Current Status and Future Directions of Self-Assembled Block Copolymer Membranes for Molecular Separations

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Abstract

One of the most efficient and promising separation alternatives to thermal methods such as distillation is the use of polymeric membranes that separate mixtures based on molecular size or chemical affinity. Self-assembled block copolymer membranes have gained considerable attention within the membrane field due to precise control over nanoscale structure, pore size, and chemical versatility. Despite the rapid progress and excitement, a significant hurdle in using block copolymer membranes for nanometer and sub-nanometer separations such as nanofiltration and reverse osmosis is the lower limit on domain size features. Strategies such as polymer post-functionalization, self-assembly of oligomers, liquid crystals, and random copolymers, or incorporation of artificial/natural channels within block copolymer materials are future directions with the potential to overcome current limitations with respect to separation size.

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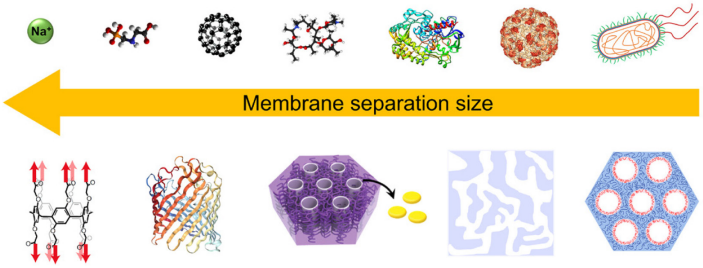

Block copolymer separation membranes are energy efficient alternatives to thermal processes but are limited to the nanometer range. Strategies such as post-functionalization, liquid crystal/random copolymer self-assembly, and hybrid channel/polymer materials are potential avenues for overcoming current limitations.

Introduction

Efficient and affordable chemical separations using nonthermal processes is a global challenge, and if successful, will significantly reduce energy consumption globally.(*1, 2*) Approximately 15% of the energy consumption within the United States is due to chemical separation processes that use thermal methods such as distillation. As an energy efficient separation technique and promising alternative to thermal processes such as distillation, membrane filtration has attracted significant attention, and is critical in building a sustainable world .(*3-5*) However, most current commercial membranes are subject to an intrinsic selectivity-permeability trade-off (*4, 6-9*), where selectivity opposes permeability. Isoporous membranes constructed using block copolymer self-assembly methods (**Fig. 1**) have shown great promise to overcome the selectivity-permeability trade-off.(*4*) Being able to self-assemble into various nanostructured morphologies in the size range from 5 to 100 nm, block copolymers have been used to fabricate membranes with very narrow pore size distributions while simultaneously exhibiting high permeability and selectivity. With several excellent reviews covering the recent progress in self-assembled block copolymer membranes,(*10-14*) here this article will place special focus on the challenge of developing isoporous block copolymer membranes with nanometer to sub-nanometer pore sizes.

Research focus of self-assembled block copolymer membranes has been primarily explored in two areas: self-assembly and block etch (SABE), and self-assembly and nonsolvent-induced phase separation (SNIPS). Due to the thermodynamic nature of block copolymer self-assembly, many membranes created using these two methods have pore size range from 10 to 100 nm.(*10, 11, 13*) With methods such as post-functionalization and utilizing kinetically trapped self-assembly, the membrane pore size can be effectively reduced to the sub-10-nanometer range.(*15, 16*) Sharing similar fundamentals and processing parameters, self-assembly of block oligomer/liquid crystals and random zwitterionic amphiphilic copolymers (r-ZACs) are also emerging methods to fabricate nanofiltration membranes in the few-nanometer range.(*17, 18*) Finally, the review will address promising strategies to build channel-based membranes with pore sizes as small as a few angstroms, which also holds the promise to explore the size limit of chemical membrane separations (**Fig. 1**). Furthermore, channel-based block copolymer membranes allow for the separation of functions similar to natural systems: transport dictated by the channel and matrix imparted by the nanostructured block copolymers.(*19*) The variety of block copolymer membrane

fabrication methods provides a library of membrane materials that find applications in a number of fields such as biomedical, waste processing, water purification, and gas separations.

