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To cite this article: Hong Ye, Caili Zhang, Chaowei Huo, Bingyu Zhao, Yuanhao Zhou, Yichen Wu & Shengpeng Shi (2021) Advances in the Application of Polymers of Intrinsic Microporosity in Liquid Separation and Purification: Membrane Separation and Adsorption Separation, Polymer Reviews, 61:2, 239-279, DOI: [10.1080/15583724.2020.1821059](https://doi.org/10.1080/15583724.2020.1821059)

To link to this article: <https://doi.org/10.1080/15583724.2020.1821059>



Published online: 25 Sep 2020.



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REVIEW



Advances in the Application of Polymers of Intrinsic Microporosity in Liquid Separation and Purification: Membrane Separation and Adsorption Separation

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ABSTRACT

Polymers of intrinsic microporosity (PIMs) are a new type of polymer material with unique microporous structure and have been widely applied in gas separation. In recent years, PIMs have also experienced rapid growth in liquid separation and purification; however, so far, no review is reported on the application of PIMs in this field. This paper reports a comprehensive and critical review on the recent research progress of PIMs in the application of liquid separation and purification including membrane separation and adsorption. First, the structural characteristics and synthesis methods of PIMs are briefly described. Subsequently, their applications in membrane separation are described in detail, including pervaporation (removal of organics from water, dehydration of solvents, and separation of organic mixtures), nanofiltration (dye rejection), and adsorption (dyes, organic contaminants, metal ions, oil/water separation, and enantiomeric separation). The effect of material structure and modification on the separation performance is emphasized, and possible new research directions are mentioned. Finally, the application of PIMs in liquid separation and purification is prospected. In conclusion, PIMs exhibit excellent separation efficiency and stable operation characteristics in liquid separation and purification, and they have attractive and broad development prospects. More valuable applications remain to be developed.

ARTICLE HISTORY

Received 28 February 2020
Accepted 1 August 2020

KEYWORDS

Polymers of intrinsic microporosity; membrane separation; pervaporation; nanofiltration; adsorption

1 Introduction

In modern chemical industry, irrespective of large-scale industrial production with automation or small-scale laboratory research, the separation and purification of raw materials and products cannot be avoided, particularly for liquid mixtures. Taking the petrochemical industry as an example, if a large amount of crude oil cannot be effectively separated, then the downstream industry cannot perform normally. The

production efficiency and product quality of downstream industry are directly related to the purity of its raw materials and products, thus directly affecting the economic benefit of enterprise. In liquid mixtures of chemical industries, often a large number of azeotropic systems exist. For example, a typical mixture of benzene and cyclohexane has a boiling point difference of only 0.6 °C. The relative volatility of benzene and cyclohexane is almost 1 in the full composition range, and they have very close molecular properties, thus making the separation very difficult.¹ Extractive distillation can separate the mixture, but the addition of third component requires a complex post-treatment process and high investment.² In addition, with the emphasis on environmental protection and to achieve circular economy, it is essential to adopt effective technologies to remove the pollutants in production sewage or recycle the high-value materials in industrial waste fluids. Therefore, the separation and purification of liquids are required in the entire process of chemical and related industries, including environmental protection, energy utilization, and recycling economy, which has great practical significance.

Liquid separation and purification technologies include both new separation technologies recently developed and some traditional unit operations. Among them, membrane separation technology is a new liquid separation technology with clean, energy-saving, and high efficiency characteristics,³ including ultrafiltration, microfiltration, nanofiltration (NF), reverse osmosis, pervaporation (PV), and other membrane processes. The key factor of this separation technology is membrane separation materials. In recent years, membrane processes and membrane separation materials have been extensively studied. In addition, adsorption separation is a typical liquid separation and purification technology in traditional chemical industry. Compared with distillation, the adsorption method is relatively convenient, but involves the regeneration of adsorbent. The adsorbent is a key factor in determining the adsorption effect. Both membrane separation and adsorbent materials should have stable chemical composition in the separation system such as water or organic solvent, especially a high specific surface area and suitable pore structure. Among many membranes and adsorbent materials used in liquid separation, polymers of intrinsic microporosity (PIMs) are very special as a type of “young” functional material with a short development time. PIMs not only have a long chain structure, but also a uniform microporous structure, making them more attractive in separation and purification.

PIMs are microporous organic polymers (MOPs), special polymers that rely on their own rigidity and nonplanar distorted structure of molecules to obtain micropores, and the distorted structure of molecular chains prevents chain packing, resulting in a higher free volume than general polymers. The pore-size distribution of PIMs is narrow, and there is no problem of pore collapse that occurs in inorganic porous materials during the removal of pore template.⁴ PIMs have been widely used in membrane separation,⁵ heterogeneous catalysis,⁶ hydrogen storage,⁷ and other fields.⁷ Gas separation in membrane separation is the most widely used field of PIMs. In the Web of science database, the number of papers on this topic can be retrieved using {“Polymers of Intrinsic Microporosity” “And” “Membrane” “And” “Gas”} as the subject, and using {“Polymers of Intrinsic Microporosity” “And” “Membrane” “NOT” “Gas”} as the subject, as shown in Figure 1. PIM membranes have been extensively studied in recent years, and the number of published research papers continues to increase. Especially after 2017, the

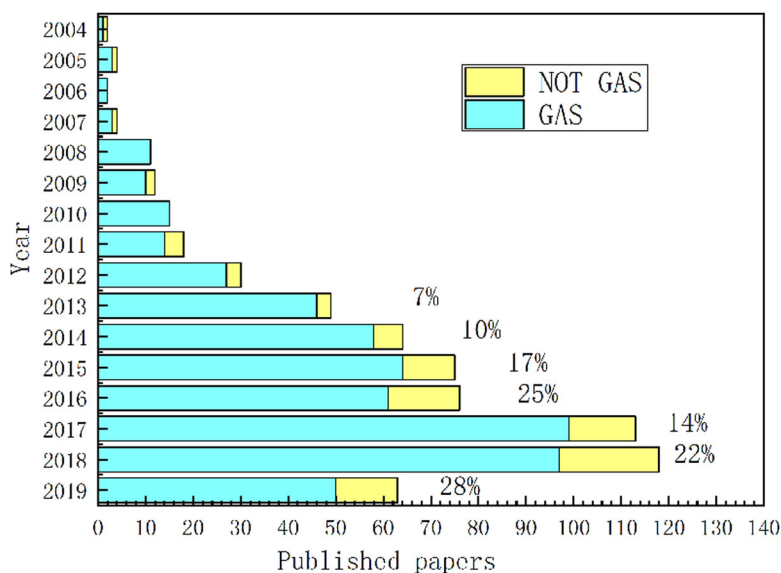


Figure 1. Number of published research papers related to PIM membrane in Web of Science database (The percentage of bars represents the percentage of nongas applications in the literature on gas separation applications) (GAS: Search topic = {"Polymers of Intrinsic Microporosity" And "Membrane" "And" "Gas"} search, NOT GAS: Search topic = {"Polymers of Intrinsic Microporosity" "And" "Membrane" "NOT" "Gas"}).

number of research papers showed a rapid growth. More notably, the number of studies in non-gas separation (mainly membrane separation and adsorption for liquid separation and purification) has also increased rapidly in recent years. As shown in Figure 1, in 2013, the number of papers published on non-gas membranes is 7% of that published on gas separation membranes. It was 17% in 2015 and reached 28% in the first half of 2019. Many studies have reported that although PIMs are highly used in gas separation, liquid separation using PIMs also has great application potential,^{8–10} and it is necessary to evaluate them.¹¹ Unfortunately, according to our literature search, no reports summarized, analyzed, and commented on the application of PIM membranes in liquid separation. This paper reports a comprehensive and critical review on the recent research progress of PIMs in membrane separation and adsorption for liquid separation and purification. First, the structural characteristics, synthesis methods, and potential separation applications of PIMs are briefly described. Then, their applications in membrane separation are described in detail, including specific applications in PV (preferential removal of organics, preferential dehydration and separation of organic mixtures), NF (dye rejection), and adsorption (dyes, organic contaminants, metal ions, oil/water separation, and enantiomeric separation). The effect of material structure and modification on separation performance is emphasized, and the possible new research directions are suggested. In addition, the role of molecular simulation in the separation applications of PIMs is described. Finally, the application of PIMs in liquid separation and purification is reviewed in order to make readers better understand the application status of PIMs in liquid separation, promote its further development, and serve as a reference for more application fields.

2. Introduction to PIMs

2.1. Structural characteristics and application potential of PIMs

Porous structure of PIMs is one of their most characteristic structural features. McKeown et al.¹² believed that the emergence of PIMs filled the gap between microporous materials and polymer materials, and also served as a bridge between them. According to the classification of pores by IUPAC, the name “microporous polymer” was derived from the fact that the pore size of such polymers is less than 2 nm.¹³ To obtain micropores, generally rigid and noncoplanar structures are necessary to construct the material. Therefore, phthalocyanine or porphyrin polymers connected with distorted spirobiindene center were first prepared; their molecular formula is shown in Figure 2 (a). Phthalocyanine-based PIMs have a crosslinked network structure with a specific surface area of up to 895 m²·g⁻¹ and 910 m²·g⁻¹.^{14,15} Furthermore, their rigid and distorted molecular chains formed many pores, which can be clearly observed from its three-dimensional structure diagram, as shown in Figure 2(b). In subsequent studies, crosslinked PIMs with a higher specific surface area were prepared; these materials were expected to be applied in gas adsorption, hydrogen storage, and heterogeneous catalysis.^{16–18} However, the first separation application of PIMs started from liquid separation and purification: Crosslinked PIMs were used to adsorb and remove phenol from water; its adsorption capacity was even higher than that of porous carbon materials with comparable specific surface area.¹⁹ However, because these materials were all crosslinked network materials, they cannot be prepared as membranes, and their application in membrane separation is limited. In addition, the distribution of partially crosslinked PIM pores was broad, affecting its application as a fine molecular recognition material.

The birth of chain-soluble PIMs opens up a new situation for PIMs.²⁰ Since then, PIMs have been widely used in membrane separation. In 2004, Budd et al.²¹ prepared a series of soluble PIMs for the first time and referred to them as PIM-1 to PIM-6. Among them, PIM-1 was synthesized by the co-condensation of two monomers, 5,5',6,6'-tetrahydroxy-3,3',3,3'-tetramethyl-1,1'-spirobiindene (TTSBI) and 2,3,5,6-tetrafluoroterephthalonitrile (DCTB), and its synthetic route is shown in Figure 3. The TTSBI structure has spiral rings of common carbon atoms, thus leading to the distorted structure of PIM-1 molecular chain. The BET specific surface area of PIM-1 was as high as 850 m²·g⁻¹, and the pore diameter was in the range 0.4–0.8 nm.²¹ Since the successful synthesis of PIM-1, the application of PIMs in separation has been significantly increased. At present, PIM-1 has become the most popular PIMs in membrane separation. Figure 1 also shows that the report on PIM separation membranes began in 2004. In the same year, Budd et al.²² first reported the application of PIM-1 membrane in the PV separation of phenol from water. After that, in 2005, Budd et al.²³ synthesized PIM-7 and for the first time applied linear PIMs (PIM-1 and PIM-7) for gas membrane separation applications. Then, the application of PIMs in gas separation developed rapidly, significantly exceeding the application breadth and depth in other fields. In 2015, the first commercial application of PIMs was achieved: 3M company adopted PIM-1 to absorb volatile organic compounds (VOCs) as an end of life service indicator.^{24,25} These academic and industrial efforts continue to extend the PIM applications as far as possible.

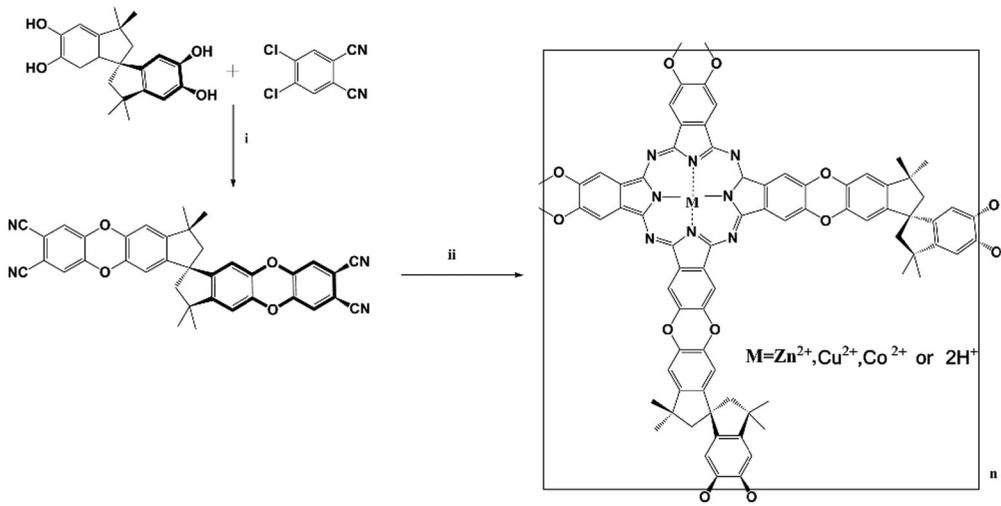


Figure 2. (a) Preparation of phthalocyanine-based microporous network polymers from spirocyclic monomer. Reagents and conditions: i) K_2CO_3 , DMF, 80°C ; ii) metal salt, quinoline, 200°C . (b) A simple three-dimensional model of phthalocyanine-based microporous network polymer with aromatic macrocycles represented by cross-like shapes.¹²

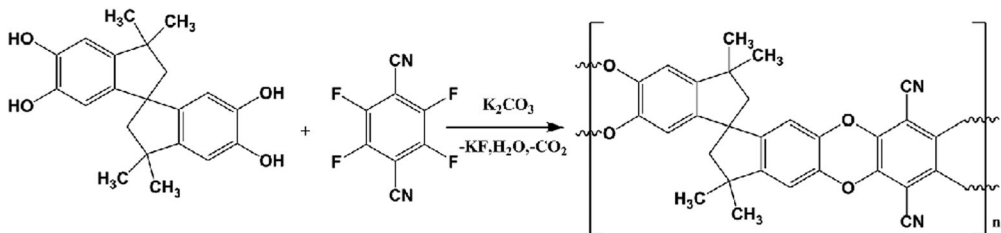


Figure 3. Synthetic route of PIM-1.

