

## 물리적 노화로 인한 미세 다공성 중합체의 투과성 저하

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(2019년 8월 15일 접수, 2019년 8월 28일 수정, 2019년 8월 29일 채택)

### Aging: Degradation of Permeability in Microporous Polymeric Membranes

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(Received August 15, 2019, Revised August 28, 2019, Accepted August 29, 2019)

**요 약:** 산업 응용에 적용할 수 있는 중합체 막의 상용화 전에, 고성능 중합체가 실질적인 도전, 즉 연장된 서비스 시간에 대한 장기 안정성을 극복해야 하는 과제가 남아있다. 매우 높은 분수 자유 부피(fractional free volume) 및 높은 투과성을 나타내는 고유한 미세 다공성 중합체(polymers of intrinsic microporosity)는 비효율적 무작위 패킹에 의해 생성된 여분의 부피가 물질의 부피적 평형에서 멀어짐과 동시에, 다시 부피적 평형 상태로 복귀하려는 특성, 즉 자유 부피를 줄여가는 특징으로 인해 투과성을 감소시키는 물리적 노화에 영향을 받기 쉽다. 본 논문에서 우리는 미세 다공성 고분자의 물리적 노화를 재검토하고 PIM에서 물리적 노화를 완화하려는 가장 두드러진 시도 중 일부를 논의할 것이다

**Abstract:** Before the commercialization of polymeric membranes applicable for industrial application, the homework remains for the high-performance polymers to overcome the practical challenge: long-term stability for prolonged service time. Polymers of intrinsic microporosity (PIMs), exhibiting exceptionally high fractional free volume and high permeability, are susceptible to physical aging where the extra volume created by the inefficient ladder-type packing will lead them from the volumetric equilibrium and reduce the free volume/permeability over time. Here, we will re-examine the physical aging of polymers of intrinsic microporosity, and discuss some of the most prominent attempts to mitigate physical aging in PIMs.

**Keywords:** *physical aging, polymeric membrane, permeability, selectivity*

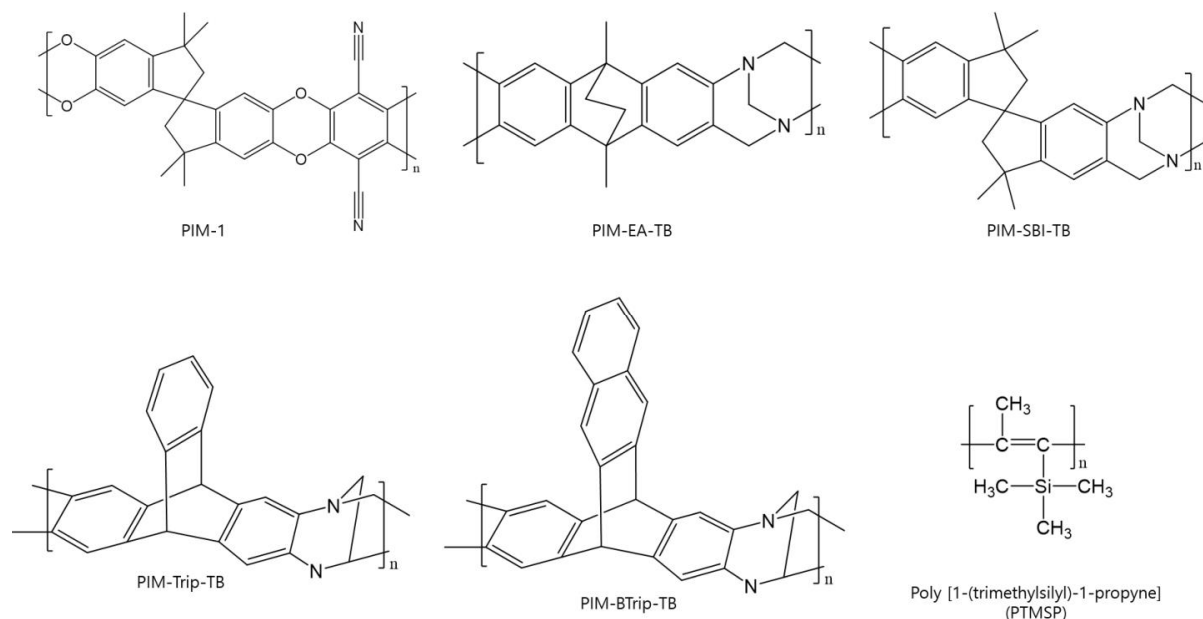
## 1. Introduction

The energy-intensive distillation processes remain as a high energy demand on this planet, and membrane-based separation is highlighted as one of the most prominent substitute technology in gas separation processes[1-3]. The pressure-driven process with a low footprint is anticipated to reduce the amount of energy consumption due to conventional thermal distillation process by 90% [1,4]. Due to advantages in energy-efficiency, easy operation, and process scalability, membranes are favored

