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Self-Assembled Materials as Novel Nanotechnology-Enabled Ultrafiltration Membranes

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Civil and Environmental Engineering

by

MaryTheresa Monahan Pendergast

2014
ABSTRACT OF THE DISSERTATION

Self-Assembled Materials as Novel Nanotechnology-Enabled Ultrafiltration Membranes

by

MaryTheresa Monahan Pendergast
Doctor of Philosophy in Civil and Environmental Engineering
University of California, Los Angeles, 2014
Professor Eric M.V. Hoek, Chair

Nanotechnology is being used to enhance conventional ceramic and polymeric water treatment membrane materials through various avenues. Among the numerous concepts proposed, the most promising to date include zeolitic and catalytic nanoparticle coated ceramic membranes, hybrid inorganic-organic nanocomposite membranes, and bio-inspired membranes such as hybrid protein-polymer biomimetic membranes, aligned nanotube membranes, and isoporous block copolymer membranes. Zeolitic and catalytic membranes appear reasonably far from commercial reality and offer small to moderate performance enhancements. Overall, bio-inspired membranes are farthest from commercial reality, but offer the most promise for performance enhancements; however, nanocomposite membranes offering significant performance enhancements are already commercially available.
Isoporous block copolymer membranes represent a fully-polymeric analog to the ordered structure associated with bio-inspired materials and are able to be produced through conventional fabrication methods. These membranes represent a possible route towards more precise particle and macromolecular separations, which are of interest across many industries. Herein, membranes with vertically-aligned nanopores are formed from a poly(isoprene-\(b\)-styrene-\(b\)-4 vinyl pyridine) triblock terpolymer via a hybrid self-assembly/nonsolvent induced phase separation process. Polymer concentration, solvent composition, and evaporation time in the fabrication process were varied to tailor ordering of the selective layer and produce enhanced water permeability. Water permeability was doubled through the optimization process, while maintaining the surface morphology and, thus, the resulting selectivity of the membrane. This was achieved by increasing volatile solvent concentration, thereby decreasing the evaporation period required for self-assembly. Fine-tuning was required, however, since overly-rapid evaporation did not yield the desired pore structure. Transport models, used to relate the in-situ structure to the performance of these materials, revealed narrowing of pores and blocking by the dense region below. It was shown that these vertically aligned nanoporous membranes compare favorably with commercial ultrafiltration membranes formed by conventional phase inversion and track-etching processes, which suggests there is practical value in further developing and optimizing these materials for specific industrial separations.
The dissertation of MaryTheresa Monahan Pendergast is approved.

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University of California, Los Angeles

2014
I dedicate this dissertation to my parents.

To Mom, for teaching me to find joy in my achievements.

To Dad, for always being my number one fan.
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REFEREED JOURNAL PUBLICATIONS


**BOOK CHAPTERS**


**SELECTED CONFERENCE PRESENTATIONS**

M.M. Pendergast, Eric M.V. Hoek, Using nanocomposite materials technology to improve the properties of RO membranes, American Institute of Chemical Engineers Annual Meeting, 2010.


CHAPTER 1

AQUATIC MEMBRANE SEPARATIONS
1.1.0. World Water Shortage

Today, we face a global water challenge. In the last century the global population quadrupled, while the world water demand increased sevenfold [1]. This global water challenge will become greater as the population and economies of developing countries expand; in the next forty years, the global population is expected to grow nearly 40%, and hence, domestic, agriculture, industry, and energy demands on water resources will continue to grow [2]. The World Water Council estimates that by 2030, 3.9 billion people will live in regions characterized as “water scarce” [3]. In addition to overall water shortage, poor water quality is near crisis in many parts of the world. According to the World Health Organization, 1.1 billion people lack access to improved drinking water and 2.6 billion lack access to proper sanitation [4]. As many as 2.2 million people die of diarrheal related disease every year most often caused by waterborne infections, and the majority of these cases are children under the age of 5 [2]. More than ever, existing fresh water resources need protection and new water resources must be developed in order to meet the world’s growing demand for clean water. This will require better water treatment technology.

