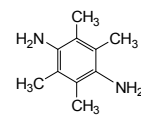
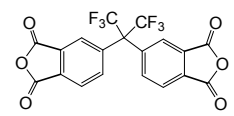
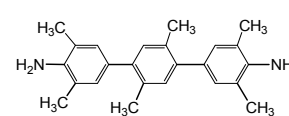
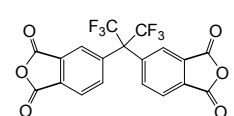
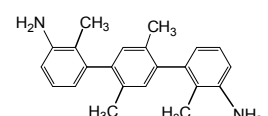
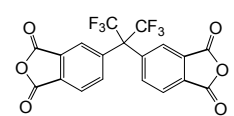






		3	/	196	10.8	14.7	18.1	13.4	73
		10	35	440	35.6	28.2	12.4	15.6	71
		1	30	360	16.5	15.0	21.8	24.0	74
		1	30	190	7.3	5.6	26.0	33.9	74

Table 2 Side Groups and gas permeability and selectivity in selected substituted polyacetylenes dense films .

$(-CR=CR^2-)_x$								
R	R ²	P (atm)	$P(\text{CO}_2)$	$P(\text{N}_2)$	$P(\text{CH}_4)$	α	α	Ref
		up/down	(Barrer)	(Barrer)	(Barrer)	CO_2/N_2	CO_2/CH_4	
Me	SiMe ₃	1	47000	11500	29900	4.09	1.57	90
C ₆ H ₄ F (<i>p</i>)		1	47000	15600	34300	3.01	1.37	90
C ₆ H ₄ F (<i>m</i>)		1	35200	12000	27800	2.93	1.26	90
C ₆ H ₃ F ₂ (<i>p</i> , <i>m</i>)		1	44200	16600	35000	2.66	1.26	90
C ₆ H ₃ F ₂ (<i>m</i> , <i>m</i>)		1	36100	13100	29100	2.76	1.24	90
C ₆ H ₄ Me(<i>p</i>)		1	16900	4100	10100	4.12	1.67	90
C ₆ H ₅		1	36400	10400	25200	3.50	1.44	90



C ₆ H ₄ SiMe ₃ (<i>p</i>)		1	2000	170	470	11.7	4.25	90
C ₆ H ₅		1	390	30	60	13.0	6.50	90
H	C(CH ₃) ₃	1 / vacuum	560	43	85	13.0	6.59	38
Me	SiMe ₂ CH ₂ SiMe ₃	1 / vacuum	310	21	45	14.8	6.89	38
Me	SiMe ₂ CH ₂ CH ₂ SiMe ₃	1 / vacuum	150	14	28	10.7	5.36	38
H	<i>o</i> -C ₆ H ₄ SiMe ₃	1 / vacuum	290	24	38	12.1	7.64	38
H	<i>o</i> -C ₆ H ₄ CF ₃	1 / vacuum	130	7.3	6.6	17.8	19.7	38
Me	<i>n</i> -C ₇ H ₁₅	1 / vacuum	130	14	40	9.29	3.25	38
Cl	<i>n</i> -C ₈ H ₁₇	1 / vacuum	170	16	46	10.6	3.70	38
Cl	<i>n</i> -C ₆ H ₁₃	1 / vacuum	130	11	33	11.8	3.94	38
Cl	<i>n</i> -C ₄ H ₉	1 / vacuum	180	10	30	18.0	6.00	38
H	CH(<i>n</i> -C ₅ H ₁₁)SiMe ₃	1 / vacuum	120	8.7	21	13.8	5.71	38

Table 3 Gas permeability and selectivity in selected PIM dense films.

Name	P up/down	$P(\text{CO}_2)$ (Barrer)	$P(\text{N}_2)$ (Barrer)	$P(\text{CH}_4)$ (Barrer)	α CO ₂ /N ₂	α CO ₂ /CH ₄	Ref
PIM-1	200-700mbar /30°C	11200	610	1160	18.4	9.6	96
PIM-7	200mbar/30 °C	1100	42	62	26.2	17.7	100, 117
TFMPSPI1	3.4 atm /25°C	731	33		22		113
DSPIM1-33	3.4 atm /25°C	1408	88		16		103
DSPIM2-33	3.4 atm /25°C	1077	52		20.7		103
DSPIM3-33	3.4 atm /25°C	2154	93		23		103
DNPIM-50	3.4 atm /25°C	2627	132		19.9		108
TOTPI100	3.4 atm /25°C	3056	190		16.1		104
DNTOTPI100	3.4 atm /25°C	3065	172		18.0		104
C-PIM-1h	3.4 atm /25°C	2543	162		15.7		112
C-PIM-2h	3.4 atm /25°C	2058	99		20.8		112
C-PIM-3h	3.4 atm /25°C	1056	48		22.0		112
C-PIM-4h	3.4 atm /25°C	620	24		25.8		112
cross-linked PIM-1/azide1(80:20)	3.4 atm /25°C	580	32		18.1		116
cross-linked PIM-1/ azide2(80:20)	3.4 atm /25°C	219	8		27.4		116

TZPIM-2	3.4 atm /25°C	3076	101		30.5		115
TZPIM-1	3.4 atm /25°C	2509	87		28.9		115
PIM-PI-1	200-500mbar /30°C	1100	48	77	22.9	14.3	57
PIM-PI-2	200-500mbar /30°C	210	9	9	23.3	23.3	57
PIM-PI-3	200-500mbar /30°C	520	23	27	22.6	19.3	57
PIM-PI-4	200-500mbar /30°C	420	16	20	26.3	21	57
PIM-PI-7	200-500mbar /30°C	510	19	27	26.8	18.9	57
PIM-PI-8	200-500mbar /30°C	3700	161	260	23.0	14.2	57
Cardo-PIM-1	200-500mbar /30°C	430	13	22	33	19.5	106
PIM-CO15	200-500mbar /30°C	2 000	83	130	24.1	15.4	114
PIM1-CO15-75	200-500mbar /30°C	2 570	110	180	23.4	14.3	114
PIM1-CO15-50	200-500mbar /30°C	4 600	210	370	21.9	12.4	114
PIMCO1-CO15-50	200-500mbar /30°C	5 400	240	350	22.5	14.3	114
PIMCO2-CO15-50	200-500mbar /30°C	5300	260	430	20.4	12.3	114
PIMCO6-CO15-50	200-500mbar /30°C	3 800	170	280	22.4	13.6	114
PIMCO19-CO15-50	200-500mbar /30°C	3 400	150	260	22.7	13.1	114
PIM-CO19	200-500mbar /30°C	6 100	320	580	19.1	10.52	114

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