over other processes, membrane-based separation processes are largely used in water purification and gas separations including hydrogen purification; O<sub>2</sub>/N<sub>2</sub> separation; natural gas purification; CO<sub>2</sub> capture; and natural gas purification (removal of higher hydrocarbon and acid gas)[5-7]. However, some of the high-performance separation membranes suffer from practical challenges such as performance degradation over usage that limit their use.

Amongst the various synthetic polymeric membranes developed until today, solution-processable polymers of

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**Fig. 1.** Molecular structures of highly permeable, high free-volume polymers[8]. Published by The Royal Society of Chemistry.

intrinsic microporosity (PIMs) are highly recognized as promising candidates for industrial application by highly selective and permeable membranes. The rigid, contorted backbone of the polymer chain results in poor chain packing, enabling polymers to have high fractional free volume, hence high permeability far surpassing the Robeson upper bound[2,8]. Since the introduction of PIM-1 in 2004[9], there has been numerous developments in this family of glassy ladder-type polymer, and today, the PIM family dominates the high-end of permeability on the 2008 Robeson plot[2,8]. Especially, advances from a single rigid spirocenters, a property which early PIMs exhibit, the addition of bridged-bicyclic contortions (i.e. Tröger's base, ethanoanthracene, triptycene)[8,10-12] to the rigid chain demonstrated higher torsion angle (Fig. 1). These advances in molecular engineering led to groundbreaking separation performances, and for the case of PIM-TMN-Trip, introduced a new moiety of inefficient 2-D chain packing, and showed excellent permeation performances compared to those of early PIMs[11,13].

The discovery and innovations on PIMs were great advancements and even led to the invention of semi-ladder type polymers such as PIM-PI group. Integration of

imide group to the ladder-type polymer enabled more mechanically robust, and highly selective separation processes[14-16]. Despite the advances in the synthesis of numerous high-performance polymers, there always remains the critical barrier of permeability/selectivity trade-off and scalability for membrane-based separation. The high permeance was definitely in favor of the industrial application, but the fundamental question remains: "Will the high permeability maintained over the period of membrane service time?"

## 2. Aging and Aging Mitigation Strategies

A critical issue that hinders those highly nanoporous polymers from actual applications, is the physical/chemical aging that retards permeability of the membrane through chain restructuring (Fig. 2, see Table 1 for permeability loss of various microporous polymers)[13,17,18]. For the semi-ladder type polymers such as PIM-PI, or even non-ladder type microporous polyimides such as 6FDA groups, the existence of the free volume within the polymer matrix makes susceptible to permeation loss due to physical aging[19,20]. Although still not clearly defined on what and how this physical aging occurs in

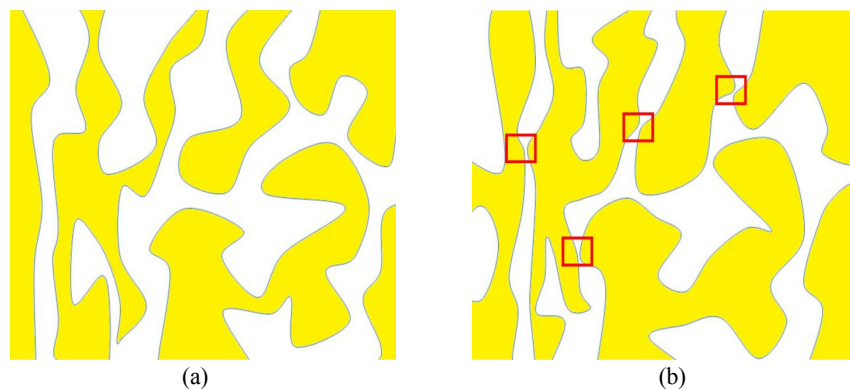
**Table 1.** Permeability and Permeability Loss due to Physical Aging of Various PIMs and Aging Mitigation Attempts

