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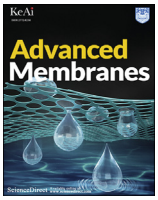

Polymer membranes for organic solvent nanofiltration: Recent progress, challenges and perspectives

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ABSTRACT

The development of polymer materials and polymer membrane fabrication techniques in recent years greatly elevates the importance and feasibility of organic solvent nanofiltration (OSN) technology, while challenges from different perspectives still hinder the wider applications of polymer based OSN membranes. This article reviews the OSN membrane research specifically from the perspective of polymer membrane materials, starting by recapping the recent progress of polymer based integrally skinned asymmetric (ISA) and thin film composite (TFC) OSN membranes. Comparing to commercially available polyimide ISA membranes and polyamide TFC membranes, multiple categories of emerging polymer materials result in membranes with much improved permselectivity for highly efficient molecular separation. In view of adopting OSN membranes for engineering applications, this review also summarizes some key challenges unique to polymer membranes including material swelling, physical aging and membrane compaction, and recent efforts to overcome them. The future research direction and application prospects of polymer OSN membranes are briefly discussed in the latter part of the article, noting that improved membrane formation control and crosslinking strategies, and the development of emerging polymer membrane materials is at high necessity to break through the application constraints of OSN in terms of permselectivity and performance stability.

1. Introduction

Separation is an essential component of industrial production processes, and the cost of separation equipment accounts for 50–90% of the total investment in chemical engineering industries [1]. Currently, most commonly used separation methods rely on energy-intensive heat-based processes, such as distillation, and account for 10–15% of the world's energy consumption [2]. Pressure-driven membrane separation is deemed as a more efficient, low-energy, and environmentally friendly separation process without phase change [3,4]. Nanofiltration is a pressure-driven membrane separation process with membranes having a pore size range of a few nanometers and a molecular weight cut-off (MWCO) between 200 and 1000 g mol^{-1} [1]. Nanofiltration has been widely used in separating substances with small molecular mass, such as inorganic salts or organic substances such as glucose, amino acids, and dyes, from water [5–7]. Meanwhile, due to the extensive use of organic solvents in daily chemical production, many high value-added substances such as active pharmaceutical ingredients (API) [8], high-value natural compounds (HVNCs) [9], etc. Need to be separated and purified from organic solvents. However, swelling or even complete dissolution of traditional polymer membranes in organic solvents makes their physical integrity in aqueous solutions difficult to maintain in organic solvents, which severely affects their separation efficiency [10,11]. Organic solvent nanofiltration (OSN) is an emerging technology where a solvent resistant nanofiltration membrane is utilized in the process of organic solvent separation and purification. The advent of OSN greatly reduces the energy consumption required for phase change-based separation methods, especially for those solvents with high boiling points [12,13]. In addition, due to the milder operating conditions of OSN, it is possible to prevent the degradation of thermal or other potentially sensitive molecular products during the separation process.

Undoubtedly, the key to OSN lies in the manufacture of an organic solvent resistant nanofiltration membrane. OSN membranes were first proposed in 1964 by Sourirajan [14] where cellulose acetate (CA)

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membranes were used for the separation of organic systems. However, the insufficient development of membrane technology at that time and the lack of materials that could withstand the challenges of the chemical environment hindered the further development of OSN. In the past few decades, the development of many polymer materials with highly robust skeletons, such as polyimide (PI) [15,16], polymer of intrinsic microporosity (PIM) [17], polybenzimidazole (PBI) [18,19], polyetheretherketone (PEEK) [20,21] and so on, has greatly broadened the scope of application of OSN. Moreover, many post-treatment modification methods further improve the solvent resistance of the materials [22, 23].

Several comprehensive review articles have been published to summarize the research on OSN processes and the development of OSN membranes [24–33]. However, there are still challenges from different perspectives to hinder the wider applications of OSN. This article aims to review the OSN membrane research specifically from the perspective of polymer membrane materials, starting by introducing the recent progress of polymer based OSN membranes in the second section. The third section focuses on the performance stability challenges of polymer-based membranes for OSN application, the reasons for these problems, and the solutions given by the researchers. The future research direction and application prospects of polymer OSN membranes are briefly discussed in the final section.

2. Preparation of polymer membranes for organic solvent nanofiltration

2.1. Integrally skinned asymmetric (ISA) membranes

Polymeric membranes can be divided into two categories, integrally skinned asymmetric (ISA) membranes and the thin film composite (TFC) membranes, based on the membrane structural conformation [34–36]. ISA membranes are usually prepared by the immersion-precipitation phase inversion method, developed by Loeb and Sourirajan [37]. By submerging the casting solution in the non-solvent phase (water), the thermodynamic state change of the homogeneous polymer solution causes phase separation: a polymer-rich phase forming the matrix of the membrane, and a polymer-poor phase forming the pores of the membrane. Due to direct contact with water, the surface region of the membrane precipitates quickly to form a dense selective layer. The formation of the selective layer delays the speed of phase inversion and results in a porous support layer. Through the control of phase inversion conditions, adjustable molecular separation performance can be obtained for many target applications. In addition, to strengthen the resistance of ISA membranes against organic solvents, cross-linking modification is commonly adopted after the membrane formation. This section summarizes some representative research work reported recently on the formation and crosslinking of ISA membranes for OSN.

2.1.1. Polymers for ISA OSN membranes

A large pool of polymer materials has been explored for ISA OSN membrane preparation, such as polyimide (PI) [38], polybenzimidazole (PBI) [39], polyacrylonitrile (PAN) [40], polytriazole (PTA) [48], polyaniline (PANI) [74,91], etc. Traditional polyimides such as P84 and Matrimid 5218 are widely used in the preparation of ISA OSN membranes due to their excellent solvent resistance, heat resistance, mechanical properties, and processability [41]. The resulting PI membranes show good performance in some alcohol solvents but instability in some polar aprotic solvents such as DMF, NMP, DMSO, etc. In order to open up the possibility of further application of ISA membranes in harsh solvent environments, many crosslinking modification methods have been proposed, such as thermal crosslinking [42], UV crosslinking [43], and chemical crosslinking [44]. Chemical cross-linking is widely studied for uniform modification of the entire membrane, and covalent crosslinking is the most widely studied type of chemical crosslinking. See-Toh et al. prepared covalent cross-linked polyimides membranes for aggressive solvents for the first time [45]. Diamine post-treatment cross-linked PI membranes have been proven to perform well in many organic solvents. To eliminate the need of an extra solvent-based production step, Vanherck and co-workers [46] added a diamine cross-linking agent to the coagulation bath to achieve the cross-linking modification of the PI membrane during phase inversion. The reaction mechanism is to open the imide bond of the polymer backbone and react with diamine to form an amide bond, thereby forming crosslinks between the polymer chains (Fig. 1a). However, when the temperature exceeds 100 °C.

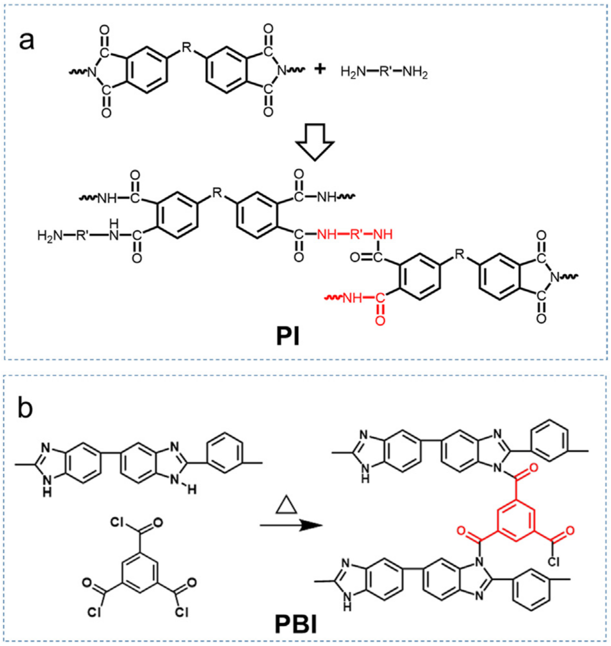

Fig. 1. The crosslinking reaction mechanism of (a) PI and (b) PBI for fabrication of integrally skinned asymmetric (ISA) OSN membranes [39,45–47].

