REVIEW ARTICLE

TECHNOLOGY

Responsive filtration membranes by polymer self-assembly

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Membrane technologies are essential for water treatment, bioprocessing and chemical manufacturing. Stimuli-responsive membranes respond to changes in feed conditions (e.g., temperature, pH) or external stimuli (e.g., magnetic field, light) with a change in performance parameters (permeability, selectivity). This enables new functionalities such as tunable performance, self-cleaning and smart-valve behavior. Polymer self-assembly is a crucial tool for manufacturing such membranes using scalable methods, enabling easier commercialization. This review surveys approaches to impart stimuli responsive behavior to membrane filters using polymer self-assembly.

***Keywords*: Membrane; Stimuli Responsive; Polymer; Self-assembly; Scalable Manufacturing; Nanostructure; Surface Chemistry; Fouling; Filtration; Ultrafiltration; Microfiltration; Water Treatment.**

INTRODUCTION

Membrane technology is crucial for many separation processes including water treatment, bioseparations, and food and beverage processing[1–3]. Membranes are widely used in seawater and brackish water desalination, generating drinking water by removing microorganisms, and treating wastewater to remove a wide range of contaminants. They also constitute an established unit operation in the manufacture of biopharmaceuticals, where they are used for the purification and concentration of protein drugs. They have many other applications, from the food and beverage industry to chemical manufacturing and to medical and research uses.

Membrane separations are energy efficient and do not require the use of added solvents. This makes membranes a green alternative to separation methods such as distillation, extraction and chromatography. Membranes are also highly modular and scalable. They can be operated in simple, low foot-print, portable systems. Driven by this promise, developing membranes with new and improved functionalities to expand their uses is an active research area.

This is, of course, only possible if membranes are capable of accomplishing the separation task in question. Most of the established applications of membranes rely on their ability to separate solutes and particles by size (e.g., removing microorganisms and viruses from water, separating proteins and salts). This means they cannot be used if the components to be separated are of similar size. Thus, for successful use in a given application, membranes should have the desired selectivity. This is typically defined by the effective pore size and pore size distribution of the membrane filter.

Another significant challenge is membrane fouling, which is defined by a loss in membrane performance due to the adsorption and deposition of feed components. Fouling leads to a drastic decline in the flow rate through the membrane, or membrane permeability, as pores clog. Up to 90% loss in permeability within hours is not unusual for feeds with high biomolecule content, such as protein solutions or wastewater. During operation, membranes are regularly cleaned by physical and chemical methods to at least partially sustain the flow rate. This leads to downtime, chemical costs, and more complicated module designs. Fouling can be a severe impediment to energy-efficient and reliable operation of membrane systems, and extensive academic and industrial research focuses on preventing and remedying fouling[1–3].

Stimuli-responsive membranes respond to changes in feed conditions (e.g., temperature, pH, ionic strength, presence of specific analytes) or external fields or stimuli (e.g., electric or magnetic fields, light exposure) and exhibit a change in performance parameters such as permeability and/or selectivity[4]. Such membranes can act as smart valves that increase or constrict flow without the need for external control, enabling the user to control and tune parameters such as pore size to suit the specific application it is used for. This capability may enable automated regulation of specific compounds or reactants upstream from the membrane without external intervention. This can be of great use in water and wastewater treatment or biomanufacturing. In addition, changes may be used in controlling the binding and release of a target compound, opening up opportunities for the design of membrane adsorbers, most commonly used in removing trace compounds for water treatment and for the downstream processing of biopharmaceuticals. Responsive surfaces that can switch between a hydrophobic and hydrophilic state can inflict a mechanical push on the pre-adsorbed proteins or other unwanted foulants, stimulating self-cleaning. This may be of great value

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in membrane operations where feeds have a high fouling potential such as domestic and industrial wastewater treatment, bioprocessing and food and dairy industries.

Membrane preparation using stimuli-responsive polymers, copolymers and polymer-additive mixtures is an attractive approach in developing responsive membranes. The conformation/polarity/reactivity of responsive polymers or functional groups integrated in the pore structure changes in response to the stimuli they are designed for, enabling their use in systems or devices that require switchable on-demand material properties. Based on the particular behavior and application, polymers can be custom-designed to respond to different external stimuli such as temperature[5], pH, magnetic or electric fields[6], ionic strength, added saccharides[7,8], antigen binding[9] or light[10,11]. Furthermore, membranes that respond to multiple types of stimuli can be developed by incorporation of different stimuli-responsive functionalities in the polymer, e.g., to respond to both pH and temperature[12].

Responsive behavior can be imparted to filtration membranes following different routes such as grafting responsive polymer layers from the external surface of a pre-existent membrane, or from the pore walls[4]. In response to changes in the environment, these functional polymers alter their chain conformation, which results in modified permeability and selectivity of the membranes. Grafting methods include photo-initiated grafting (UV and non-UV), redox-initiated grafting, plasma-initiated grafting, thermal grafting and controlled radical grafting methods such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. Other methods to develop responsive membranes include integrating stimuli-responsive groups in the bulk of the membrane material or applying the responsive polymer as a physical coating onto a macroporous base membrane[4,13]. In these systems, changes in membrane permeability and selectivity are driven by the changes in degree of swelling of the membrane barrier, again arising from the conformational changes. This can also be achieved by surface-initiated polymerization.

In contrast to these methods, polymer self-assembly can lead to membranes with exceptional performance and added functionality without the need for added processing steps, often through processes that can directly be plugged into existing manufacturing methods[14]. With well-designed polymers, interesting and functional nanoscale structures can be achieved spontaneously, and surface chemistry of various materials can be controlled to impart desired function. Technologies that utilize self-assembly thus face fewer barriers to scale-up and translation into real products.

There are several comprehensive reviews in the literature that elaborate on stimuli-responsive membranes[4,15–17]. This review focuses on the use of polymer self-assembly, and hence will specifically describe instances of self-assembling polymers to impart responsive behavior to selective membranes. We first give a short introduction on how membranes are made and comment on different approaches for incorporating responsive self-assembling polymers into scalable membrane manufacture. Then, we describe specific examples of these approaches, classified by the main stimulus the membranes respond to. Finally, we end with an outline of unresolved questions and a future outlook.

INTEGRATING POLYMER SELF-ASSEMBLY INTO MEMBRANE MANUFACTURE FOR STIMULI RESPONSIVE MEMBRANES

State-of-the-art in membrane manufacture

Membranes on the market today are typically classified according to their pore size[2,3]. Microfiltration (MF) membranes have pore sizes between 0.1 and 10 μm and are typically used for removing bacteria and particulates. The pores of ultrafiltration (UF) membranes are 2–100 nm in diameter, although the effective pore size commonly is reported in terms of molecular weight cut-off (MWCO), described as the molecular weight of components retained by 90%. They are capable of retaining viruses, macromolecules and emulsified oils. MF and UF membranes are porous materials, and operate based on a pore flow mechanism that sieves solutes or particles larger than the pore size. Nanofiltration (NF) and reverse osmosis (RO) membranes are designed to retain salts and small molecules. NF membranes retain doubly charged salts and are used in water softening. RO membranes are used for desalination. Both of these membranes typically have a thin film composite (TFC) morphology, where a very thin (~100 nm), selective polymer layer is deposited onto a porous support, typically an MF or UF membrane.

The most common manufacturing method for porous membranes for MF and UF is non-solvent induced phase separation (NIPS). A polymer solution is cast on a solid substrate or support fabric, and then immersed in a coagulation bath filled with a non-solvent or a mixture of non-solvents. The non-solvent in the coagulation bath diffuses into the polymeric solution and the solvent in polymeric solution diffuses into the non-solvent bath. The polymer precipitates on the substrate, forming a polymer-rich and polymer-poor phase. These two phases form the solid membrane matrix and the membrane pores, respectively[2,3].