Table 1. Porous structure of PIMs.

PIMs	Specific surface area $\text{m}^2\cdot\text{g}^{-1}$	Pore size	Chain structure	Reference
Phthalocyanine or porphyrin based PIM	450–1000	Micropore (<2 nm), mesopore (2–50 nm)	crosslinked	14,15
CTC-PIM	830	0.6–0.7	crosslinked	26
Triptycene-PIM	1065	<0.7	crosslinked	16
PIM-1	850	0.4–0.8	linear	21
		0.3–1.1 ^a		27
PIM-7	680	subnanometer	linear	28
PIM-8	677	Not mentioned	linear	28

^aTaken from the pore-size distribution map of the original literature

Both crosslinked and linear PIMs have several typical characteristics: (1) Both are glassy polymers with a relatively rigid structure; their molecular structures are often rich in benzene rings. (2) Both have a high specific surface area and relatively narrow pore-size distribution. Table 1 summarizes the specific surface area and pore size of several crosslinked or linear PIMs widely reported in the literature. We hope that readers will understand the porous properties of several typical PIMs and then attempt to expand and explore the applications of PIMs according to their pore size.

Table 1 shows that the pore size of PIMs was stable within the range of micropores. For the originally developed crosslinked PIMs (such as phthalocyanine or porphyrin based PIM), there were many mesoporous pores as well as micropores. Whereas, for the cross-linked PIMs synthesized in the later stage, especially the linear PIM-1 series developed in recent years, had a pore structure mainly composed of micropores with only a few mesopores. The pore structure and molecular properties of PIMs determine its potential in liquid separation, mainly reflected in the following three aspects:

1. The pore size of PIMs perfectly covered the required size range of membrane pores in NF and reverse osmosis; thus, they can be used in separation involving NF and reverse osmosis membranes.
2. The pore size of soluble PIM-1 covered the size of common target compound to be separated such as water, ethanol, butanol, benzene, and phenol in PV. Considering the hydrophobicity of PIM-1, it can be used in the PV recovery of organic compounds from water.
3. The porosity and high specific surface area of PIMs made it have similar adsorption capacity as activated carbon, which can be used for adsorption extraction separation.

The applications of PIMs reported so far are summarized in Figure 4. Crosslinked PIMs were first applied to adsorption separation, and soluble PIMs were rapidly developed for gas membrane separation. Next, the applications of PIMs in the liquid separation such as PV and NF were developed. The application of PIMs was not limited to this. More separation systems for existing applications and more separation applications of PIMs are still being explored.

Whether PIMs can be widely used is also related to whether the synthetic method can be easily implemented. The synthesis of PIMs will be briefly described below.

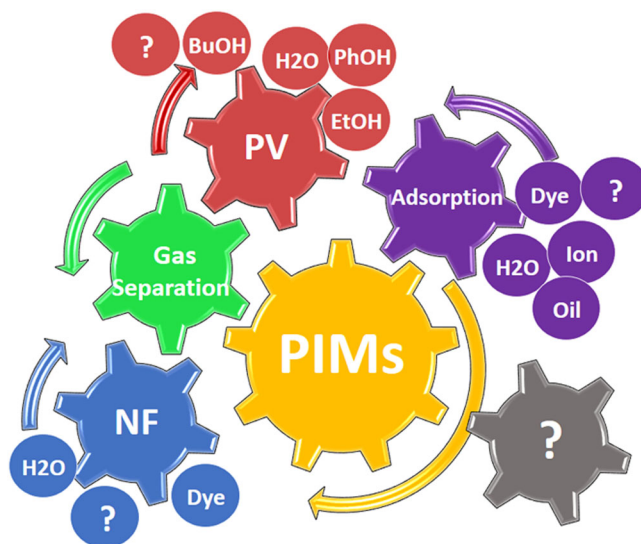


Figure 4. Current application areas of PIMs.

2.2. Synthesis of PIMs

Because PIM-1 is one of the most concerned PIMs in the current PIMs family, it was taken as an example to describe the synthesis. McKeown²⁵ reported that PIMs can be synthesized using three main methods: formation of dibenzodioxin,²² Tröger's base,²⁹ and formation of imide linkages³⁰ between monomers. PIM-1 was synthesized using the first method, and the reaction is shown in Figure 3. Song et al.³¹ evaluated the effect of monomer/catalyst ratio, reaction temperature, and time on the molecular weight of PIM-1 in detail and synthesized linear soluble PIM-1 with an average molecular weight of up to $2,11,900 \text{ g}\cdot\text{mol}^{-1}$. The reaction conditions used in this study can be classified as the so-called "low temperature method," i.e., the reactants were reacted at $\sim 50\text{--}60^\circ\text{C}$ for 24–72 h or even longer.²² The concentration of monomer was a key controlling factor during the synthesis, because crosslinks were formed at high concentrations, while oligomers with a low molecular weight were formed at low concentrations. The optimal reaction condition was to add $\sim 3 \text{ mmol}$ of each monomer in every 10–15 mL of dimethyl formamide (DMF).²⁵ Another so-called "high temperature method" was proposed by Du et al.,³² where the reaction was performed at $150\text{--}160^\circ\text{C}$ for 0.5–2 h using dimethylacetamide (DMAc) as the reaction solvent (toluene was added later to ensure normal stirring).^{32,33} If the solvent was changed to dimethyl sulfoxide (DMSO), the appropriate reaction temperature was 120°C .³⁴ PIM-1 used in most studies was synthesized using the high temperature method; the synthesis cycle should be shortened to improve the research efficiency. Regardless of the low temperature method or high temperature method, PIM with a molecular weight of $M_n > 30 \times 10^3 \text{ g/mol}$ or $M_w > 100 \times 10^3 \text{ g/mol}$ can be generally obtained, and the membrane obtained by casting the PIM-1 solution satisfies the requirements of membrane separation test. Most studies on the modification of PIM-1 started from the cyano group ($-\text{CN}$) in the PIM-1 structure; the most common modification method was to hydrolyze $-\text{CN}$ to carboxyl group ($-\text{COOH}$),³⁵ followed by further modification. The degree of hydrolysis

determined the amount of -COOH, affecting the hydrophilicity of membrane. This significantly affects the separation effect of membrane, thus making it suitable for the separation application of different liquid mixtures. In addition, PIMs and their modified membranes showed a relatively rigid structure, good thermal stability, and excellent solvent resistance. They were only soluble in chloroform, dichloromethane, and tetrahydrofuran, making them unique in liquid separation such as the PV separation of organic compounds and organic solvent NF. By adjusting or modifying the structure of PIMs, the pore size could be precisely regulated, and the polymer exhibited different selective separation effects on different molecular pairs with different sizes.

3. Application of PIM membranes in PV

Pervaporation (PV) achieves mass transfer by the chemical potential difference of a component upstream and downstream of the membrane as the driving force of mass transfer, and realizes the separation by the difference in affinity and mass transfer resistance of the membrane to different components in the feed.³⁶ The principle is based on the “solution–diffusion” model.³⁷ Like other membrane separation processes, membrane materials are the key to determine the PV separation efficiency.³⁸ PV has diverse applications, which can be applied in the dehydration of organic solvents,^{39,40} recovery of organics from water,^{41,42} and separation of organic mixtures.^{2,43} For dense PV membranes, small molecules permeated through the randomly distributed free volume among the polymer chains.⁴⁴ If the polymer has a higher effective free volume, it will certainly improve the problem of low PV flux and reduce the PV membrane area required for separation. Hydrophobic PIMs have more free volume and can satisfy this requirement; thus they are first applied to PV separation of organic matter from water.

3.1. Removal of organic matter

3.1.1. Alcohols

Because of the shortage of fossil energy, the preparation of biofuels has received much attention.⁴⁵ PV can be coupled with fermentation to continuously remove bioethanol (or butanol) from the fermentation system, thus reducing the inhibitory effect on microorganisms, and improving the fermentation yield.^{46,47} Rubbery polydimethylsiloxane (PDMS) is one of the most commonly used membrane material for the separation of alcohols from water.⁴⁸ Glassy polydimethylsilylpropyne (PTMSP) has also good separation performances for alcohols.⁴⁹ More glassy polymers were rarely reported for this separation until PIMs were used for preferential separation of alcohols.

In 2008, Adymkanov et al.¹⁰ first used PIM-1 to preferentially separate alcohols from water. The flux of PIM-1 to methanol, ethanol, and *n*-butanol decreases in the following order: methanol > ethanol > *n*-butanol, obviously related to molecular size. In a PV separation experiment of ethanol and water mixture (containing 10% ethanol), the normalized permeation flux increased from $14.6 \text{ kg} \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ to $43.3 \text{ kg} \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ as the feed temperature increased from 30°C to 60°C (flux increased from $0.47 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ to $1.4 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$), and the separation factor decreased from 10.7 to 9.3. Compared with the traditional PDMS membrane, the flux of PIM-1 membrane was

similar to that of PDMS, whereas the thickness-normalized flux was higher than that of PDMS, showing the advantage of PIMs in permeation compared with rubber polymers. In addition to ethanol, Žák et al.³³ further explored the use of PIM-1 for the separation of butanol and investigated the PV separation performance of PIM-1 membrane for butanol aqueous solution. PIM-1 membrane can preferentially separate butanol from water, but there was an aging phenomenon that often existed in glassy polymer (such as PTMSP) membranes. When the storage time of PIM-1 membrane was extended to 370 days, the butanol permeability coefficient of PIM-1 membrane decreased from 9×10^{-5} to $1.1 \times 10^{-5} \text{ mol}\cdot\text{m}^{-1}\cdot\text{kPa}^{-1}\cdot\text{h}^{-1}$ under the feed solution of 50°C , and the degree of decline exceeded 87%. The permeability coefficient of water decreased from 3.2×10^{-5} to $2.2 \times 10^{-6} \text{ mol}\cdot\text{m}^{-1}\cdot\text{kPa}^{-1}\cdot\text{h}^{-1}$, which decreased more than butanol. Therefore, the selectivity increased from 2.8 to 5.1. The attenuation of flux was caused by the slow and spontaneous rearrangement of molecular chain, which was transformed from the thermodynamic nonequilibrium state to the equilibrium state. During physical aging, the renewed soaking of PIM-1 membrane by methanol also failed to achieve satisfactory results. This is because the permeability attenuation of butanol did not slow down, but increased the permeability of water, thereby reducing the membrane selectivity. However, such attenuation is not inevitable. In gas separation applications, addition of 2% carbon nanotube modifier to PIM-1 can significantly mitigate flux aging.⁵⁰ Consequently, when using pure PIM-1 PV membrane for dealcoholization, some porous modifiers should be added in advance to avoid this phenomenon. For PV, this is also a meaningful research direction.

In fact, in PV membranes, a very small amount of pure membrane is present that can satisfy the separation requirements; the membrane was usually modified. Blending is one of the most common methods for membrane modification. The addition of inorganic fillers to organic membranes is a simple and feasible method to prepare mixed matrix membranes (MMMs). However, because the preparation of MMMs requires good dispersion of particles in the polymer, surface modification is essential. Lan et al.⁵¹ added nanoscale silica (SiO_2) modified with γ -methacryloxypropyltrimethoxysilane (KH570) to PIM-1 membrane and prepared composite membrane supported by cellulose acetate membrane. This membrane was used for the preferential separation of butanol in water. The addition of particles increased the hydrophobicity and restrained the swelling of membranes. When the particle loading was less than 4 wt%, the separation factor of membrane increased by more than 2 times, while the permeation flux slightly decreased. A higher filling will lead to the agglomeration of particles. Thus, the flux increased significantly, and the separation factor decreased greatly. When the particle content was 4 wt%, for a butanol aqueous solution containing 5 wt% butanol at 20°C , the separation factor of SiO_2 /PIM-1 composite membrane was 15.47, and the permeation flux was $511 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. In the latest study, Lan et al.⁵² added a kind of nano-sized carbon black modified with a silane coupling agent (aminopropyltriethoxysilane) into the PIM-1 membrane matrix; a loading of 6 wt% of inorganic particles reduced the swelling of PIM membrane by 23% and improved the hydrophobicity of membrane, thus simultaneously improving the permeability and selectivity of PIM-1 membrane. The best performance was achieved when the modified particle content was 4 wt%. For a butanol solution containing 5 wt% butanol at 30°C , the permeation flux was

$1116 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and the separation factor was 19.7. SiO_2 and carbon black used in the above studies were solid particles, and the improvement in their selectivity can be mainly attributed to the hydrophobicity of interfacial channels of organic-inorganic phase and the inhibition of swelling, and SiO_2 and carbon black provided no internal channels. Porous zeolite is the most commonly used modifier for dealcoholized membranes, and its properties of internal channel significantly affect the properties of membrane. Mason et al.⁵³ grafted an ethylbenzene group $(-\text{CH}_2)_2\text{-Ph}$ on the surface of silicalite-1 zeolite and then added the modified MFI zeolite to PIM-1 to improve the dispersion of particles in the polymer matrix by taking the advantage of the affinity between benzene ring structure on the surface of modifier and PIM-1 structure. This study is also the first report on the MMMs of PIM-1 and zeolite. The inorganic particles were still well dispersed in PIM-1 matrix under a high filling amount of zeolite with a volume content of 35.5 v%. Moreover, because only one functional group of the modifier can be anchored on the surface of zeolite, it will not block the pore passage of zeolite, i.e., the surface modification will not sacrifice the specific surface area of zeolite.⁵⁴ PV experiments were carried out for an ethanol aqueous solution containing 9 wt% ethanol at 50°C . A zeolite loading of 35.5 v% increased the separation factor of PIM-1 membrane from 3.21 to 4.7, but the permeation flux significantly reduced from $46.7 \text{ kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $18.6 \text{ kg}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$.