Possible re-imidization leads to cross-linking failure, which limits the scope of application of the membranes. In addition, the insufficient alkaline resistance of polyimides also limits their use, as high concentrations of organic and inorganic bases would cause degradation of PI. Polybenzimidazole (PBI) is also a promising material for OSN membranes preparation. In addition to mechanical, thermal, and solvent stability, PBI also has good stability to acids and bases. Valtcheva and coworkers [39] tested the stability of the cross-linked PBI membranes under acidic and alkaline conditions and the results show that the membrane exhibits good acid and alkali resistance and restores its original performance after neutralization. Moreover, due to the existence of intramolecular hydrogen bonds, the PBI OSN membranes has excellent swelling resistance. Like PI, cross-linking modification is also adopted to expand the scope of application of PBI OSN membranes. Various compounds can be used for cross-linking through the reaction between the N–H functional group of the imidazole ring in PBI and the reactive functional group of the cross-linkers [19]. Recent works by Farahani et al. [47] proposed a green crosslinking PBI method through trimesoyl chloride (TMC) and an environmentally friendly solvent 2-methyl tetrahydrofuran (2-MeTHF). The reaction mechanism can be seen in Fig. 1b, and the resulting membrane has good permeability and separation performance in organic solvents.

2.1.2. Types of crosslinking

Covalent crosslinking modification is usually adopted by post-processing the ISA OSN membrane to further enhance its solvent resistance as well as to finetune the membrane pore profile. Besides chemically crosslinking with small molecule crosslinkers, Nunes et al. [48] reported a simple strategy to fabricate thermally crosslinked PTA-OH asymmetric membranes recently. The membrane fabrication process

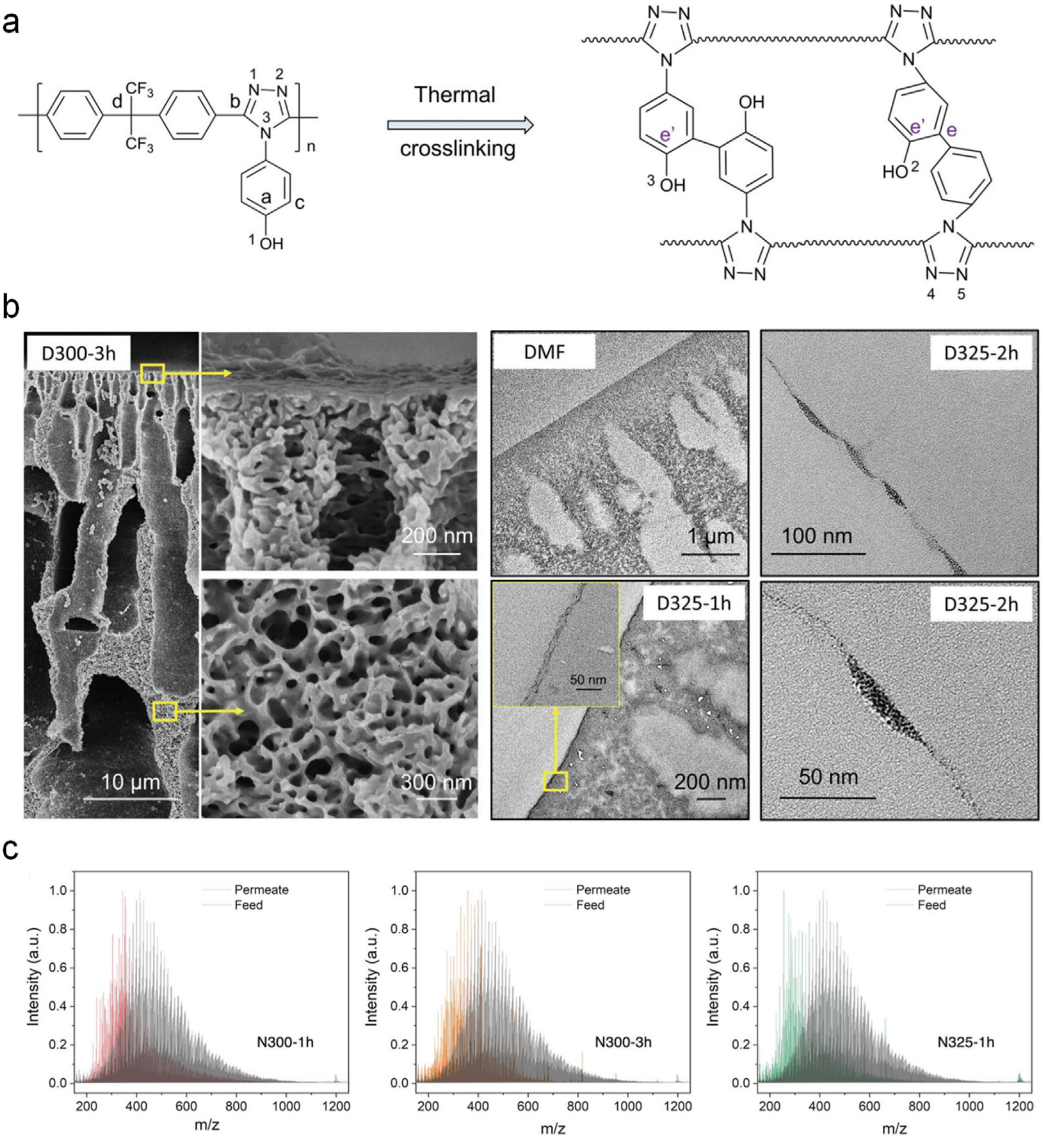

Fig. 2. Thermally cross-linked PTA-OH membranes: (a) Thermal crosslinking mechanism of PTA-OH; (b) Cross-sectional SEM and TEM images of thermal crosslinked membranes; (c) FT-ICR MS spectra of hydrocarbon feed and permeate [48].

involves non-solvent-induced phase separation (NIPS) method and thermal cross-linking. The selective layer of the asymmetric membrane was controlled within 10 nm thickness (Fig. 2). The resulted polymer membranes are endowed with interconnected free volumes with subnanometer-level selectivity for the transport and separation of hydrocarbons. The membrane selectivity can be tuned to the lower end of typical nanofiltration range (200–1000 g mol^{-1}). The polytriazole membrane achieves up to 95% enrichment of hydrocarbon contents with less than 10 carbon atoms (140 g mol^{-1}), revealing great potential in the field of crude oil fractionation.

Generally, the introduction of covalently crosslinking agents led to significant decreased initial flux and reduced mechanical strength of membranes. Therefore, many works have been studied to propose other strategies to replace covalent crosslinking. Jin et al. [49] reported a new strategy to fabricate OSN membranes through facile metal ion cross-linking of ISA polyimide membranes (Fig. 3a). Among them, a Cu^{2+} cross-linked membrane exhibits good resistance to harsh organic solvents like DMF or NMP. In Fig. 3b, the initial solvent flux change of the membrane before and after crosslinking is very small, signifying negligible change of the membrane free volume. At the same time, due to the coordination crosslinking of metal ions, the membrane's resistance to compaction has been significantly improved, which will be further discussed in Section 3.3. Zhao and co-workers [50] formed an interpenetrating polymer network (IPN) via in-situ polymerization of dopamine in the PBI ISA membrane matrix, and achieved excellent solvent resistance and permeability of polar aprotic solvents without covalently crosslinking the PBI backbone. The separation performance of the final membrane can be controlled by adjusting the polymerization time. This method provides a simple green alternative to covalently cross-linking.