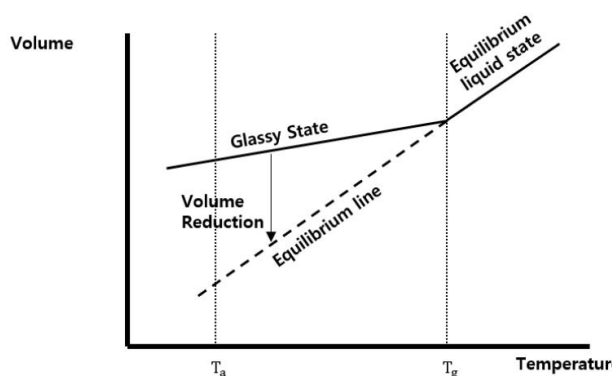
Polymer	Treatment		Permeability					Selectivity				Ref	
	Age		H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> /CH <sub>4</sub>		CO <sub>2</sub> /CH <sub>4</sub>
PIM-1	N.A	1	3,623		1,076	308		6.1	16.5	2.8	3.7	10.0	[13]
		1,380	1,544		317	64		24.1		5.0			[13]
PIM-TMN-Trip	N.A	1	16,900	33,300	4,600	2,230	3,420	7.6	14.9	2.1	4.9	9.7	[11]
		365	9,840	14,100	3,160	727	943	13.5	19.4	4.3	10.4	15.0	[11]
PIM-TMN-SBI	N.A	1	7,190	17,500	3,200	1,080	2,100	6.7	16.2	3.0	3.4	8.3	[11]
		14	1,370	2,980	485	160	300	8.6	18.6	3.0	4.6	9.9	[11]
PIM-EA-TB	N.A	1	7,760	7,140	2,150	525	699	14.8	13.6	4.1	11.1	10.2	[42]
		470	4,442	2,644	933	188	219	23.6	14.1	5.0	20.3	12.1	[12]
PIM-Trip-TB	N.A	1	8,039	9,709	2,718	629	905	12.8	15.4	4.3	8.9	10.7	[12]
		100	4,740	3,951	1,073	189	218	25.1	20.9	5.7	21.7	18.1	[12]
PIM-Btrip-TB	N.A	1	9,976	13,205	3,292	926	1,440	10.8	14.3	3.6	6.9	9.2	[43]
		166	4,280	4,147	1,166	216	283	19.8	19.2	5.4	15.1	14.7	[43]
TOX-PIM-1	Thermal crosslink	1	1,820	1,100	245	30.1	15.9	60.5	36.5	8.1	114.5	69.2	[36]
		455	1,380	310	30	8.1	4.1	170.4	38.3	3.7	336.6	75.6	[36]
TOX-PIM-1 (200 ppm O <sub>2</sub> )	Thermal crosslink	1	2,768	3,945	853	196	145	14.1	20.1	4.4	19.1	27.2	[36]
		355	1,967	995	262	34.4	18.9	57.2	28.9	7.6	104.1	52.6	[36]
PIM-CD-0.5	Filler addition	1	2,994	5,435	944	214	315	14.0	25.4	4.4	9.5	17.3	[33]
		120	2,672.8	4,609.8	787.7	148.1	198.2	18.0	31.1	5.3	13.5	23.3	[33]
PIM-CD-1.0%	Filler addition	1	3,356	6,574	1,123	283	447	11.9	23.2	4.0	7.5	14.7	[33]
		120	3,059.5	5,781.5	958.4	213.6	317.4	14.3	27.1	4.5	9.6	18.2	[33]
PIM-CD-2.0%	Filler addition	1	3,889	8,812	1,671	481	716	8.1	18.3	3.5	5.4	12.3	[33]
		120	3,664.7	8,139.8	1,521.8	391.5	552.2	9.4	20.8	3.9	6.6	14.7	[33]
KAUST-PI-1	N.A	1	4,183		827	169		24.8		4.9	24.8		[13]
		150	3,431		542	87		39.4		6.2	39.4		[13]
KAUST-PI-2	N.A	1	2,436		582	131		18.6		4.4	18.6		[13]
		870	1,522		205	39		39.0		5.3	39.0		[13]
KAUST-PI-7	N.A	1			865	240		0.0		3.6	0.0		[13]
		15	3,198		842	224		14.3		3.8	14.3		[13]
		660	2,164		490	115		18.8		4.3	18.8		[13]
PIM-PI-EA	N.A	1	2,966		850	226		13.1		3.8	13.1		[13]
		273	2,860		659	131		21.8		5.0	21.8		[13]
PIM-CD-0.5	Filler addition	1	2,994	5,435	944	214	315	14.0	25.4	4.4	9.5	17.3	[33]
		120	2,672.8	4,609.8	787.7	148.1	198.2	18.0	31.1	5.3	13.5	23.3	[33]

To be continued.