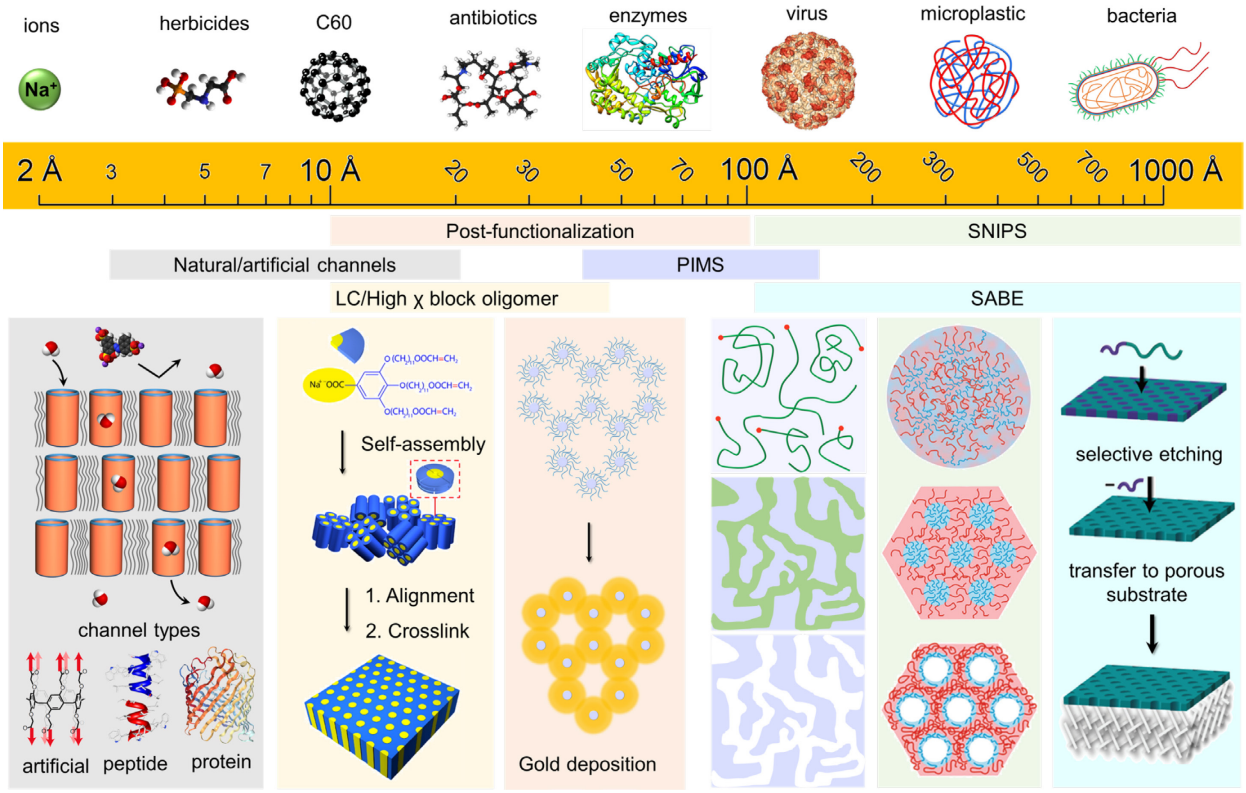

Fig. 1. Summary of membrane fabrication membranes using polymer self-assembly methods and corresponding separation size ranges. SABE: self-assembly and block etch. Copyright 2010 American Chemical Society. SNIPS: self-assembly and nonsolvent-induced phase separation. Copyright 2014 Royal Chemistry Society. LC: liquid crystal. Copyright 2014 American Chemical Society. PIMS: polymerization-induced microphase separation.

First introduced as an empirical observation among gas separation membranes in 1991 by Robeson,(*7*) the selectivity-permeability trade-off, also known as the "upper bond" relation, describes the performance limit of different polymer materials for gas separations (**Fig. 2a**). The molecular basis of this contradiction between selectivity and permeability was later explained by Freeman (*6*) in 1999. Similar trade-offs were later described for almost all types of membranes, such as desalination membranes,(*20*) ultrafiltration membranes,(*21*) and ion exchange membranes.(*22*) Isoporous membranes, where the pore size distribution is very narrow, enable both high permeability and selectivity at the same time (**Fig. 2b**).(*21*) For isoporous membranes, the pore geometry will effectively reduce tortuosity for high permeability while the uniform pore size guarantees high selectivity.(*4*) As shown in **Fig. 2b**, membranes with narrower pore size distribution will have much higher separation factors compared to membranes with wider pore size distributions. This effect is particularly prominent when the size of separation target is similar to the mean size of membrane pore.(*21*)

Block copolymer self-assembly has provided a convenient and powerful way for building isoporous membranes. Covalently-connected, incompatible polymer blocks will microphase separate to form various ordered structures, and the resulting nanoscale morphologies are controlled by balancing unfavorable pairwise monomer interactions (i.e., enthalpy) and chain configurational degrees of freedom (i.e., entropy).(*23, 24*) The morphology and associated length scale depend on the volume fraction of different blocks (f_A, for the A-block volume fraction of an AB diblock copolymer), the incompatibility between the blocks quantified by the Flory-Huggins interaction parameter (χ), and the degree of polymerization (N). Nanostructures such as body-centered sphere, lamellar, hexagonally-packed cylinders (HCPs), and gyroids are readily prepared through equilibrium self-assembly.(*25, 26*) Beyond equilibrium, kinetic-trapping strategies further expand the type of possible self-assembled structures.(*16, 23, 27-32*) Structures from block copolymer self-assembly typically have feature size ranging from 5 nm to 100 nm, which is particularly suitable for ultrafiltration applications.(*13*)

Thermodynamic and Kinetic Factors in Block Copolymer Membrane Fabrication

The first construction of nano-porous materials from block copolymer self-assembly dates back to 1988,(*33*) which has opened new avenues for using block copolymers in membrane applications

such as (*34*) polymer electrolytes,(*35*) virus removal,(*36*) and water filtration.(*37*) In SABE (**Fig. 2C**), equilibrium self-assembly structures of block copolymers are typically obtained through spin-coating or solvent-casting followed by annealing, and then one of the blocks was selectively etched to form pore structures. PS-*b*-PLA,(*37-39*) PI-*b*-PLA,(*40*) PS-*b*-PMMA,(*36*) and PB-*b*-PDMS(*41*) are common block copolymers used in SABE, where the PLA, PMMA, and PDMS blocks can be readily etched. The self-assembly and etching methods are now straightforward especially since the morphology and length scale of self-assembled structures are under thermodynamic equilibrium control and precise synthetic processes lead to desired materials. Structures such as HCP and lamellar are widely explored for membrane applications.(*36-38, 42*) However, SABE involves expensive fabrication process such as directed self-assembly,(*43*) which makes it economically less competitive compared to traditional roll-to-roll membrane fabrication techniques.

