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BIOSEPARATIONS APPLICATIONS

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Nanoporous membranes generated from self-assembled block polymer precursors: *Quo Vadis?*

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ABSTRACT: Nanoporous membranes based on self-assembled block polymer precursors are an emerging class of promising separation, purification, and sensing devices due to the ability of researchers to control the nanostructure and chemistry of these multifunctional materials and devices. In fact, modern polymer chemistry provides techniques for the facile, controlled synthesis of the block polymers that constitute these devices. These designer macromolecules, in turn, can then self-assemble into functional nanostructures depending upon the chemical identity of the synthesized block polymers and the thin film fabrication methods employed. After fabrication, these nanoporous membranes offer a highly tunable platform for applications that require high throughput, high surface area, homogeneous pore size, and varying material properties. And, with these readily tunable chemical and structural properties, block polymer membranes will allow for significant improvements in myriad applications. In this Review, we summarize the key advances, with a specific emphasis on the previous 5 years of work, that have allowed block polymer-based membranes to reach their current level of technology. Furthermore, we project how these state-of-art, self-assembled block polymer membrane technologies can be utilized in present-day and future application arenas. In this way, we aim to demonstrate that the rigorous work performed on block polymer-based membranes has laid a strong foundation that will allow these macromolecular systems to: (1) be major avenues of fundamental scientific research and (2) be parlayed into transferable technologies for the betterment of society in the imminent future. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41683.

INTRODUCTION

The first nanoporous membrane fabricated from a synthetic polymer was developed over a century ago, and since that time, this class of membranes has found application across a vast number of technological fields.[1–3] However, prior to the 1960s, membranes were difficult to manufacture on large-scales, little was known about their nanostructure, and their performance was moderate at best. As such, they were used primarily for simple, laboratory-scale tasks such as dialysis and filtration.[1] In 1963, Loeb and Sourirajan introduced the first example of the nonsolvent induced phase separation (NIPS) technique, which enabled the high-throughput processing of synthetic polymers into functional membranes.[4] Spurred by innovations in synthetic chemistry, further breakthroughs in membrane fabrication, and the advent of nanotechnology, the performance of porous membranes has advanced rapidly. As a result of these advances, porous membranes are now used commonly in several sectors of industry (e.g., water purification and treatment,[5–9] biopharmaceutical separations,[10–12] and electronics

processing).[13] However, despite the significant progress made in the development of fundamental scientific insights and engineering principles, their primary use within industry remains filtration and dialysis.[1–3]

Industrial applications of membranes have not moved beyond filtration, in large part, due to the limitations that the nanostructures of membranes generated using modern fabrication methodologies impose on their performance.[8,12,14–16] That is, an ideal filtration membrane would have a high density of pores that all possessed a single, well-defined size. In this case, the membrane would demonstrate both a high permeability and a high selectivity. Currently, however, a tradeoff between permeability and selectivity exists (Figure 1).[14] In particular, the performance of membranes fabricated using phase separation techniques have high permeability values due to their high porosities, but are limited by nonuniform pore size distributions that lower their ability to distinguish between molecules of differing sizes.[30] Conversely, track-etched membranes have nearly uniform pore size distributions, which makes these

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membranes highly size-selective, but are plagued by low permeability values due to the fact that they contain sparsely distributed pores.[14]

To harness the beneficial attributes of these two membrane geometries, a third class of membrane structures has been introduced recently; these membranes are based on nanoporous thin
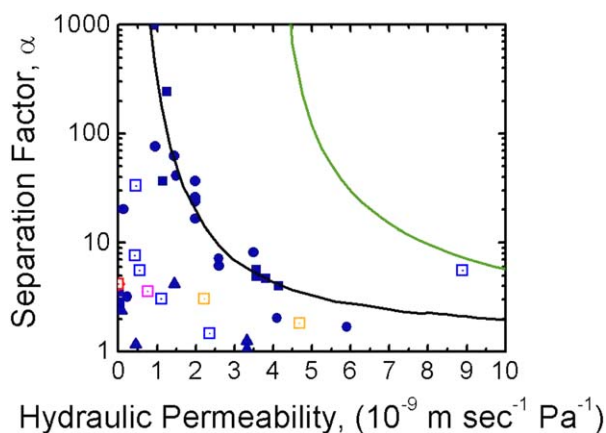
Figure 1. The selectivity-permeability trade-off (i.e., Robeson Plot)[17] for state-of-the-art, commercially available ultrafiltration membranes (filled navy points) and self-assembled block polymer membranes (open points in other colors). In this Robeson Plot, the black solid line indicates the "upper bound" suggested for conventional membranes[14] and the green solid line represents the "upper bound" calculated for block polymer membranes.[18] The upper bound for conventional membranes was developed by fitting experimental data for the rejection of BSA to well-established theories for solvent flow (i.e., the Hagen-Poiseuille equation)[19] and solute rejection.[20,21] The upper bound for block polymer membranes was calculated using the same theories and assuming a membrane with a 200-nm-thick active layer and a porosity of 30%, which is consistent with the nanostructural characterization of the membranes. A solute diameter of 7.3 nm, which is equivalent to the hydrodynamic diameter of BSA, and membranes with a monodisperse pore diameter ranging from 7.3 to 10.1 nm were assumed.[18] The difference between the two upper bounds results from the well-defined nanostructure of the block polymer membranes. That is, the high density of pores with a narrowly distributed pore size results in more selective separations at higher permeabilities. The summarized data were collected from Refs. 14,18, and 22–29. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

films derived from block polymer templates.[31–33] Due to their high density of well-defined pores, the nanostructures of assembled block polymers show great promise in being able to produce membranes that are both highly permeable and highly selective.[34]

The potential for self-assembled block polymers to serve as an innovative platform for the development of next-generation membranes has been demonstrated. In particular, Figures 1 and 2 present experimental evidence demonstrating that the performance of block polymer membranes can surpass that of current commercial membranes. In Figure 1, the Robeson Plot[17] provides a facile visualization tool for the inherent permeability-selectivity trade-off associated with filtration membranes.[14] The ideal membrane would be situated in the upper right corner of the plot; however, the current membranes made using the NIPS process are clustered toward the lower left side of the plot. Initial studies regarding block polymer membranes focused primarily on directing the self-assembly of these materials, and the membranes produced in these early studies possessed transport properties similar to commercial membranes. Recently, block polymer membranes are being optimized for

higher performance. For example, the membrane that lies significantly above the current upper bound (solid black line in Figure 1) was fabricated from a block polymer precursor. In addition, Figure 2 displays the molecular weight cut-off (MWCO) curves for three membranes, a commercial NIPS membrane and two membranes produced from block polymer precursors.[35] The steepness of cut-off curve for the block polymer membranes relative to the commercial membrane is a clear indication of their ability to distinguish between solutes of differing size selectivity. These results demonstrate that the promise of block polymer membranes is real. However, several important technological hurdles remain before this potential is translated to the large-scale applications.