**Table 1.** Continued

Polymer	Treatment	Age	Permeability						Selectivity				Ref
			H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>	
PTMSP (Approximate)	N.A	1	14,000	30,000		5,000	1,300	2.8	6.0		10.8	23.1	[34]
		60	9,520	19,800		2,750	650	3.5	7.2		14.6	30.5	[34]
PTMSP/NH <sub>2</sub> - PDCX (Approximate)	Filler addition	1	16,000	29,000		4,000	7,500	4.0	7.3		2.1	3.9	[34]
		60	14,080	26,970		3,360	7,050	4.2	8.0		2.0	3.8	[34]
PTMSP/PDCX (Approximate)	Filler addition	1	20,000	44,000		6,500	7,500	3.1	6.8		2.7	5.9	[34]
		60	19,400	43,120		3,900	7,050	5.0	11.1		2.8	6.1	[34]
PIM-300-2.0d	Thermal cross- linking	1	3,872	4,000	582	96	73	40.3	41.7		53.0	54.8	[35]
		10	3,678.4		529.6	82.5	59.1	44.6			62.2		[35]
CoPIM-TB-1	Cross- linking	1	6,534	7,835	1,569	367	575	17.8	21.3		11.4	13.6	[37]
		40	5,216	4,977	1,210	235	308	22.2	21.2		16.9	16.2	[37]
CoPIM-TB-1	Cross- linking	1	5,873	6,767	1,554	347	448	16.9	19.5		13.1	15.1	[37]
		40	5,092	4,969	1,204	227	298	22.4	21.9		17.1	16.7	[37]
C-CoPIM-TB-1	Cross- linking	1	4,887	4,251	856	144	169	33.9	29.5		28.9	25.2	[37]
		40	5,373	4,937	996	157	214	34.2	31.4		25.1	23.1	[37]
C-Co-TB-2	Cross- linking	1	8,039	9,709	2,718	629	905	12.8	15.4		8.9	10.7	[37]
		40	4,560	4,019	768	110	157	41.5	36.5		29.0	25.6	[37]
PIM-1/PAF-1	Filler addition	1	5,533.1		1,191.4	2,233.3		2.5		0.5			[30]
		400	5,165.5		400.7	466.7		11.1		0.9			[30]

**Fig. 2.** Illustration of internal polymer structure of porous membranes (a), and reduction of fractional free volume and (b) pore shrinkage caused by physical aging.



**Fig. 3.** Schematic drawing of glassy polymers in out of equilibrium state below glass transition temperature ( $T_g$ ), and free volume reduction over time[21]. Copyright 2004 for John Wiley and Sons.

glassy polymers, it is apparent that below the glass transition temperature ( $T_g$ ), the molecular motion of the polymer chains is not zero[18-20]. There is a gradual restacking of the polymer matrix in order to recover from the out-of-equilibrium excess enthalpy or free volume. In other words, moving for the unreachable thermodynamic equilibrium regardless of the high chain rigidity of the ladder-type polymers. This phenomenon is more apparent with PIMs since there is no clearly defined  $T_g$  for most, if not all, PIMs below the decomposition temperature. Through the process that involves densification of the polymer film, the chain conformation will collapse the micropores over the extent of time and reduce the free volume.

$$V_f \rightarrow \text{segmental motion} \rightarrow \frac{dV_f}{dt} \rightarrow V'_f \quad (1)$$

As shown in (1)[21], the fractional free volume (FFV,  $V_f$ ) of a porous membrane, will be reduced by the segmental motion of the polymer chain, leading to the re-defined FFV ( $V'_f$ ). By the definition of the unreachable thermodynamic equilibrium, the process will be infinitely repeated over time in the direction of diminishing the FFV (Fig. 3). Relevance to the hindrance of the chain motion that allows gas molecules to diffuse through the membrane as we commonly acknowledge in the solution-diffusion model, the collapse of the free

volume will result in a decrease in the diffusion jump frequency[19,21]. Although this may somehow act as a benefit for gas separation in the way of increasing the selectivity of two different gases, the severe decrease of permeability paramount the benefit of selectivity[24].