The SNIPS method to create membranes is more compatible with industrial roll-to-roll methods, (**Fig. 2d**),(*15, 44-47*) and is based off the widely applied method "NIPS" from industry, which therefore possess great potential in terms of scalability. The use of diblock copolymers PS-*b*-P4VP,(*15, 44, 48-52*) PS-*b*-PEO,(*53*) PS-*b*-PHEMA,(*54*) and triblock copolymers PS-b-PI-*b*-PS-*b*-P4VP (*45, 46, 55, 56*) and PI-*b*-PS-*b*-PDMA(*47, 57*) are widely explored in SNIPS. Unlike the SABE process, SNIPS affords asymmetric membranes with kinetically trapped structures which are out of equilibrium.(*58*) In this method, it is believed that the polymers self-assemble into micelles first, and then develop into ordered structure in a thin skin layer during solvent evaporation (solidification), which will finally form open pores when being immersed into non-solvent.(*11*) Beneath the "active" skin layer of SNIPS membranes, a much thicker and more porous substructure (similar to that of NIPS membranes) can be found, which provides an integral support for the whole membrane. Due to the kinetic nature of SNIPS membrane structures, they can be easily tuned through various phase separation parameters such as solvent/non-solvent, temperature, additives, evaporation conditions, and film thickness.(*12*) A composite structure with a thin skin-layer on top of a porous substrate support structure is especially beneficial for simultaneously maintaining mechanical properties and high-water permeability. Water permeability is generally defined as volumetric flux normalized to hydraulic pressure (usually expressed in units of Liters per squared meters per hour per bar or LMH/bar) is an important

performance parameters for ultrafiltration membranes.(*13*) The composite structure allows for selectivity maintenance through the skin layer while the thinness of the skin layer enabled by the porous support structure allows the permeability to remain high.

Although block copolymer self-assembly has been widely used to create nanostructured membranes with well-defined pore sizes and morphologies, statistical copolymers in which monomers are randomly distributed (e.g., the reactivity ratios for monomer A and B are both equal to 1)(*59*) along the polymer chain will self-assembly into co-continuous morphologies in which there is local microsegregation of the two different species.(*60-66*) Recently, the Asatekin group has shown that zwitterionic statistical copolymers such as poly (trifluoroethyl methacrylate-*r*-sulfobetaine methacrylate) (P(TFEMA-*r*-SBMA)) and poly (allyl methacrylate-*r*-sulfobetaine methacrylate) (P(AMA-r-SBMA)) are viable alternatives compared to block copolymers to create membranes with small pore sizes.(*18, 67-70*) The self-assembly method to synthesize zwitterionic membranes results in pore sizes as small as one nanometer, or even sub-nanometer, in addition to exhibiting superior anion selectivity.(*18, 70*) In such membranes, statistical copolymer containing zwitterions and hydrophobic monomers undergo microphase separation and form co-continuous networks with ionic and hydrophobic nanodomains. Such membranes are especially attractive due to the ease to scale up and their anti-fouling properties.(*67-69*) An added benefit of using random copolymers for self-assembled membranes is that domain alignment is not an issue as it is in ordered block copolymers. Co-continuous morphologies percolate the volume of the material and diffusing species will not be impeded by grain boundaries, similarly to ion-conduction in polymer electrolyte membranes.(*71*)