Most RO and NF membranes today are TFC membranes with cross-linked polyamide selective layers, prepared by interfacial polymerization on the surface of the porous support. TFC membranes for these and other applications can also be prepared by coating the porous support in a roll-to-roll system using well-established technologies such as doctor blading, dip coating and spray coating. These coating methods are also applied on other membranes to prepare fouling resistant coatings and to seal defects[3].

New technologies to prepare responsive membranes should, if possible, be amenable to easily integrating into these well-established manufacturing processes (i.e., NIPS for MF and UF membranes, coating or interfacial polymerization for smaller pore sizes). This is one of the great strengths of polymer self-assembly for developing new membranes: most approaches described here are compatible with either the NIPS process or only require coating a porous support with the desired polymer. Polymer chemistry and physics then act in parallel to impart the desired functionality into the membrane, without additional human intervention. This improves the translational potential of these technologies into commercial products. In addition to imparting responsive behavior, the described self-assembly methods can offer benefits of improved size-based selectivity, better productivity, longevity and fouling resistance. Thus, polymer self-assembly is a potent approach for designing new and better membranes[14].

Copolymer microphase separation and formation of nanostructures

Polymers are a very interesting class of materials due to the large number of degrees of freedom in their design. The properties of polymers are affected not only by their chemical structure, but also with the shape, or architecture of the molecules. Copolymers, which contain more than one kind of repeating unit, form various nano- and microstructures with little or no intervention through self-assembly. The resultant structures cover a wide range of characteristic sizes, from less than a nanometer to microns. They can be of many shapes, regular or irregular, discrete or continuous, aligned or random, etc.

One significant approach to using polymer self-assembly in membrane technologies utilizes these nanoscale features as the pores of the membrane. The majority of work to date on copolymer self-assembly has focused on block copolymers (BCPs). Block copolymers show microphase separation with complex and periodic geometry, affording substantial engineering opportunities at the nanoscale[18]. Immiscible blocks of block copolymers microphase-separate into domains which typically feature an equilibrium domain size of 3–100 nm. The equilibrium domain size and structure geometry are a function of the Flory–Huggins interaction parameter between blocks and the degree of polymerization. Self-assembly of diblock copolymers may lead to spheres, lamellae, cylinders, and complex bicontinuous nanostructures (**Fig. 1**)[19]. Triblock copolymer

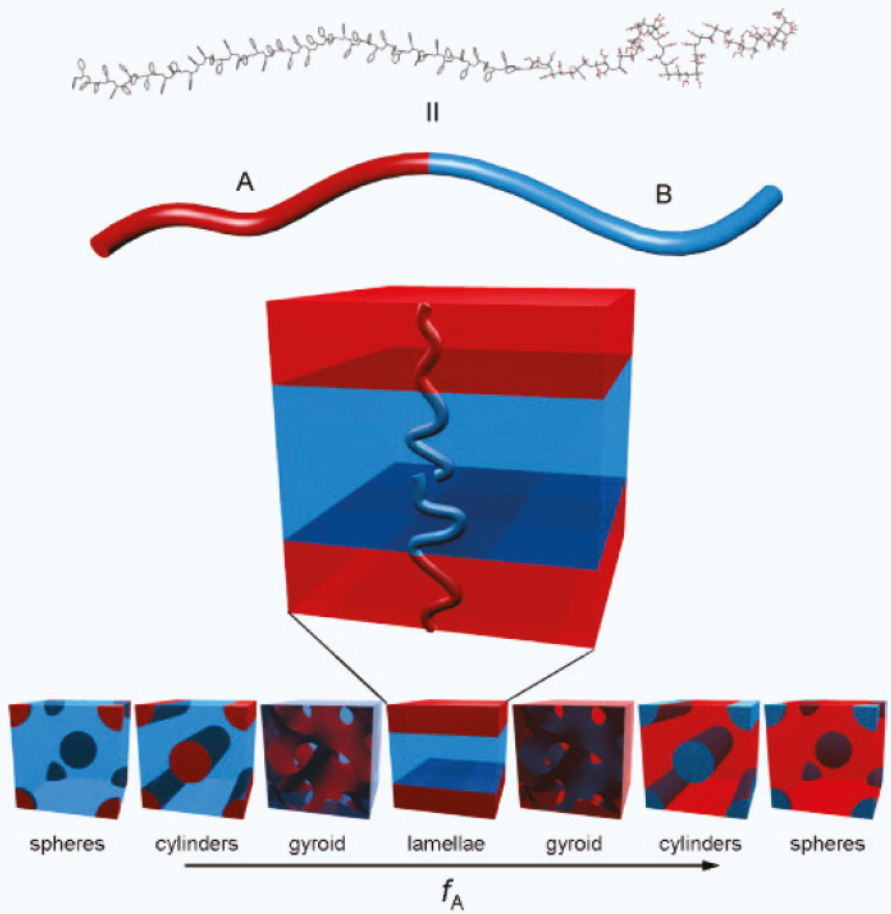

Figure 1 Schematic of thermodynamically stable diblock copolymer phases. The A-B diblock copolymer, such as the PS-b-PMMA molecule represented at the top, is depicted as a simple two-color chain for simplicity. The chains self-organize such that contact between the immiscible blocks is minimized, with the structure determined primarily by the relative lengths of the two polymer blocks (f_A). Reprinted with permission from [19], Darling, S. Directing the self-assembly of block copolymers. *Progr. Polym. Sci.* **32**, 1152–1204 (2007). © 2007, Elsevier.

assembly may result in even more complicated structures[20]. Among these, the cylinder and gyroid phases have found promising use in membrane science, enabling high porosity nanoporous membranes with narrow pore size distributions essentially by controlling the copolymer architecture. These membranes are inherently stable in terms of thermodynamics, chemical and mechanical resistance because the physically phase-separated polymeric blocks are covalently bonded at a molecular level.

Cylindrical microphases are especially interesting for membrane applications, because they make perfect pores with minimum tortuosity, and hence highest flux. But cylindrical microphases must be aligned perpendicular to the membrane surface and percolate continuously through the whole membrane cross-section (<1 μm for coatings, >10 μm for free-standing membranes to impart mechanical integrity) using specific and tightly-controlled processing conditions to provide high permeability[21–23]. Alternatively, the gyroid phase is bicontinuous (i.e., both domains create networks) and hence does not require any alignment, but is only stable in a very narrow region of the phase diagram[24]. Copolymers with designed monomer sequences can access a broader set of conditions where these bicontinuous microphases can be accessed, but the careful control of polymer synthesis conditions can add to manufacturing costs[25,26].