The aging phenomena are not only limited to microporous, high free volume polymers. Ultramicroporous membranes based on carbon molecular sieve (CMS) are known to show aging-related performance degradation over time as well. Even though it is classified as a molecular sieve with MOFs (metal-organic frameworks), ZIFs (zeolitic imidazolate frameworks), zeolites, and etc, CMS membrane discriminates itself from other microporous frameworks in chemical stability and processability. The production of CMS is still being widely studied for tailoring separation efficiency and higher permeability, but it doesn't leave the large boundary of the method of pyrolysis of precursor polymeric membrane in controlled atmosphere and temperature. Recently, the processability and scalability of CMS have been taken to the new level by modification of hollow fiber membranes[19,20] and is showing great promises as an option in membrane-based separation. Unlike conventional polymers, CMS provides two discrete range of pores for molecular diffusion. Pyrolysis of precursor polymers in oxygen controlled conditions forms "turbostratic" carbon structure, where irregular packing of  $sp^2$ -hybridized carbon sheets occurs. This leads to the coexistence of two different pore morphologies, which are micropores (7-20 Å) created by the irregular stacking of two different of  $sp^2$ -hybridized carbon sheets, and ultramicropores (< 7 Å) which are the intrinsic pores of the individual sheets. This unique combination of two different pore size distribution enables high-frequency diffusion in the micropores and selective material sieving in the ultramicropores, which allows high flux and selectivity for separation.

In fact, just like the glassy polymers, where performance of the membrane is mostly affected by chain conformation change (physical aging), CMS will go through similar mechanism in physical aging, during which the random stacking of the  $sp^2$ -hybridized carbon plates will

collapse the micropores, where aforementioned, much of the diffusive jumps will take place for the permeates. As a result, just like that of glassy polymers, the permeability of the membrane will decrease over time, whereas selectivity will increase. Due to the abundant carbon edge sites, the aging of CMS is different from that of glassy polymers in that it will be highly influenced by the chemical aging as much as physical. It has been reported that water adsorption of the CMS has a high influence on the decreased gas permeability of the carbon films. Menendez *et al.*, hypothesized that the defective edges of the carbon sheets will act as a reactive site for the oxygen or water molecules for chemisorption[27]. Also, when CMS films were exposed to volatile organic compounds or other chemical contaminants, due to the hydrophobic/organophilic nature of the micropores, adsorption of organic chemicals blocked the micropores and membrane performance was highly diminished, which was then regenerated upon exposure to propylene as cleaning agent[28].

### 2.1. Microporous filler addition

In an effort to increase the efficiency of membrane-based separation and exceed polymer performance limitations, the addition of filler materials to the membrane offers promising results for the next generation of membrane-based separation. Although PIMs by themselves are an excellent choice of materials due to their high permeability, there is always a room for improvement in selectivity. One of the popular strategies to enhance the selectivity in the polymeric membrane is the addition of highly-selective microporous fillers to the polymer matrix. When the proper filler-matrix combination is selected, as predicted by Maxwell's equation[29], the addition of the size-selective molecular sieving nanoparticle such as zeolite and metal-organic frameworks (MOFs), enhances the selectivity as well as the permeability of the polymeric membranes. More importantly, some fillers strongly interact with the polymer matrix to greatly enhance the age-resistance via rigidification of the backbone of the polymer.

Lau *et al.*, proposed addition of nanoparticles of the

porous aromatic framework (PAF-1) to the polymer matrix[28,29]. It was hypothesized that the high BET surface area up to  $5,200 \text{ m}^2\text{g}^{-1}$  and the average pore diameter of 1.2 nm of PAF-1 formed interwoven structure with the super glassy polymers matrix. With the addition of PAF-1 nanoporous particles to three different super glassy polymers, (poly[4-methyl-2-pentene] (PMP), poly[1-(trimethylsilyl)-1-propyne] (PTMSP), and PIM-1) the study showed that the decrease in permeability of gases due to physical aging of PIM-1/PAF-1 over the time was greatly improved down to 7%, whereas that of a pristine PIM-1 film was 62%. As a follow up, Lau *et al.*, introduced various functionalized PAF-1 (PAF-1, PAF-1-NH<sub>2</sub>, PAF-1-SO<sub>3</sub>H, PAF-1-C<sub>60</sub>, PAF-1-Li<sub>6</sub>C<sub>60</sub>) nanoparticles to PTMSP[32]. Although most of the functionalized PAF-1 particles had little or no effect on H<sub>2</sub>, N<sub>2</sub> or CH<sub>4</sub> permeability change over a year, it showed only 9% decrease permeability for CO<sub>2</sub> with PTMSP/PAF-1-Li<sub>6</sub>C<sub>60</sub>. The analysis of the PAFs showed that except PAF-1-Li<sub>6</sub>C<sub>60</sub> and PAF-1-C<sub>60</sub>, the BET surface area of the nanoparticles has decreased compared to that of normal PAF, indicating that the pore volumes of PAF-1 have been already filled up by the chemical moieties of sulfonic and amine groups. Li<sub>6</sub>C<sub>60</sub> functionalized PAF-1 measured exceptionally high BET surfaced area of  $7,360 \text{ m}^2\text{g}^{-1}$  compared to that of normal PAF-1, which was  $3,760 \text{ m}^2\text{g}^{-1}$  for this study. In addition, it was suggested the Pseudo-chemisorptive behavior between CO<sub>2</sub> and the lithium ions enabled not only much higher CO<sub>2</sub> permeation but also selective aging of the polymeric membranes.