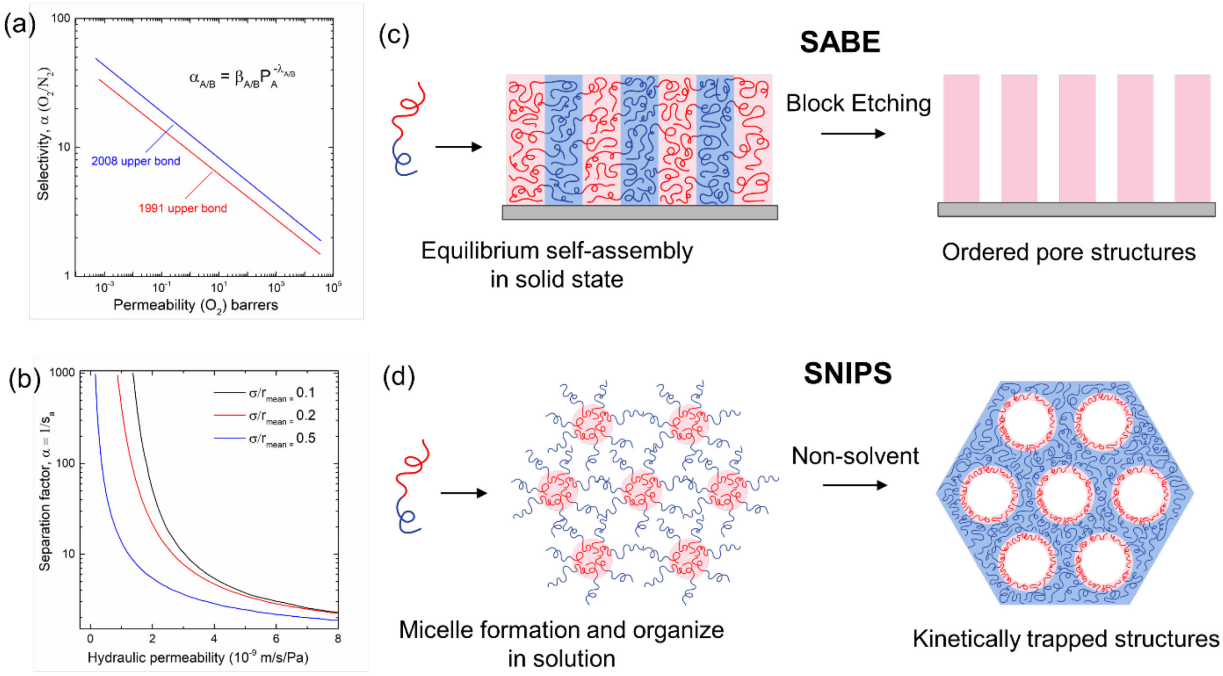

Fig. 2. Isoporous block copolymer membranes made from self-assembly and block etching (SABE) and self-assembly and non-solvent induced phase separation (SNIPS). (a) Permeability-selectivity trade-off of different membrane materials for O_2/N_2 separation.(*9*) Copyright 2008 Royal Society of Chemistry. (b) Effect of membrane pore size distribution on trade-off between membrane separation factor and permeability.(*21*) Copyright 2008 Royal Society of Chemistry. Schemes showing (c) SABE and (d) SNIPS processes to create isoporous block copolymer membranes.

Reactive Systems and Post-Polymerization Methods

With SABE and SNIPS being the two dominant methods for preparing self-assembled block copolymer membranes, the majority of the prepared membranes utilize anisotropic structures such as HCP and lamellae, where the pore structures need to be well aligned for separation purposes. On the other hand, gyroids (**Fig. 3a**) are isotropic ordered structures that can provide interconnected and easily accessible pore structures without the requirement for alignment.(*41*) However, the application of gyroid structures have been greatly limited by the narrow phase space window with respect to block copolymer composition and molecular weight (**Fig. 3b**). As replacements, kinetically trapped bi-continuous morphologies can be easily prepared through crosslinking or thermal processing.(*16, 27, 72-75*) As shown in **Fig. 3c**, one kinetic trapping strategy is polymerization-induced microphase separation (PIMS) developed by the Hillmyer group.(*16, 72-74*) In this method, an etchable polymer (PLA) end-functionalized with chain transfer agent (e.g., macro-CTA) is first dissolved in a mixture containing monomer (styrene) and crosslinker (divinylbenzene). Upon UV or thermal initiation, polymerization will lead to the formation of block copolymers in situ. As N increases, microphase separation will take place due to an increase in segregation strength (χN). As a result of the crosslinking reactions, a disordered bi-continuous structure that resembles spinodal decomposition in binary polymer blends or the fluctuating disordered state in volumetrically symmetric diblock copolymer systems, is kinetically trapped before the system reaches thermodynamic equilibrium. PIMS results in membranes with pore sizes as small as 4-8 nm, which is significantly smaller than the majority of membranes made from SABE and SNIPS.(*16*) Recent work has shown that related in situ polymerization schemes that results in grafted block copolymer architectures versus crosslinked linear block copolymers leads to ordered and metastable phases including hexagonally perforated lamellae,(*32, 76*) which is potentially useful in membrane separation applications.(*77*)

A related kinetic-trapping method to PIMS recently developed by the Hillmyer group is to directly crosslink block copolymers above their order-disorder transition temperature (T_{ODT}) (**Fig. 3d**).(*27, 75*) Here, microphase separated block copolymer materials, PLA-*b*-P(S-*s*-GMA) or PLA-*b*-P(S-*s*-B), are heated above T_{ODT}, resulting in a disordered polymer melt that exhibits concentration fluctuations resembling a bi-continuous morphology.(*78*) At $T > T_{ODT}$, the sample is crosslinked, and when cooled below T_{ODT}, the bi-continuous disordered state is kinetically trapped at room

temperature. After selectively etching one domain of the material, nanoporous membranes with pore size ranging from 7.5-10 nm are readily prepared.(*27*)