In addition to traditional carbon-based and silico-alumina-based fillers, graphene, a typical two-dimensional sheet material, is an extremely attractive filler to PV membrane materials owing to its high specific surface area and controllable physicochemical properties.^{55–57}

Molecular simulation showed interaction between PIM-1 monomer and GO; therefore, PIM-1 and GO could have good compatibility.⁵⁸ However, the dispersion problem of GO in PIM-1 still needed to be solved first. Alberto et al.⁵⁹ modified the hydrophobicity of graphene oxide (GO) by reacting with octylamine (OA), octadecylamine (ODA), and carboxyl groups at the edge of GO. As a result, ODA-modified GO (GO-ODA) has good dispersion in chloroform, while OA-modified GO (GO-OA) was not highly dispersed in chloroform. However, both GO-OA and GO-ODA obtained by hydrazine hydrate reduction exhibited good dispersion in the membrane solution of PIM-1 in chloroform. For butanol/water mixture, the addition of 0.1 wt% of reduced GO-ODA and reduced GO-OA to PIM-1 membrane increased the separation factor of PIM-1 from 13.5 to 26.9 and 32.9, respectively, and the permeate flux was maintained at about $1 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Reduction reaction removes the hydrophilic group of GO and increases the affinity of the membrane to butanol. However, no significant improvement was observed in the ethanol/water system, as shown in Figure 5, because of no significant difference in the dissolution/diffusion coefficient of ethanol and water in PIM-1 membrane.

In addition to adding inorganic particles to prepare MMMs, the addition of a suitable polymer to a membrane matrix is also an effective method to modify the membrane. This method avoids the aggregation of inorganic particles in the organic matrix or the loss of inorganic particles in the application. However, their compatibility or phase separation should be considered. Zhang et al.⁶⁰ fabricated a PIM-1/PDMS hybrid PV membrane by innovatively introducing a “hard material” PIM-1 as an organic porous

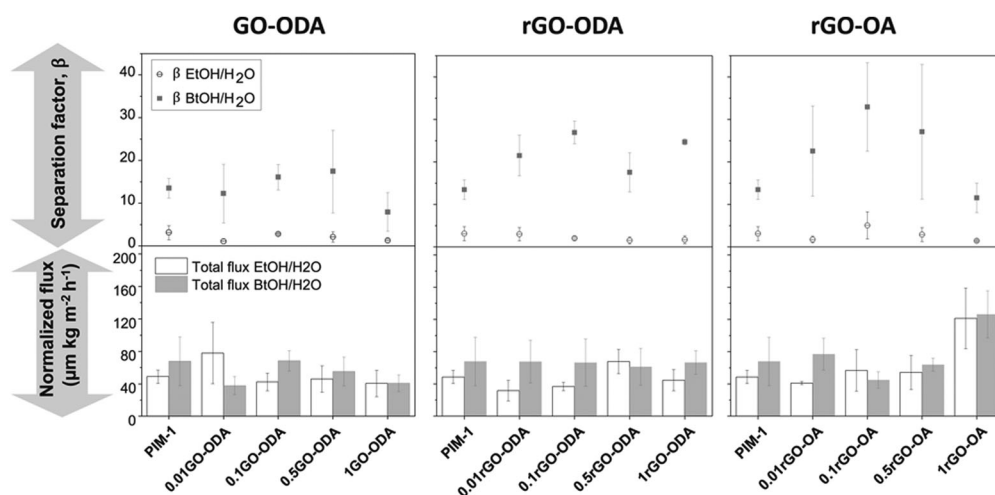


Figure 5. PV performance of PIM-1 membranes and MMMs composed of PIM-1 and graphene-like fillers. (aqueous feed solutions at 65 °C containing 5 wt% of alcohol).⁵⁹



Figure 6. Preparation of PIM-1/PDMS membrane.⁶⁰

modifier to a “soft material” PDMS. The preparation of hybrid membrane is shown in [Figure 6](#). Compared with traditional inorganic fillers, PIM-1 exhibited better interfacial compatibility with PDMS matrix membrane and endowed PDMS with better permeability and hydrophobicity simultaneously. The hybrid membrane showed no significant phase separation within 8 wt% of PIM-1 content. PV separation was carried out for an aqueous solution with a butanol content of 1 wt% at 60 °C; the permeation flux and separation factor increased with the increase in PIM-1 content. At a PIM-1 content of 8 wt%, the permeation flux was doubled, and the separation factor increased by ~35% compared with the pure membrane. The membrane still exhibited good structural stability and integrity after continuous operation for more than 240 h, which has a broad application prospect in industry. In addition, in the preparation of hybrid PDMS membrane, the commonly used solvent for PDMS, *n*-heptane (or other alkane solvents), was not used. Instead, PDMS was directly dropped into the chloroform solution of PIM-1 by utilizing the fluidity of linear PDMS. This is not common in the preparation of PDMS-modified membranes in the past, providing a good reference for the modification of PDMS membranes.

In most studies on the application of PIM-1 PV membranes for dealcoholization, self-supporting PIM-1 membranes were used, and in a few studies, PIMs were used to prepare ultrathin composite membranes, i.e., thin-film composite (TFC) membranes. The positive significance of TFC membranes for industrial applications was self-evident. Some studies prepared PIM-1 TFC membranes with polyacrylonitrile (PAN) as the support membrane for the PV separation of phenol from water.⁶¹ However, due to the condensation of water vapor in PAN pores, the composite membrane became hydrophilic and the flux of composite membrane is lower than that of self-supported PIM-1. Therefore, Gao et al.⁶² replaced the support membrane with hydrophobic polyvinylidene fluoride (PVDF) as the base membrane to obtain composite membranes by “dip-coating” in a PIM-1 solution. The thickness of separation layer can be adjusted by varying the concentration of PIM-1 solution. For the PV separation of *n*-butanol (5 wt%)/water mixture, the total flux increased gradually as the thickness of active layer of PIM-1 decreased from 2.8 μm to 1.0 μm , whereas the thickness-normalized flux decreased as the thickness of PIM-1 layer decreased. This indicates that in fact better membrane separation properties could be achieved. The permeation flux of TFC membrane with an active layer of 1 μm reached $9.08 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and the separation factor was 13.3. However, the total flux of self-supporting PIM-1 membrane with a thickness of 27 μm was only $1.85 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and the separation factor was 19.6. It can be observed that PIM-TFC membrane structure significantly improved the permeability of PIM-1 without sacrificing selectivity. The separation performance of PIM-TFC membrane was also higher than that of commercial PDMS membrane. Therefore, it was very interesting to develop TFC membranes with a nanometer active layer. The study also reported that the surface porosity of PVDF support membrane was the main factor affecting the performance of TFC membrane, because the reduction of surface porosity leads to the reduction of effective permeable membrane area. Therefore, when evaluating the permeate flux, surface porosity of support membrane can be combined with membrane thickness in the calculation of normalized flux.

From the application of PIM-1 PV membrane in preferential separation to alcohols, the separation efficiency on butanol was found to be better than that on ethanol. Furthermore, compared with other literature reports on the removal of alcohol, although the selectivity of PIM-1 based membranes should be improved, the permeability was extremely advantageous.⁶³

3.1.2. Phenol

Phenol and its homologs are important chemical raw materials and toxic pollutants that cause pollution to water bodies.⁶⁴ The solubility of phenol in water is limited, so the content of phenol in waste is relatively low. Therefore, it is suitable to recover phenol by PV technology.⁶⁵ In the researches of membranes for phenol separation, the depth and breadth of studies were inferior to those of membranes for alcohol separation. The traditional hydrophobic PDMS membrane showed medium separation efficiency when used for the separation of phenol.⁶⁶ Polyether block amide copolymer (PEBA) membrane has excellent permeability and selectivity to phenol, but it was difficult to be used commercially.⁶⁶ However, a series of studies by Ye et al.^{42,67–69} on polyurethane (PU) PV membrane showed that PU membranes have great advantages in selectivity, but the

permeability should be improved. More and more effective membranes have yet to be developed.

After the development of soluble PIMs, it became possible to prepare PIM membranes. Considering that the structure of PIMs is rich in benzene ring and contain cyano group (-CN) which can interact with the benzene ring electron cloud of phenol, PIM membranes were first used for the PV separation of phenol in water, earlier than that in gas separation. In 2004, Budd et al.²² first casted PIM-1 solution into a membrane and separated the aqueous solution containing 1–5 wt% phenol at 50–80 °C. The total permeation flux was 0.20–0.67 kg·m⁻²·h⁻¹, the separation factor was 16–18, and the membrane thickness was 40 μm. This performance result is similar to the PV separation performance of PDMS composite membranes in the report,⁷⁰ which initially showed that PIM-1 has potential application in PV. Unfortunately, no more reports have appeared on PIM application in PV for phenol separation for a long time after that.

In a recent study from our group, the membrane was prepared with different molecular weights of PIM-1, and PIM-1 was blended with polyether-based PU for modification,⁷¹ and the effects of PIM-1 molecular weight and PU content on the PV performance to separate phenol from water were evaluated. In the PV experiment performed on a phenol aqueous solution containing 5 wt% of phenol at 80 °C, the number-average molecular weight (M_n) of PIM-1 increased from 3.6×10^4 g/mol to 9.0×10^4 g/mol, and the thickness-normalized flux increased from 26.6 kg·μm·m⁻²·h⁻¹ to 42.7 kg·μm·m⁻²·h⁻¹, respectively. The separation factor also increased from 11.03 to 16.02 (as shown in Figure 7). It can be observed that the longer the chain, the fewer the free chain ends, providing more effective free volume for phenol. For a phenol aqueous solution containing 1 wt% phenol at 60 °C, the total permeation flux and separation factor of PIM-1 (M_n : 9.0×10^4 g/mol) prepared by our group were 12.6 kg·μm·m⁻²·h⁻¹ and 26.8, respectively. This was significantly higher than the PV performance of PIM-1 (M_n : 9.6×10^4 g/mol) membrane under the same feed concentration at 70 °C reported by Budd et al.²² (the permeation flux and separation factor were 8.4 kg·μm·m⁻²·h⁻¹ and 16, respectively), even though the molecular weight of PIM-1 used in both studies was very close. The molecular weight of PIM-1 had a significant effect on the PV separation performance, which has not been paid attention to in previous studies. In addition, PIM-1 with the same molecular weight had different separation properties, probably relates to the thermal history of polymer membrane formed under the preparation conditions, or the aging phenomenon caused by the PIM-1 chain rearrangement as described above. All of these remind us to pay attention to the heat treatment and storage history of the membrane in the literature on PIM membrane separation.

In the study of blended membranes,⁷¹ when 1 wt% PIM-1 was blended into a PU membrane matrix, a severe phase separation would occur due to the large polarity difference between them, leading to the increase in permeation flux and decrease in separation factor. However, when 0.125 wt% poly (styrene-butadiene-styrene) (SBS) block copolymer was added to the blend system, SBS acted as an interface agent and compatibilizer, reducing the size of PIM-1 aggregates in PU and increasing the permeation flux and separation factor of the modified membrane to a level higher than pure PIM-1 membrane.