Liu *et al.* incorporated microporous fillers to the polymer matrix by mixing  $\gamma$ -cyclodextrin ( $\gamma$ -CD) to PIM-1 [33]. The asymmetric porous structure of  $\gamma$ -cyclodextrin with inner pore diameter 6.0~7.8 Å and outer pore diameter of 15.3 Å induced extra porosity to the membrane for increased FFV and hence higher permeability was achieved. Unlike mixed-matrix membrane,  $\gamma$ -CD was added to PIM-1 during the polymer synthesis step, where the outer hydroxyl group of  $\gamma$ -CD allowed  $\gamma$ -CD to act as a monomer during polymerization, triggering aromatic nucleophilic substitution to form PIM-CD.

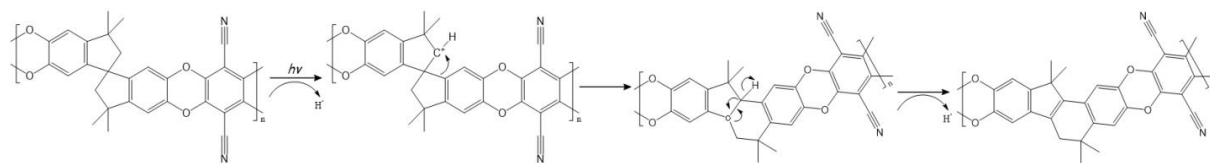
Ideally, in order to achieve PIM-CD with maximum FFV, each -CD would react per TFTP (tetrafluoroterephthalonitrile) during polymerization, however, the higher polydispersity of PIM-CD compared to that of pristine PIM-1 is an indication that there may possibly have been multiple attachments of TFTP to the multiple hydroxyl reactive sites of -CD. Nevertheless, despite the hint of “crosslinked” polymer matrix, the permeability of CO<sub>2</sub> was increased by over 2 folds. Moreover, the rigid -CD showed a prominent effect on the physical aging of the polymer. The new PIM-1 matrix with -CD blend showed less than 20% decrease in permeability with only 2% addition of -CD, with the trend of more physical aging resistance with more -CD added, leading to the conclusion that the intrinsic chemical bonds are grasping the polymer chains and holding the architecture.

Despite the success in containing physical aging with nanoparticle filling, the problem of scalability of the filler preparation was still at hand. Again, Lau *et al.*, proposed the idea of the addition of hypercrosslinked polymer (HCP) to PTMSP to tackle both performance loss by physical aging and scalability of filler production fit for industrial application[34].  $\alpha, \alpha'$ -dichloro-*p*-xylene was polymerized to form *p*-DCX, some of which were further treated with aniline to produce NH<sub>2</sub>-*p*-DCX. The significance of this study was in that the HCPs were prepared in relatively large scale (~30 g) which, considering the 10 wt% filler/polymer loading, would be enough for a substantial amount of polymer as well as showing scalability of the HCP production. Evidently, the addition of *p*-DCX to PTMSP matrix enhanced the membrane performance in both permeability and selectivity, as well as showing loss of CO<sub>2</sub> permeation of ~2% when the film was aged for 60 days. The investigation of chain mobility showed that the good interaction between the *p*-DCX and PTMSP restricted the mobility of the bulky trimethylsilyl group of PTMSP, the group which allows high permeation of PTMSP. Also, it was reported that the trimethylsilyl free carbon atom's mobility was increased unlike that of the carbon connected to the trimethylsilyl. The im-