Herein, we detail recent progress in the development of membranes derived from block polymer precursors. Much like the progress required to translate the current generation of porous polymeric membranes from the laboratory scale to industrial applications, the development of block polymer membranes will rely on advances in the synthesis of the novel macromolecules, high throughput processing of these novel macromolecules into functional membranes, and a better elucidation of the structure-property-performance relationships of block polymer membranes at the nanoscale. As such, we highlight significant advances in these areas before discussing how the synthetic flexibility, well-defined nanostructures, and the easily tailored functionalities of block polymer membranes will enable the
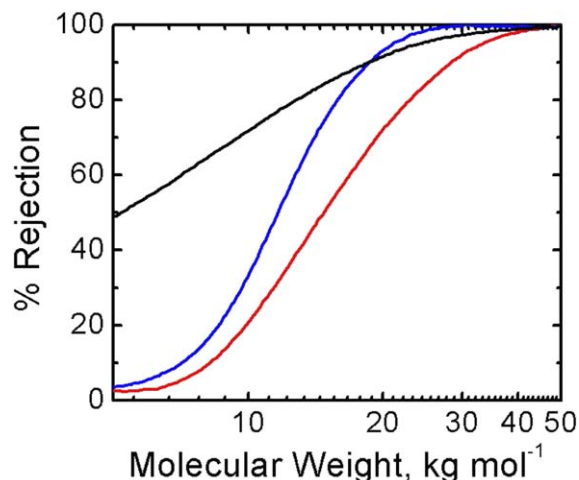
Figure 2. MWCO curves for different types of filtration membranes. The black line represents data that were collected for a commercial membrane made using a standard NIPS technique; the blue line and red line are data obtained for membranes generated through the phase separation of block polymers. Block polymers with a pore-forming-block that had a molecular weight of 32 and 65 kg mol^{-1} were used to prepare the membranes that resulted in the blue line and red line, respectively. Each membrane was challenged with dextran molecules of varying molecular weights. The sharper MWCO of the block polymer membranes indicate that they have more well-defined pore sizes than the commercial membrane. The shift of the MWCO between the two block polymer-templated membranes demonstrates that the pore size of block polymer membranes can be tuned through the controlled synthesis of the block polymer template. These data are reproduced from Ref. 35. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
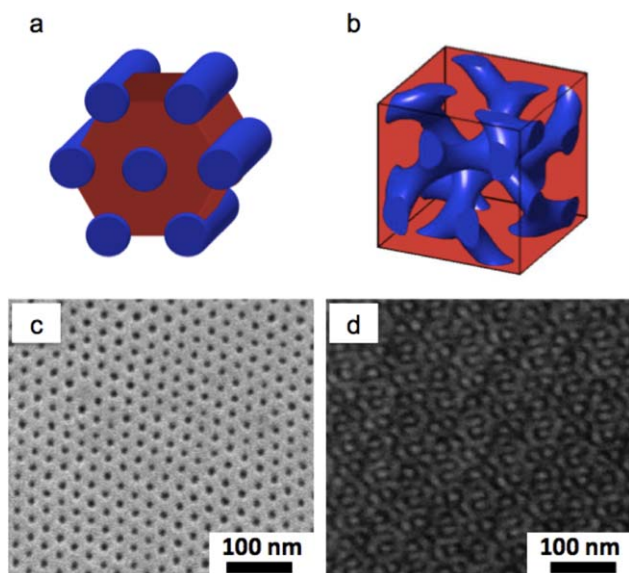
Figure 3. Representative images of common microstructures used in the fabrication of nanoporous membranes from block polymer templates. The (a) cylindrical and (b) gyroid structures are depicted in cartoon form and SEM micrographs of membranes fabricated using the (c) cylindrical and (d) gyroid phases as structural templates are shown. The SEM micrograph in panel (d) is reproduced with permission from Ref. 81. Copyright 2011 American Chemical Society. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

implementation of next-generation membranes in applications beyond simple filtrations. These advances, which address the limitations of current membranes, will help to overcome the pressing challenges of our times.

**Facile and Tunable Syntheses of Myriad Block Polymers**

The synthetic flexibility associated with block polymers makes them an attractive material of construction for nanostructured, functional membranes, and the polymerization mechanisms that can be employed offer macromolecular architects a wide variety of tools by which to generate these next-generation macromolecules.[36–41] Of critical import to the synthetic pathway chosen, however, is the fact that in many polymer systems a relatively narrow molecular weight distribution, or dispersity ($Đ < 1.5$),[37] must be maintained in order to facilitate block polymer self-assembly,[32,33,42] although recent theoretical and experimental efforts have demonstrated that block polymers with high dispersity values can self-assemble into ordered structures.[43–49] Furthermore, most instances of block polymer synthesis require the consecutive growth of subsequent blocks from the previous polymer moiety (or moieties in the case of block polymers containing more than two macromolecular segments). Therefore, "living" or controlled polymerizations, reactions where all chains are allowed to propagate at almost exactly the same rate and irreversible termination is suppressed,[50] have become the synthetic route of choice. Although many systems have been deemed "living," most of the controlled polymerization mechanisms for block polymer membrane materials are performed through ring opening polymerization (ROP),[51] anionic polymerization,[52] controlled radical polymerization (CRP),[53] or a

combination of these mechanisms [i.e., the change of mechanism polymerization (ChOMP) strategy[36,54,55]].

The selection of which polymerization mechanism to employ must be tailored to the needs of the polymer scientist with respect to the ultimate chemical functionality of the membrane platform. For example, ROP offers access to practically any cyclic monomer with a wide range of catalytic systems,[54,56,57] and recent efforts have demonstrated that organic catalyzed-ROP reactions can make the metal-free synthesis of block polymers a reality.[58,59] Furthermore, controlled anionic polymerizations offer excellent control of the block polymer molecular weights, and molecular weight distributions,[60] which allows for exceptional model block polymer systems to be fabricated readily. However, both of these synthetic routes can be limited to a select number of monomers, and the synthesis of multiblock polymers, especially for three or more blocks, can require the utilization of *in situ* solvent exchange procedures or polymer end-capping strategies that are difficult to perform beyond the laboratory scale.[61,62]

Conversely, CRP mechanisms are compatible with many different monomer types, are not as sensitive to ambient conditions as many other controlled polymerization mechanisms, and the scalability of these reactions is well known.[40,63,64] As such, implementation of these synthetic protocols could enable block polymer-based membranes to reach commercial levels in a ready manner. Among the three most common types of CRP are: (1) nitroxide-mediated polymerization,[63] (2) atom-transfer radical polymerization,[64,65] and (3) reversible addition-fragmentation chain transfer (RAFT) polymerization.[40,50] In fact, all three of these types of polymerization mechanisms have been used to generate nanostructured membranes from block polymer templates with a high degree of success.[66,67] And, while each of these CRP strategies has its own unique set of positive aspects and potential drawbacks,[63,65,68,69] RAFT-mediated polymerizations do tend to have unique advantages (i.e., the inherent lack of metal contaminants, the wide range of compatible monomers and solvents, and the relatively short polymerization reaction times) that make the wide-scale implementation of this synthetic protocol very attractive for membrane fabrication. In a RAFT-mediated polymerization, a chain transfer agent (CTA) is added to a conventional free radical polymerization that contains a monomer and an initiating species.[70] This CTA typically is a thiocarbonylthio compound[50] that can be removed easily at the end of synthesis, if necessary for particular applications.[71] In practice, the CTA prevents chain termination and promotes a mediated polymerization rate, which results in high molecular weight polymers that have narrow molecular weight distributions.[50]