2.2. *Thin film composite (TFC) membranes*

Thin film composite (TFC) membranes are usually composed of an ultra-thin dense barrier layer and a porous support layer, which can be designed and assembled separately to optimize the membrane performance [51]. The nature of the support layer is important for TFC membranes, which provides membrane mechanical stability and allow the formation of a defect-free skin layers [52]. The design of the solvent-resistant support layer is usually similar to the ISA membranes as mentioned above, which are achieved by phase conversion and post-crosslinking modification. The nature of the barrier layers

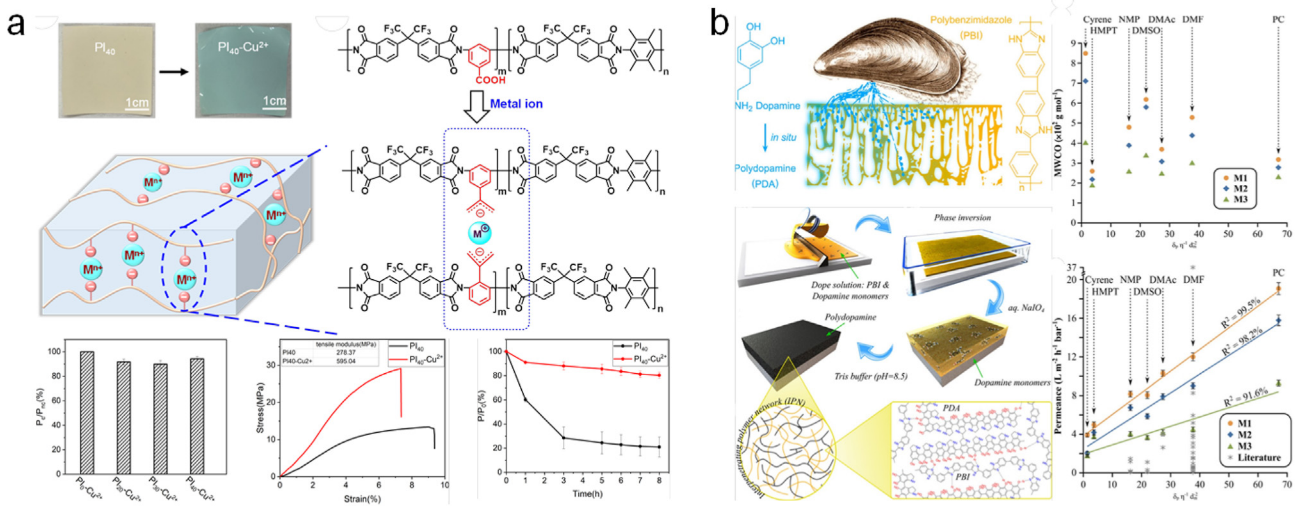

Fig. 3. Strategies for making non-covalently cross-linked ISA membranes, and their OSN performance: (a) Metal ion coordination induced cross-linking of polyimide membranes [49]; (b) PDA/PBI interpenetrating polymer network membranes [50].

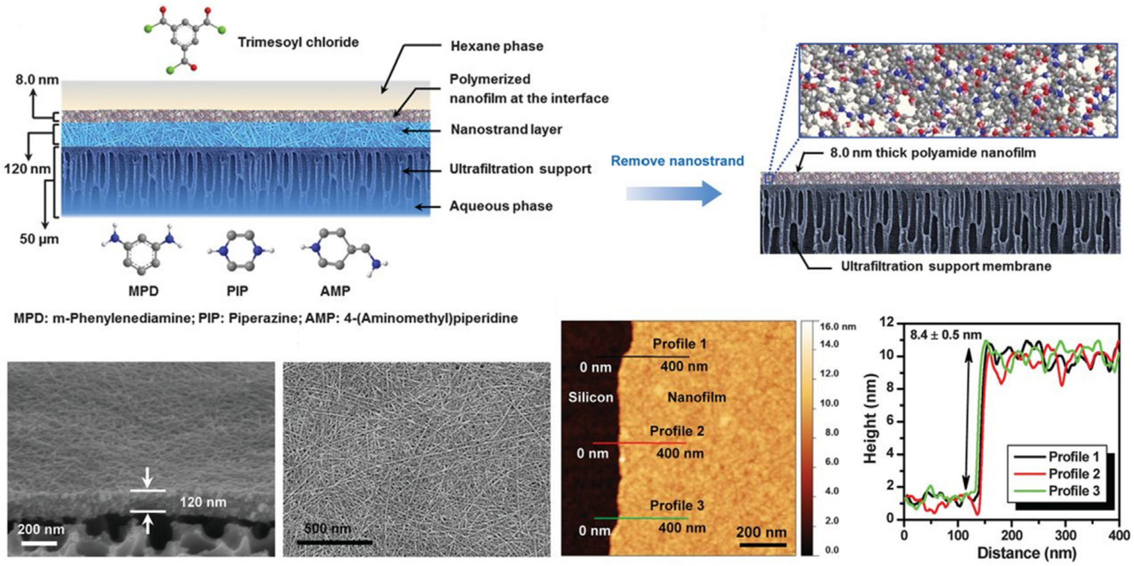

Fig. 4. Ultrathin polyamide films prepared by controlled interfacial polymerization on a nano-strands gutter layer [53].

determines the permeability and selectivity of the TFC membranes. Interfacial polymerization and polymer coating has been widely employed to form the barrier layer. Interfacial polymerization is a process where the polymerization occurs at the interface between two immiscible phases. TFC membranes can also be prepared by dip- or spin-coating a dense polymer layer of different composition on top of a porous ultrafiltration (UF) support. In this section, representative research work on OSN TFC membranes reported recently will be elaborated.

2.2.1. *Interfacially polymerized thin films*

The most used dense selective layer material for TFC OSN membranes are polyamides, which is usually synthesized by interfacial polymerization of trimesoyl chloride (TMC) and *m*-phenylenediamine (MPD) on a solvent-stable porous substrate. As the core of TFC membranes, this selective layer has great influence on membrane flux and selectivity. Reducing membrane thickness and increasing microporosity to decrease mass transfer resistance and increase separation factor, have proved to be effective ways to obtain high-performance membranes. Karan et al. [53] reported a representative work by using a sacrificial layer of cadmium hydroxide nano-strands to synthesize a free-standing network polymer nanofilm with a thickness of less than 10 nm (Fig. 4). The resulting ultra-thin film exhibits high methanol flux of 11–12 L m^{-2} h^{-1} bar^{-1}. By further controlling the interface reaction conditions to control the morphology of the nanofilm, a crumpled PA active layer was obtained. Due to the significant increase in the effective permeable area, the methanol flux increases by more than 4 times, reaching 52 $Lm^{-2}h^{-1}bar^{-1}$, without sacrificing selectivity. In addition, the crumpled nanofilms are sufficiently rigid and stable under pressure filtration. As the pressure increases, it does not fold or flatten to form overlapping layers.

Increasing microporosity of barrier layer material to decrease mass transfer resistance and increase separation factor, have proved to be an effective strategy to obtain high-performance membranes. Jimenez-Solomon et al. [54] prepared polymer nanofilm with enhanced microporosity by involving contorted phenols 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (TTSBI) and 9,9-bis(4-hydroxyphenyl)fluorene (BHPF) as interfacial polymerization monomers to produce