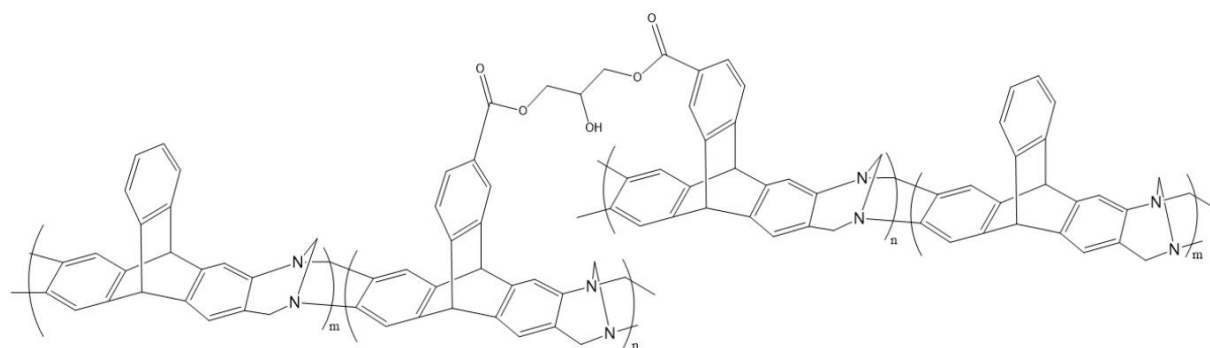
obilization/mobilization of different carbons of the polymer chain allowed selective aging of PTMSP.

## 2.2. Crosslinking

Thermal crosslinking of the polymer membrane is very much well known and practice for enhancing polymer stability and selectivity. Due to the relatively low selectivity (e.g. H<sub>2</sub>/N<sub>2</sub> ~6.1) of PIM-1, intentional densification of the polymer matrix is somewhat favored under the circumstances of low permeability loss. Li *et al.*, proposed a thermal crosslinking reaction of PIM-1, where the polymer film was left at 300 °C under vacuum[35]. It was proposed that PIM-1 underwent internal covalent bonding, and the -CN nitrile groups are converted into -CN imine group in the PIM-1 structure to form triazine rings. During the thermal crosslinking period from 0.5 to 2 days, it was found that the degree of crosslinking highly affects the fractional free volume in a very interesting way. Of course, the common conjecture is that a crosslinked polymer will exhibit lower fractional free volume, therefore having less gas permeability. This was the case for PIM-1 put into 300 °C for 0.5 days (PIM-300-0.5d) compared to a pristine film. However, contrary to the expectation that PIM-300-2.0d would have lower permeability compared to that of PIM-300-0.5d, the permeability of the different gases increased along with the time of thermal crosslinking, and permeability of PIM-300-2d actually surpassed that of pristine PIM-1. The calculation of the free volume (FFV) of the thermally crosslinked polymers showed that the FFV, when calculated based on Bondi's method, actually increased along with the duration of the crosslink. With this, Li *et al.*, proposed that the higher extent of crosslinking induced further chain “tightening” which caused the chain rearrangement in favor of increasing the FFV. In addition to the interesting permeability measurements results, a short term membrane stability was measured for physical aging of the membrane. Although the membrane was put into testing for only ~10 days period, PIM-200-2.0d presented approximately 50% less decrease in relative permeability compared to that of pristine PIM-1, in-



**Fig. 4.** Proposed mechanism of UV-crosslinking of PIM-1[39]. Copyright 2012 for John Wiley and Sons.



**Fig. 5.** Proposed molecular structure of CoPIM-TB-1 and CoPIM-TB-2, where carboxylic acid groups react with glycidol to crosslink two different polymer chains[37]. Copyright 2018 for Elsevier.

dicating possible improvement in resistance to physical aging of PIM-1.

A couple of years later, Song *et al.*, proposed thermal oxidation of PIM-1 (TOX-PIM-1) in an oxygen controlled environment in order to increase the selectivity of PIM-1 as well as increasing physical aging endurance[36]. They proposed that the membrane matrix itself acts as a reactor where the traces of oxygen (ppm level) will cause oxidative crosslinking of polymer chains at bottlenecks of the micropores by oxidative chain scission and *in-situ* covalent crosslinking. To check, they observed that the loss of ultra micropores (smaller than 7 Å). They confirmed the crosslinking of PIM-1 by mechanical testing of TOX-PIM-1, produced at 385 °C in 200 ppm O<sub>2</sub> with a sufficient amount of time, by checking its stability in chloroform. In correlation with most crosslinked polymers, the BET surface area of TOX-PIM was significantly reduced compared to that of original PIM. This supported the claim on the loss of ultra micropores as well as diminished gas permeability (down to ~30% in CO<sub>2</sub>) after the crosslink. However, by thermal crosslinking, significant enhancement in selectivity was achieved. It is noteworthy the H<sub>2</sub>/CH<sub>4</sub> selectivity was enhanced from 8.6 to 114, after

the crosslinkage, and 114 to 340 by followed aging. This opens much potential for selective aging since H<sub>2</sub> permeability was dropped by only 25% during 455 days whereas that of CH<sub>4</sub> dropped down to 25% of its original value of TOX-PIM-1