While several groups have shown that block copolymer self-assembly to create cylindrical or gyroid phases leads to thin polymer films capable of operating as membranes with high selectivity and monodisperse pores, it was a challenge to incorporate this into scalable roll-to-roll manufacturing methods. In 2007, Peinemann *et al.* reported the first membranes manufactured by NIPS whose pore structure is driven by block copolymer self-assembly[27]. They used the diblock polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) as the self-assembling block copolymer. For membrane preparation, they used a mixture of two solvents, volatile tetrahydrofuran (THF) and less volatile dimethyl formamide (DMF), to allow for assembly of the microphase-separated morphology during the NIPS process. In this dual solvent system, THF evaporates rapidly after casting, enabling polymer congregation on the membrane surface. Water is used as non-solvent. This approach is known as self-assembly and non-solvent induced phase inversion (SNIPS) because phase changes are induced by both self-assembly and the non-solvent immersion. **Figure 2** shows the SNIPS procedure for PS-*b*-P4VP membrane manufacture and FESEM surface images of the membranes manufactured from ternary solutions of different concentrations[28]. The product membrane features a thin layer (~200 nm) of precisely oriented cylindrical pores on top of a very porous support layer. This morphology allows the cylindrical domains to persist through a much thinner selective layer while maintaining the exceptional selectivity and surface porosity obtained by this self-assembled morphology. The highly porous support layer also enables higher flux. The effective pore size of the membrane is 8 nm, potentially due to swelling of P4VP in water and partial blockage of the pores. Since this report, membranes with improved mechanical properties have been prepared utilizing SNIPS[29]. SNIPS membranes promise very high permeability[30,31] and efficient protein separation[31,32]. The pore size can be adjusted by controlling the molecular weights of the two blocks, or by using additives in the solvent system[32–34]. The process has already been implemented in roll-to-roll systems[32,33] and hollow fiber geometries[35,36]. Catalytic gold nanoparticles can be integrated into these membranes to impart reactivity (e.g., reduction of toxic 4-nitrophenol to 4-aminophenol) in addition to separation application[36]. With the right choice of self-assembling block copolymer, SNIPS can also be used to manufacture membranes with different properties as in responsive or fouling resistant membranes[37–40]. These responsive membranes will be discussed further below.

Block copolymer self-assembly is typically confined to domain sizes 10–100 nm[18], where the lower bound is set by the inverse relationship between molecular weight and the Flory interaction parameter directing the self-assembly. The smallest domain size reported is ~3 nm[41], substantially larger than required for membranes with MWCO below 5,000 g/mol. This limitation renders the application of block copolymer membranes impractical in size-based exclusion of small organic solutes and ionic species in water treatment. This brings up the motive to pursue alternative approaches for designing low MWCO membranes to perform highly selective small molecule separations.

To achieve smaller pore sizes, microphase separating block copolymers have been used to guide the alignment and order of other

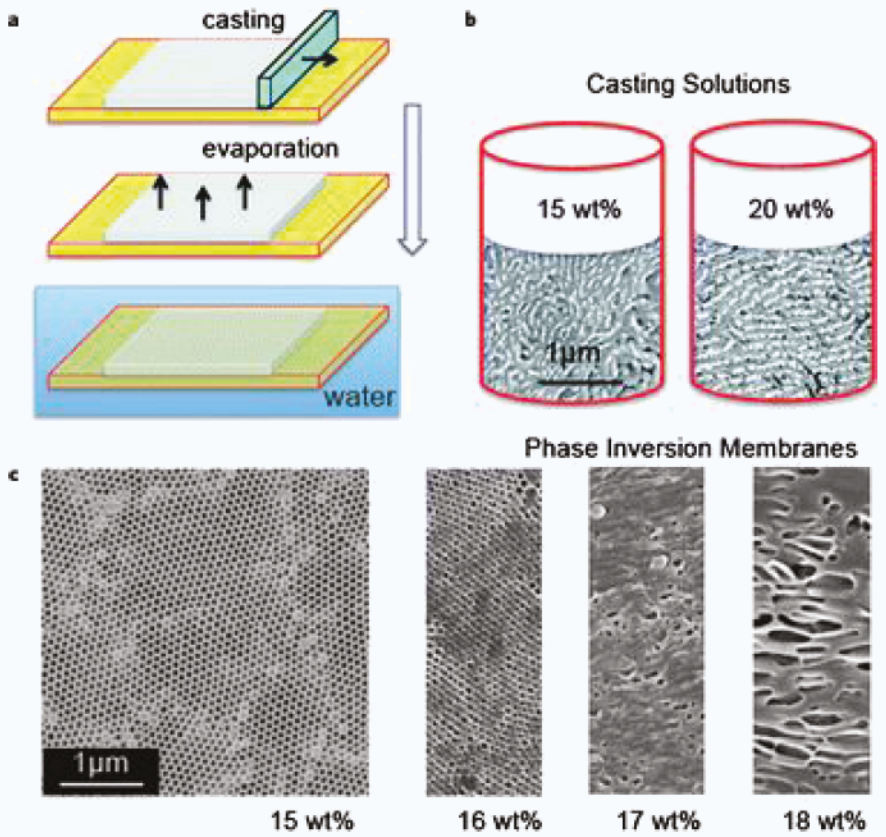

Figure 2 (**a**) Membrane casting of PS-*b*-P4VP 175k-*b*-65k membranes prepared from a copolymer solution in 1DMF : 1THF : 1DOX. (**b**) Cryo-FESEM images of the fractured face of frozen casting solutions after sublimation. The higher concentration gel (20 wt%) shows more order when compared to the 15% wt% gel. Samples were sublimed at -90°C and coated with 5 nm of platinum. Secondary electron images were taken with a through-the-lens detector at 5 kV and spot sized 1.0. (**c**) FESEM of the manufactured membrane surfaces made from ternary solutions of different initial concentrations. Scale bars equal 1 µm. Reprinted with permission from [28], Marques, D.S., *et al.* Self-assembly in casting solutions of block copolymer membranes. *Soft Matter* **9**, 5557-5564 (2013). © 2013, The Royal Society of Chemistry.

nanomaterials that act as nanopores such as carbon nanotubes[42], cyclic peptides[43] and biological water channels[44]. These approaches are quite promising, with the potential to reach pore sizes small enough to retain salts. However, they have not yet been demonstrated in highly scalable membrane systems. Furthermore, most of these nanomaterials are fixed in their chemical structure, with no responsive behavior. Future work may show that these approaches can be scaled up to roll-to-roll systems. Some of the proposed nanomaterials (e.g., carbon nanotubes) may potentially be modified to show responsive behavior.

Microphase separation also occurs in copolymers of other architectures, such as random, bottle-brush star-block and comb-shaped copolymers. These systems result in less regular/periodic nanostructures, but a regular structure is not needed for engineered membranes. All three of these architectures form bicontinuous domains in wider parameter ranges than BCPs, provided the repeat units are sufficiently incompatible and there is a sufficient amount of each monomer[45–50]. For example, while block copolymers require low polydispersity and highly controlled polymerization conditions to achieve the bicontinuous gyroid phase[51,52], side-chain length polydispersity actually increases the range of conditions where bicontinuous domains form in the case of comb-shaped copolymers[53]. Furthermore, these architectures can access smaller domain sizes, and hence separations of smaller solutes, due to the connectivity of their chains.

Alternatively, membranes can be coated with microphase separating polymers that serve as selective layers. This approach is somewhat similar to SNIPS in relying polymer self-assembly for pore formation. But it decouples the mechanical property restrictions from selective layer nanostructure by providing a porous support for the self-assembled selective layer. Membrane coating is easily scalable, and already widely used in the field for various purposes. Doctor blading, spray coating, dip coating and other approaches can be used, and integrated into roll-to-roll and hollow fiber manufacturing lines easily. This approach works especially well for polymers that self-assemble into bicontinuous nanostructures such as comb-shaped and random copolymers[49,50,54,55]. If sections of these copolymers are responsive, the resultant membrane is also responsive.

Polymer self-assembly at interfaces and membrane surface modification

Copolymers show interesting interfacial and surface behavior. They can expose one or more of their components to the surface, form self-assembled brushes, stabilize and/or form colloids and expose or hide functionalities at the surface. Furthermore, these surface properties often respond to environmental factors. These qualities arise not only from the chemistry of the copolymers, but also from their architecture. Copolymers that contain repeat units of different chemical structures, and hence chemical compatibility and interaction capabilities, lead to their segregating at interfaces (e.g., polymer–polymer, polymer–air, polymer–water). This property has been extensively used in other fields, where copolymers of various architectures are used as compatibilizers, surfactants and biomaterials that modulate cell adhesion. This feature can also be used to modify membrane surfaces.