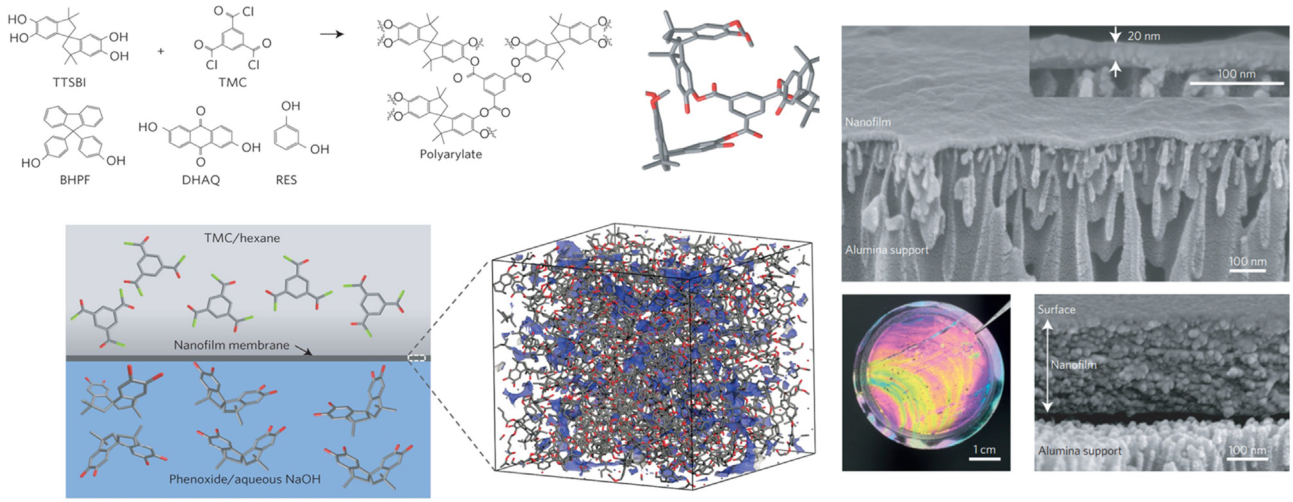

Fig. 5. Interfacially polymerized aromatic polyester nanofilms. Cross-sectional SEM image of a freestanding polyarylate film [54].

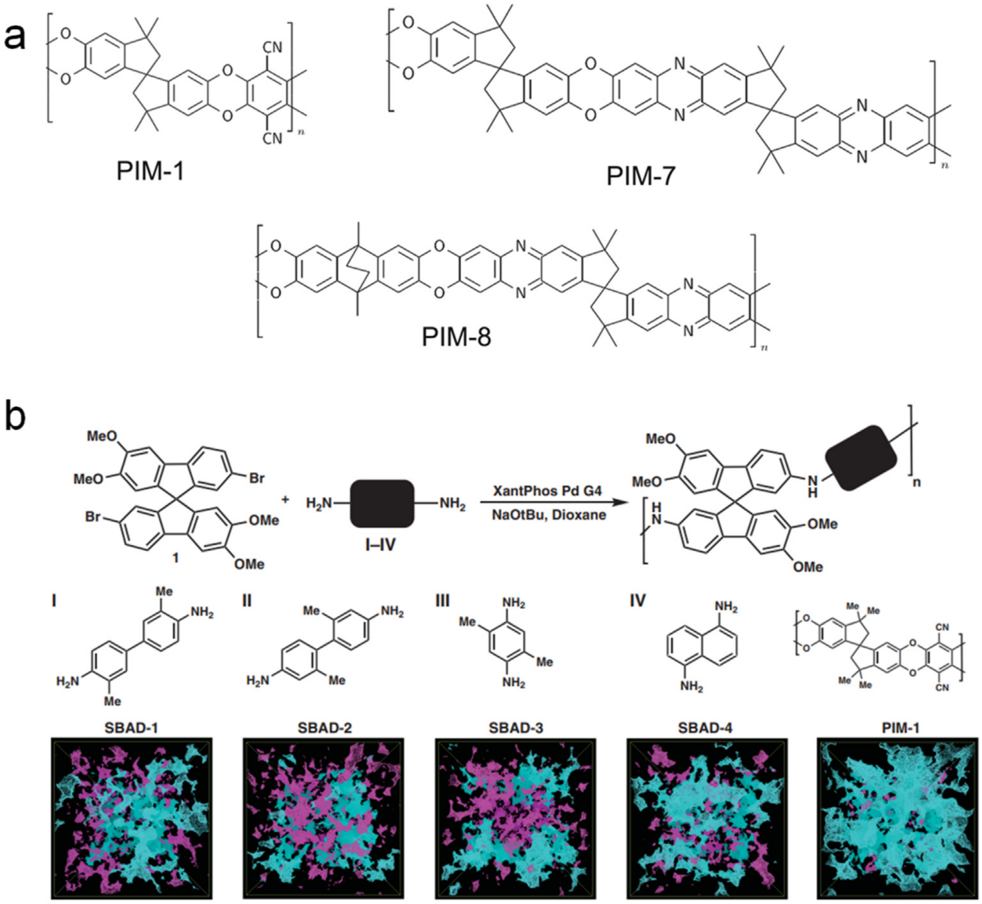

Fig. 6. (a) Chemical structures of various liner PIMs [54]; (b) Polymerization of the SBAD class of materials: SBAD-1 to SBAD-4. Pore surfaces computational modeling for the SBAD series and PIM-1, teal presents for accessible (interconnected) pores, and magenta presents for nonaccessible pores [57].

polyarylate membranes with enhanced micropores (Fig. 5). At the same time, the planar structure of non-contorted phenols dihydroxyanthraquinone (DHAQ) and (1,3-benzenediol) RES were used as controls. The results show that solvent flux of the microporous membranes is 2 orders of magnitude higher than that of the non-microporous membranes.

2.2.2. *Emerging polymer thin films for OSN*

Besides interfacially polymerized thin films, TFC OSN membranes can also be prepared by dip- or spin-coating or locally growing a dense polymer layer of different composition on top of a porous support. This approach is more straightforward to explore new types of polymers as the material for TFC OSN membranes.