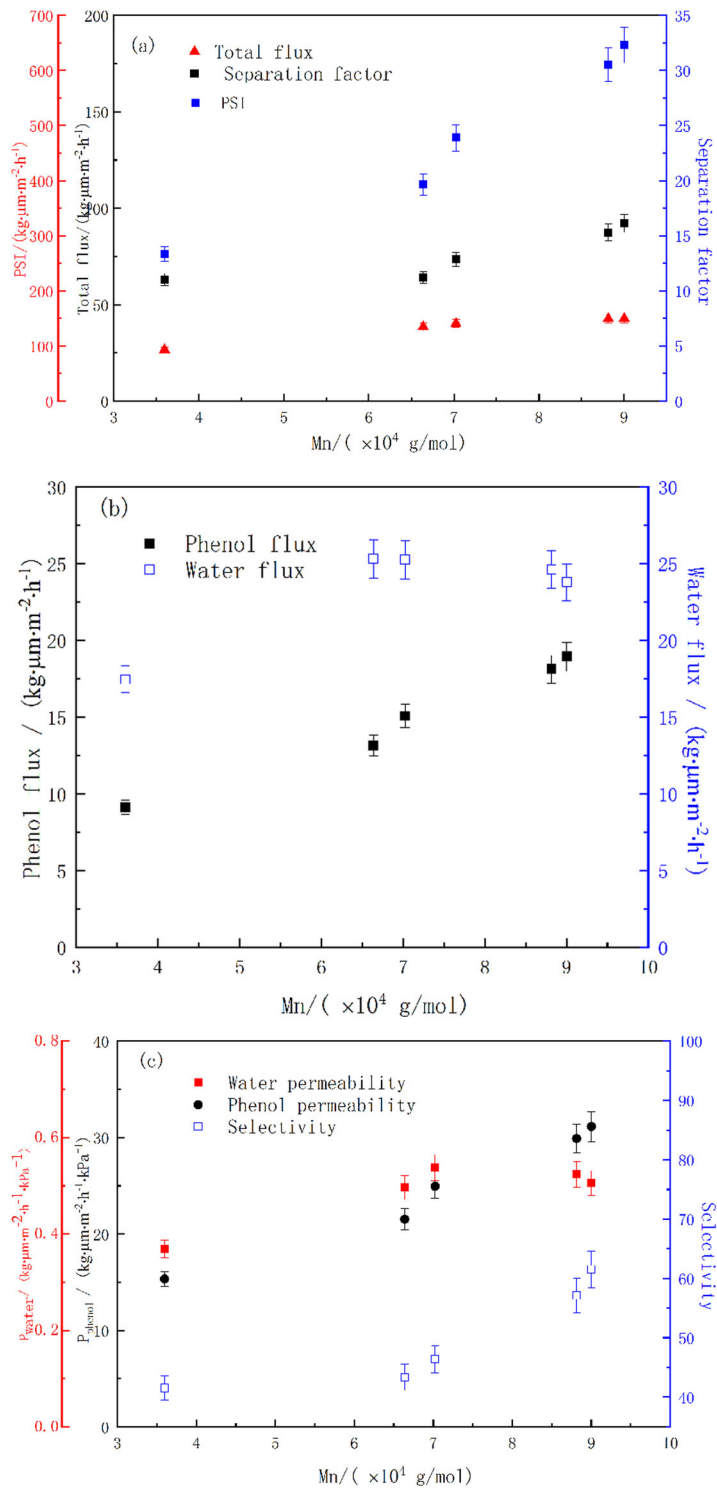


Figure 7. Effects of molecular weight on separation performance: (a) total flux, separation factor, and PSI, (b) partial flux, and (c) permeability and selectivity (feed concentration: 5 wt% and temperature: 80 °C).⁷¹

Although the separation of phenol in PV is the earliest application of PIM-1 membranes in liquid separation, few in-depth studies are reported on this field. Structurally, PIM-1 is not only suitable for the recovery of phenol from water, but also for the recovery of other aromatic substances (such as benzene) in water. Previous studies⁷² have shown that PIM-1 has a high affinity for a mixture of benzene, toluene, and xylene (BTX), and more separation systems where PIMs can be used should be developed.

3.1.3. Other organic matter

In addition to alcohols and phenols, in 2015, Wu et al.⁷³ also studied the PV separation performance of PIM-1 membranes on VOCs in water. The VOCs used included 10 types of organic matter such as ethyl acetate, diethyl ether, acetonitrile, tetrahydrofuran, acetone, acetic acid, and dioxane. The results show that PIM-1 membrane exhibited very good preferential separation to VOCs for aqueous solutions containing 1 mol% ethyl acetate, and its permeation flux and separation factor (ethyl acetate/water) were $39.5 \text{ kg} \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and 189, respectively. This is more than those of PV membranes for ethyl acetate separation reported in most studies and provided a layered aqueous-rich phase and an ester-rich phase on the downstream side. Moreover, the solubility parameters (mainly affecting selectivity) and molecular volume (mainly affecting permeability) of VOCs jointly affected the PV performances (as shown in Figure 8), and the effects on permeation flux and separation factor were similar. For instance, PIM-1 membrane exhibited a lower permeability flux and separation factor for organic compounds with a higher solubility parameter (i.e., it was far from the solubility parameter of PIM-1) and a larger van der Waals volume and vice versa. Therefore, PIM-1 membrane did not exhibit the common compensation effect of flux and separation factor common in previous membrane separation, but showed the same high and low permeability flux and separation factor for specific VOCs. In addition, the molecular shape also significantly affects the separation. For example, chain molecules such as ethyl acetate can easily pass through narrow channels, while circular molecules such as tetrahydrofuran cannot. Therefore, although their solubility parameters were similar and the van der Waals volume of the latter was smaller, the separation factor of membrane to tetrahydrofuran was still more than 10 times smaller than that of ethyl acetate. In this study, the dissolution and diffusion in PIM-1 membrane were analyzed and discussed in detail, laying a foundation for the research group to conduct a series of subsequent studies on the application of PIM-1 membrane PV in dehydration.

3.1.4. Summary of removal of organic matter by pervaporation using PIM membranes

It is well known that a tradeoff phenomenon exists between permeation flux and selectivity of membranes in pervaporation. Figure 9 shows the reported total flux and separation factor for the separation of ethanol, butanol, and phenol from water. It can be observed that the PIM membranes show better selectivity to butanol than phenol and ethanol, probably owing to the more hydrophobicity of butanol. Relatively, the separation of butanol has attracted most attention.

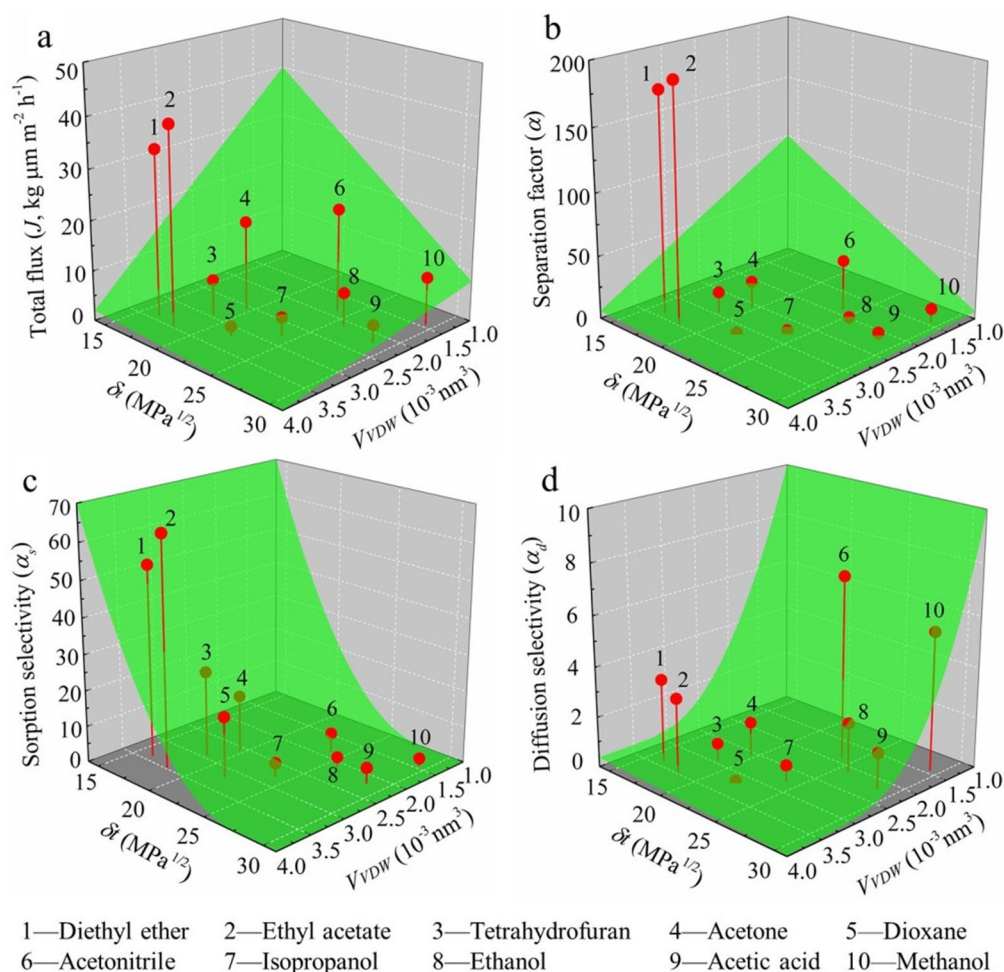


Figure 8. Effect of solubility parameter (δ) and van der Waals volume (V_{VDW}) of VOCs on the PV of 1.0 mol% VOC aqueous solutions using PIM-1 membrane at 30 °C: (a) flux (J), (b) separation factor (α), (c) sorption selectivity (α_s), and (d) diffusion selectivity (α_d).⁷³

The fluxes of PIM membranes for separating butanol are under $2 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ except for PIM-TFC membrane with a flux of $9.08 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and separation factor of 13.3. Undoubtedly, PIM-based TFC membrane is quite promising for industrial applications. Currently, successful examples of PIM-TFC membranes are not extensive in liquid mixture separation. For the design of PIM TFC membranes, the method to combine PIM dense layer with supporting layer should be considered. The supporting layer should be insoluble in the solvent of PIM membrane solution. Available methods to fabricate PIM thin layer could be dip-coating and spin-coating, while it is difficult to obtain a thin film by the common solution-casting method. More novel approaches should be further developed and applied. Except for TFC membranes, most PIM separation layers were modified by different modifiers including polymer and inorganic filler. The modification seems to be more effective to enhance the separation factor than flux. It is supposed to

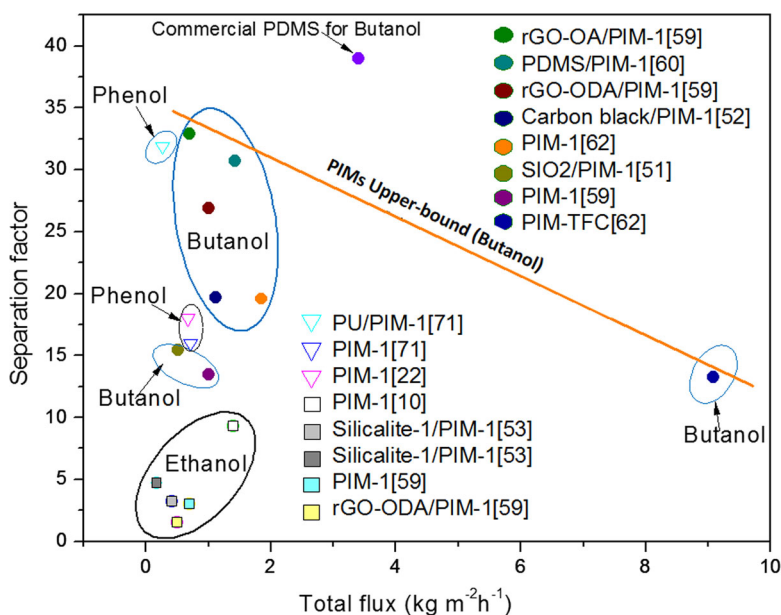


Figure 9. Comparison of PIM-based materials in the application for separation of organics. (The data are retrieved from the figure, table, or the main text in the corresponding references.)

be promising that modified PIMs are designed as a dense thin layer of TFC membranes, combining the advantages of TFC and modified dense membranes and exhibiting outstanding separation performance with a high flux and separation factor.

The commercial PDMS membrane known as PDMS Pervap 4060 (Sulzer) exhibited a separation factor of 39 and flux of $3.4 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for butanol-water mixture,⁴⁹ which is over but near to the upper-bound of PIM membranes. This indicates that PIM membranes have the potential to become comparable to popular commercial PDMS membranes.

3.2. Dehydration

Among the commonly used PV membrane materials, PDMS is commonly used for the preferential removal of organics, whereas polyvinyl alcohol (PVA) is a typical dehydration membrane material. If their application fields were exchanged, it was difficult to use PDMS for dehydration or PVA for preferential separation of organic matter from water. This has not been reported in the literature. However, in addition to the above reported applications of PIM-1 membrane as the preferential removal of organic membrane, PIMs can also be used as a dehydration membrane. Such membranes are very rare in membrane separation. Hydrophobic membranes used in preferential dehydration applications can avoid the decrease in separation performance due to swelling, which has a great application prospect in this field.

The research group of Zhang (Xiamen University, China) conducted a series of excellent studies on the use of PIM-1 membranes in PV dehydration of alcohols. In 2016, Wu et al.⁷⁴ systematically studied the PV separation performance of PIM-1 membrane

for the preferential separation of water from ethylene glycol (EG) based on the needs of industrially refined EG products. Although the solubility parameter of EG is closer to that of PIM-1 compared with water, PIM-1 membrane still exhibited hydrophilicity. The water/EG mixture with a water content of 18.5 wt% at 30 °C exhibited a permeation flux of $2.94 \text{ kg} \cdot \mu\text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and a separation factor of 42.93. Moreover, its diffusion selectivity reached hundreds of times of adsorption selectivity. The separation process is dominated by the diffusion process, i.e., the preferential permeation of water mainly depends on its own size advantage. The total flux and separation factor increased with the increase in water (or methanol) content in the feed, because the swelling degree of PIM-1 membrane decreased with the increase in water (or methanol) content. This was very different from a typical dehydration membrane.

The hydrophilicity of pure PIM-1 was limited; therefore, Chen et al.⁷⁵ prepared carboxylated PIM-1 membrane by hydrolysis to improve the dehydration efficiency of EG. The hydrophilicity of membrane linearly increased with the increase in carboxylation degree, and the separation performance also increased. Compared with other dehydration membranes for water/EG mixture, the carboxylated PIM-1 membrane clearly exhibited permeability advantage, but the separation factor still should be further improved. In the latest study, Liu et al.⁷⁶ cleverly designed a new type of PIM-1/polysulfone (PSF) copolymer membrane, and its synthesis route is shown in Figure 10. The hydroxyl group of PSF allowed it to participate in the copolymerization reaction as a macro-monomer of PIM-1. The introduction of PSF reduced the chain spacing of PIM-1, thereby improving the diffusion selectivity of water molecules and making the membrane exhibit hierarchical pores: (1) The solvent rapidly volatilized to form mesopores during the preparation of membrane; (2) the molecular chain of copolymer was packed to form uniform pores of 0.95 nm (as shown in TEM of Figure 11); (3) chain packing also formed smaller pores, ~ 0.49 nm in size obtained by XRD. The formation of hierarchical pores was beneficial to the diffusion of water. The alcohol molecules were adsorbed on the surface of well-defined micropores of 0.95 nm, resulting in the formation of rapid water transport channels at the center of the micropores, while the pore of 0.49 nm can achieve a high selectivity to water by size sieving. In addition, water molecules can also gather in the mesopores when diffusing through the membrane.