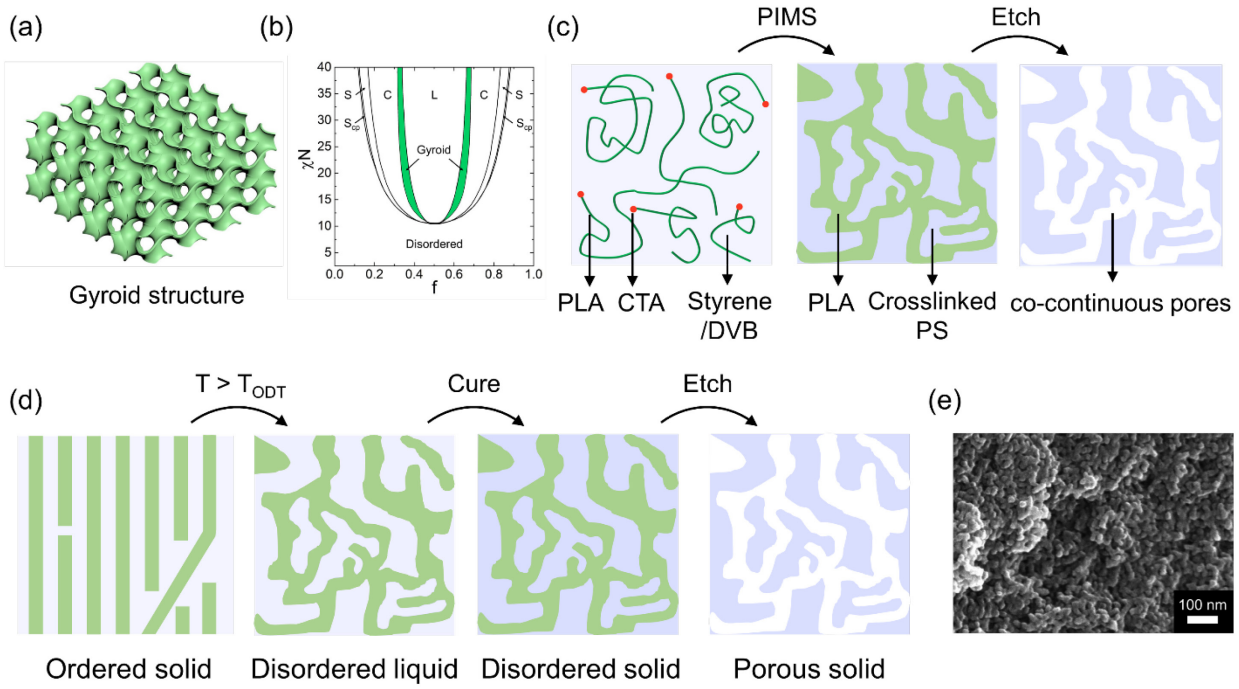

Fig. 3. Co-continuous block copolymer membranes using reactive methodologies. (a) A model of gyroid structure shows ordered and interconnected pore structures. (b) A phase diagram of block copolymer where the window of gyroid structure is very narrow. (c) Polymerization-induced microphase separation (PIMS) for making isoporous membrane utilizing disordered co-continuous phase. (d) Disordered isotropic membranes made through kinetically trapping disordered structures by curing above the order−disorder transition temperature (T_{ODT}). (e) SEM image of a disordered isotropic membrane.(*27*) Copyright 2017 American Chemical Society.

Another widely explored and more straightforward way to reduce pore size is post-functionalization of block copolymer membranes. For example, Yu et al.(*51*) has shown that through a two-step gold decoration and deposition process, the pore sizes of PS-*b*-P4VP membranes are dramatically decreased from 20 nm to 3 nm (**Fig. 4a**). Tuning pH is an alternative way of decreasing pore size, especially due to the fact that the hydrophilic blocks used in a lot of SNIPS membranes are pH sensitive, such as P4VP,(*15, 44-46, 48, 49, 55, 79*) P2VP,(*80-82*) and PAA(*47, 52, 57*). Nunes et al. has shown that the pore size of PS-*b*-P4VP membranes can be switched from 21 nm at basic condition (pH = 10) to 1-3 nm at acidic condition (pH = 2).(*15*) The Peinemann group has reported a PS-*b*-PAA and PS-*b*-P4VP blended block copolymer membrane with pore size as small as 1.5 nm.(*52*) The Phillip group has successfully converted the carboxylic acid groups inside PI-*b*-PS-*b*-PAA membrane pores into ethane-1,1-disfulonic acid groups (**Fig. 4c**),(*83*) and achieved pore size as small as 0.8 nm (**Fig. 4d**).(*57*) Despite its success, the pH dependence of such membranes can also limit their application in certain environments while providing benefits in other applications.