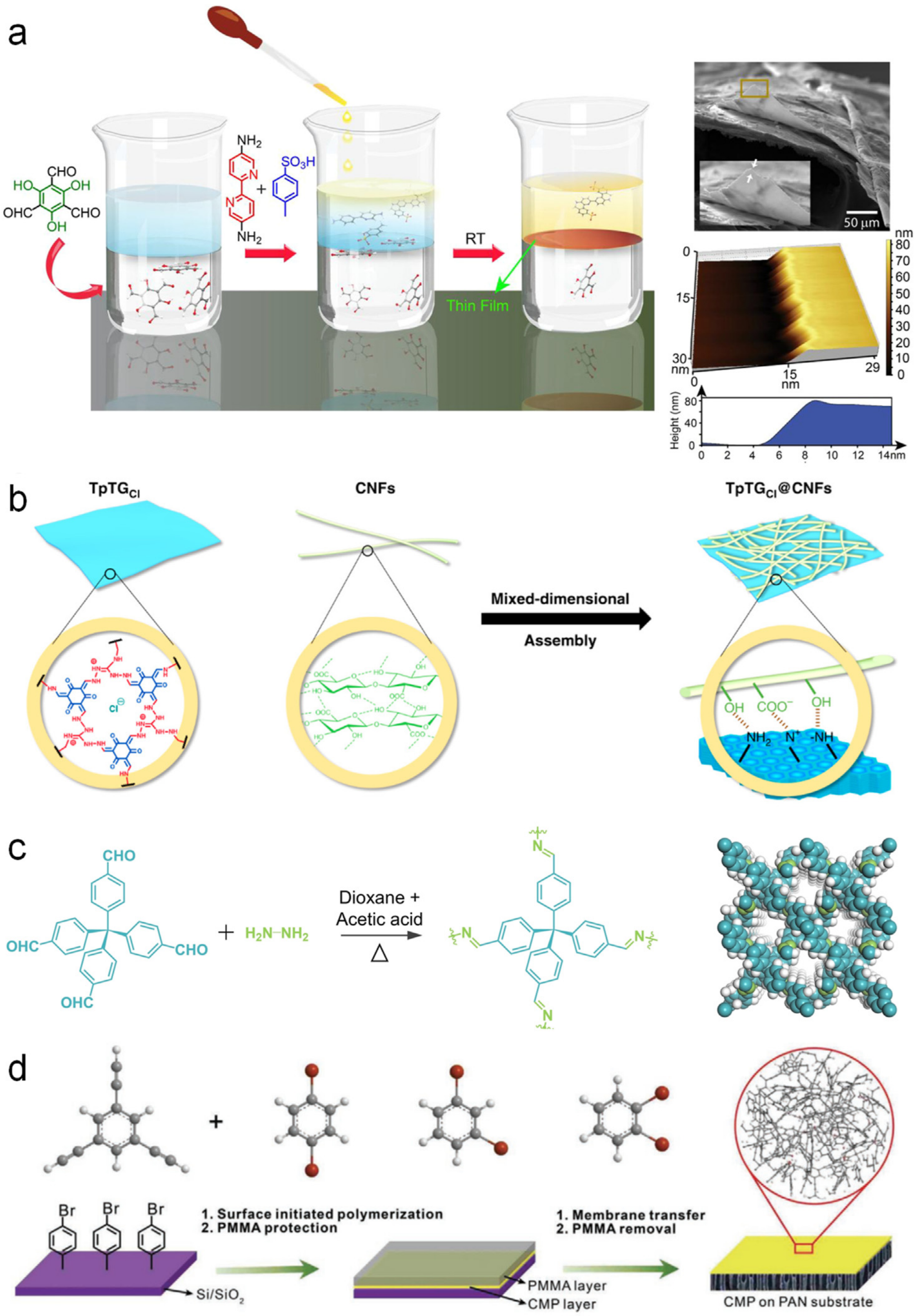

Fig. 7. (a) Tp-Bpy thin film synthesized via interfacial crystallization process used to the for OSN [58]; (b) COF membranes fabricated by COF nanosheets and CNFs assembly [59]; (c) Synthesis of 3D COF membranes [60]; (d) CMP membranes prepared on the PAN substrate [61].

Polymers of intrinsic microporosity (PIMs) firstly proposed by Budd and McKeown in 2004, possess interconnected micropore structure (<2 nm) as result of the inefficient chain packing induced by stiff and twisted polymer chain structures (Fig. 6a). The solution-processable microporous PIMs bring rich imagination for enhancing OSN membranes permeance and selectivity. PIM-1 TFC membranes were firstly fabricated for OSN application on PAN support through a dip-coating coating method by Fritsch and co-workers [55]. The resulted membranes exhibited 3000% n-heptane permeance higher than commercial membrane. A much thinner PIM-1 membrane with thickness between 35 nm and 660 nm were prepared by spin coating method by Patricia et al. [56]. These membranes show fast penetration of n-heptane and the rejection rate of hexaphenylbenzene (MW = 534.6 g mol^{-1}) is about 90%. The 140 nm thick films obtained the best performance with a permeance of 18 L m^{-2} h^{-1} $bar^{-1}$of n-hexane. The high flux is attributed to the use of high specific surface area polymers and ultra-thin films. Unexpectedly, when the thickness of the membranes is less than 100 nm, the flux of the membranes decreases instead as attributed to the structural relaxation effect of linear polymer ultra-thin films. Due to the scale of micropore sizes, PIM-like polymers are generally incapable of separating small molecules in the organic solvent reverse osmosis (<200 g mol^{-1}) and “tight” organic solvent nanofiltration (200–300 g mol^{-1}) regimes. Lively et al. [57] proposed a series of spirocyclic polymers linked with single N-aryl bond, endowed with non-interconnected microporosity owing to the enhanced interchain interaction (Fig. 6b). The spirocyclic polymers were casted on the polyimide substrate to form

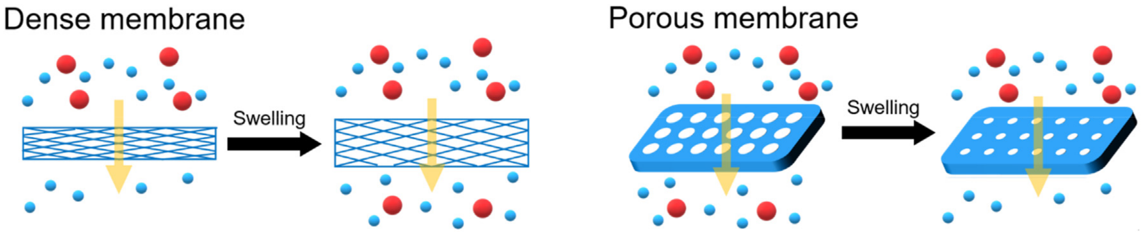

Fig. 8. Schematic diagram showing the influence of polymer swelling on dense and porous membranes.

a 200 nm thickness selective layer. The resulting membranes demonstrated fractionation of liquid light-crude-oil through a combination of class- and size-based separation mechanism without phase transition process. Molecules lighter than 170 Da or a boiling point less than 200 °C in the permeate are intensively enriched. The scalability and high selective efficiency endow the membranes with great substitute potential of conventional separation process such as distillation.

Covalent organic frameworks (COFs) as newly developed crystalline porous polymers attract great attention in molecular separations owing to their regulated and tunable microporous structure. In recent years, researchers are focus on COF membrane fabrication to play the full roll of COFs in membrane separation. Up to now, COF membranes could be prepared on support in the form of TFC membranes via interfacial synthesis. Banerjee et al. [58] firstly proposed a thin films fabrication protocol for crystalline COF through an interfacial crystallization approach at room temperature. Highly crystalline COF thin films in the thickness of 50–200 nm are prepared in liquid-liquid interface under ambient conditions., A salt-mediated technique was developed to enhance crystallization of COF film as shown in Fig. 7a. This interfacial strategy was extended to prepare 4 types of COF films with different pore sizes. These thin COF films exhibit much higher solvent-permeance over conventional nanofiltration membrane. Nevertheless, the pore sizes of current COFs range between 5 and 58 Å [5], which is usually larger than most OSN-interested target molecules. And the fabrication of defect-free COF membranes remains a challenge owing to the weak intermolecular interaction. A series of COF membranes were thus constructed through assembly of COF nanosheets and cellulose nanofibers (CNFs) as demonstrated in Fig. 7b by Jiang et al. [59]. The membrane pore size was controlled in range of 0.45–1.0 nm owing to the sheltering effect of CNFs, which endowed resulting membranes with more precise sieving property. Accordingly, the membranes demonstrate a high separation factor of 3876 for water/n-butanol, and high-water flux of 42.8 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ with 96.8% rejection of Na_2SO_4. Besides 2D COF membrane, Wang et al. [60] recently reported an advanced OSN processes using newly developed three-dimensional (3D) COF membranes as shown in Fig. 7c. The crystallization of 3D COF membranes were moderated by nanoporous supports. Sub-nanometer and anti-swelling channels are given inside the three-dimensional crosslinking structure of 3D COF. Therefore, the resulting membranes possess sharp selectivities to small molecule and a high permeance. Moreover, a record stability against high solution concentration feeds and long-term operation time are obtained.

Conjugated microporous polymer (CMP) membranes, an emerging type of polymer membranes besides COF membranes, have also been adopted for OSN applications. Tang's group prepared CMP membranes through C–C coupling reactions via a surface-initiated polymerization strategy as shown in Fig. 7d [61]. The membranes consist of conjugated backbone network structure, demonstrating high resistance to organic solvents. The conjugated skeletons of CMPs designed by molecular engineering endowed the resulted membrane with tunable pore structure and highly anti-swelling structure. The CMP membranes was fabricated in an ultra-thin thickness around 42 nm. The PAN supported CMP membranes demonstrate high solutes rejection and wide range of nanofiltration in both non-polar and polar solvents.

3. Challenges of polymer membranes towards OSN application

With the development of various polymer modification methods and new rigid backbone polymers, the choices of polymer materials for making OSN membranes have been expanded. Polymers with good solution processability and mechanical properties are developed, and crosslinked polymer membranes can withstand a wide range of solvents including polar aprotic solvents. However, there are still challenges from different perspectives to hinder the wider applications of OSN. This section analyzes several OSN performance stability problems unique to polymer membranes, the reasons for these problems and solutions given by researchers.