To further improve the hydrophilicity of PIM-1 for wider application, Salehian et al.⁷⁷ designed a novel CPIM-1/P84 blend membrane for the PV dehydration of isopropyl alcohol (IPA) by utilizing the high permeability of carboxylated PIM-1 (CPIM-1) and high selectivity of polyimide (PI). Hydrogen bonding existed between the two polymers; when the content of CPIM-1 was less than 10 wt%, the two polymers were completely miscible. PV dehydration experiments showed that the addition of 10 wt% of CPIM-1 to the P84 matrix can improve the permeability of water by 87% without affecting the selectivity. At this time, the selectivity of IPA/H₂O can reach 6263. Yong et al.⁹ blended carboxylated PIM-1 (hPIM-1) with several PIs and calculated their mixed free energy by molecular simulation to study the compatibility between the two polymers. By optimizing the blending ratio, a blending membrane was obtained with both high permeation flux and separation factor. For a water (15 wt%)-*n*-butanol mixture, the permeation flux of Matrimid membrane containing 20 wt% of hPIM-1 was $47.8 \text{ g m}^{-2} \cdot \text{h}^{-1}$, and the separation factor exceeded 5000. In particular, the study found that unlike the design of a

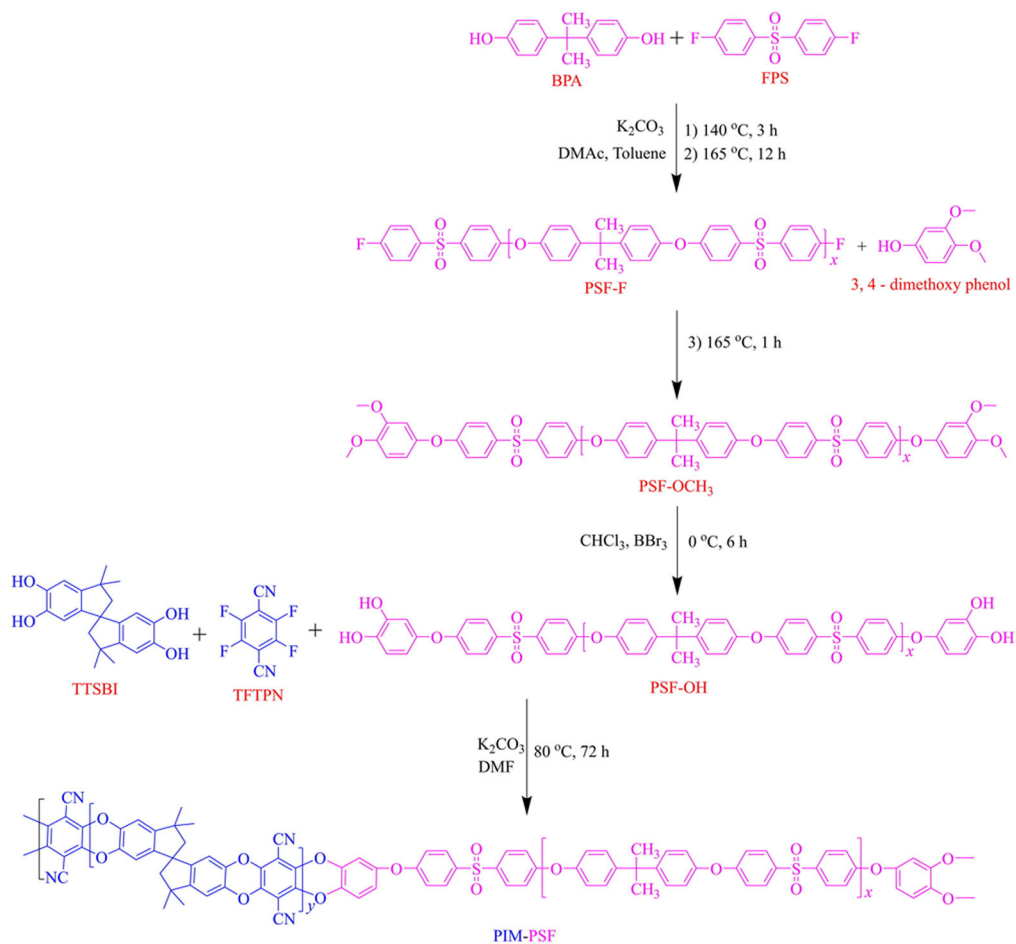


Figure 10. Synthesis of PIM-PSF copolymer.⁷⁶

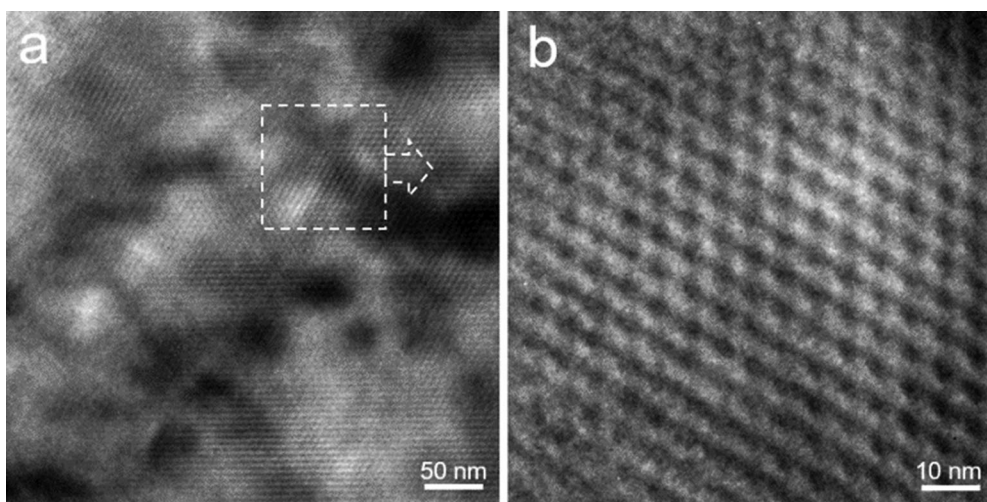


Figure 11. TEM images of PIM-PSF membrane with (a) low and (b) high magnification.⁷⁶

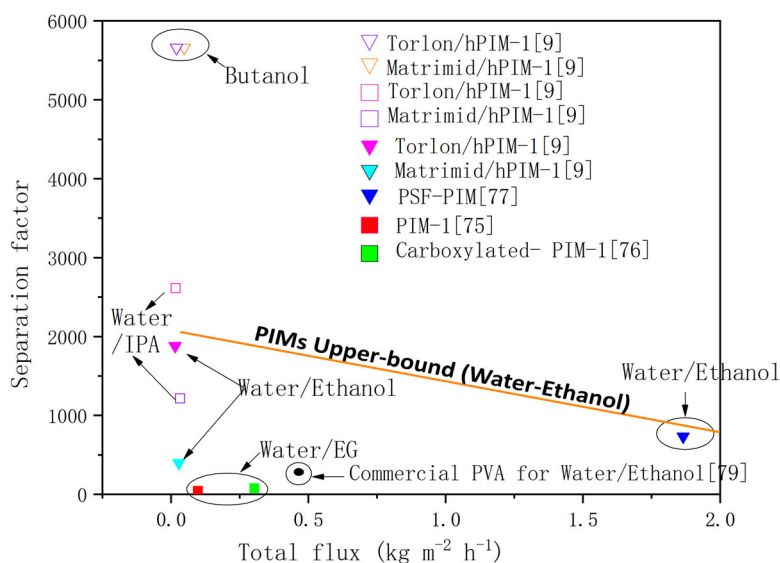


Figure 12. Comparison of PIM-based materials in the application for dehydration. (The data are retrieved from the figure, table, or main text in the corresponding references.).

gas separation membrane, the design of structure of PI/hPIM-1 PV membrane should consider the compatibility of two polymers, effect of swelling on the interaction between small molecules and polymer membranes, and adsorption and dissolution selectivity of blends. This study provides a reference for designing PV membrane structures, organic solvent NF, and developing next-generation water purification membranes, thus laying a foundation for evaluating the applications of gas separation membranes in PV.

Figure 12 shows a comparison of the separation performances of different PIMs and their modified membranes for dehydration from C_2 – C_4 alcohols via pervaporation. The membranes show a higher separation factor to water in water/butanol than in water/IPA, ethanol, and EG, although the dehydration of PIM membranes has been rarely reported. Interestingly, the performance of commercial PVA membrane (PERVAP2200) (flux: $0.45 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, separation factor: 287^{78}) is below the current upper bound of PIM dehydration from ethanol. Especially, the PSF-PIM membrane showed more excellent performance with a flux of $1.87 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and separation factor of 732, indicating that PIM membranes have more potential in the dehydration application than traditional PVA membranes.

To explain the excellent dehydration performance of PIM membranes, solution-diffusion mechanism could be used to describe the transport process of small molecules in these PIM membranes. According to the solution-diffusion mechanism, the water and alcohol molecules first dissolve in the membrane and then diffuse through the membrane. The separation factor (α) is the product of diffusion selectivity (α_{dif}) and sorption selectivity (α_{sorp}).^{74,75} A comparison between α_{dif} and α_{sorp} will be helpful to understand the separation mechanism of PIM pervaporation membranes. The limited data of α_{dif} and α_{sorp} reported in the literature are summarized in Table 2. As shown in Table 2, it is interesting that α_{dif} is almost thousands of times higher than α_{sorp} when PIM membranes are used for the dehydration of EG and IPA. Obviously, the good selectivity

Table 2. Diffusion selectivity (α_{dif}) and sorption selectivity (α_{sorp}) of PIM membranes.

PIMs	Feed mixture	α_{dif}	α_{sorp}	$\alpha_{\text{dif}}/\alpha_{\text{sorp}}$	Reference
P84/c-PIM-1	Water-IPA	3625	1.324	2737.9	77
PIM-1	Water-EG	390.27	0.11	3547.9	74
PIM-1	methanol-EG	27.83	0.87	32.0	74
PIM-1	Water-EG	553.14	0.107	5169.5	75

of PIM membranes to water is derived from the diffusion priority of water with smaller size than alcohol molecules. Finally, the unique porous structure of PIMs induces the “molecular sieving effects” during diffusion. That is the reason why hydrophobic PIMs could be used for in preferential dehydration applications. A similar phenomenon has also been observed in the separation of methanol from methanol-EG mixtures.⁷⁴ Unfortunately, no more data are available for the application of removal of organic matter from water. Further studies in this field should be conducted in the future.

Regarding material structure and performance, the flux of most membranes falls below $0.5 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ except for PSF-PIM. Unlike the carboxylation modification of CN group, the structural design of PSF-PIM is derived from the synthesis of macromonomer.⁷⁶ The novel monomer rearranges the original chain packing of PIM-1 and endows the membrane with hierarchical microporosity that will greatly benefit the mass transfer. It is suggested that more backbone modification of PIMs could be done by introducing some novel monomers with functional groups or distorted structures, although the current research on PIM modification is almost exclusively focused on the carboxylation of CN.

3.3. Separation of organic mixtures

In the three applications of PV, the selection and design of separation membranes for the separation of organic mixtures were more difficult. Hydrophilic membranes can be used for the application of preferential dehydration separation, and hydrophobic organophilic membranes can be used for the preferential removal of organics, both of which are commercially available for industrial use at present. It is usually difficult to separate organic/organic mixtures, and it should be designed according to the physicochemical properties of separation system with a specific target. However, organic mixtures are mostly azeotropic and widely present in petrochemical industry. The development of PV separation membranes for organic mixtures has important practical significance such as energy saving. Systems that relatively received attention are aromatic/aliphatic hydrocarbon mixtures,^{79,80} gasoline desulfurization,^{81,82} methanol/dimethyl carbonate (DMC) mixture,^{83,84} isomer mixture,^{85,86} and other systems.

Wu et al.⁷⁴ evaluated the PV separation performance of preferential separation of methanol from a methanol/EG mixture when studying the separation performance of PIM-1 in the dehydration of EG. The solubility parameters of methanol and EG are almost the same, but the molecular size of methanol is smaller than that of EG. Therefore, PIM-1 membrane could preferentially separate methanol; a separation factor of 24.21 was obtained. Similar to dehydration of EG, this is a diffusion-controlled process. In the latest report, PIM-1 membranes were used to separate methanol and DMC mixture.⁸⁷ Unlike previous preferential separation of methanol, PIM-1 membrane can preferentially separate DMC from its azeotropic system (DMC accounted for 18 mol%,

methanol accounted for 82 mol%) by PV or vapor permeation, which can make the PV more efficient and saving energy. Unlike previous TFC membranes⁸⁸ highly admired in PV membrane separation, this study used a “thick” PIM-1 membrane with a thickness of ~0.5 mm. For a mixture at 40 °C, PIM-1 membrane exhibited a separation factor of 2.3 in PV separation comparable to PDMS, but the permeation flux was higher than PDMS membrane. When using a feed of azeotropic vapor for vapor permeation experiments, the separation factor could be increased to 5.1, which is the best selectivity currently obtained by membrane technology for the preferential separation of DMC.