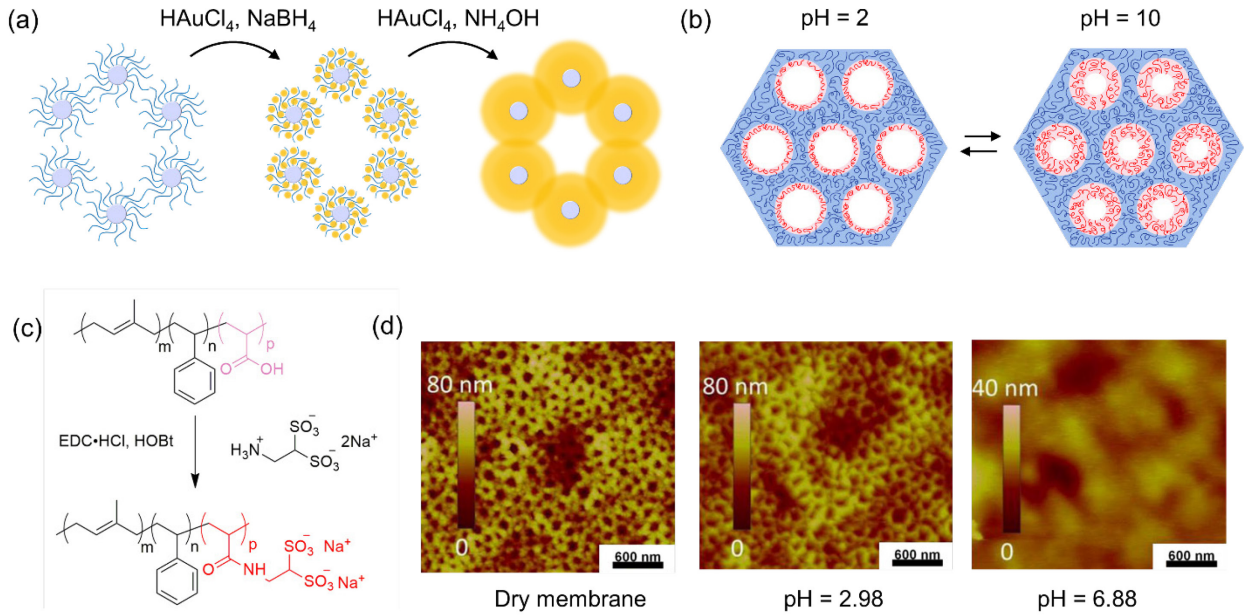

Fig. 4. Isoporous membranes with nanometer pore size using post-functionalization methods. Decreasing block copolymer membrane pore size through (a) gold deposition and (b) pH adjustment. (c) Reaction scheme for converting the carboxylic acid groups inside membrane pores into ethane-1,1-disfulonic acid groups. (d) AFM height images show size change of membrane pore as the environmental pH values change. Copyright 2014 Royal Society of Chemistry.

Oligomeric and Liquid Crystalline Copolymers Systems

Although there has been significant progress in creating block copolymer membranes, there is a fundamental lower limit with respect to achievable pore size. Two simultaneous requirements need to be fulfilled to decrease the pore size in block copolymer membranes: high χ and low N.(*84*) For example, in AB lamellar block copolymer systems in which $f_A = 0.5$, the domain spacing, d, is expected to scale as $d \sim N^{2/3}$,(*85-87*) which means that the pore size of one of the domains would be $d/2$. Therefore, to reduce the pore size for membrane applications, one would need to reduce N, but at reasonable χ values, as N decreases, the material will disorder. To circumvent the thermodynamic limits on block copolymer pore size, researchers have synthesized high χ block oligomers or liquid crystalline molecules, which is an effective strategy for fabricating membranes with pore size that are only a few nanometers.(*17, 88-90*) Utilizing crosslinked liquid crystal mesophases, the Osuji group has developed a series of ordered nanostructured membranes with pore size of 1-2 nm (**Fig. 5**).(*17, 88-90*)

Different liquid crystal molecules have been exploited in this type of membrane fabrication (chemical structures listed in **Fig. 5a**). Several strategies have been proven effective in developing efficient and robust membranes.(*17, 88-91*) One strategy is to target vertically aligned HCP structures and drive liquid crystal molecules into anisotropic self-assembly. Through magnetic alignment or soft confinement annealing (**Fig. 5b**), the pore structures were aligned perpendicular to the membrane plane, which will then be crosslinked at this desired orientation and form tough membrane materials with pore size from 1 to 2 nm.(*17, 88*) Liquid crystals can also be co-assembled with a template molecule, which will be later washed out from the membrane to form open pores.(*89*) More recently, the Osuji group has also developed a new membrane model utilizing the isotropic HCP structures, where the separation pathways are similar to that of bi-continuous structure membranes.(*90, 92*) The isotropic HCP membrane model(*40, 90*) does not require an alignment step, which could be advantageous in terms of production cost and scalability.

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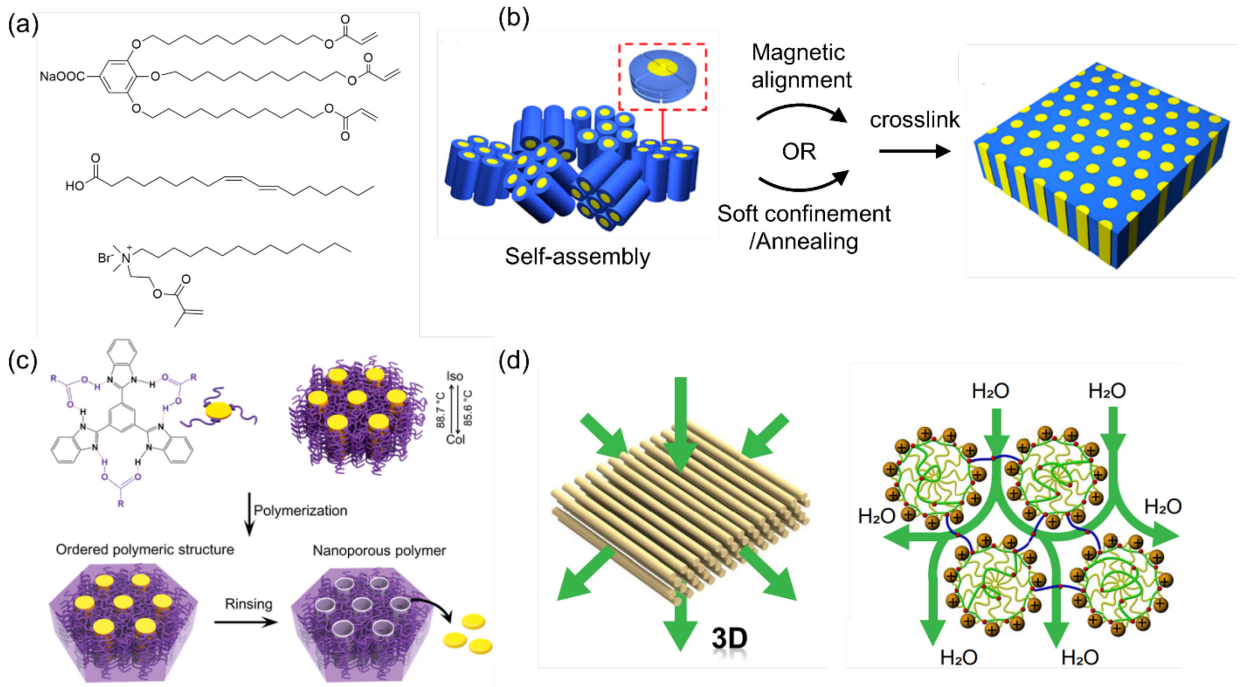