Most of the work in this field focuses on preventing fouling, utilizing amphiphilic copolymers. Typically, the copolymer is designed so that the hydrophobic section is compatible with the base polymer used to prepare the bulk of the membrane (e.g., polyvinylidene fluoride, polyacrylonitrile, polysulfone), and the hydrophilic section is designed to prevent the adsorption of foulants and microorganisms (e.g., polyethylene glycol, PEG). The amphiphilic copolymer is added to the membrane casting solution along with the base material[56–61]. During precipitation in a water-based coagulation bath, the additive acts as a macromolecular surfactant, segregating to all polymer–water interfaces, and self-assembling to expose the hydrophilic functional groups at all membrane surfaces. The coverage extends throughout the internal pores, thus preventing internal pore fouling by biomolecules that permeate the membrane. The method has several unique advantages in requiring no additional processing steps, yielding substantially higher pure water fluxes than in the absence of additive.

Most of these studies focus on membranes with poly(ethylene oxide) (PEO) side-chains, considered to be the gold standard in fouling resistance. On the other hand, this approach can also be used to impart stimuli responsive properties by selecting the hydrophilic component

accordingly as the chains cover the membrane surface and the pore walls. Therefore, if the degree of swelling of the polymer brush changes in response to solution properties (e.g., temperature, pH, ionic strength), the flux and pore size is also modified[13]. Alternatively, the stimulus may change the surface properties of the membrane, modulating adsorption of solutes within pores.

STIMULI RESPONSIVE MEMBRANES

Temperature, pH and dual responsive membranes

Temperature and pH are likely the most widely used stimuli in the membrane literature, in part due to the ease of controlling these factors and in part due to the wide availability of information on how polymers behave in response to these parameters. Several researchers have prepared membranes that respond to one or both of these stimuli. Temperature-responsive membranes are usually prepared using polymers which show a characteristic lower critical solution temperature (LCST). At temperatures below the LCST the polymer dissolves perfectly in the solvent, where at temperatures above the LCST the polymer precipitates out of solution[62]. Poly(N-isopropylacrylamide) (PNIPAAm) has been a widely preferred material for the manufacture of temperature-responsive membranes. PNIPAAm is water soluble at low temperatures, but it precipitates out of water at temperatures above its LCST, around 32°C[5]. Intramolecular hydrogen bonding within and between PNIPAAm chains gets stronger than intermolecular hydrogen bonding with water molecules above 32°C, leading to thermal dissociation of water molecules from the hydrated polymer chains. This results in the collapse of PNIPAAm chains out of aqueous solution. This has been used to control changes in membrane structure and transport properties in response to temperature stimuli.

Self-assembling polymers containing PNIPAAm have been used to produce temperature-responsive microfiltration membranes from poly(vinylidene fluoride) (PVDF)-*graft*-PNIPAAm copolymers using NIPS, where water at 27°C was used as the non-solvent[63]. The copolymer was synthesized using thermally induced graft copolymerization of NIPAAm with ozone-pretreated PVDF. PNIPAAm segregation to the surface was confirmed by X-ray photoelectron spectroscopy (XPS) analysis and it was found that increasing NIPAAm content in the copolymer led to membranes with enhanced temperature-responsive swelling in aqueous solutions. The transport properties of model drugs, calcein and fluorescein isothiocyanate-dextran in phosphate buffer solutions were shown to reversibly change with varying permeate temperature in the range 4–55°C. The steepest change in permeability was observed between 27 and 32°C, matching the reported LCST range for PNIPAAm.

PNIPAAm containing copolymers were also used to prepare composite membranes by coating them onto a porous support. For example, a series of triblock polystyrene-*block*-poly(N-isopropylacrylamide)-*block*-polystyrene copolymers, PS-*b*-PNIPAM-*b*-PS, were synthesized at various weight fractions of the PS block[64]. Triblock copolymers with varying PS block lengths and fractions were used to create novel thermo-responsive membranes based on lamellar, gyroid, cylindrical and spherical block copolymer morphologies. **Figure 3** shows the chemical structure of PS-*b*-PNIPAM-*b*-PS triblock copolymer and a schematic illustration of temperature-induced conformational change of aqueous hydrogel comprising self-assembled morphology with spherical PS domains[65]. Composite membranes for separation studies were prepared by spin-coating thin films of PS-*b*-PNIPAM-*b*-PS onto a meso/macroporous polyacrylonitrile (PAN) support membrane. Permeability tests were carried out at different temperatures using aqueous solutions of model PEG molecular weight standards. A reversible temperature-responsive behavior was observed in permeability, where increased permeability and pore size was attained below the transition temperature of PNIPAM.

pH-responsive membranes are useful for filtration applications that require flow regulation, self-cleaning surfaces, size- and charge-selective

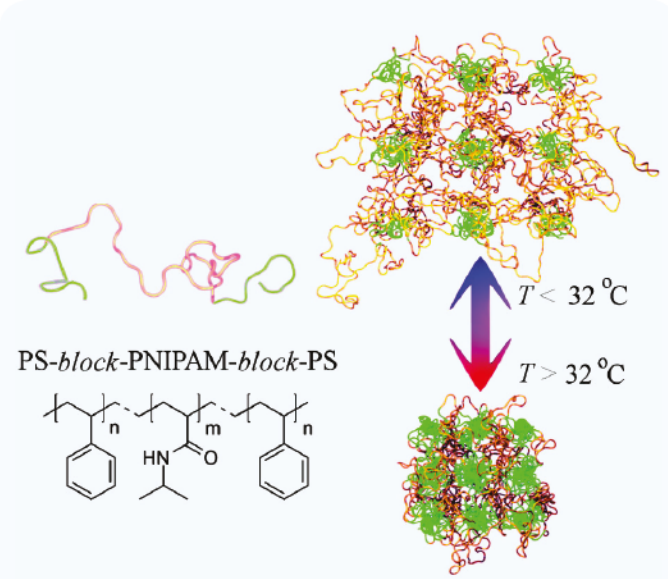

Figure 3 Left: Chemical structure of polystyrene-*block*-poly(N-isopropylacrylamide)-*block*-polystyrene triblock copolymer. Right: Schematic illustration of temperature-induced conformation transition of aqueous hydrogel having self-assembled morphology with spherical PS domains. The latter domains act as physical cross-links for the hydrogel, and as the temperature is raised above the coil-globule transition temperature the PNIPAM chains become hydrophobic and the gel collapses. Reprinted with permission from [64], Nykänen, A., *et al.* Phase behavior and temperature-responsive molecular filters based on self-assembly of polystyrene-*block*-poly(N-isopropylacrylamide)-*block*-polystyrene. *Macromolecules* **40**, 5827–5834 (2007). © 2007, American Chemical Society.

features. Typically, self-assembling polymers used in such membranes incorporate polymer segments with weakly acidic or basic functional groups. For example, carboxylic acid groups are charged at higher pH levels, but switch to their protonated, less hydrophilic form at low pH. Weakly basic polymers such as poly(2-vinyl pyridine) (P2VP), poly(4-vinyl pyridine) (P4VP) and amine-functional acrylics show the opposite response, becoming charged and hydrophilic at low pH upon protonation. This leads to a change in polymer swelling and conformation in water, which can be used to alter pore size, water permeability and surface hydrophilicity.