These types of advances in block polymer synthesis have made possible the systematic design and ready synthesis of multicomponent polymers comprised of nearly any monomers desired, which proves of critical import in the design of tailored soft materials. This capability enables chemists and device engineers to work collaboratively to build a library of block polymers with mechanical, nanostructural, and chemical properties tailored to the specific needs of a device. In this way, true structure-property-performance relationships can be elucidated, and research teams can optimize material and module designs in an expedient manner.
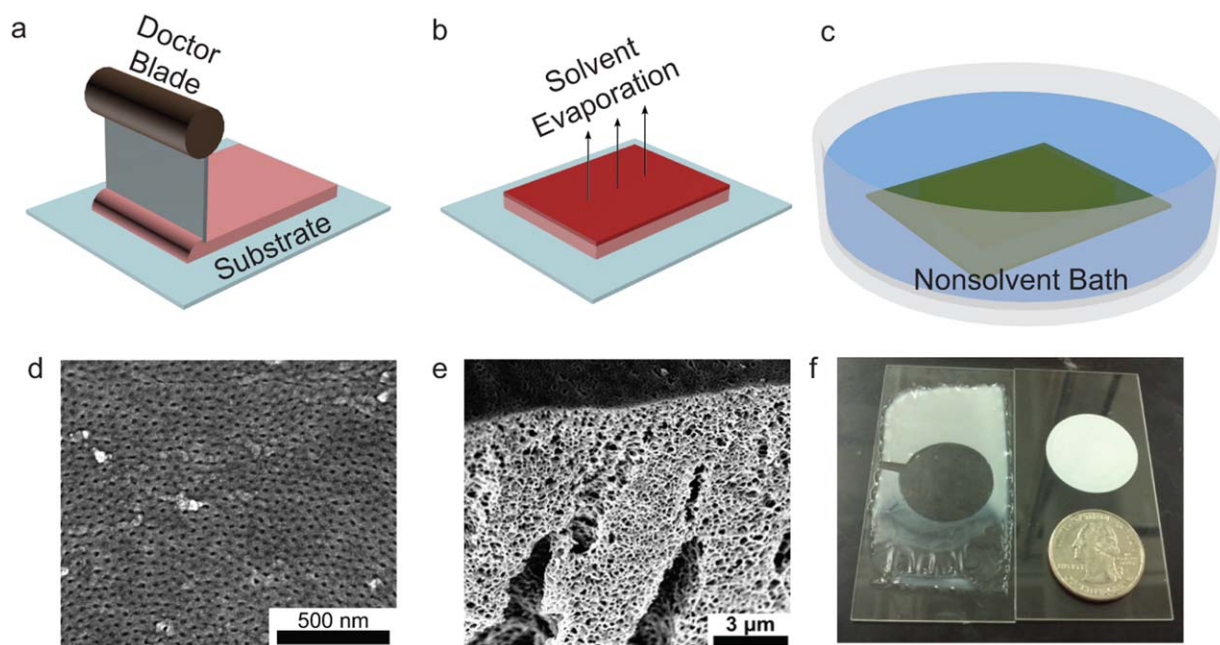
Figure 4. A schematic of the SNIPS membrane fabrication technique, and the resulting membrane. (a) A polymer solution is prepared by dissolving a block polymer in a solvent or mixture of solvents. The solution is then drawn into a thin film through simple casting techniques (e.g., using a doctor blade). (b) Solvent is allowed to evaporate from the thin film in a controlled manner for a predetermined period of time. (c) Then, the thin film is plunged into a nonsolvent bath. The nonsolvent causes the polymer to precipitate, which kinetically traps the nanostructure of the membrane. The result is a nanoporous membrane with an asymmetric structure that comprises a highly selective active layer situated on top of a gutter layer with a high porosity. (d and e) SEM micrographs of the top and cross section of membranes made using the SNIPS process. The image in (e) is reproduced with permission from Ref. 97. (f) The fabricated membrane next to a US quarter showing the laboratory-scale of the membrane. However, the size of the membranes made via the SNIPS technique are limited simply by the dimensions of the casting substrate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Emerging Techniques Allow for the Scalable Fabrication of Membrane from Self-Assembled Block Polymer Precursors

Critical to the success of nanostructured membranes is the deliberate preparation of block polymers that possess specific constituent polymer moieties, which are chemically unique enough to self-assemble at the nanoscale when the polymer is processed into a membrane.[72,73] Many times, this self-assembly relies on the natural chemical dissimilarity, which is characterized by the interaction parameter (χ), and the overall (i.e., for all of the moieties of the polymer chain) degree of polymerization (N) of the block polymer.[32,33,74–78] Therefore, microphase separated block polymer membranes can be produced simply by coating a thin film of solution on a substrate and allowing the solvent to evaporate. For instance, spin-coating a solution containing a block polymer onto a support makes manufacturing ultra-thin, microphase separated block polymer films with smooth, uniform surfaces readily feasible.[72] The thicknesses of these films are controlled by tuning the angular velocity of the substrate, the polymer concentration in solution, and the solvent used to dissolve the block polymer;[79] and, a host of examples have demonstrated the potential of this membrane fabrication strategy. We note that, when implementing this strategy, it is essential to ensure that the permeable domains of the membrane (e.g., the pores in a filtration membrane) are accessible to the feed and permeate sides of the membrane and that they transverse the entire thickness of the film.[35,80]

Two general strategies have been implemented to address this key concern (Figure 3). Researchers: (1) have used a block polymer that forms a cylindrical morphology and taken steps to ensure that the cylindrical domains are oriented perpendicular to the thin dimension of the film or (2) have used a block polymer with a bicontinuous morphology (e.g., a gyroid-like phase) that obviates the need for alignment.[13] In both these instances, the minority phase is chosen carefully such that it can be removed selectively to produce a nanoporous material.[81–85] At first pass, the second strategy, which does not require alignment of the block polymer, would seem to be a more popular route towards the high-throughput production of functional block polymer membranes. However, the narrow compositional window of stability of the gyroid phase in diblock polymers makes the realization of this morphology difficult in practice.[32,86] Nonetheless, porous membranes have been prepared from 1,2-polybutadiene-b-polydimethylsiloxane (1,2-PB-b-PDMS) block polymers that form the gyroid phase.[81,87] After coating thin films of this block polymer, the 1,2-polybutadiene was cross-linked and the polydimethylsiloxane was etched selectivity to yield a nanoporous membrane. Even though the gyroid morphology presented by the 1,2-PB-b-PDMS system eliminated the need to orient the block polymer template, a wise choice of the casting substrate was necessary to produce membranes that possessed pores accessible to both sides of the thin film. Specifically, enthalpic interactions between some substrates and the
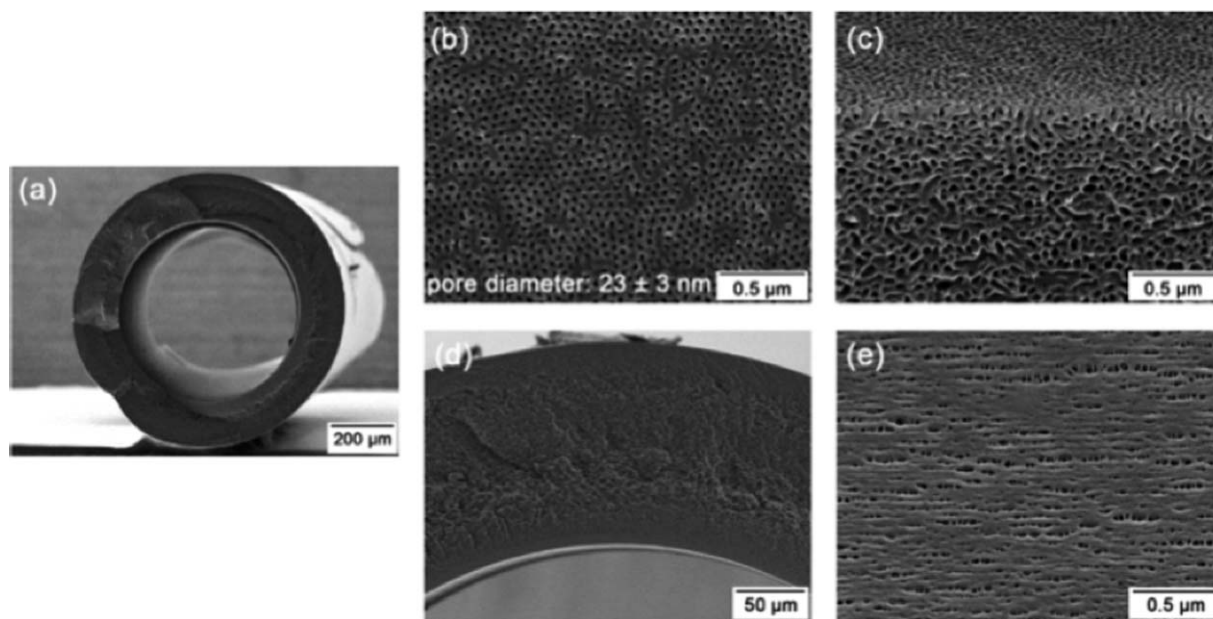
Figure 5. SEM micrographs for the PS-P4VP-based hollow fiber membranes are shown. (a) A cross section of a fiber demonstrating that it is free of macrovoids. (b) A membrane surface containing well-defined pores of a narrowly distributed size (c) A cross-sectional view of a hollow fiber showing the graded support structure underlying the active layer. (d) A higher magnification micrograph of the membrane cross section. (e) The porous structure on the core side of the hollow fiber. These images are reproduced with permission from Ref. 111.

cast polymer altered the self-assembly of the block polymer in the region near the substrate, and resulted in the formation of nonporous, impermeable skin layers.[81] Preferential interactions between one block and the substrate, which drive the formation of dense skin layers, are not uncommon for membrane fabrication methodologies that evaporate all of the solvent from the as-cast films. On the laboratory scale, plasma etching is typically used to remove the skin layers—the application of this technique to large-scale membrane fabrication, however, is suspect. Thus, future large-scale processing of these membranes will require new techniques to address this concern.