The above studies show that PIM-1, a hydrophobic membrane, can be used for the effective recovery of alcohols in water depending on its affinity to organic matter, thus exhibiting potential application in the separation and purification of biomass fuels. PIM-1 can also be used for the removal of VOCs in water and has application potential for environmental protection. Some studies on PIM-1 have been reported in azeotrope separation, but still have several problems: (1) The types of PIMs application are very simple; only the application of PIM-1 is reported at present. (2) The application of separation system is narrow, mainly used for alcohol recovery in water. More examples of organic matter recovery from water and organic mixture separation should be obtained. Besides, another suggestion worth mentioning for the readers is that the intrinsic flux normalized by pressure and thickness such as permeability or permeance^{89,90} should be used and discussed more in the studies of PIM pervaporation membranes. Although the real flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) can demonstrate the direct separation performance of membranes, the normalized flux can help to elucidate the polymer structure/property relationship.

4. Application of PIM membranes in NF

NF is a membrane separation process between ultrafiltration and reverse osmosis. As the NF driving pressure required is less than reverse osmosis, it is sometimes known as “loose reverse osmosis.” The Molecular Weight Cutoff (MWCO) is 200–1000 g/mol (or 200–500 g/mol); it is generally used for the separation of dissolved components with a molecular size of 0.5–2 nm.^{91,92} The microporous range of PIMs is suitable for the NF process, making them ideal materials for the preparation of high-flux NF membranes.

In 2005, McKeown et al.⁹³ first reported the application of PIM-1 membrane for organic solvent nanofiltration (OSN) and applied for a patent. Unfortunately, the used solvents acetone and toluene severely swell the membrane, thus exhibiting a high permeation flux and low rejection rate for polyethylene glycol (PEG). In 2012, Fritsch et al.⁹⁴ in this research team prepared a kind of TFC membrane of PIM-1 and PIM copolymers (PIM1-CO6-50 and PIM1-CO1-50) on a PAN porous support by dip coating. The molecular structure of active layer of the membrane is shown in [Figure 13](#). In addition, unlike previous studies, to control swelling in a simple and feasible method, the PIMs were blended with polyethylene imine (PEI) and then crosslinked with PEG diglycidyl ether to obtain a crosslinked separation thin layer. In this way, a higher rejection rate can be achieved. The results show that thermal and chemical crosslinking with PEI can effectively inhibit swelling, so that PIM-1 can be used as the separation layer of NF membrane in organic solvent systems of ketones, aromatic hydrocarbons, halogenated hydrocarbons, and tetrahydrofuran, exhibiting superior performance than the commercial membrane

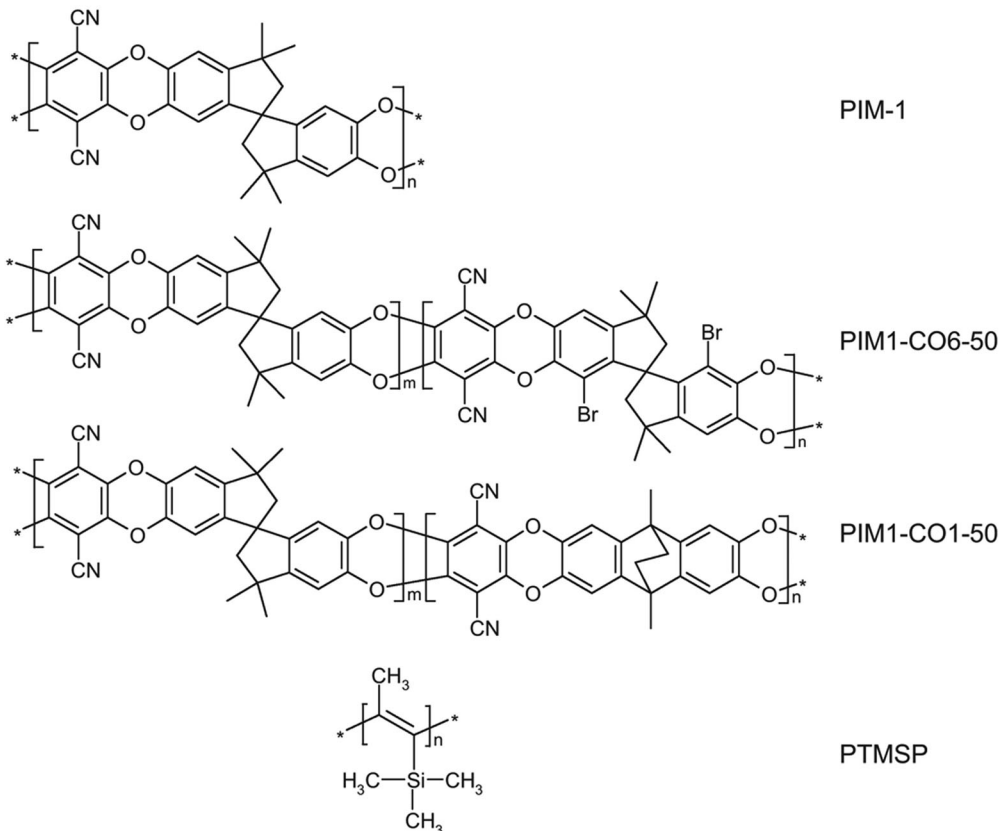


Figure 13. Molecular structures of PIM-1 and PIM copolymers.⁹⁴

StarmemTM240. The study also found that if the PAN support membrane was precoated with a layer of PDMS as the intermediate layer, the crosslinked PIM-TFC membrane could achieve 97% rejection rate of hexaphenylbenzene in *n*-heptane and guarantee a high flux. If no intermediate layer was present, the permeability will be much lower.

Next, Tsarkov et al.⁹⁵ and Volkov et al.⁹⁶ from the same group prepared three types of glassy polymer NF membranes including PIM-1, PTMSP, and poly(4-methyl-2-pentene) (PMP) and evaluated the effects of the properties of solvents and polymers on the rejection of dye molecules. For dyes with a low molecular weight ($M_w = 350$ Da) such as Safranin O and Orange II, the membrane retention values were similar, and the order of retention value for different dyes was also the same. This is slightly related to the properties of the polymer, but related to the size of interaction between the polymer membrane and dye. Therefore, solvent Blue 35, which slightly differed from the solubility parameter of polymer, was negatively intercepted in the membrane separation of different polymers. For dyes with higher molecular weights, the rejection rate was mainly determined by the size of free volume in polymer. PIM-1 showed a rejection rate of 98% for Remazol Brilliant Blue R, higher than PTMSP and PMP. It was also found that PIM-1 has a high distribution coefficient for several dyes studied in the dye adsorption experiment; therefore, it can be predicted that PIM-1 has the potential to be used in the adsorption field. On this basis, Anokhina et al.⁹⁷ found that in the NF application of

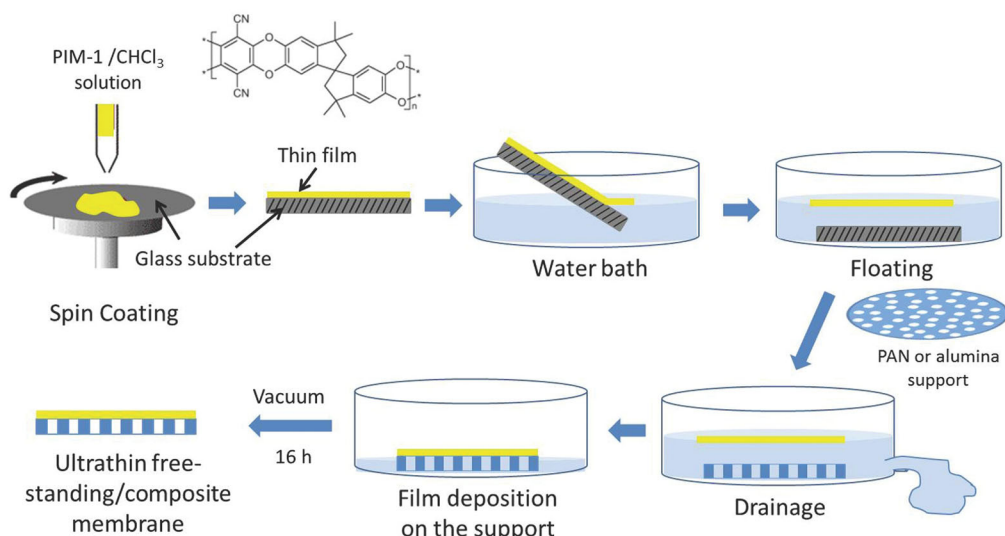


Figure 14. Schematic of preparation for ultrathin PIM-1 membranes via spin coating on glass and transfer to a porous support (PAN or anodized alumina). Concentrations of PIM-1 in chloroform (CHCl₃) used for spin coating were in the range 0.25–2.5 wt% (w/w).⁹⁸

PIM-1 membrane, the solvent properties also significantly affect the separation performance. In a nonpolar solvent, oil red O can be rejected, while in a polar solvent, it was negatively intercepted.

In the above studies, the thickness of PIMs active layer was at least 300 nm⁹⁴, and the thicker one was at 20–30 μm.⁹⁵ To further improve the performance of OSN membrane with PIMs as the active layer and more fully exhibit its characteristics of high permeability, the thickness of active layer for separation was reduced using different methods in the following studies.

Gorgojo et al.⁹⁸ from Livingston group (Imperial College London, United Kingdom) prepared a TFC membrane with a thickness of 35–140 nm using PIM-1 as the raw material. The specific preparation process is shown in Figure 14. The PIM-1 membrane was first formed on a glass substrate by spin coating and then suspended in a water bath to separate the membrane from the substrate. Then, the support membrane required for preparing the TFC membrane was placed under the PIM-1 membrane floating on the water surface, and the water in the water bath was released slowly. Finally, the PIM-1 thin layer was deposited on the support, where the deposition of PIM-1 thin layer on the support was the key for the success of ultrathin TFC membrane preparation. The SEM characterization showed that the TFC membrane with a separation layer of less than 1 μm was successfully obtained (as shown in Figure 15), and no defect was observed on the surface. The obtained PIM-1-TFC membrane exhibited a very good separation effect on the hexaphenylbenzene/*n*-heptane system. When the thickness of PIM-1 was 140 nm, the permeability of composite membrane was two orders of magnitude higher than that of commercial PI-based OSN membrane Starmem240. Moreover, the rejection rate of hexaphenylbenzene reached 90%, and it had excellent mechanical strength and high-pressure operation stability. It is interesting to note that when the thickness of PIM-1 layer was less than 140 nm, the permeance

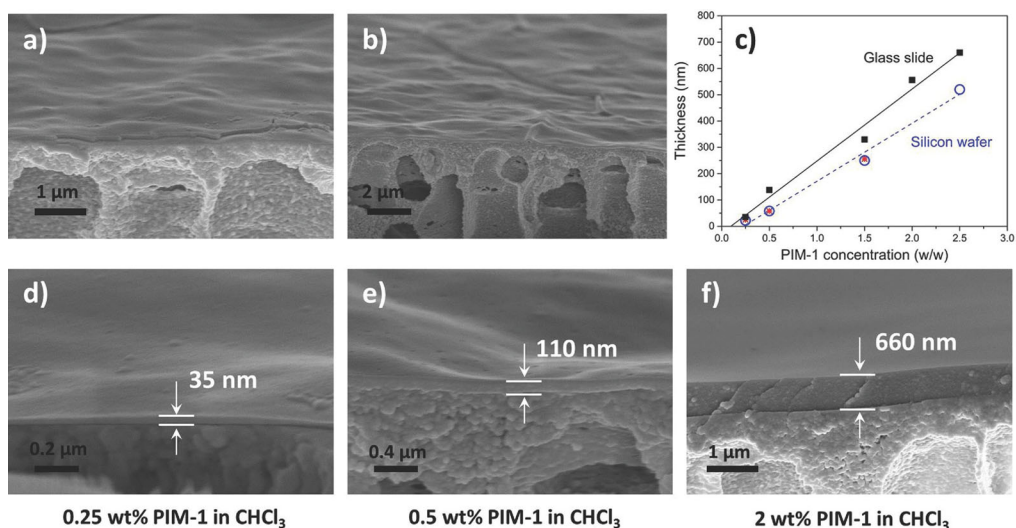


Figure 15. SEM images of ultrathin PIM-1 membranes at different magnifications on a porous PAN support. Thin membranes were prepared on a glass plate via spin coating a solution of PIM-1 with different polymer concentrations in chloroform and then transferred to PAN supports. (a,d) 0.25 wt.%; (b,e) 0.5 wt.%; (f) 2.5 wt.%. (c) Dependence of membranes thickness on PIM-1 solution concentration and (■) glass and (○,*) silicon substrates, spin coated at 2000 rpm. Thickness values were obtained by scanning electron microscopy (SEM, ■), atomic force microscopy (AFM, ○), and light interferometry (*).⁹⁸

($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) decreased with the decrease in the thickness of separation layer. According to the calculation performed by the author in this paper, its thickness-normalized flux (permeability, $L \cdot \mu m \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) had the same change trend. This can be attributed to the change in the glassy polymer chain stack within the thin-film confinement. Gao et al.⁶² also found a similar phenomenon in the PV of butanol using a PIM-1-TFC membrane. This prompted scientists to reconsider the relationship between the thickness of separation membrane and its permeability. In addition, this method of preparing TFC required extremely delicate experimental operation and a large amount of time, and its industrial application prospect was questionable. In another study, Cook et al.⁹⁹ in the same group fabricated a series of composite membranes of PIM-1, PIM-7, and PIM-8 for OSN using “roll-to-roll” dip coating method on two different support membranes including PAN and crosslinked polyetherimide (PEI), and obtained a PIM separation thin layer of 100–300 nm by adjusting the concentration of casting solution. It was found that PIMs can obtain a coating with fewer pinholes and higher quality on crosslinked PEI compared with PAN supporting membrane, which is related to PEI’s ability to maintain molecular flexibility in dry state. Compared with PIM-1 and PIM-7, PIM-8 exhibited a higher separation factor for straight hydrocarbons in mixed alkanes of straight chain and branched chain C_{16} . This report introduced PIMs other than PIM-1 into OSN application for the first time.