Zhang *et al.*, proposed a modification of PIM-Trip-TB by copolymerization of 2,6-diaminotryptycene (m) and 2,6-diaminotryptycene-14-carboxylic acid (n) to produce CoPIM-TB-1 and CoPIM-TB-2, both of which contains m : n ratio of 9 : 1 and 8 : 2 respectively[37]. After polymerization and membrane preparation, both of these polymers were crosslinked with glycidol by soaking followed by heat treatment for 120 °C to obtain C-CoPIM-TB-1 and C-CoPIM-TB-2 (Fig. 5). The scheme of this study was to solve not only the physical aging effect of PIM-Trip-TB, one of the most permeable glassy polymers synthesized but also to solve the plasticization of polymers during the separation processes. As shown in Fig. 5, it was anticipated that the glycidol would provide additional FFV to the polymer matrix, as well as stability of the membrane[38], but the permeability of the membrane decreased for about ~50% for all single gases (8,616 Barrer to 4,251 Barrer in case of CO<sub>2</sub>). Even after 40 days of aging, the



separation performance was kept at a high level, where the crosslinked films C-CoPIM-TB-1 showed 10, 9, and 8% in a decrease in permeability for H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub> gases respectively. The higher crosslinkage of the polymer chain did adhere to the less loss of permeability because C-CoPIM-TB-2 only lost 7, 5, and 9% decrease in permeability for the same gases. Considering the high separation performance that PIM-Trip-TB demonstrates, it may still be considered a candidate for high-performance gas separation membrane.

### 2.3. UV treatment

It is a well-known trait of polymeric membranes will undergo UV-photochemical reaction under certain conditions via UV light[37-39]. Li *et al.*, proposed a mechanism of restructuring of PIM-1 sandwiched between two quartz plates under UV radiation of  $\lambda = 254$  nm (Fig. 4)[39]. It was proposed that the UV radiation removed radical hydrogen, which will cause electron migration that will end up with the elimination of the spiro-carbon center in the UV-rearranged PIM-1.

The absence of the spiro-carbon center and non-rigid longer chain did indeed influence the permeability of the membrane. The positron annihilation spectroscopy (PALS) showed that the average free volume radius shrinkage from 3.08 to 1.93 Å after 4 hours of UV exposure. Throughout all the samples with the variation of UV exposure time, from 10 minutes to 4 hours, the permeability of all gases except for that of H<sub>2</sub> decreased to below one magnitude and the H<sub>2</sub> permeability dropped to 12% of its original value. However, there was a significant increase in H<sub>2</sub> selectivity, where the ideal H<sub>2</sub>/N<sub>2</sub> selectivity surged from 12.1 to 166. As for the mitigation of aging, UV treated PIM-1 showed better leveling on the decrease of permeability on the relative scale with less than 20% loss for all gases in 30 days period, but the severe loss of permeability during the UV rearrangement outweighed the advantage from reduced aging effect.

On the other hand, Song *et al.*, proposed a completely different interpretation of the UV effect on PIM-1[40]. When PIM-1 film was exposed to UV with

the wavelength  $\lambda = 254$  nm, they observed a drop in permeability and drop in molecular weight and polydispersity index (PDI). They proposed that the PIM-1 chain did not rearrange or change chain conformation, but the UV/ozone radiation caused oxidation of PIM-1 that caused chain scission to the depth of UV penetration. Smaller polymer chains packed themselves in between the large chains, therefore reducing the micropore volume. Although UV exposure was conducted in a controlled atmosphere, the remainder O<sub>2</sub> within the polymer matrix and since any chamber cannot be removed of O<sub>2</sub> entirely in the non-ideal world, the small trace of remaining O<sub>2</sub> was enough for photo-oxidation. This caused the pore volume to be reduced by 0.6-0.7 nm, thus reduced the BET surface area. The permeation properties of the UV treated PIM-1 were similar to that of the finding in Li *et al.* However, there is an open room for debate on the mechanism for pore shrinkage caused by UV radiation on PIM-1.

### 3. Conclusions

In this review, we have addressed the aging phenomena of membranes produced from polymers of intrinsic microporosity (PIMs) and post-synthetic modifications as aging mitigation strategies. To summarize, several different approaches indicate a plausible solution to the physical aging in high free volume polymers with attractive gas separation performance that exceeds conventional synthetic polymer membranes, to be continued over membrane product service period. These approaches will need to be applied to the thin-film composites of PIMs (selective layer thickness < 1 μm) or asymmetric hollow fiber membranes that represent the commercially viable architecture of polymeric membranes.

### Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2018R1C1B6002461)

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