The limited compositional window for the gyroid phase in diblock copolymers has been addressed by recent efforts that have fabricated membranes using the polymerization induced phase separation technique.[33,35,83,88] While this technique does not rely strictly on the self-assembly of block polymers, it does rely on the chemical dissimilarity between the two constituent blocks of the block polymer to template a bicontinuous nanostructure with well-defined pore sizes. Another alternative route toward the production of robust membranes from bicontinuous morphologies is a transition to triblock polymers, which exhibit a greater number of bicontinuous morphologies and larger compositional windows where these morphologies form.[89–91] However, no reports on the use of this methodology to produce filtration membranes with bicontinuous structures (e.g., the double gyroid structure) are present within the literature to date.

The majority of membranes fabricated from self-assembled block polymers have used hexagonally ordered cylindrical templates, and, in these efforts, researchers have been able to identify various techniques to align the cylinders normal to the

substrate.[13,34,80] In some cases, casting conditions that result in the spontaneous alignment of the cylindrical domains perpendicular to the substrate surface have been identified.[26] In fact, ultrafiltration membranes have been fabricated using self-assembled polystyrene-*b*-polyisoprene-*b*-polylactide block polymers that adopt a core-shell cylindrical morphology with polylactide and polyisoprene forming the core and the shell of the cylinder, respectively. By controlling the block polymer design and coating conditions, the core-shell cylinders were aligned with their long axes normal to the membrane surface upon spin coating. Subsequently, the polylactide moiety could be etched selectively to create a nanoporous polystyrene-polyisoprene membrane.[26]

The spontaneous generation of perpendicular cylinders is convenient but uncommon. Instead, the parallel orientation of the cylinders relative to the substrate is often preferred thermodynamically due to the higher chemical affinity of one of the blocks to the substrate.[13,22,82] Therefore, researchers have turned to using directed assembly of these macromolecules. In this way, the thermodynamically driven microphase separation of the block polymers is combined with one or more external stimuli to provide a driving force for the perpendicular orientation of the cylindrical block polymer domains. For instance, one alternative membrane fabrication technique calls for the application of an electric field to reorient the block polymer through a disorder-to-order transition. By minimizing the orientation-dependent free energy, the applied electric field induces compositional fluctuations from a disordered state to oriented cylindrical micro-domains.[92,93] These important initial studies established the ability to control the thin film alignment of block polymers; however, the scalability of electric field-aligned mechanisms is of concern.[94,95] As such, researchers have
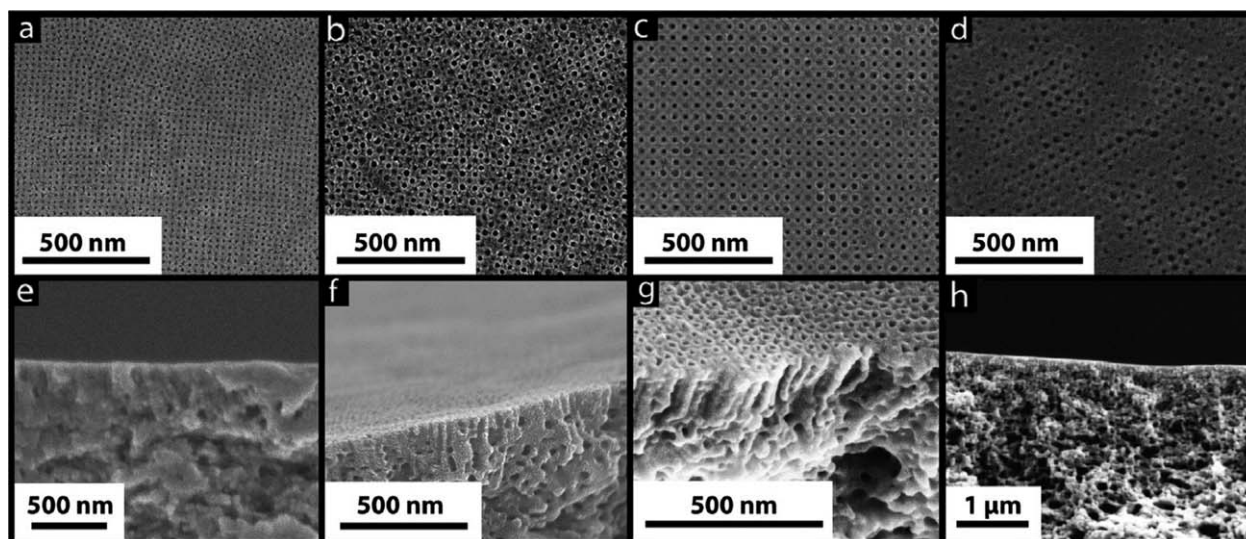
Figure 6. Scanning electron micrographs of the surface (top row) and cross section (bottom row) of membranes fabricated using polyisoprene-*b*-polystyrene-*b*-poly(4-vinylpyridine) triblock polymers of varying molecular weights. The molecular weights of the triblock polymers were (a,e) 43, (b,f) 77, (c,g) 91, and (d,h) 115 kg mol^{-1}. Using transport tests, the pore diameter for the membranes shown in panel (a–d) were 7, 16, 17, and 36 nm, respectively, which compared well with the pores sizes determined from the SEM micrographs (i.e., 8, 14, 14, and 20 nm). These data are reproduced with permission from Ref. 23.

turned to more easily scaled directed assembly methods for block polymers, and one of the more promising mechanisms is one that includes the utilization a magnetic field.[94,95] That is, if the block polymer contains a suitable magnetically anisotropic moiety, the domains of the block polymer will respond to an external magnetic field. In fact, impressive results have demonstrated recently that highly ordered nanoporous membranes with low tortuosity have been made from cylinder-forming brush-like polymers containing a magnetically anisotropic moiety and a hexagonally packed cylinder-forming moiety.[96] When the magnetic field is applied, the magnetically anisotropic moiety responds by aligning parallel to the applied field, which then directs the cylindrical domains to align in the desired orientation. Following crosslinking of the matrix and selective degradation of the cylindrical domains, a self-supporting membrane containing nanopores is produced.[94,96] Therefore, these types of directed assembly protocols must be investigated, as capitalization of these initiatives could result in large intellectual returns.

To date, however, the most successful methodology for directing the assembly of nanostructured block polymer-based membranes has been the self-assembly and nonsolvent induced phase separation (SNIPS) procedure (Figure 4).[97–99] This membrane fabrication protocol combines the thermodynamically driven self-assembly of block polymers in solution with the oft-used membrane fabrication technique of NIPS. As such, the SNIPS protocol is consistent with existing large-scale industrial phase-inversion membrane fabrication methods[99] and provides an ideal platform for directing the manufacturing of self-assembled block polymers towards a commercial market.[100,101] In the SNIPS process, a controlled solvent evaporation period allows for the self-assembly of the block polymer chains into nano-structured domains at the solution-air interface. This occurs

because the local concentration of the block polymer at the interface is much greater than that of the original solution, and this increase in polymer concentration drives self-assembly in solution.[22,80,102–104] In fact, a very recent result has demonstrated that the self-assembly in solution can be monitored using small-angle X-ray scattering (SAXS) and that the collected SAXS data can be used to predict the nanostructure of the thin film at the surface near the solution-air interface.[105] After this self-assembly occurs, the partially evaporated film is plunged into a nonsolvent bath to kinetically trap the nonequilibrium membrane microstructure. Because the lower portion of the membrane is far-removed from the air-solvent interface and contains polymer at roughly the same concentration as that of the original solution, this portion of the film precipitates in a manner similar to that seen in the NIPS procedure.

The combination of these two phenomena results in an asymmetric membrane with an ordered, highly selective top layer [Figure 4(d)] that is connected to a nonordered support/gutter layer [Figure 4(e)].[97,99] As such, using the SNIPS process enables the fabrication of membranes with both high permeability and high selectivity. Furthermore, the versatile method makes the production of membranes for multiple applications compatible with high-throughput (i.e., roll-to-roll) manufacturing-scale processes.