Gao et al.¹⁰⁰ modified PIM-1 into thioamide-containing PIM-1 (TPIM) and prepared a membrane (as shown in Figure 16) for dye NF separation with ethanol and acetone as the solvents. The introduction of amino groups in the structure allowed PIM-1 to be easily crosslinked with acyl chloride without using external components⁹⁴ or by the

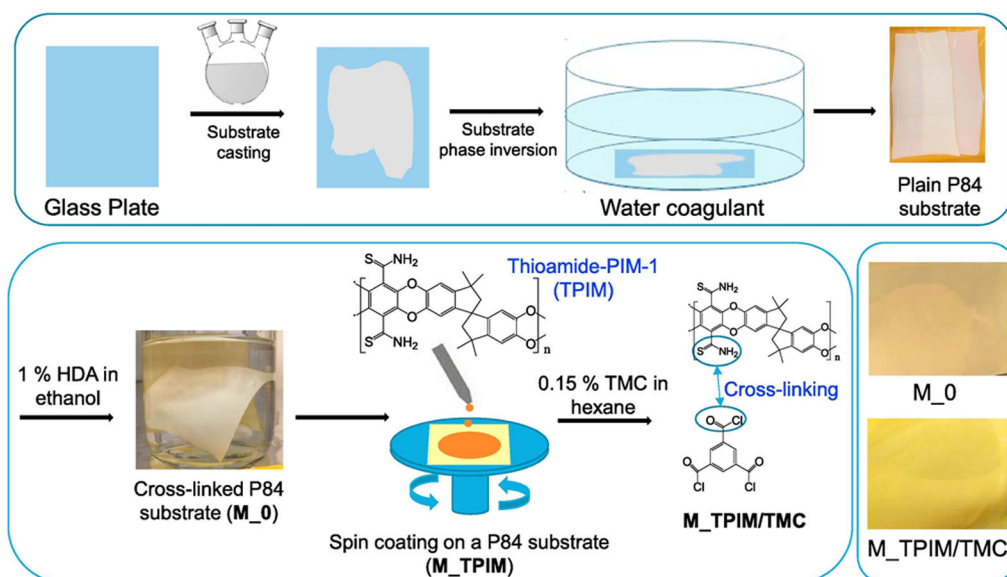


Figure 16. Formation of P84 substrates and TPIM/TMC membranes and their appearance.¹⁰⁰

crosslinking of carboxyl group after the hydrolysis of PIM-1.¹⁰¹ The thickness of TPIM layer supported by crosslinked P84 was less than 150 nm, with not only smaller free-volume voids, but also better chemical stability and rejection. The rejection rate of obtained TFC membrane to Remazol Brilliant Blue R reached 90%, and the permeability of pure ethanol was $3.4 \text{ L} \cdot \text{m}^{-2} \cdot \text{bar}^{-1} \cdot \text{h}^{-1}$. This study provides a good learning for the modification of PIM-based membranes.

Generally, organic solvents should be added to the preparation of casting solution for PIMs membranes. For example, the solvents used in typical PIM-1 were chloroform and tetrahydrofuran; usually the polymer concentration in the membrane solution was relatively low (<10 wt%), i.e., the solvent consumption was large. From the perspective of environmental protection, the green solvent should be further developed. In a recent study, Agarwal et al.¹¹ prepared Troger's base PIMs with hydroxyl functionalization, which was positively charged by quaternary amination and negatively charged by sulfonation. The obtained two charged polymers were soluble in water, and the TFC NF membrane of charged Troger's base PIM was prepared using layer-by-layer self-assembly (LBL) technology with PAN as the support. The thickness of separation layer increased by 2 nm per layer. The flux can reach 5-6 LMH/bar, and the rejection rate of PEG (molecular weight of 500 g/mol) was 95%. This study significantly improved the applicability of PIMs in liquid separation, expanded the alternative materials of TFC active layer, and promoted the application of PIMs in liquid separation.

5. Application of PIM membranes in adsorption

Adsorption is one of the common separation methods for removing organic or inorganic pollutants in solutions. In the above-mentioned applications of PIMs in NF, some PIMs exhibited strong interaction with some organic dye molecules, resulting in a

negative interception in NF separation.⁹⁶ This indicates that PIMs can be used as porous adsorbent materials with excellent properties.

5.1. Adsorption of dyes

Anokhina et al.⁹⁷ applied a PIM-1 solution many times to a stainless steel screen mesh, which was used for solid-phase extraction (or swing adsorption). For an ethanol solution with neutral solute (oil red O), the degree of enrichment of oil red O in PIM-1 was up to 4300 times, and it even reached 53,000 times using a water/ethanol (30/70) mixture as the solvent. However, PIM-1 had no effect on anionic dyes. In addition to the attachment of PIM-1 to the support, more studies used the method of preparing electrospun fiber membranes for adsorption experiments, making them easier to recover and reuse the adsorbent.

The following studies on adsorption were generally carried out using PIMs fiber membranes, and the PIMs were modified with different strategies.

Zhang et al.^{102–104} published a series of research papers on the application of electrospun microfibrillar membranes prepared by PIM-1 and its hydrolysis modification materials in adsorption separation. First, based on the hydrophobicity of PIM-1 itself, PIM-1 is more suitable for the removal of pollutants in the oil phase, unlike the conventional adsorbent including activated carbon and porous silicon. In the study,¹⁰³ a PIM-1 spinning fiber membrane was used for the adsorption of dye in oil phase. The BET specific surface area and pore volume of the fiber membrane were higher than those of PIM-1 powder, because of the rapid evaporation of solvent in spinning. In addition, because the PIM-1 fiber membrane had more “open pores” than “closed pores,” it had a faster adsorption rate than the PIM-1 dense membrane, but the saturated adsorption amount was close to that of dense membrane. Second, the hydrolyzed PIM-1 fiber membrane can be used for the adsorption of dyes in the aqueous phase owing to its hydrophilicity.¹⁰⁴ The hydrolyzed PIM-1 fiber contained carboxyl groups, increasing its dispersibility in water. It also exhibited a good adsorption to cationic dyes in water by charge interaction. The saturated adsorption amounts of methylene blue and methyl violet were $424.80 \text{ mg}\cdot\text{g}^{-1}$ and $317.26 \text{ mg}\cdot\text{g}^{-1}$, respectively, both higher than the adsorption activity of activated carbon. In addition, PIM-1/POSS spinning fiber membranes¹⁰² can also be used for oil/water separation. POSS increased the surface roughness of fiber, and under the operating conditions of spinning, even if the POSS content was high, it was not easy to cause severe agglomeration, whereas the casting membrane formation process under the same content was not so. When the content of POSS in the fiber membrane was 40%, the water contact angle was 155° , and the oil contact angle was 0° . Thus, a fiber membrane surface with superhydrophobicity was obtained. The obtained fiber membrane can also be used for the adsorption separation of dyes in the oil phase.

Satilmis et al.^{105–108} conducted a series of studies on the adsorption properties of PIM-1 and modified PIM-1. Carboxylated PIM-1 spinning fiber membranes with different hydrolysis degrees (65–99%) were prepared.¹⁰⁶ Similar to the research results of Zhang,¹⁰⁴ carboxylated PIM-1 showed better adsorption performance for cationic dyes than for anionic dyes. In addition to carboxylation modification, to use PIM-1 in the adsorption of anionic dyes, amination modification of PIM-1 fiber was conducted.¹⁰⁶

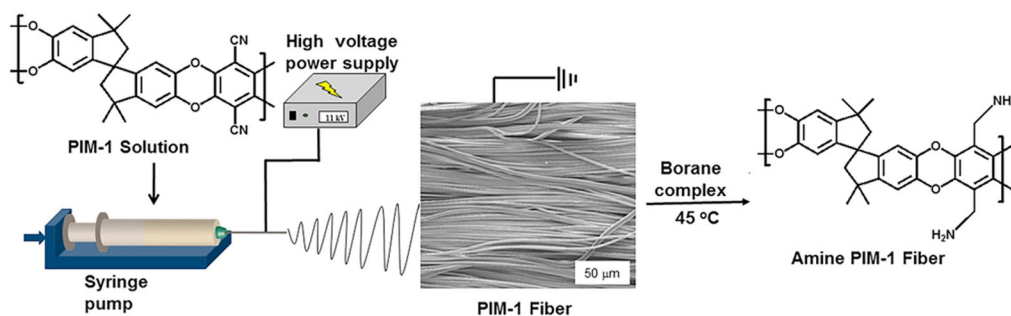


Figure 17. Illustration of electrospinning and production of AM-PIM-FM.¹⁰⁶

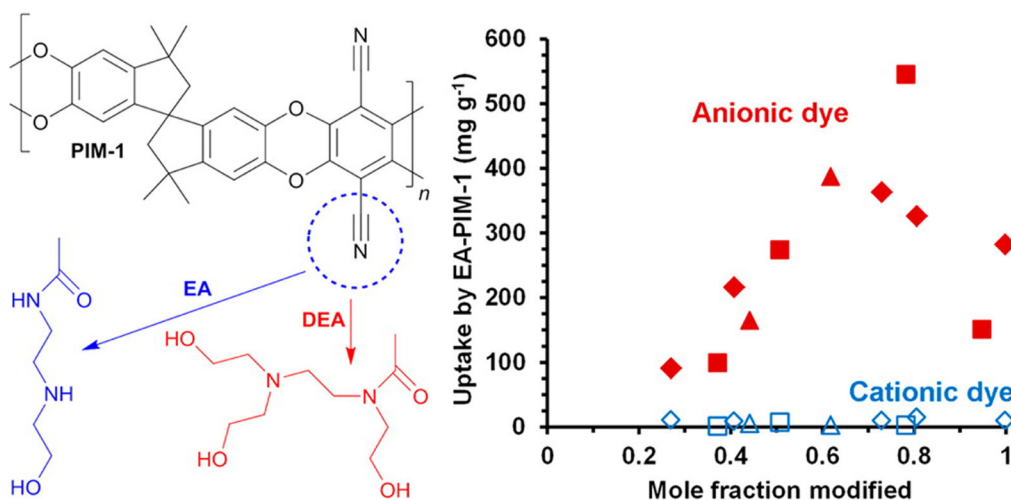


Figure 18. Ethanolamine- and diethanolamine-modified PIM-1 and uptake of selective adsorption of dye.¹⁰⁸

The method was to convert the cyano group (CN) of PIM-1 into an amino group (NH₂) using borane complex, as shown in Figure 17. The amino-modified PIM-1 fibrous membrane showed a stronger anionic dye adsorption capacity than the unmodified PIM-1 fibrous membrane and amine-modified PIM-1 dense membrane. Aminated PIM-1 can also be obtained by the reaction of ethanolamine with PIM-1^{107,108} After the modification, aminated PIM-1 showed better adsorption performance for anionic dyes than cationic dyes, as shown in Figure 18, exactly opposite to the adsorption of carboxylated PIM-1 obtained via hydrolysis. By complementation, dyes with different properties in water can be removed, as shown in Figure 19.

5.2. Adsorption of toxic organic matter (no dye) in water

The earliest adsorption application of PIMs started before the linear PIMs was synthesized. Budd et al.¹⁹ used crosslinked PIMs to adsorb phenol from water and found that the adsorption capacity of phenol was significantly higher than that of common activated carbon. After soluble PIMs were developed, the electrospinning membranes of

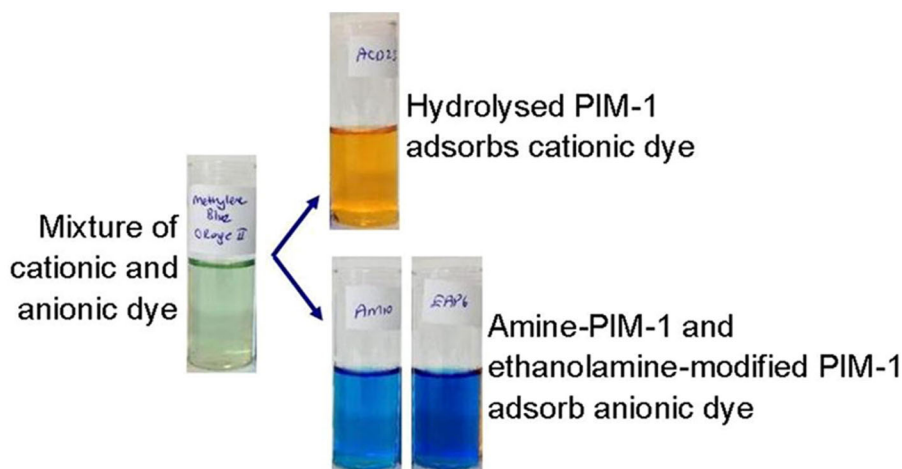


Figure 19. Adsorption performances of amine-PIM-1, ethanolamine-modified PIM-1, and hydrolyzed PIM-1.¹⁰⁷

different PIMs were generally used to study the adsorption. Satilmis et al.¹⁰⁹ used PIM-1 electrospinning membrane to adsorb aniline in both water and air and found that its adsorption capacity and adsorption rate were higher than those of dense PIM-1 membrane and PIM-1 particles; the maximum adsorption capacity reached up to $138 \text{ mg}\cdot\text{g}^{-1}$, exceeding the adsorption capacity of most adsorbents reported in the literature. In the latest study, PIM-2¹¹⁰ spinning fiber membrane was also used for adsorption experiments. PIM-2 showed a strong hydrophobicity and high specific surface area, and it can adsorb DMSO and silicon oil, ~ 20 times of its own weight.