In that regard, ultrafiltration membranes prepared using SNIPS of the PS-*b*-P4VP block copolymer are pH-responsive[27,28,34,36,65,66]. They exhibit significantly higher water permeability and pore size at high pH values, where the P4VP segments are deprotonated, hydrophobic and collapsed onto the pore walls. pH changes can be used to change the permeability by 1–3 orders of magnitude, and widely vary the effective pore diameter[35]. The same is true for membranes prepared from the triblock copolymer poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) (ISV), designed to offer better mechanical properties[67,68]. The effective pore size and flux depend on the state of P4VP block, which can switch between a highly swollen, protonated form and a less hydrophilic deprotonated form. **Figure 4** shows the pH-dependent pore size change in a PS-*b*-P4VP membrane whose formation is directed by micellar assembly due to complexation between bivalent cations and pyridine in the casting dope[66]. SNIPS of PS-*b*-P4VP can also be used to create membrane selective layers with alternate morphologies, such as overlapping networks of cylindrical micelles[69]. These membranes also show pH response.

Derivatives of PS-*b*-P4VP can enable the combination of pH response with additional functionality. For example, the triblock copolymer

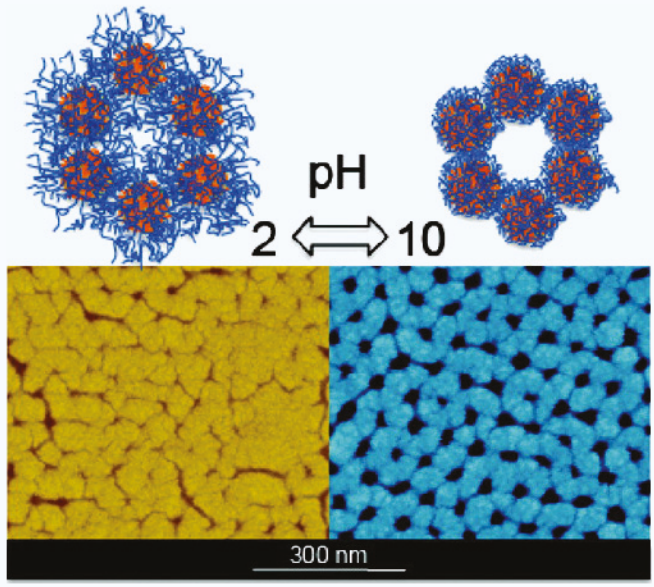

Figure 4 Micelle size change in casting dope as a function of pH, and cryo-field emission scanning electron microscopy (cryo-FESEM) of PS-*b*-P4VP membranes cast from solution in DMF/THF/Cu(acetate)2, immersed in HNO_3 (pH 2) and NH_4OH (pH 10) aqueous solutions. Reprinted with permission from [66], Nunes, S.P., *et al.* Switchable pH-responsive polymeric membranes prepared via block copolymer micelle assembly. *ACS Nano* **5**, 3516–3522 (2011). © 2011, American Chemical Society.

poly(styrene)-*block*-poly(4-vinylpyridine)-*block*-poly(propylene sulfide) (SVPS), still shows comparable pH response but also includes short functionalizable poly(propylene sulfide) blocks exposed within the pores[70]. While experiments to date only demonstrate the proof of concept by attaching dyes into the pores, the thiol-ene functionalization chemistry could enable the attachment of proteins and dyes into the pores, opening the way to additional application.

PS-*b*-P4VP can also be chemically modified to alter its pH response. For example, the P4VP blocks in the PS-*b*-P4VP copolymer was oxidized to P4VP-N-oxide by immersion into acetic acid/H_2O_2 mixtures after membrane formation[71]. The resultant membranes showed low permeability above pH 5, as the pyridine oxide groups got deprotonated and hence uncharged and hydrophobic. This is, as described above, the opposite trend when compared with the unmodified P4VP-containing membranes.

Studies that utilize SNIPS of terpolymers that feature poly(acrylic acid) (PAA) segments exhibit even stronger and more interesting pH response[72–74]. These membranes also showed the ability to uptake copper ions by complexation, and permeability that is responsive to the concentration of copper ions[74]. To achieve this, membranes were first prepared from the triblock copolymer poly(isoprene-*b*-styrene-*b*-N,N-dimethyl acrylamide) (PI-PS-PDMA) triblock copolymer using SNIPS. These membranes exhibited the regular, monodisperse surface pores and improved mechanical properties similar to those reported for the ISV membranes, but exhibited no pH response, retaining a permeability of ~6 L/m^2.h.bar and a constant MWCO over a wide pH range. Then, the PDMA segments lining the pores were converted to PAA using acid catalyzed hydrolysis at 85°C. The permeability of this membrane remained at ~0.6 L/m^2.h.bar between pH 12 and pH 4. Below this pH, permeability increased sharply as the PAA chains were protonated and collapsed onto the pore walls, reaching 16 L/m^2.h.bar at pH 1[72]. Further studies of these membranes, however, showed hysteresis in their pH response. When the pH was gradually decreased, the behavior described above was observed. When the membrane was equilibrated at pH 2 and then the pH was increased gradually, the permeability decreased only partially between pH 3 and 4. Then, the permeability showed a partial decline to ~6 L/m^2.h.bar, stayed there till pH 5.5, and showed a much more gradual decline up to pH 8.5. Above this pH, the permeability was in agreement with the values reported in the first experiment. Similar hysteresis was also observed in analyzing the degree of ionization of PAA and copper uptake. This hysteretic effect is long-lived, and arises from hydrogen bonding between protonated PAA chains at low pH that persists until higher pH levels are reached that forces the deprotonation of the carboxylic acid groups.

pH-responsive behavior can be achieved using copolymers with various architectures. In addition to block copolymers, random and graft copolymers have been used. For example, pH-sensitive UF membranes using random copolymers poly(acrylonitrile-*co*-acrylic acid) (P(AN-*co*-AA)) and poly(acrylonitrile-*co*-methacrylic acid) (P(AN-*co*-MA)) have been prepared by phase inversion[75]. Filtration studies showed that the permeance rate decreased and dextran rejection increased in both membranes when the pH was changed from acid to alkali.

Similarly, PAA-*graft*-PVDF copolymers were used to produce pH-responsive MF membranes by phase inversion[76]. The permeability of aqueous solutions increased with a decrease in feed solution pH from 6 to 1, and the most significant increase was obtained in the pH range of 2–4. Conformational changes in AA polymers upon pH stimuli were deemed effective in causing the reversible changes in permeability. A highly extended conformation is attained at high pH due to strong interaction with water and electrostatic repulsion between the negatively charged groups. At low pH, a collapsed conformation adopted by the chains prevents blockage of pores, allowing larger pore size and higher permeability.

Graft copolymers of PVDF with 2-vinylpyridine (2VP) and 4-vinylpyridine (4VP) polymer side chains, termed P2VP-*g*-PVDF and P4VP-*g*-PVDF, have been used to prepare pH-responsive MF membranes using NIPS[77]. The permeability of both PV2VP-*g*-PVDF and PV4VP-*g*-PVDF membranes varied significantly with feed solution pH changing from pH 1–6 due to protonation/deprotonation of the pyridine groups.

pH-responsive copolymers can also be used blended with commodity polymers (e.g., PVDF) in NIPS to prepare membranes with similar properties. This approach combines the performance features arising from the designed self-assembling copolymer with the lower cost and optimized mechanical properties of the base/commodity polymer. For example, blends of PVDF containing up to 10 wt% of amphiphilic comb copolymers with a PVDF backbone and PMAA side chains, PVDF-*g*-PMAA, were manufactured by NIPS[78]. The PVDF-*g*-PMAA containing membranes showed fast and reversible permeability change upon pH stimuli over an order of magnitude when the feed solution pH changed between 2 and 8.

UF and MF membranes have been designed to exhibit double stimuli-responsive behavior also, changing their behavior upon changes in both temperature and pH. This gives the user multiple tools to tune and control membrane performance. Dual stimuli responsive membranes either use copolymers that combine two types of monomers that respond to different stimuli (e.g., PNIPAAm and PAA), or utilize a polymer that responds to both temperature and pH. A common polymer that fits the latter description is poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA). The PDMAEMA homopolymer contains a tertiary amine group the gets protonated and charged at low pH. It also exhibits an LCST of 50°C in aqueous environment, imparting it temperature responsive behavior for filtration applications.