Fig. 5. Isoporous membranes with nanometer pore size made from self-assembly of block oligomer/liquid crystals. (a) Molecular structures of the membrane building motif. (b) Anisotropic membranes prepared through a two-step process of self-assembly and magnetic alignment/soft confinement annealing.(*17*) Copyright 2014 American Chemical Society. (c) Anisotropic membranes made through a sacrificial template molecule.(*89*) Copyright 2017 American Chemical Society. (d) Isotropic membranes made utilizing mesophases of hexagonally packed cylinders.(*90*)

Channel-Based Membranes

Although block copolymer/oligomer/liquid crystal and random copolymer self-assembly is a powerful approach to reduce membrane pore sizes, the materials are experimentally limited to the nanometer range. The stated self-assembly methods alone are not sufficient for applications that require molecular level separations.(*4*) To this end, channel-based membranes inspired by cell membrane models have shown great promise to overcome current challenges.(*4, 93-96*) Channel proteins present in cell membranes are exquisite molecular machines with exceptional transport efficiency and selectivity, which are far beyond the reach of current commercial membrane materials.(*97, 98*)

However, before biomimetic membranes can be widely applied for real-world applications, several challenges need to be addressed. The first challenge is how to design or modify channel molecules to fulfill desired separation tasks. Although natural channel proteins, such as Aquaporins, are very efficient, their high cost and low stability have become a major hurdle for scalability. These proteins are also often "over-qualified" for simple separation tasks, where certain structural and functional features are necessary for life but are excessive for membrane applications. One possible solution to the problem is to redesign more robust membrane proteins specifically for separation purposes.(*99*) Chowdhury et al. have shown that through computational design, beta-barrel Outer Membrane Protein F (OmpF) can be used as a scaffold to exclude specific solutes ranging from 58 Da to 360 Da (**Fig. 6a**). Compared to Aquaporins, these redesigned channels have higher permeability and selectivity that are better suited for desalination applications, rendering them possibly better candidates for desalination membranes.

Compared to protein redesign, a more scalable approach may be to develop artificial channels using synthetic methods.(*100-107*) Since the first report of artificial channel in 1982,(*108*) a large number of synthetic structures have been reported to simulate natural channel and pore proteins. These synthetic channels were designed to transport different target molecules, including water,(*104, 105, 109-111*) protons,(*107, 112, 113*) cations,(*113-116*) anions,(*117, 118*) amino acids,(*119*) sugars,(*120*) nucleic acids,(*121*) and proteins.(*122*) Some of these channels have already been reported to show efficiency and selectivity comparable to their natural counterparts. For example, Song et al.(*105*) have reported cluster-forming organic nanostructures that enable

water transport at a rate of 10^9 water molecules per second per channel molecule (**Fig. 6b**). Foldamer-based artificial water channels can even reach a higher water permeability of 2.7×10^{10} water molecules per second, which is 2.5 times of AQP1.(*104*) These highly efficient artificial water channels have opened new avenues for developing high performance channel-based water purification membranes.

A recently reported method for promoting proton transport through lipid bilayers is the use of random single chain heteropolymers, which were polymerized using both polar (oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and 3-sulfopropyl methacrylate potassium salt (SPMA)), and nonpolar monomers (methyl methacrylate (MMA) and 2-ethylhexyl methacrylate (EHMA)).(*107*) The polymer chains will insert into the lipid bilayers in which the hydrophobic segments enter the internal bilayer domain while the hydrophilic segments reside at the water infaces. The organization of the polymer chain at the bilayer surfaces and internal regions is hypothesized to promote hydrogen-bonded chain formation, which is necessary for proton transport in biomembranes.(*123*) The ability of random heteropolymers to favorably interact and self-organize in lipid bilayers, and to mimic protein channels in natural systems, highlights how critical monomer sequence within single chains is for tailoring polymers for specific applications.

With highly efficient artificial channels available for use, a critical challenge is to properly incorporate channel molecules into membrane materials. A key factor for building channel-based membrane is to align the channel molecules in the right orientation so that the channels can optimally perform their function.(*124-127*) Due to the rich self-assembled structures and similar amphiphilicity of block copolymers as compared to lipids, a natural progression is to co-assemble channel molecules and block copolymers. Among different morphologies from self-assembly, flatsheet-like structures such as lamellae or 2D crystals are more desirable and convenient for membrane fabrication (**Fig. 6c, 6d**).(*19, 94, 128-131*)