The SNIPS methodology is not limited to flat sheet membranes. Developing techniques that transform block polymer membranes from two-dimensional thin film devices into more complex three-dimensional structures has the potential to extend further the potential range of applications for these next generation membranes. Of particular interest to separation scientists, is the ability to fabricate hollow fiber membranes from self-assembled block polymer materials.[106] When implemented in full-scale modules, hollow fiber membranes provide larger
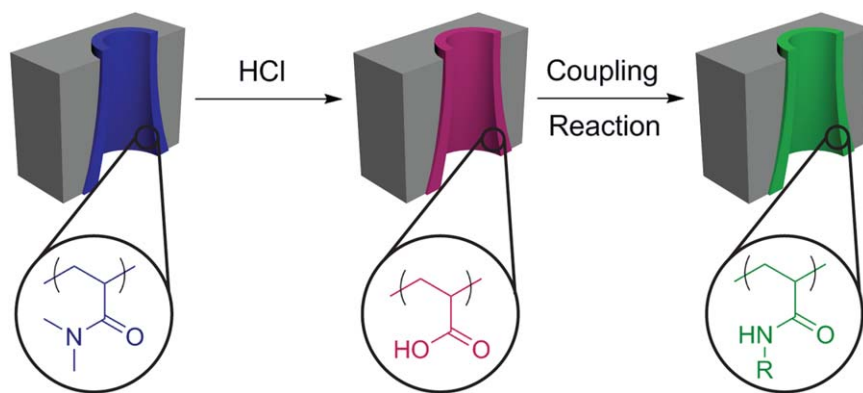
Figure 7. The versatility of modern block polymer syntheses allows for the fabrication of membranes with pore walls that can be chemically tailored to the needs of a variety of applications. In the example shown here, the hydrolysis of the PDMA moieties that line the nanopores of a self-assembled PI-PS-PDMA membrane to poly(acrylic acid) enables the functionalization of the pore functionality through straightforward coupling reactions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface areas per module volume, which results in higher productivity per module.[2,107–110] Several initial studies have demonstrated the feasibility of producing hollow fiber membranes from self-assembled block polymers. For example, the SNIPS process has recently been combined with standard wet spinning techniques to produce hollow fiber membranes that possess a selective layer with a structure directed by a PS-P4VP template (Figure 5). Using a dry-jet wet spinning process, hollow fiber membranes with pore sizes ranging from 20 to 40 nm in diameter were produced by adjusting the ratio of THF to DMF in the casting solution, polymer molecular weight, and spinning conditions. This capability is particularly exciting given the trend toward the use of hollow fiber modules for large-scale membrane separations.[106,111,112]

These types of developments in the scalable manufacturing of block polymer-based membranes will allow large areas of flat sheet or hollow fiber membranes to be fabricated reproducibly. By relying on the self-assembly of block polymer templates to direct the nanostructural and chemical features of the membranes, the ultimate properties of the membranes can be controlled precisely. Importantly, this relies on developing robust structure-property-performance relationships such that block polymer synthesis can be guided for targeted membrane performance.

Controllable Macromolecular Architectures of Block Polymers Enables the Design of Membranes with Targeted Performance Profiles

As well-documented across the polymer literature, the selection of the macromolecular architecture of the polymer template can alter many tangible properties of the ultimate device.[14,34] For example, mechanical integrity is of particular import to the operation of filtration membrane systems as the pores in these thin films reduces the mechanical toughness of the membrane relative to dense (i.e., nonporous) materials. Therefore, the use of higher molecular weight polymers as templates for nanoporous membranes is preferred due to the increased mechanical toughness imparted by the high molecular weight polymers (i.e., those beyond their entanglement molecular weight) relative to their low molecular weight analogs. However, it must be stressed that

an increase in molecular weight also necessarily increases the pore diameter of the nanoporous membrane (Figure 6).

To increase the mechanical robustness of self-assembled polymer thin films to a greater extent, many polymer chemists have combined moieties that are rubbery at room temperature (e.g., polyisoprene) with moieties that are glassy at room temperature (e.g., polystyrene), and tailored the precise composition of these two segments such that the desired self-assembled morphology is achieved.[23,25,26] For example, this strategy has been implemented for PI-PS-P4VP,[23,25] which is the triblock analog of PS-P4VP. The addition of the low glass transition temperature (T_g) PI block[113] produced membranes that were tougher than comparable membranes made from diblock templates; ultimately, this transition allowed smaller pore sizes to be realized. These two examples of block polymer design (i.e., polymer molecular weight and constituent blocks) are just two simple handles by which polymer scientists can control the nanostructural, thermal, and mechanical properties of the resulting membranes, and it is anticipated that even more unique synthetic protocols will allow this arsenal to be expand greatly in the future.

However, it must be stressed that the ability to direct the structure and properties of the nanoporous membranes is not limited to the macromolecular architecture of the block polymer template employed. This has been demonstrated for a number of systems, and is perhaps best illustrated by membranes fabricated using the SNIPS protocol. For instance, the nanostructure generated by the SNIPS process can be tuned by varying a number of engineering parameters. Included in these are: (1) the composition of the solvent and nonsolvent,[29,102,114,115] (2) the polymer concentration in solution,[24,25,80,114] (3) the polymer molecular weight,[23,114] and (4) the use of additives in the casting solution[28,104,116–119] (e.g., salts that complex with a specific moiety in the block polymer).

The composition of the casting solvent can affect the final nanostructure of membranes fabricated using the SNIPS technique greatly. As such, there are multiple requirements placed on the solvent selected for the process. In particular, when using solvent evaporation to direct self-assembly, the solvent mixture

should (1) facilitate block polymer self-assembly and alignment and (2) produce an asymmetric membrane microstructure upon evaporation.[28,99] While how the SNIPS process proceeds at the nanoscale remains an open question in the literature, there is strong experimental and theoretical evidence suggesting that the solvent mixture chosen does drive the formation of block polymer micelles in solution.[23,120] This can be accomplished by choosing solvents that dissolve one of the blocks selectively; tabulated solubility parameters have been helpful in identifying "selective" solvents.[121,122] For example, a binary mixture of tetrahydrofuran (THF) and 1,4-dioxane (DOX), which dissolve PS and P4VP preferentially, was shown to produce PI-PS-P4VP micelles packed on a BCC lattice in sufficiently concentrated casting solutions, and similar evidence exists for other self-assembled systems (e.g., PS-P4VP,[105] PS-PLA[22]) block polymer systems. To generate an asymmetric microstructure, the solvent mixture should contain a more volatile solvent that will evaporate to a greater extent than the less volatile co-solvent of the block polymer solution. The optimal solvent mixture results in a film that is dense at the film-air interface, where the polymer concentration is highest after evaporation and prior to phase inversion, and gradually decreases into a more open substructure with larger pore sizes toward the bottom.[24,99] In the case of THF $[P^{vap}(20°C) = 140$ mmHg] and DOX $[P^{vap}(20°C) = 30$ mmHg],[123] the evaporation of THF is more rapid. This rapid evaporation increases the polymer concentration at the thin film-air interface significantly, which causes the block polymer molecules to interact and induces self-assembly.[80,103] Furthermore, there is some experimental evidence to suggest that the rapid evaporation also helps to orient the permeable domains of the block polymer perpendicular to the surface of the film.[80]