3.1. Swelling

Swelling is a phenomenon unique to polymer materials, where the solvent molecules diffuse into the polymer matrix and cause an abrupt change in polymer volume [62]. The size of the solvent molecules and the polymer are very different, which results in a large difference in their speed of movement. The diffusion of solvent molecules into the polymer is much faster, causing the polymer to expand. Different from aqueous environment, the strong interaction between organic solvents and polymer membranes lead to changes in the pore structure, thereby affecting the permeability and selectivity of the membranes. Hanson solubility parameters are often used to predict the interaction between solvents and solutes [63,64]. The solubility parameters of each solvent and solute are composed of three parts: dispersive, polarity, and hydrogen bonding. In general, closer solvent and polymer Hansen solubility parameters correspond to stronger interactions between the, and more solvent molecules diffuse into the polymer matrix to causing more severe swelling.

Polymer swelling is common in organic solvent systems and it affects the permeability and selectivity of the membranes. For example, PIMs have received great attention as a polymer membrane material for OSN because of their good permselectivity and stability in organic solvents. However, it is found that PIMs are more prone to swelling than conventional polymers in some organic solvents, which results an increased flux and reduced rejection [65,66]. Pinnau et al. reported the swelling of PIM-based ultrathin films in organic solvents with a swelling factor as high as 2.5 [67]. Understanding the interaction between organic solvents and polymer membranes is therefore important. Basically, for dense membranes, the diffusion of solvent molecules causes the increasing of free volume between polymer chains, thereby increasing the permeability of the membrane while making it easier for solute molecules to pass and leading to a decrease in selectivity. On the contrary, for the scenario with porous membranes, swelling of the polymer makes membrane pores smaller, resulting in lower permeability and higher selectivity. The different effects of swelling on dense and porous membranes are schematically illustrated in Fig. 8. Furthermore, for TFC membranes and dual-layer membranes, the difference of swelling degrees for the two independent layers must also be considered. Large differences in the swelling degree may cause layer delamination in certain organic solvents, i.e. the functional layer eventually detaches partially or fully from

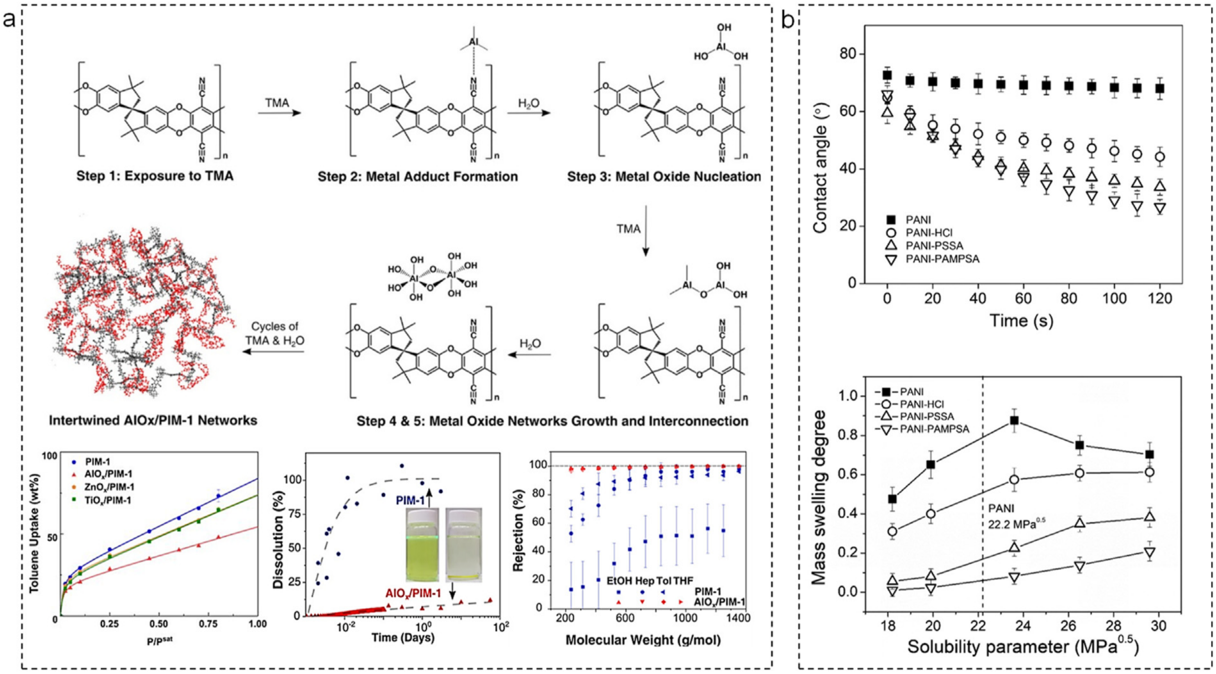

Fig. 9. (a) Vapor phase infiltration of metal oxides into nanoporous polymers improves the membrane's anti-swelling properties [69]. (b) Swelling mitigation by involving polyacid dopants into polyaniline membranes [76].

the underlying substrate [68,69].

Various approaches have been reported to mitigate the effect of swelling on OSN membrane performance [70–73]. Chemical cross-linking is a classic and effective method to overcome the swelling issue of polymer membranes [74,75]. The three-dimensional network structure formed by cross-linking enhances the interaction between the polymer chains and hinder the swelling effect of the solvent molecules. Recently, McGuinness and co-workers reported an innovative vapor phase infiltration (VPI) technique for membrane post-treatment to improve the membrane swelling stability [69]. As shown in Fig. 9a, an AlO_x/PIM-1 membrane was formed by interweaving an atomic-scale metal oxide network with a nanoporous polymer membrane such as PIM-1. A significant reduction in swelling of the hybrid membranes was observed in the toluene adsorption. The hybrid membranes also achieved stable performance in organic solvent environments like THF where the pristine polymer can be completely dissolved. Shen and co-workers prepared a stable nanoporous polyaniline (PANI) membrane by polyacid doping for OSN applications [76]. It can be seen in Fig. 9b that the swelling degree of the membranes decreases with polyacid doping. It is explained by the significantly improved hydrophilicity of the PANI membranes with the acid doping. The doped hydrophilic PANI membranes have a higher solubility parameter than that of the undoped one, and a higher solubility parameter moves further away from the solubility parameter of common solvents. Additionally, polyacid dopants can strongly interact with PANI through hydrogen bonding and electrostatic interactions, which also allows the doped membranes to maintain its physical integrity in a variety of organic solvents. Meanwhile, regarding the swelling-induced layer delamination issue of composite membranes, Fontananova and co-workers proposed an innovative solution by using the same P84 copolyimide material to prepare the dense selective layer and porous support layer [77]. Such a polymer homogeneous composite (PHC) OSN membrane design ensures a high affinity between the two layers, increases the long-term stability of the composite membrane, and reduces the possibility of delamination.

3.2. *Physical aging*

Physical aging commonly exists in organic solvent nanofiltration membranes materials, which significantly affect the performance of the membrane. As the polymer materials used for OSN usually have a glass transition temperature (Tg) much higher than room temperature, they are non-equilibrium materials with considerable free volumes in their structure. The physical aging process is the relaxation process of glassy polymers transitioning from the non-equilibrium state to the equilibrium state through the micro-Brownian motion of the polymer segments [78,79]. Especially for ultrathin polymer films, it is found that the Tg decreases as the thickness of the film is reduced, and simultaneously leads to faster physical aging and structural relaxation [80]. As illustrated in Fig. 10, the free volume of the polymer loses gradually during the advance of the relaxation process, leading to the densification of the polymer membrane and decrease of its solvent permeability. Accessing the physical aging of polymer membranes throughout their whole

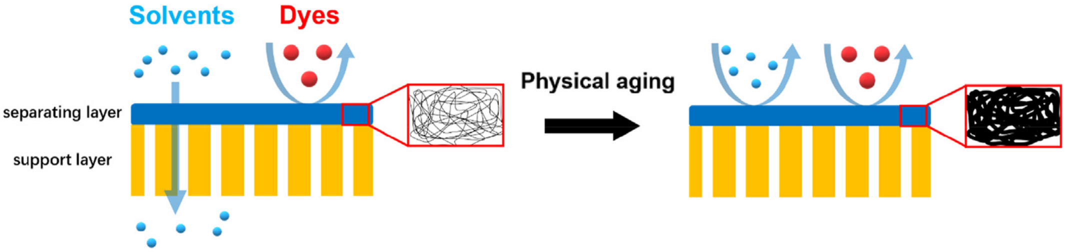

Fig. 10. Schematic diagram showing the influence of physical aging on OSN membranes.