For instance, double stimuli-responsive porous membranes have been reported, cast with polystyrene-block-poly(N,N-dimethylaminoethyl methacrylate) (PS-*b*-PDMAEMA) diblock copolymers in THF/DMF mixtures following NIPS procedure[79]. The hydrophilic block PDMAEMA

provides responsive behavior to two stimuli, pH and temperature. The membranes showed a thin separation layer with pores in the range of 20–80 nm and an approximate thickness of 1 mm, where constant and reproducible flux values could be obtained. At feed solution temperatures below the LCST of PDMAEMA (50°C), the polymer chains are hydrophilic and they adopt an extended conformation resulting in partial blockage of the pore opening. At temperatures above the LCST, the chains become less hydrophilic, collapse to the pore walls and increase pore opening and aqueous solution permeability. The effect of pH on pore size and separation properties was evaluated by pH-dependent filtration of silica particles with sizes of 12–100 nm. At 25°C, under acidic conditions silica particles with a diameter of 15 nm or larger were completely rejected from the membrane, whereas particles with 15–22 nm diameter range could pass through the membrane at pH 6–10.

Alternatively, PVDF-*g*-PDMAEMA copolymers were synthesized by the controlled grafting of PDMAEMA side chains from PVDF by VDF-initiated ATRP of DMAEMA[80]. The PVDF-*g*-PDMAEMA copolymers were then used to create pH- and temperature-responsive MF membranes by phase inversion in deionized water. The permeability of aqueous solutions through the membranes increased with increase in pH from 3–11 and in feed temperature from 30–70°C.

An example of combining two polymers with separate responsive capabilities involves MF membranes prepared from blends of PAA-*g*-PVDF and PNIPAAm by NIPS[81]. The permeability of the blend membranes was found reversibly responsive to both pH and temperature, with the most significant changes in permeability observed at feed solution pH between 2 and 4, and temperature around 32°C, the LCST of PNIPAAm.

Alternatively, a pH-responsive membrane can be further functionalized with a thermally responsive component. For example, PS-*b*-P4VP isoporous membranes prepared by SNIPS were further functionalized with PNIPAAm chains by first coating the membrane pores by a polydopamine layer, and then exposing this adhesive coating to PNIPAAm-NH2 chains[82]. The resultant membranes showed changes in permeability and contact angle in response to both pH and temperature.

These studies focus heavily on porous membranes where self-assembly leads to pores lined with responsive polymer chains. There are few studies of pH or temperature responsive membranes that focus on the separation of small molecule solutes, prepared by forming TFC membranes whose selective layers are formed of the self-assembling copolymers. One of these studies utilizes a comb-shaped copolymers with a hydrophobic PVDF backbones and hydrophilic PEO-based side-chains that microphase separates into ~1 nm bicontinuous domains[50]. The hydrophilic domains act as PEO-filled nanochannels through which water and other solvents can permeate through. Further studies of these membranes show that the effective channel size depends strongly on the degree of swelling of PEO chains[54,83]. These membranes exhibit increased water flux and decreased dye rejection with increasing temperature, pressure and ionic strength[54]. These factors work synergistically; while the effect of increased pressure is minimal at room temperature and deionized water, it becomes visible at 50°C and in saline solutions. These results correlate closely with reported phase diagrams of PEO in water, which show an LCST for PEO at around 100°C that is depressed at higher ionic strengths and pressures.

A study by Phillip and coworkers utilized a terpolymer that includes a PAN backbone, PEO side-chains and epoxide groups to prepare such membranes with multiple functionalities[84]. PAN-*g*-PEO was previously reported to form a bicontinuous microphase separated structure with permeation occurring through the interconnected PEO phases, acting as effective pores ~1 nm in diameter[56]. This recent study introduced epoxide moieties lining the pore walls by synthesizing a terpolymer. This allows for introduction of both positively charged and negatively charged moieties to the membrane through a post-modification process. Amine groups were introduced through ring opening reaction of epoxide and a primary amine. These amine groups can be reacted with sulfophenyl isothiocyanate sodium salt to generate a negatively charged, sulfonic-acid-functionalized membrane. The incorporation of these functional groups leads to charge-based rejection and pH dependent transport behavior. The surface charge of sulfonate functionalized membranes was found to remain constant due to low pK_a of the sulfonic acid. Thus, no change in salt rejection over the wide pH range of 2.5–10.5. In contrast, membranes functionalized with amine groups with a pK_a of 10.7 show a significant decrease in salt rejection at pH value of about 10, with the most notable decrease in rejection of $MgCl_2$ with about 60% decrease in rejection. This demonstrates that small molecule and salt ion rejection can also be tuned using a pH-responsive polymer with careful polymer design.

Ionic strength responsive membranes featuring zwitterionic groups

Zwitterionic groups, with equal number of positive and negative charges, are found to be highly responsive to changes in electrolyte concentration of solutions. Owing to the presence of strong electrostatic interactions between zwitterions, they form strong dipole–dipole assemblies that may be in a collapsed or globular conformation in aqueous solution. In the presence of low molecular weight salts, these dipole–dipole assemblies may disassociate and become charged to varying extents. Each co-ion of the zwitterionic head group is expected to be surrounded by counter-ions and a hydration shell, which may lead to increased hydrophilicity of the zwitterionic groups and/or the formation of highly swollen chains and increased coil size (**Fig. 5a**). This phenomenon is known as the anti-polyelectrolyte effect[85]. The behavior of zwitterions in electrolyte solutions depends on the zwitterionic functional group, polymer architecture, degree of polymerization as well as electrolyte concentration. This electrolyte responsiveness of zwitterions has been utilized to prepare ionic strength-responsive membranes by modifying the surface of commercial porous membranes with zwitterionic polymers[86–88]. Studies on the effect of ionic strength on self-assembled membranes are relatively limited, and focus on large pore size membranes (UF, MF) prepared by graft and random zwitterionic copolymers.

A graft copolymer with a PVDF backbone and sulfobetaine methacrylate (SBMA or PDMAPS) side chains (labeled PDMAPS-*g*-PVDF) has been used in the manufacture of MF membranes by phase inversion in aqueous media of different ionic strength and temperatures[89]. The researchers were able to tune the pore size by changing the grafting density of side-chains, casting membranes in aqueous media of varying ionic strength, and also filtering feeds with varying ionic strengths. They found that temperature of the casting bath did not have a significant effect on membrane performance. However, as the ionic strength in feed increased, the zwitterionic side chains became swollen, exhibiting anti-polyelectrolyte effect, and extended into the pores. This led to a decrease in pore size and flux as the ionic strength in feed increased (**Fig. 5b**), allowing facile tuning of membrane performance.

A random copolymer of acrylonitrile (AN) and sulfobetaine methacrylate monomers (PAN-*r*-SBMA) has been used in the manufacture of UF membranes by phase inversion[90]. These membranes are reported to be ionic strength-responsive, and the responsive behavior was reversible. At low sodium chloride concentrations, proteins adsorb onto membrane surface and pore walls, causing pore narrowing and hence proteins cannot go through (closed channels, **Fig. 5c**). At high salt concentrations, the interactions between the zwitterionic groups and proteins are weakened, and the hydrophilicity of the zwitterionic groups is enhanced as they become more dissociated and surrounded by counter ions and a hydration shell. As a result, protein adsorption is suppressed and protein permeation is allowed through the membranes (open channels, **Fig. 5c**). In this way, the membranes were found to open and close channels for protein transport in response to feed ionic strength.