Utilizing the co-assembly of a crosslinkable ABA triblock copolymer (PI-*b*-PEO-*b*-PI) with natural/artificial channels, Lang et al. have developed a channel-based membrane platform where the block copolymer matrix provides mechanical and structural support similar to lipid bilayers in cell membranes. Furthermore, different channel molecules can be then be added to the

hydrophobic domains to determine the separation function (**Fig. 6c**).(*19*) Channel-based 2D crystals is another successful strategy for building channel-based membranes.(*130-133*) Widely applicable to different types of channel proteins, this strategy allows for fabrication of highly porous 2D nanosheets, which can be further converted to large scale membranes through layer-by-layer deposition and crosslinking.(*130, 131, 133*) Through this method, both natural and artificial channels have been exploited to co-assembly with lipids or block copolymers (PB-*b*-PEO) and form defect-free flat-sheet crystals (**Fig. 6d**). Using β-barrel membrane protein as separation elements, biomimetic membranes with separation in the sub-nanometer to few-nanometer range have demonstrated an extremely high water permeability that is up to 1000 times higher than that of commercial membranes.(*131*)

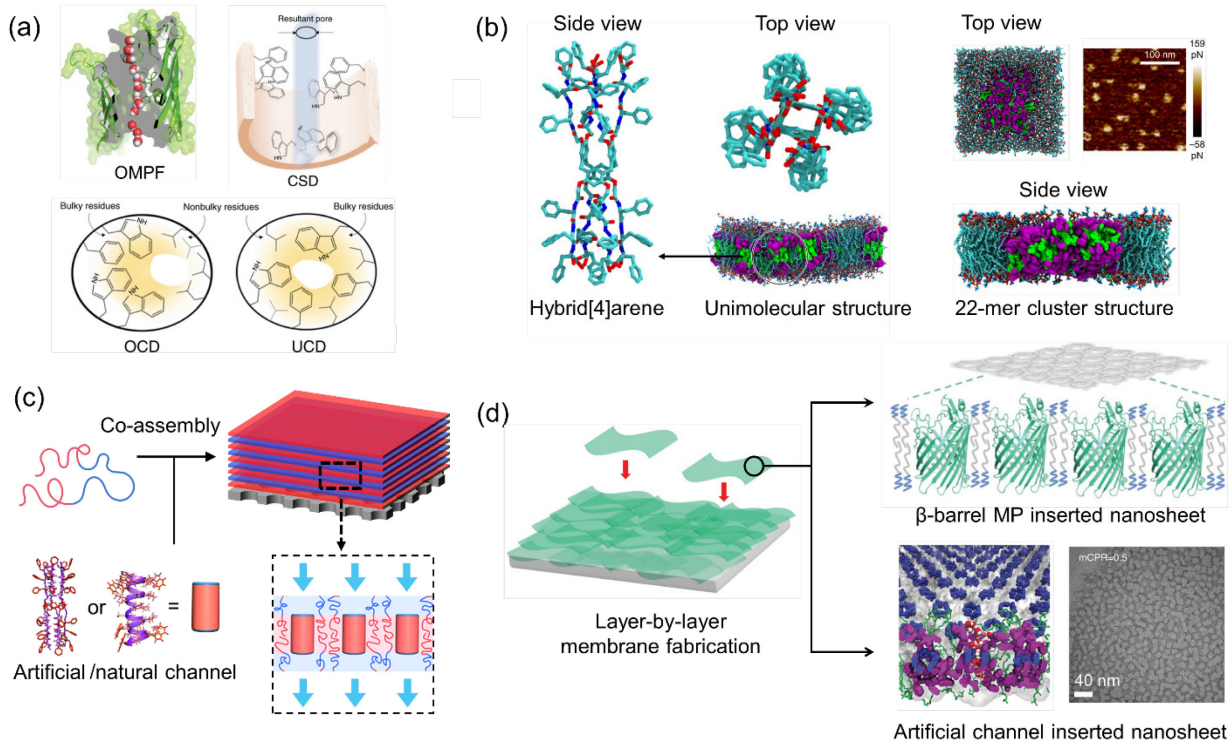

Fig. 6. Isoporous membranes using block copolymers scaffolds and natural/artificial channels as separation elements. (a) Design and modification of pore structures based on OmpF channel proteins.(*99*) Copyright 2018 Nature Publishing Group. (b) Artificial water channel with anisotropic water-wire network designs.(*131*) Copyright 2020 Nature Publishing Group. (c) Channel-based membranes through co-assembly of channel molecules and block copolymers into lamellae structures.(*19*) Copyright 2019 American Chemical Society. (d) Channel based

membranes made from lay-by-layer deposition of channel inserted nanosheets.(*130, 131*) Copyright 2020 Nature Publishing Group.

Summary and Outlook

Block copolymer self-assembly promises disruptive technology advancements in the membrane separation field. Attributed to uniform self-assembled pore structures, selectivity and permeability of block copolymer membranes have been shown to exceed current commercial membranes in lab scale experiments. However, before such technologies can be scaled up and become commercially competitive, more robust, and cost-effective fabrication process are necessary. Large-scale tests under harsh conditions are further required to address real world operational challenges such as the long-term stability and fouling issues. Membrane mechanical properties also need to be considered due to the high hydraulic pressures that are employed in certain applications with ultrafiltration pressures ~ 2-5 bars and reaching as high as ~70 bars for seawater desalination.(134) Synthesis of mechanically robust membranes is particularly challenging for many self-assembled block copolymer membranes, where thin membrane thicknesses is necessary for high water permeability but may lead to lower pressure resistance. Through fundamental concept innovation such as kinetic trapping, liquid crystal self-assembly, and biomimetic channels, the separation size range of isoporous membrane have been significantly expended, which represents new opportunities in application fields such as in hydrocarbon processing, food processing, antibiotics and biologics manufacturing, and gas separations.

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Conflicts of interest

The authors declare no competing financial interest.

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Bios

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