Additionally, in SNIPS processing, the selection of the solution to be used as the nonsolvent quenching bath is important to the membrane fabrication process.[115] The liquid used must be miscible with the solvent,[29,99,115] and the exchange of solvent and nonsolvent must occur rapidly in order to produce a highly porous gutter/support layer.[124] The rate of solvent-nonsolvent exchange directly influences the size of the voids formed in the lower portion of the membrane, while the self-assembled portion of the film precipitates almost immediately upon immersion in the nonsolvent.[102,103,115] This almost instantaneous precipitation kinetically traps the nonequilibrium membrane nanostructure with a high density of accessible pores on the top surface. The graded pore structure that results from this process can be idealized as two resistances in series. To maximize the permeability of the composite, the selective layer should be as thin as possible and the gutter layer should be as porous as possible, while still providing adequate support to the selective layer. The solvent composition, length of the evaporation period, and the composition of the nonsolvent bath are three design parameters that can be modified to tailor the nanostructure of the composite for optimal membrane performance.[24,29,115] Therefore, polymer scientists and engineers have multiple handles they can use to tune the final nanostructures of membranes fabricated by the SNIPS process. However, it should be stressed that the exact impact of each one of these engineering handles has on how the SNIPS process proceeds at
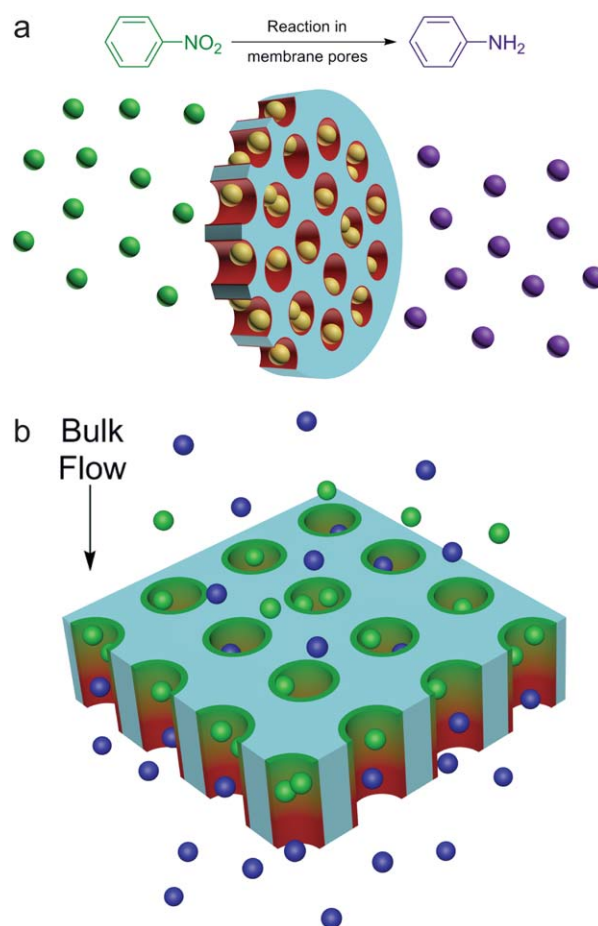
Figure 8. (a) Reactive membranes can be used to chemically convert dissolved molecules as they flow through the pores of the membrane. In this example, nitrophenol is converted to aminophenol by gold nanoparticles tethered to the pore walls. The chemically tailored pore walls of self-assembled block polymer membranes will allow a large number of reactive moieties to be implemented within the pores, while the tunable nanostructure is able to provide a large surface area and uniform flow in each pore. (b) By tuning the chemical functionality of the pore walls, membrane adsorbers that bind molecules selectively while allowing others to pass through can be generated. These membrane adsorbers reduce the mass transfer limitations associated with standard chromatography and adsorption columns packed with selective resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the nanoscale is not well known currently. Therefore, optimization of the SNIPS casting procedure often is based on chemical intuition, and as such, performed in a rather Edisonian manner for current state-of-the-art devices. Future work on developing proper structure-property-performance relationships to elucidate how all of these myriad parameters in the macromolecular design and SNIPS casting process affect the structure formation pathway and the final nanostructure of the membrane is of the utmost import.

The Synthetic Flexibility of Block Polymers Enables the Design of Membranes with Tailored Pore Functionalities

The recent advances in the synthesis of block polymers and the fabrication of membranes from these novel macromolecules

have propelled this emerging membrane platform forward in the past decade.[13,14,31,34,125] While significant work remains to be done to elucidate fully the structure-property-performance relationships for membrane derived from block polymer templates, early efforts in this field demonstrate clearly that the synthetic flexibility provided by block polymers allows for the systematic tuning of membrane nanostructures through the controlled synthesis of the macromolecular template.[82,126] In addition to this work that demonstrates the ability to control structure, recent efforts have demonstrated that the pore functionality of membranes generated from block polymer templates can be tailored to meet the specific needs of a multitude of applications.[82,97,127,128] Recently, a binary mixture of polystyrene-*b*-poly(4-vinyl pyridine) and poly(ethylene glycol)-*b*-poly(4-hydroxystyrene) was utilized to form nanoporous membranes that could be modified to form cationic polyelectrolytes. Negatively charged gold nanoparticles were then successfully introduced to these positively charged pore walls, providing a functionalized membrane for applications such as catalytic reactions and opening the door for chemically defined nanochannels with a high density of reactive sites.[128] Researchers also have successfully deprotected poly(methyl methacrylate-*r*-trimethylsilyl)prop-2-ynyl methacrylate)-*b*-poly(4-bromostyrene) (P(MMA-*r*-TMSPYMA)-PBrS) block polymers to form poly(methyl methacrylate-*r*-propargyl methacrylate)-*b*-poly(4-bromostyrene) (P(MMA-*r*-PgMA)-PBrS) prior to solvent annealing without sacrificing the block polymer's capacity to self-assemble into cylindrical domains. This process resulted in thin films with an alkyne-functionalized pore wall that can be further modified by alkyne/azide click chemistry for applications such as biosensing and cell-adhesion controlling.[129] Another example of this transformative capability is detailed in a report regarding the fabrication of membranes from a poly(isoprene-*b*-styrene-*b*-N,N-dimethylacrylamide) (PI-PS-PDMA) triblock polymer. The *N,N*-dimethylacrylamide moiety of the PI-PS-PDMA block polymer can be functionalized selectively to produce pores lines by an acrylic acid moiety.[97] Subsequently, the acrylic acid moiety can then be functionalized with simple coupling chemistry (Figure 7) to produce a membrane with functionality tailored to the needs of a given process. It is anticipated that this capability will be of utility to researchers who are developing membrane devices for a variety of biological and environmental applications.

APPLICATION OF NANOPOROUS BLOCK POLYMER MEMBRANES IN BIOLOGICAL PROCESSES

Pharmaceutical Separations

Block polymer membranes provide the possibility of highly selective separations based on size-selective and/or chemically-selective mechanisms. This capability is of particular interest to those in the field of biotechnology due to the stringent regulations surrounding the purity of modern therapeutics.[130] For example, viral contamination can result in a whole bioprocess being taken offline for cleaning, a procedure which can take months to complete. Therefore, the separation of microorganisms and viruses from fermentation titers is a key step in the production of modern biopharmaceuticals.[12,131] Membrane separations are already making inroads into this application, as witnessed by the increasing number of companies using this technology for viral clear-

ance.[12] A final purity of less than one retrovirus per million doses is targeted for most biotherapeutics. Therefore, the membranes utilized in these processes are often required to withstand high pressures, be resistant to organic solvents, operate at elevated temperatures, and perform well in highly acidic or basic conditions.[132] Furthermore, it is beneficial if these membranes can resist the nonspecific adsorption of the dissolved solutes in the process streams.[133,134] Block polymer membranes can provide all of these properties through the selection of appropriate chemical composition and post-synthesis treatments. In one example, researchers fabricated ultraviolet light-crosslinked (UV-crosslinked) polystyrene-*b*-poly(methyl methacrylate) (PS-PMMA) membranes that could withstand pressures up to 2 bar and many organic solvents while maintaining high selectivity for human rhinovirus type 14.[132] The selectivity of these membranes was comparable to that of polycarbonate track-etched membranes but the throughput was notably higher.[135,136] These attractive qualities can be attributed directly to the well-defined nanostructure of block polymer membranes as well as the mechanical and chemical stability afforded by crosslinking the material.