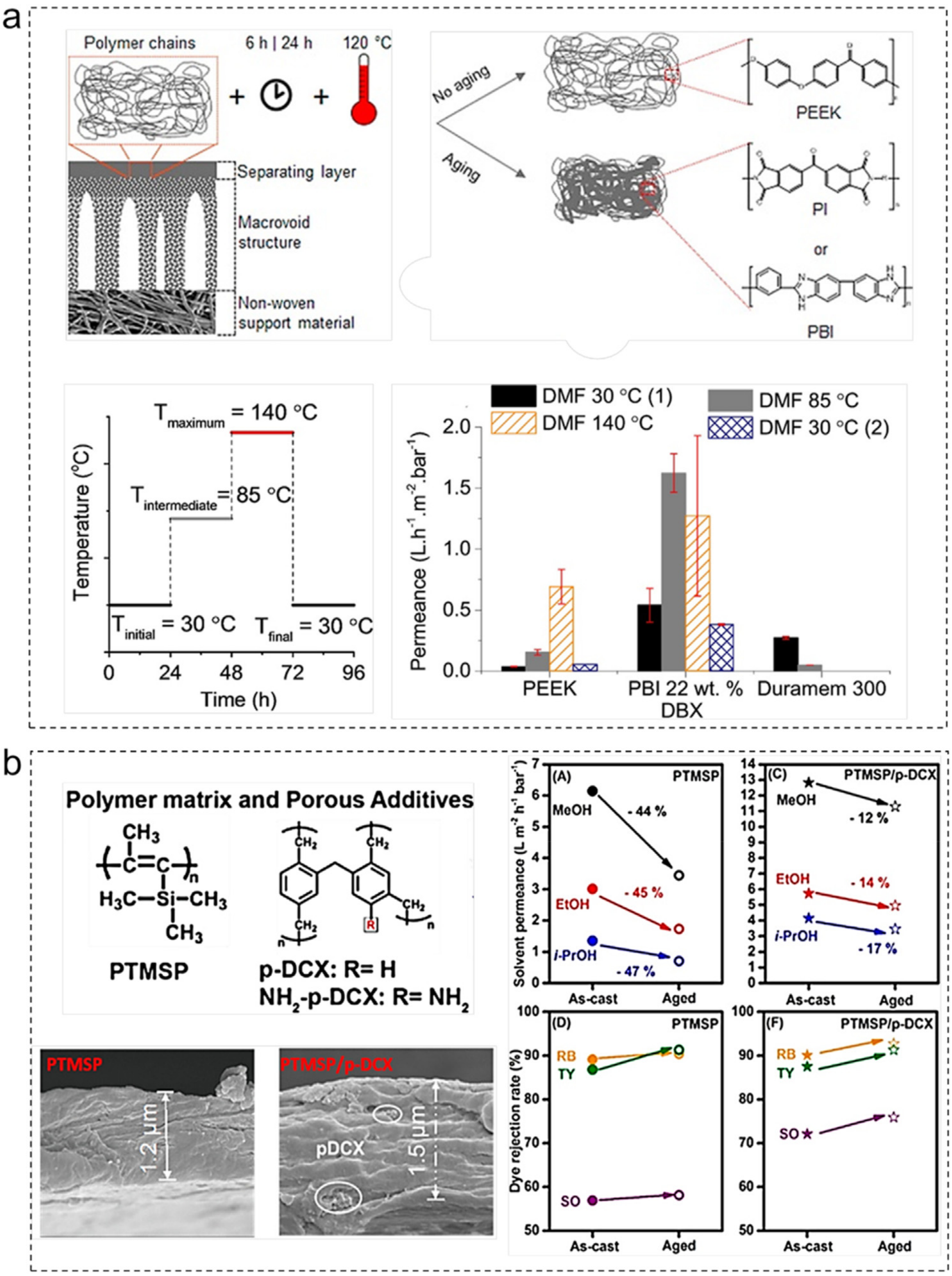

Fig. 11. (a) Physical aging of PEEK, PBI and PI membranes with respect to time and temperature [84]. (b) Hyper-crosslinked polydichloroxylene (*p*-DCX) additives that achieve impeded aging and enhanced permeability of polyacetylene membranes for OSN [86].

lifespan is thus important, but it is difficult to collect OSN performance data over months or years for scientific research. Instead, the effect of thermal annealing on the membrane OSN performance is reported more widely to amplify the micro-Brownian motion and accelerate the physical aging process of the polymer [15,65,81]. For instance, See-Toh and co-workers studied the effect of annealing temperatures on the OSN performance of Lenzing P84 polyimide membranes [15]. When the annealing temperature was increased to 200 °C, the solvent flux of the membrane decreased from 68 $L\,m^{-2}\,h^{-1}$ at the beginning to a solvent flux close to zero, but resulted in little change in the MWCO curves. SEM pictures also suggest that the annealing causes the nodule structure of the separation layer to disappear and become a continuous non-porous dense layer.

Researchers have devised different strategies to alleviate the physical aging issue. Chemical cross-linking has a positive effect on the anti-aging properties of the existing polymer membrane, but the introduction of chemical cross-linking agents usually results in a decrease in organic solvent permeability. da Silva Burgal and co-workers reported the use of polyetheretherketone (PEEK) as a new alternative polymer of OSN membranes [82,83]. As shown in Fig. 11a, PEEK membranes are found to remain flexible and retain a constant permeance after air annealing, revealing excellent anti-aging properties compared to commercial PI membranes and cross-linked PBI membranes. This finding is likely due to the reason that PEEK is a semicrystalline thermoplastic polymer with a rigid aromatic backbone structure, and that PEEK membranes formed via phase inversion is close to the equilibrium.

Glass state with closed polymer chain packing [84]. Recently, Abdulhamid et al. reported an intrinsically microporous PEEK membrane, and found that the membrane undergoes negligible OSN performance change throughout a six-month aging experiment, confirming that the anti-aging feature of PEEK extends to polymers of intrinsic microporosity [85]. Meanwhile, the incorporation of nanomaterials is also