Light responsive membranes

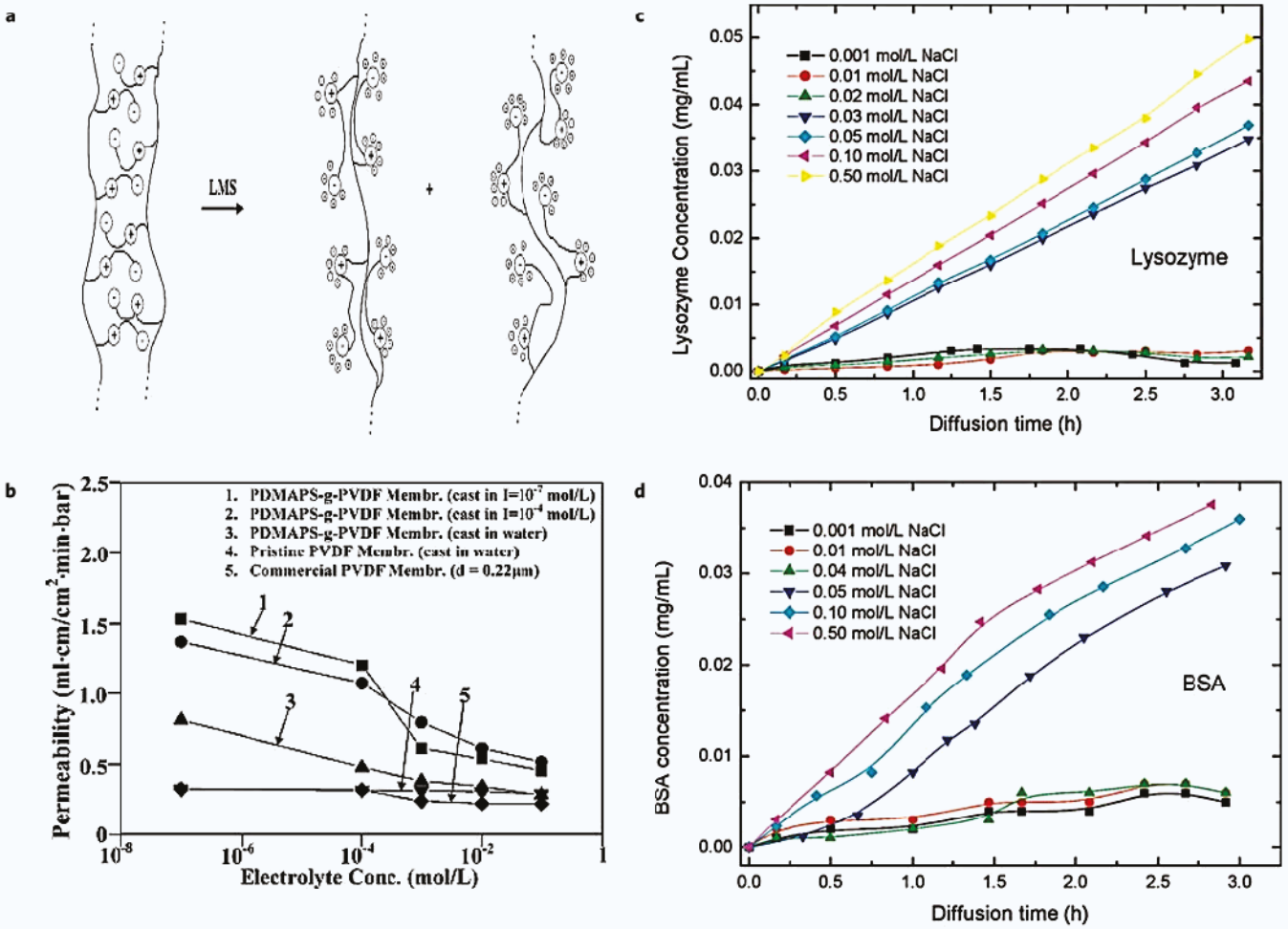

Figure 5 Some examples of ionic strength response of zwitterions. (**a**) Schematic representation of antipolyelectrolyte effect. At low or no ionic strength, the zwitterions self-assemble with their dipoles aligned in an antiparallel fashion (left). Upon the addition of a low molecular weight salt (LMS), these assemblies disintegrate. Each co-ion is surrounded by other counter-ions and a hydration shell (right), leading to highly swollen and expanded chains. Reprinted with permission from [91], Georgiev, G.S., *et al.* Self-assembly, anti polyelectrolyte effect, and nonbiofouling properties of polyzwitterions. *Biomacromolecules* **7**, 1329–1334 (2006). © 2006, American Chemical Society. (**b**) Permeability of electrolyte solutions through a MF membrane prepared from a comb shaped copolymer, PDMAPS-*g*-PVDF. As electrolyte concentration increases, zwitterionic chains swell and extend into the pores leading to pore narrowing, and hence decreased salt permeability through the membrane. Reprinted with permission from [92], Zhai, G., *et al.* Poly(vinylidene fluoride) with grafted zwitterionic polymer side chains for electrolyte-responsive microfiltration membranes. *Langmuir* **19**, 7030–7037 (2003). © 2003, American Chemical Society. (**c,d**) Diffusion of two proteins, lysozyme (**c**) and bovine serum albumin (**d**), at different electrolyte concentrations through PAN-*r*-SBMA UF membranes. As the electrolyte concentration increases, protein permeation increases due to increased hydrophilicity of zwitterions and weakened interactions between proteins and zwitterions. Reprinted with permission from [90], Su, Y., *et al.* Smart zwitterionic membranes with on/off behavior for protein transport. *J. Phys. Chem. B* **112**, 11923–11928 (2008). © 2008, American Chemical Society.

Self-assembling polymers offer a variety of approaches to new light-responsive membranes with tunable, responsive selectivity without the need for additional manufacturing steps. Light as a stimulus enables remote control of materials without physical contact or a mechanical apparatus. Light-induced changes in the geometry and dipole moment of photo-switching molecules lead to macroscopic changes that alter final material properties such as wettability, permeability, charge, 3-D shape, color, binding and alignment.

Light-responsive membranes can be created by incorporating photochromic moieties into copolymer structure as side groups of one of the blocks. In these systems, the photo-isomerization of photo-chromic groups incorporated into polymeric systems allows light-induced variations in polymer structure, conformation and solvation because of the altered interactions between photo-chromic groups and polymer chains, solvent molecules or polymer side groups. Several photochromic molecules have been used in designing light-responsive block copolymers such as anthracene, azobenzene (Azo), spiropyran, dithienylethene, diazonaphthoquinone and stilbene[93,94]. Most of these systems show a reversible photo-isomerization reaction upon ultraviolet (UV) and visible light absorption, such as the photo-dimerization of anthracene, the *trans-cis* isomerization with Azo and stilbene, the isomerization of spiropyran to merocyanine, and conversion between ring-open and ring-closed forms of dithienylethene. These photo-induced changes of chemical states have the potential to enable creation of intelligent filtration membranes that feature switchable surface wettability[95,96] and solvent permeability[97,98] in response to light stimulus.