In addition to viral clearance, biopharmaceutical separations require the isolation of the active pharmaceutical element. For example, recombinant proteins are in high demand, but in order for these proteins to benefit patients in clinical settings a fast and efficient separation process is required to produce them in an economical manner.[130] Current processes typically use an affinity-based purification that relies on packed columns filled with selective, but costly, resins.[137] Unfortunately, this method requires large pressure drops, and is hindered by mass transfer limitations and relatively low binding capacities.[11] Therefore many efforts are being conducted to develop membrane separations capable of isolating therapeutic proteins.[130,138–140] The high density of pores with well-defined diameters between 3 and 70 nm[97,114] and tailored surface chemistries of block polymer membranes make them a strong candidate for application in this important separation. Recently, block polymer membranes fabricated via SNIPS casting of PS-P4VP were utilized in the separation of two similarly sized proteins.[139,140] By quaternizing the P4VP moiety of the block polymer membrane, it was possible to impart positive charge to the pore walls. This charge made it possible to separate two biomacromolecules of very similar sizes. That is, bovine serum albumin (BSA) was separated successfully from bovine hemoglobin based on electrostatic interactions between the membrane and proteins because of the chemistry of the block polymer membrane.[139,140]

The ability to tailor the chemical functionality of recently reported block polymer membranes should allow the interactions between membrane and solute to be extended from nonselective electrostatic interactions to more selective interactions (e.g., chelating or complexation). This would make membranes derived from self-assembled block polymers ideal platforms for the development of membrane adsorbers. These membrane-based adsorbers would provide improved capacity for protein binding, faster separations, and minimized nonspecific binding while requiring lower pressure drops.[141] And while no reports

on the use of self-assembled block polymer membranes to fabricate membrane adsorbers exist in the literature currently, several works demonstrate the promise of membrane adsorbers by modifying commercially available membranes.[141–143]

For instance, membrane adsorbers that bind proteins selectively have been designed using polymeric membranes functionalized with a variety of moieties (Figure 8).[141,142,144] Yang and Ulbricht designed a stimuli-responsive ion-exchange membrane adsorber consisting of zwitterionic polymer brushes for which chain stretching can be optimized for protein-binding through the addition of an intermediate concentration salt solution.[141] These membranes, as well as those designed by Bruening et al. using Cu^{2+} coordination, are able to be flushed of proteins and, in the case of copper, regenerated, without loss of their high binding capacity.[141,143] Membrane adsorbers have been designed using a combination of layers[145] and post-synthesis modification[138,142,145] to create polymer chains that recognize the target molecule through coordination[143] or charge-exchange.[142] On the other hand, and despite promising initial results demonstrating proof of the concept, membrane adsorbers based on track-etched membranes as the separation platform demonstrate relatively low binding capacities. Conversely, the distribution of pores sizes characteristic of phase inversion membranes increases dispersion greatly,[146] which limits the overall efficacy of adsorbers built from these membranes. In this way, the well-defined nanostructure of block polymer membranes should be able to address these materials challenges that hinder commercially available membranes by providing high binding capacity due to the high density of pores with minimal dispersion due to the single, well-defined pore size afforded by these materials.

The advantages that block polymer membranes present for the fabrication of membrane adsorbers also can be utilized in the development of membrane reactors. For example, researchers have designed reactors for protein digestion via protease-modified membranes.[147,148] In these, the facile control of the residence time of the protein within the pores of the membrane (i.e., through changes in membrane thickness or feed solution flow rate) allows for control over the size of the resulting peptide.[148] Membranes have also been implemented to enrich phosphopeptides, which can be used to induce immune responses.[149] In both cases, functionalized block polymer membranes would be capable of preventing proteins from passing through undigested, yielding a pure product without unreacted molecules.

Controlled Release of Therapeutic Drugs

In addition to being used to separate and purify biopharmaceuticals, functional block polymer membranes can function as a delivery vessel for the controlled release of therapeutic drugs.[150,151] For example, recent studies describe the development of nanoporous block polymer membranes that result in the single-file diffusion of therapeutic molecules. This novel transport mechanism, which relied on the tunable nanostructure of block polymer membranes, was shown to provide continuous controlled release[152] over a period as long as two months without denaturation of the delivered proteins.[153] Furthermore, researchers have shown that anodic aluminum oxide nanoporous

devices can deliver drugs on-demand through pulsatile changes in pore size through electrical stimulation.[154] In this way, the pores could be opened for a predetermined length of time due to an external electrical signal to allow the appropriate amount of the drug to diffuse through the membrane before swiftly returning to the "closed" pore size when the signal is removed.

Many of the recent studies regarding block polymer membranes as controlled release devices revolve around stimuli-responsive polymers because the tunable functionalities of block polymers allow for easy tailoring of the pore walls in order to respond to different external stimuli. Block polymer membranes have been tailored to respond to pH[155,156] and thermal stimuli,[127,157] making them a promising, affordable, and scalable route for improved drug delivery. For instance, using other block polymer assemblies, microspheres,[151,155,158] and micelles[156,157] can be used for stimuli-responsive, targeted drug release. Thermally responsive micelles have proven stable for over 72 h and are able to target release to sites with elevated local temperatures.[159] pH-responsive micelles have been developed for intracellular delivery of hydrophobic drugs,[156] and pH-responsive microspheres offer gated pores for drug release with high internal porosity lending itself to high sorption and sustained release behavior.[155]

Biomedical Engineering Devices

Block polymer-based membranes can be implemented in a number of other devices that are relevant to biological applications.[136,158] For example, block polymers have been used to develop biosensors[159,161] and protective coverings.[160] Both implantable, autonomous biosensors and long-term protective coverings must be biocompatible, antifouling, chemically resistant, flexible, and tough, which are all properties that can be achieved with block polymers.[162] In fact, it has been demonstrated that mechanically robust nanoporous membranes based on a polyethylene-b-polystyrene template possess monodisperse pores that allow for the diffusion of glucose while fully blocking BSA.[159] With further development, these membranes could be applied as glucose monitors for diabetes patients, using electrochemical detection of the membrane potential to determine glucose levels.[159] Additionally, devices capable of high resolution single nucleotide polymorphism (SNP) detection have been fabricated using functionalized membranes derived from a PS-PMMA block polymer. Unlike other SNP detection devices, the device based on block polymer membranes could operate without an external electrical or chemical signal.[163] In another example of a promising application for block polymer membranes, a modified polystyrene-b-polybutadiene-b-polystyrene (PS-PB-PS) ionomer was used to produce a membrane that has demonstrated potential as a dressing for wounds. It showed high water vapor permeability, bactericidal activity, and cell viability while preventing fibronectin adsorption, all of which will expedite healing while minimizing the risk of infection.[160] Utilizing the myriad capabilities possessed by block polymers, such as a variety of available structures via self-assembly, chemical tunability, mechanical and chemical stability, stimuli-responsivity, and antifouling properties, these materials provide endless possibilities for use in biological applications.

POTENTIAL USES OF NANOPOROUS BLOCK POLYMER MEMBRANES IN ENVIRONMENTAL APPLICATIONS

Providing contaminant-free water is of critical import for many residential, commercial, and industrial applications, and porous filtration membranes play a major role in meeting the ever-increasing demand for water.[3,6,9,161] Filtration membranes are used in the pretreatment of seawater prior to desalination by reverse osmosis as well as to ensure viral clearance from municipal water supplies.[8,161] They also are used in membrane bioreactors, which are increasingly popular wastewater treatment processes.[6] The application of membrane devices in a large number of water treatment processes suggests strong opportunities for block polymer membranes to make a positive impact on these applications.

In the simplest example, the nanostructured membranes designed to possess high permeability values and a uniform pore sizes provide an excellent platform by which to perform size selective filtration. The range of pore sizes that are accessible to self-assembled block polymer membranes can be leveraged to filter solutes over a wide span of sizes selectively. For example, a recent effort has demonstrated that particles as small as 2.6 nm in diameter can be removed effectively by these devices.[97] On the other side of the spectrum, pores sizes as large as 70 nm have been reported.[114] With access to this range of pore sizes, block polymer membranes can be tailored to remove small solutes of concern, such as divalent ions, as well large solutes, such as semiconductor nanoparticles. In addition to the advantages provided by the self-assembled selective layer, the ability to modify the porosity of the phase inverted support layer enables the fabrication of more permeable membranes, which can help improve energy efficiency and process throughput. For example, the co-assembly of a PS-P4VP block polymer with TiO_2 nanoparticles produces modified finger-like supporting layer with enhanced membrane permeability.[28] In fact, this membrane exceeded the upper bound for traditional UF membranes, and there is still a great deal of phase space remaining by which to improve the performance of UF membranes before reaching the ultimate limit of the membrane separation. By tuning parameters from the block polymer membrane fabrication process, there are numerous possibilities waiting to be discovered towards making a better self-assembled block polymer UF membrane.