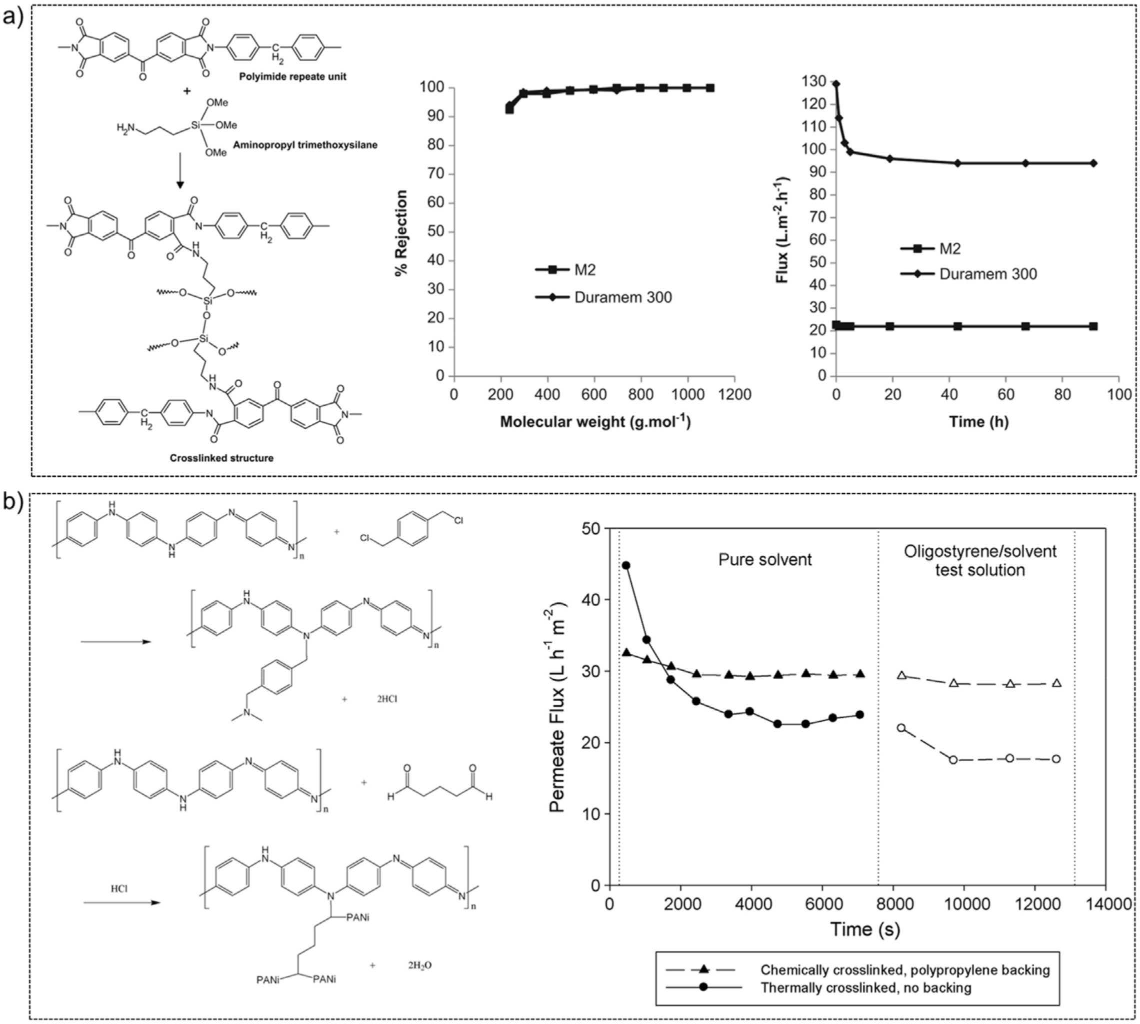

Fig. 12. (a) Introduction of an organic-inorganic hybrid network to improve the compaction resistance of the OSN membrane [91]; (b) chemical crosslinking of ISA polyaniline (PANI) membrane for compaction resistance improvement [93].

found effective to reduce the membrane aging. Cheng and co-workers added the hyper-crosslinked porous additive polydichloroxylene (*p*-DCX) into the Poly [1-(trimethylsilyl)-1-propyne] (PTMSP) membrane matrix to achieve impeded aging and enhanced permeability [86]. As shown in Fig. 11b, the resulting mixed matrix membrane shows enhanced anti-aging properties in continuous long-term operation, owing to the polymer chain immobilization by the strong interaction between the polymer chain and the hyper-crosslinked additives.

3.3. Compaction

It is common to observe that the initial operation stage of a fresh OSN membrane is accompanied by a significant drop in permeation flux. Such flux drops can be exceeding 50%, which is usually attributed to the compaction of membranes under the mechanical effect of trans-membrane pressure. Compaction leads to a tightening of the membrane polymer matrix, which result in lower flux and higher retention capability of the membrane comparing to the initial state before compaction. For instance, the commercial STARMEM 122 membrane exhibits a 60% decline of methanol flux after compaction at 30 bar pressure, while its rejection to tetra butyl ammonium bromide (MW = 322) increases from 88% to 97% after compaction [87]. Membrane compaction can be divided into recoverable elastic deformation and unrecoverable plastic deformation [88,89]. It is usually necessary to pre-condition an OSN membrane before each operation cycle to reach its steady state, which greatly reduces the efficiency of the entire OSN process. In addition, the compaction effect of the membrane substrate also has a significant influence on the final performance of the OSN membranes. Karan et al. [90] reported that the sub-10 nm PA nanofilm on the porous support film of cross-linked P84 shows a large flux decline with the running time, but such compaction phenomenon on the alumina film does not seem to occur.

Apart from engineering approaches like membrane pre-conditioning, it is important to alleviate the membrane compaction from the perspective of membrane materials. Many methods have been proposed to improve the compaction resistance of OSN membranes. Siddique et al. introduced an organic-inorganic hybrid network into the membrane matrix to enhance the compaction resistance of the membrane [91]. As shown in Fig. 12a, 3-aminopropyltrimethoxysilane (APTMS) is used as a cross-linking agent and an organic silicone precursor to form an organosiloxane network with polyimide. The resulting mix matrix membrane shows good stability and negligible compaction (<2%). This improvement.

Is due to the presence of an inorganic filler that enhances the rigidity of the membranes. But the existence of organic-inorganic network also reduces the free volume fraction and overall porosity of the membrane, resulting in lower flux. Karimi et al. [92] reported that the introduction of metal-organic framework (MOF) also significantly improves the anti-compaction performance of membranes due to the additional rigidity of MOF. Besides inorganic fillers, proper chemical cross-linking could enhance the mechanical strength of the OSN membrane and effectively improve the compaction resistance as well. Loh et al. [93] studied chemical cross-linking of ISA polyaniline (PANI) membranes for organic solvent nanofiltration, where the introduction of chemical cross-linking agents significantly improves the membrane's resistance to compaction (Fig. 12b). However, chemically cross-linked membranes usually possess significantly reduced solvent permeation, as free volumes between the polymer chains are occupied by the chemical cross-linkers. Whereas the recently reported metal ion coordination cross-linked polyimide observed a similar improvement in compaction resistance without significantly reducing the initial solvent permeability (Fig. 3a) [49]. The involvement of metal ion crosslinkers significantly enhances the polymer-chain rigidity without occupying as much free volume as traditional chemical cross-linkers.

4. Conclusions and perspectives

We have recapped the recent developments of polymer membranes for OSN from the perspectives of traditional and emerging polymer materials. Generally, the research of polymer OSN membranes in the past few years highly focuses on improving the separation performance in terms of solvent permeance and solute selectivity. Both the introduction of emerging polymer materials and innovative design of membrane fabrication/post-treatment methods contribute to such performance advancements. Comparing to the commercially available polyimide ISA membranes and polyamide TFC membranes, PBI, PEEK, PIMs, COFs and CMPs are several types of promising polymer membranes materials for OSN in terms of much improved permselectivity for highly efficient molecular separation.

In view of adopting OSN membranes for engineering applications, we have also summarized some key challenges unique to polymer membranes and recent efforts to overcome them. The material swelling in organic solvent environments, the physical aging against prolonged membrane lifespan, and membrane compaction against elevated operating pressure are among the key challenges of polymer OSN membranes. Vapor phase infiltration, hyper-crosslinked additives, inorganic fillers, and metal ion coordination crosslinking are some recently developed innovative approaches to overcome the aforementioned challenges related to membrane performance stability in OSN applications.

Despite the high demand of organic solvent related separations, the engineering application of OSN processes is still highly constrained to few scenarios like waste solvent and/or solute recovery, solvent exchange, etc. Polymer membranes with highly tailored features for OSN processes are required to broaden their applications in various industries. The key requirements for the future polymer OSN membranes from the application perspective would thus include (1) resistance to a wide range of both polar and non-polar solvents, (2) high selectivity to species with close MWs, (3) higher rejection to solutes of smaller sizes, and (4) higher solvent permeance for reduced membrane area. In order to fulfill the application requirements of OSN, future research of polymer OSN membranes should continue to improve the separation performance of conventional ISA and TFC polymer membranes via improved membrane formation control and crosslinking, and concurrently focus on the development of emerging polymer membrane materials like PIMs, COFs, CMPs, etc. to break through the limit of existing OSN membranes in terms of permselectivity and performance stability.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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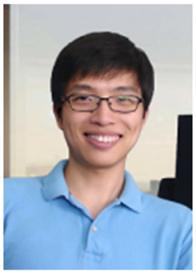

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