Yushkin et al.⁷² found that the adsorption capacity of PIM-1 for nonpolar solvents such as BTX was higher than that for polar solvents (e.g., DMF and DMSO). This is consistent with the solubility parameter theory, because two components with similar solubility parameters would have a higher affinity. This also indicated that PIMs have a good affinity for other benzene pollutants, and its adsorption application system can be further expanded. Pan et al.¹¹¹ applied PIM-1 spinning fiber membrane for the adsorption of phenol in water and also the adsorption of broad-spectrum pesticide carbendazim. The coexistence of mesoporous and microporous structure of fiber membrane reduced the mass transfer resistance and showed a high adsorption capacity.

5.3. Adsorption of metal ions in water

Zhang et al.¹⁰⁴ found that although PIM-1 fiber membrane before hydrolysis almost exhibited no adsorption capacity for heavy metals, the hydrolyzed PIM-1 fiber membrane exhibited strong adsorption capacity for Pb^{2+} and Cu^{2+} in water due to the action of carboxyl groups. This led to expectation that PIMs might be used for the adsorption of metal ions in water.

Uranium is an important energy source with a great significance to industry, agriculture, national defense, as well as science and technology development. Uranium is enriched in sea water. If uranium can be extracted from seawater with appropriate technology, it is of strategic significance for the sustainable development of nuclear energy.

Sihn et al.¹¹² converted the cyano group of PIM-1 by the reaction between PIM-1 and hydroxylamine into an amoxime group, and achieved the rapid adsorption and recovery of uranyl ions using amoxime-PIM-1. Because the adsorbent was in the particle state, it was not easy to use in practical industrial applications. In the latest study, Satilmis et al.¹¹³ modified PIM-1 with amidoxime and prepared modified PIM-1 into a fiber membrane. The adsorption capacity of modified PIM-1 fiber membrane reached 20 times higher than that of unmodified PIM-1 fiber membrane. Although the adsorption performance of the fiber membrane was slightly lower than that of the granular material, it has greater industrial application and feasibility.

5.4. Separation of oil/water mixture

PIM fiber membranes with nanoparticles can also be used for oil/water separation. As mentioned in Section 5.1. PIM-1 fiber membrane containing 40 wt% POSS can be used to separate a series of oil/water mixtures and emulsions with a separation efficiency of higher than 99.95%.¹⁰² Furthermore, the contact angle and flux of the membrane did not change much after repeated use. To further increase the hydrophobicity of PIM-1 fiber membrane, the solution formed by PIM-1 and perfluoro-*n*-octyl-triethoxy silane (PTES) (PIM-1/PTES = 9/1 w/w) was soaked and coated on the alkali-corroded polyester fiber membrane to obtain a superhydrophobic and oleophilic fiber membrane.¹¹⁴ Alkali etching endowed higher roughness to the fiber substrate. PIM-1 and PTES endowed good oleophilicity to the membrane. The separation efficiency of oil/water mixture was still up to 99.96% even if used for more than 30 cycles.

5.5. Enantiomeric separation

Weng et al.³⁵ used PIM-1 membrane for the resolution of enantiomers for the first time, and the molecular design of separation membrane was also very creative. Starting from the monomer required for the synthesis of PIM-1, a single enantiomer of TTSBI with optical purity above 99% was obtained by asymmetric crystallization, and then it was polymerized with DCTB to obtain chiral PIM-1 and carboxylated chiral PIM-1 membranes. In an osmotic chiral separation experiment, the membrane successfully separated mandelic acid, binaphthol, Fmoc-phenylalanine, and its own monomer TTSBI; the enantiomeric excess (ee%) could reach 32%, 53%, 75%, and 87%, respectively, with a high permeability rate. The application of such chiral PIMs is not limited to enantiomeric separation, but it can also be used as a chiral stationary-phase material.

The above studies show that the application of PIMs in adsorption separation mainly focused on the adsorption of dye using PIM-1. Its specific adsorption characteristics can be regulated by its own chemical structure. From the perspective of adsorption morphology, it was mainly for the application of PIMs as spinning fiber membranes. Compared with dense membranes, this change of morphology significantly expanded its application space, and its application in other liquid separation fields is also being developed.

6. Molecular simulation study of PIMs

With more and more attention paid to PIMs in PV, NF, adsorption, etc., the study on its separation performance became more and more essential. However, because of the limitations of experimental conditions and equipment, the properties of membranes were restricted by various complex factors. This also limited the understanding and interpretation of microstructure of membrane and the mechanism of small-molecule transmembrane diffusion and solute retention at atomic and molecular scales. Molecular simulation can overcome these shortcomings and transform the molecular-scale process into a visual process, to help understand the problems including the structure and performance of membranes and guide the design and optimization of membrane materials and processes.

In the molecular simulation of PIM membranes, Jiang's group (National University of Singapore) conducted a series of valuable studies, and the following studies which will be discussed are all from this research group. Xu et al.¹¹⁵ simulated the adsorption of liquid in PIM-1 membrane and predicted the permeability of liquid in the membrane based on this simulation. For the water permeability prediction of amorphous PIM-1 membrane, the solution-diffusion (SD) model is consistent with the results of molecular dynamics (MD) simulation, and water tends to move randomly during the penetration in PIM-1 membrane with occasional jumps to migrate. The method only required one simulation of liquid adsorption to estimate the solubility and diffusion coefficient, and then permeability was predicted. Shi et al.⁸ first simulated the swelling behavior and performance of PIM-1 membrane in reverse osmosis desalination and bioethanol fuel dehydration. The prediction results of swelling degree are consistent with the reported values in the literature. In the simulation of desalination, water appeared the jumping and to-and-fro motion in the membrane with a permeation flux of $8.6 \times 10^{-7} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and a rejection of 100%. In the simulation of PV of ethanol dehydration, the diffusion of ethanol was inhibited by its larger molecular size than that of water as well as its interaction with the polymer. Thus, the predicted dehydration performance of PIM-1 membrane was higher than that of dehydration membrane such as PVA. Thus, PIM-1 membrane has great application prospects in reverse osmosis and PV, and its application in NF can also be predicted.

In the following study, to quantitatively understand the separation mechanism of PV from the molecular scale, Gupta et al.¹¹⁶ evaluated the separation performance of PIM-1 membrane on an ethanol/water mixture by maintaining the vapor-liquid equilibrium on the feed side and simultaneously an extremely low permeate pressure throughout the simulation. The permeation flux and separation factor were consistent with the experimental results of Mason et al.⁵³ as mentioned above.

In the NF molecular simulation, Gupta et al.¹¹⁷ simulated the separation of ethanolamine in ammonia by NF with PIM-1 membrane. Both water and ammonia molecules exhibited good permeability in PIM-1, but ethanolamine also penetrated through the PIM-1 membrane, making it difficult to achieve 100% rejection. Liu et al.¹¹⁸ conducted molecular simulation to study the swelling of PIM-1 membrane in methanol, ethanol, acetonitrile, and acetone and evaluated the organic solvent NF performance of swelling membrane. The application of this simulation method to simulate the swelling process was one order of magnitude faster than the common method, and the simulation results

were consistent with the trend of experimental results. The rejection rate of swelling PIM-1 membrane to methyl blue was 100%, and the predicted permeability flux was consistent with the experimental value. This study led to understand the swelling and NF of membranes from a microscopic perspective; the key factors affecting membrane swelling and NF were revealed and analyzed. It laid a foundation for the development of new OSN membranes for solvent recovery.

7. Application challenges of PIMs in liquid separation and purification

Since the birth of PIMs, the applications have been extended from gas separation to adsorption, PV, NF, and other chemical engineering processes in less than 20 years. When readers browse the related literature of PIMs materials, it is easy to see the advantages of PIMs in separation, especially in the permeability and efficiency of separation. However, from the perspective of this paper, further applications of PIMs in liquid separation and purification still have many challenges:

1. Scalable synthesis and membrane fabrication of PIMs: As mentioned above, the synthesis of PIM-1, the most typical representative of PIM family, was achieved by the polycondensation between DCTB and TTSBI. Moreover, both monomers, even the solvent and catalyst, were all purified by recrystallization, sublimation, or vacuum drying, and the synthesis ratio should also be very accurate. Otherwise, it is difficult to obtain the product with a high molecular weight. In addition, if the reaction was carried out using the “low temperature method,” the time required is at least three days. The high temperature method can shorten the reaction time, but crosslinked insoluble substances are easily formed, and the molecular weight distribution is also widened. Although a promising fast (15 min) and solvent-free mechanochemical approach is reported to be used for the synthesis of PIMs with a high molecular mass and low polydispersity by solid grinding,¹¹⁹ all the current studies are based on small-batch feed synthesis in laboratory; no reports on pilot scale test or large-scale synthesis have been reported. Furthermore, the molecular weight difference of PIM-1 is also large in the literature, and the number-average molecular weight ranged from $3 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ to $20 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$. These indicate that the mass industrial production of PIMs is not easy. The fast and solvent-free mechanochemical approach is probably a new developing direction, promising for the scalable green synthesis of PIMs. Besides, studies on PIM membranes are almost exclusively focused on dense flat sheet or TFC membrane morphologies. However, due to limited space or extreme pressure requirements, flat sheet membranes—and by extension plate and frame membrane modules—are often not suitable for processes. Fortunately, Hollow fiber membranes are another membrane morphology utilizing asymmetric membranes to create high-flux devices with very high pressure resistance. In recent years, some studies have been conducted on the preparation and application of PIM-1 hollow fiber membranes, such as for gas separation and NF.^{120–123} Hollow fiber membranes could be promising PIM membrane morphology for industrial-scale utilization.

2. **Material cost problem:** A comparison of the cost has been made between PIM-1 and the common commercial polyether-based PU.⁷¹ The cost of PIM-1 material is $\sim 3107.0 \text{ \$kg}^{-1}$, whereas that of PU is only $14.5 \text{ \$kg}^{-1}$. Obviously, the application of PIMs is difficult to popularize, which is not like some cheap membrane materials. PIMs are more suitable for some limited special separation applications, which will limit some extended applications of PIMs. For example, carbon molecular sieve (CMS) membranes based on pyrolyzed PIM-1 dense films have been reported for excellent organic separation performances.¹²⁴ That will be the more promising growing point in PIM application, if the cost of PIMs could be reduced more via optimizing the synthetic route and method.
3. **Aging of PIMs:** The slow rearrangement of molecular chains leads to the aging of PIMs. As a result, the separation efficiency decreases with time when PIMs are applied to membrane separation, which should be paid enough attention. When the separation performance of PIMs membrane is investigated, the change in its performance over time should also be evaluated, even though this problem was not considered for some rubber membranes in the past. If excellent separation performance can only be obtained from freshly prepared materials, its application prospect is significantly weakened. The addition of different modified fillers has different effects on relieving aging, which should be considered when designing a mixed matrix membrane structure of PIMs.
4. **The swelling problem of membrane and the solution:** Soluble PIMs are easy to prepare as membranes, but simultaneously they are easily swelled, especially when used in the presence of organic solvents. In general, current studies chemically converted the CN group of PIM-1 to other functional groups such as carboxyl or amino groups which can be further crosslinked or added polymers that can be crosslinked. The available functional group in the molecular structure of PIM-1 is CN. Many other reactive groups are available in other soluble PIMs. The development of more types of PIMs in liquid separation and purification may provide more meaningful results.
5. **Chemical engineering processes** involve many unit operations such as distillation, absorption, extraction, adsorption, and membrane separation. Currently, PIMs are only used in adsorption and membrane separation, and more applications in other separation operations should be further developed. A combination of new materials and traditional technologies is expected to provide new vitality to the latter.

8. Conclusions and prospects

PIMs with a high specific surface area, good mechanical strength and chemical stability, and uniform micropores formed from the packing of molecular chain have been widely used in gas separation in the past decade, whose applications in liquid separation and purification also rapidly increased and occupied an increasingly important position. Most of the current studies focused on membrane separation processes such as PV and NF; many studies focused on the adsorption and removal of toxic and harmful organic pollutants and metal ions. In the study of PV, PIMs not only achieved the preferential removal of a

small amount of water from organic matter, but also removed a small amount of organic matter from water, which had the flexibility and applicability unavailable to common membrane materials. In the separation of NF membranes, PIMs exhibited a high rejection rate. Moreover, it can reject different charged pollutants by different modification methods, thus exhibiting variability. However, the biggest advantage of PIM membranes is permeability. If the PIMs separation layer cannot be made thin, the advantage of PIMs membranes can hardly be utilized. In the traditional adsorption separation field, PIMs are mainly used in the form of spinning fiber membranes and have generally achieved higher adsorption capacities. Compared with gas separation membranes, the types of PIMs introduced into liquid separation and purification are not rich enough, and the types of unit operations covered are not wide enough. More PIMs that have been used as gas separation membranes have the potential for use in liquid separation and purification, which still needs further efforts. From our point of view, PIMs, especially PIMs membranes, will be developed at a faster speed, and it is expected to be combined with other porous materials such as metal organic framework compounds to obtain pore structures of different levels to achieve better tailored precise separation of molecules. It is believed that the application of PIMs in liquid separation and purification will be further expanded and PIMs will become the “star material” that can satisfy the different separation requirements in modern chemical industry.

Disclosure statement

The authors declare no conflict of interest.

Funding

The authors gratefully acknowledge the financial support provided by National Key Research and Development Program of China (2017YFC1600401), National Natural Science Foundation of China (31871749), Beijing Natural Science Foundation (2172020), National Key Research and Development Program of China (2017YFC1600605), and National Natural Science Foundation of China (grant no. 21503007).

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