In addition to the improved size-selectivity and membrane throughput provided by block polymer membranes, the ability to tailor the surface chemistry of block polymer membranes also is of great utility for a number of environmentally relevant applications.[3,6,9] Ensuring complete removal of some dilute contaminants requires that they be degraded into benign products. Nanoporous membrane reactors [Figure 8(a)] are one advanced reactor design where the well-defined nanostructure and tailored pore chemistry of block polymer membranes could provide advantages over the current state-of-the-art.[6] When nanoporous membranes are compared with other catalyst supports (e.g., porous particles) the overall reaction efficiency of the membrane reactor is higher, because the reaction rate is not hindered by mass transfer limitations such as bulk-to-core diffusion.[164,165] In one important demonstration of this principle, modified nanoporous alumina membranes were used as a platform for the development of a membrane reactor that reduced 4-nitrophenol to 4-aminophenol. A stable value of nearly 100% conversion was observed even after a feed volume equivalent to 140,000 membrane volumes was processed.[165] The high porosity and uniform pore size of nanoporous alumina membranes result in high surface area to volume ratio, high values for the hydraulic permeability, and constant contact times for flow through each individual pores, all of which contribute to the high conversion at high throughput. However, anodized alumina membranes are exceedingly brittle and costly. Block polymer based membrane reactors possess the same nanostructural advantages as the alumina membranes, but take advantage of the better mechanical integrity and lower costs of polymeric systems.[9] Specifically, a recent demonstration of a block polymer-based reactor used gold nanoparticles deposited in the active layer of a PS-P4VP hollow fiber membrane to reduce 4-nitrophenol to 4-aminophenol. With an effective area 2.16 cm^2, the system was capable of reducing the 4-nitrophenol concentration from 0.1 to 0.023 mM.[106] This, in turn, highlights the potential of future nanoporous membrane reactors, which could be used to remove harmful contaminants selectively. The membrane reactor provides an effective pathway for degrading environmental contaminants into benign products,[166–168] which provides a solution to issues associated with disposing of a concentrated stream of the contaminants.

In addition to being used to purify water, self-assembled block polymer membranes may also serve as real–time, on-site sensors for the monitoring and quantification of harmful contaminants (e.g., heavy metal ions).[6] For instance, researchers have immobilized a Pb(II)-specific DNAzyme on an gold-coated polycarbonate track etched membrane to build a heavy metal biosensor. Once Pb(II) is present in the water stream, it reacts with DNAzyme and releases the cleavable substrate strand, which contains a fluorophore that is detected through optical means.[169] While the fundamental sensing and reporting of this work is exquisite, the higher surface area to volume ratio afforded by block polymer-based membranes may further improve the lower detection limit that is achievable using membrane sensors. Furthermore, the chemical functionality of the block polymer-based membrane could be tuned to offer stimuli-responsive properties in a manner that would allow for the nanoporous channels to open or close depending on the absence of presence of trace materials. Initial evidence for this type of response in block polymer-based membranes has been demonstrated previously, and key instances are pH or temperature responsiveness of polymer chemistry that alter the interior lining of the membrane pore walls.[25,97,106,117,127,170] Extension of this phenomenon beyond this initial, relatively straightforward example, would allow for a powerful tool capable of providing an important responsive diagnostic system to a host of application communities.

NANOPOROUS BLOCK POLYMER MEMBRANES WITH REDUCED FOULING PROPENSITIES

Fouling (i.e., the nonspecific deposition and adhesion of dissolved solutes on a surface) is a ubiquitous challenge in membrane processes, and its causes and effects are detailed at length in several review articles.[171–179] In filtration separations, it reduces throughput and increases the energy demands associated with the

membrane process.[134] In controlled release and sensing applications it compromises reliability.[180] Despite its well-documented effects and extensive research into mitigation strategies, universal solutions to this large challenge are slow to come. In fact, there is currently no membrane that can resist fouling completely.[172] Instead, the surface chemistry of each membrane must be tailored to resist fouling from the specific feed stream that the membrane will encounter.[171–173,175,179,181–185] This complexity is highlighted by studies demonstrating that a moiety that reduces fouling propensity for one feed stream can exacerbate fouling for another.[173,183–185] However, the ability to tailor the chemistry of block polymer membranes to the needs of each specific feed stream could help to address this important challenge. For instance, the chemical modification of a block polymer to create a membrane with targeted amphiphilic nanoscale domains is one well-discussed strategy for designing fouling resistant membranes.[133,186] In one example, chemical functionalization of the 4-vinyl pyridine moiety of a poly(styrene-b-4-vinylpyridine) block polymer by mixing with 2-(4-hydroxy-benzeneazo) benzoic acid results in the formation of a supramolecular complex, which is then fabricated into membrane. This nanostructured material is subsequently treated to quaternize the functional groups lining the surface of the pore walls. The resulting membrane shows very low albumin bovine adsorption capacity, which indicates good anti-fouling properties for biochemical separations.[187] The versatile and tunable chemistry structures of emerging block polymer systems affords membranes derived from these materials the capacity to be fabricated and functionalized with specifically designed moieties membrane when needed.

SUMMARY AND FUTURE OUTLOOK

Block polymers have provided a key area of thinking with respect to the design of next-generation materials in the membrane community, and the future of these materials will remain bright for many years to come. These future successes will be built from the initial efforts in the field that relied solely on the thermodynamically driven self-assembly of block polymers with chemically distinct segments and the subsequent removal of one of these moieties. In this manner, which is akin to the wealth of work regarding block polymers for nanolithographic applications,[13,188–191] these pioneering works established the ability of membranes based on block polymer templates to provide highly selective separations. However, the inability to reproducibly generate large membrane areas with well-aligned pores in a low-cost and high-throughput manner stymied implementation of these materials at the industrial scale. In order to address this critical issue, the community recently has turned to the SNIPS membrane fabrication process in order reap the benefits associated with both block polymer self-assembly and traditional membrane fabrication processes. In this way, asymmetric membranes with highly selective nanoporous layers that quickly taper into high-flux microporous layers are formed from a single material. Furthermore, this processing technique is compatible with existing roll-to-roll membrane manufacturing techniques. As such, a clear pathway for technology transfer to society is present.

Despite the initial successes of block polymer-based membranes, many fundamental scientific questions still exist for block polymer-based membranes, and these challenges present themselves as excellent opportunities for creating the next archetype of membranes. Fortunately, many of these questions can be addressed in a systematic manner due to the synthetic flexibility associated with block polymers. That is, by generating macromolecules with distinct and tailor-made chemical moieties, researchers will be able to isolate exquisitely the mechanism behind some of the most pressing challenges of membranes today. For instance, elucidating fully the structure-property-performance relationships of the SNIPS casting process through tailored macromolecular design is of critical import. Only with complete control of these key parameters will large-scale nanomanufacturing be guided by more than just Edisonian design of experiments. Addressing this large challenge will require the synergistic efforts of polymer chemists and physicists, rheologists, and membrane scientists. Additionally, the exciting research regarding block polymers for antifouling or self-cleaning membranes through the use of mixed hydrophobicity or zwitterionic block polymer segments should be expanded upon as these materials could aid in overcoming one of the largest challenges facing membrane separations currently. Finally, the next-generation applications of block polymer-based membrane devices (e.g., nanoscale reactors, biocompatible systems) promise to provide the new archetypes that will allow nanostructured polymer membranes to go beyond size-selective separations and step into the realm of simultaneous synthesis and purification of tailored materials.

For these paradigm-altering motifs to be realized, we envision a future where the fundamental science of membrane technologies must be necessarily intertwined with the needs of these devices at the industrial scale. Through proper collaboration between membrane-based scientific disciplines (e.g., polymer science, chemical engineering, materials engineering, and environmental engineering) and sectors (i.e., academia, national laboratories, start-up companies, and established industrial entities) these opportunities will be addressed such that true technological impact is had. Therefore, this is an exciting time for block polymer-based membranes, and the originality and resourcefulness of the scientists and engineers that compose this community will allow these functional macromolecules to go quickly and with great strides both in the laboratory and in the marketplace.

AUTHOR CONTRIBUTIONS

CONFLICT OF INTEREST

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