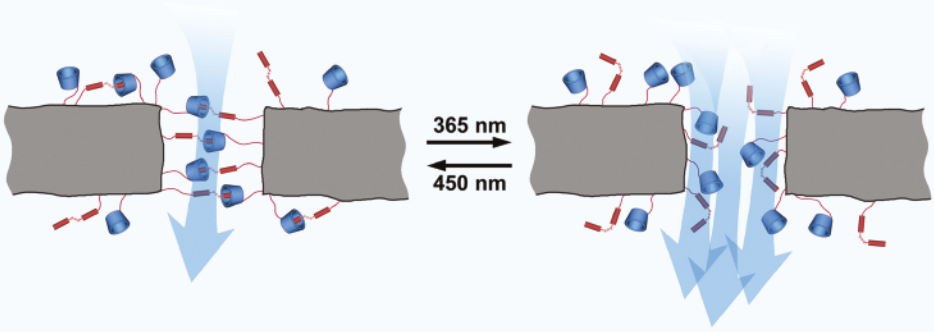

Figure 6 PES membranes with photo-responsive permeability. Under the external irradiation at 450 nm, due to the complex between Azo and β-CD, the pores in the membranes are closed and the membranes show low permeability; after switching the external irradiation to 365 nm, due to the collapsing of the complex between Azo and β-CD, the pores in the membranes are opened and the membranes show high permeability. Reprinted with permission from [103], Shi, W., *et al*. Poly(ether sulfone) membranes with photo-responsive permeability. *J. Membr. Sci*. **455**, 357–367 (2014). © 2014, Elsevier.

The first study that reports the combination of light response in block copolymer membranes prepared by SNIPS was recently published[99]. In this work, a poly(styrene-*b*-anthracene methyl methacrylate-*b*-methylmethacrylate) (PS-*b*-PAnMMA-*b*-PMMA) triblock copolymer was chosen for membrane formation. The anthracene methyl methacrylate block provided the light response, and the amphiphilic character of the block copolymer led to either hexagonally ordered or cylindrical pores, based on the molecular weight used. The anthracene moiety converts to cyclic adduct photodimers in the solid state upon exposure to long-wave UV (365 nm), and then the original monomers can be restored by exposure to short-wave UV (264 nm). With that, the flux and retention of the membranes could be switched by longer or shorter wavelength UV irradiation. Photo-responsive polymers that include Azo groups have been the most widely studied examples[100,101]. However, it should be noted that the use of Azo-containing block copolymers for forming light-responsive SNIPS membranes remains relatively unexplored. The photo-induced *cis*-to-*trans* isomerization of Azo is coupled with a rapid and complete change in its electronic structure, geometric shape, and polarity[102]. Implementation of Azo derivatives into polymer structure enables photo-responsive membranes with variable polarity, wettability, permeability and self-assembly behavior. For example, the ability of β-cyclodextrin (β-CD) groups to form host-guest complexes with Azo (but not stilbene) has been used to prepare light-responsive membranes[103]. In preparing these membranes, first Azo and β-CD terminated poly(ether sulfone) (PES) were synthesized, then PEG was implemented as the binding agent between Azo/β-CD and PES to create the Azo modified PES (PES-PEG-Azo) and β-CD modified PES (PES-PEG-β-CD). The synthesized PES-PEG-Azo and PES-PEG-β-CD were blended with PES polymer to form the final designed PES membrane. **Figure 6** shows the photo-responsive permeability of the designed PES membrane based on the host-guest complex between Azo and β-CD groups.

In addition to Azo, spiropyran (SP) is also a well-known photochromic group that, in response to UV light irradiation, undergoes a photoreversible isomerization from the neutral hydrophobic SP form to a zwitterionic hydrophilic merocyanine (MC) form. The MC form can return to the initial SP state by visible light irradiation. This is especially important for fouling resistance and self-cleaning behavior. Spiropyran derivatives can be embedded, cross-linked, and introduced as side chain or part of the main chain in polymer matrices to obtain photo-regulation of membranes. These photo-functional groups can be attached onto the pores of porous membranes to achieve responsive behavior[98,104,105], or spiropyran-containing chains can be grafted from a pre-existent membrane surface[97,98,106]. However, these approaches often focus on post-processing membranes with often harsh or sensitive treatments to incorporate these functional groups. Simpler coating or membrane formation methods that would rely on the self-assembly of the polymeric materials for pore formation or surface functionalization that induce photo-responsive behavior are not widely studied.

UNRESOLVED QUESTIONS AND FUTURE OUTLOOK

While extensive work has focused on functionalizing existing membranes by post-processing to impart responsive behavior, approaches using polymer self-assembly to achieve this task in a single step are still limited. While self-assembly approaches for membrane pore size control and surface functionalization exist[49], most of these approaches focus on fouling prevention. Approaches to impart responsive and multi-functional behavior are limited in comparison. This is especially evident from the small number of studies listed here that focus on preparing membranes that respond to stimuli other than pH (e.g., light, specific chemical compounds, electric and magnetic fields).

There are many interesting studies that demonstrate approaches to incorporate response to more complex stimuli into membranes. For example, incorporating biological macromolecules into membranes can enable responsive behavior to specific chemicals through powerful protein-ligand or receptor–ligand interactions. In many applications, from wastewater treatment to biomanufacturing, this approach could be used as a smart valve that responds to the presence of a specific problem (or desired) solute in the membrane feed, regulating upstream reactions. While a few reports of such membranes prepared by grafting methods have been reported[107], this is still a very open field.

Membranes that react to electrical stimuli are also of great interest. For example, conductive polymers have been used as membrane materials[108,109], and have the potential to exhibit not only pH response but some interesting capabilities upon exposure to external electric fields, such as the removal of foulant layers[110] or acting as reversible ion exchangers for wastewater treatment[111]. A big challenge for utilizing these conjugated polymers for membrane applications is their formation into porous membranes. Furthermore, it is very difficult to synthesize copolymers of such conducting polymers, which limits opportunities for leveraging polymer self-assembly.

Stimuli that rely on solution properties (e.g., pH, temperature, etc.) tends to slowly modify membrane behavior, and relies on changing the feed composition, which may not always be feasible. Electrical contacts or UV lamps are hard to integrate into a membrane module filled with water. In contrast, external magnetic fields are easy to apply externally. Thus, more research on membranes that respond to magnetic fields is needed. Some studies have utilized post-processing methods to incorporate magnetic nanoparticles onto membrane surfaces to prevent fouling[112]. Scalable manufacturing of similar membranes using polymer self-assembly, exploration of their responsive properties, or the utilization of similar approaches for membranes with additional functionality, would be of great interest. Alternatively, superparamagnetic nanoparticles have

been combined with temperature-responsive hydrogels or grafted brushes to control their swelling remotely[113,114]. This could enable temperature-responsive membranes to be controlled remotely using external magnetic fields. However, there is still a significant knowledge gap in using this principle to manufacture responsive membranes using scalable, single-step approaches and with competitive performance.

There are also very few technologies that exhibit responsive behavior in membranes aimed at small molecule separations. This is because membrane technologies capable of achieving these separations by polymer self-assembly in general are relatively few, and quite recently developed. Most membranes with effective pore size smaller than 1–2 nm are RO and NF membranes that have cross-linked polyamide selective layers. This well-established technology does not utilize of the advantages of polymer self-assembly, and is in itself not very amenable to significant modification beyond the formation of coatings on existing membranes. Creating ~1 nm and smaller features by self-assembly is challenging, but a few research groups are recently expanding the options and starting to report the addition of new functions, including responsive behavior, to these platforms.

Most research focuses on the use of stimulus response only after the membrane is formed. Careful design of membrane manufacturing methods based on our knowledge of the responsive behavior of selected polymers can enable better control of membrane pore size and selectivity.

Finally, most studies in this area are limited to proof of concept demonstrations of membrane manufacture and function. There are few published studies on practical applications of these highly promising membranes, demonstrating their use in real separation challenges with commercial impact. This also impedes the translation of these new technologies to industrial-scale production and use, despite the relatively low technological barriers to large scale manufacturing. Addressing these two limitations requires extensive collaboration between the academic researchers who develop these technologies and industrial partners. This would enable the identification of most relevant applications and markets, demonstration of the use of these technologies and their commercial potential and foster work that bridges the gap between lab scale research and products with true impact on manufacturing, economy and environment.

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