1.2.0. Membrane Technology

1.2.1. Principles of Membrane Separations

A membrane is a semi-permeable barrier that allows passage of certain compounds, but not others (Figure 1-1). In 1861, Maxwell wrote of “a being whose faculties are so sharpened that he can follow every molecule in its course” [5]. Maxwell’s theorized ‘sorting demon’ would be able to perfectly recognize and separate individual
molecules. While such an ideal barrier has not yet been fabricated, 150 years later commercially available membrane technologies reliably perform a wide range of separations and the application of membrane technology continues to grow.

![Figure 1-1](image)

**Figure 1-1.** A schematic depicting two reservoirs separated by a semi-permeable membrane. Initially, there is a mixed solution containing multiple species. Some species are able to pass through the membrane while the others are not, resulting in a separation of the species.

Separation processes create order from disorder; therefore, there is an inherent energy input required to enable them. This energy is termed the minimum work of separation ($\Delta W_{\text{min}}$). Mixing of two solutions occurs spontaneously if the free energy of the mixture is less than the sum of the free energies of the pure solutions. Alternately, the minimum work required to separate a mixture is equal to or greater than the free energy ($\Delta G$) of mixing,

$$\Delta W_{\text{min}} \geq \Delta G = \Delta H - T\Delta S.$$  (1)
This free energy can be related to the chemical potential difference between the mixture and the pure solutions,

$$\partial G = -S \partial T + V \partial P + \Sigma \mu_i \partial n_i.$$  \hspace{1cm} (2)

The gradient of the chemical potential is the driving force for mixing and determines the minimum energy that must be input to achieve separation.

**Figure 1-2.** A schematic depicting the phenomenon of natural osmosis (left) and pressurized reverse osmosis (right). If a semi-permeable membrane, which allows for the passage of water, but not salt, separates a salt solution and pure water osmosis dictates that water will pass through the membrane to dilute the salt solution until equilibrium across the membrane is reached. In reverse osmosis, pressure is applied to overcome the osmotic pressure difference between the two sides causing pure water to pass in the opposite direction and concentrate the salt solution.
Take osmosis and reverse osmosis as a practical example. A semi-permeable membrane (ideally, infinitely permeable to water and infinitely impermeable to salt) separates a salt solution from pure water. The chemical potential of the solution is reduced in proportion to the amount of salt, which increases the entropy (S) and decreases the free energy. The higher chemical potential of the pure water drives water molecules through the membrane until the two solutions achieve osmotic equilibrium—this is osmosis. To reverse the spontaneous process of osmosis and drive water from the salt solution side to the pure water side (to “reverse osmosis”), energy equal to the original osmotic pressure difference (i.e., chemical potential difference) between the two solutions must be input to the salt solution side. Energy in excess of this amount must also be exerted to account for any irreversible losses.

![Figure 1-3](image_url)  

**Figure 1-3.** A process design showing a pressure-driven membrane separation, indicating the influent feed stream and two outflows of permeate (product) and retentate (concentrate).

In order to quantify the performance of a membrane separation, two primary metrics are used: selectivity and permeability. Selectivity is the starting point as
separation is the primary objective. Selectivity of a membrane can be expressed in terms of solute rejection (especially for pressure driven liquid separations),

\[ R = 1 - \frac{c_p}{c_f}, \quad (3) \]

where \( c_p \) is the concentration of the solute in the permeate stream and \( c_f \) is the concentration of the solute in the feed stream. This equation has the same form as the conversion in a chemical reactor. Alternatively, selectivity of a membrane can be expressed as a separation factor,

\[ \alpha_{A/B} = \frac{S_A}{S_B}, \quad (4) \]

where \( S (= c_p/c_f) \) is the sieving coefficient and \( A \) and \( B \) denote the components being separated. Separation factor is more commonly used in solute separations (e.g., protein fractionation) or phase separations (e.g., \( \text{O}_2/\text{N}_2 \) gas separation, ethanol/water pervaporation).

After it is established that the selectivity of a membrane is appropriate for a given separation, the permeability of a membrane (to a large extent) dictates the cost of the ultimate separation. Lower permeability translates into larger membrane area required (increased capital investment) and/or more energy input required (increased operating expense). Flux \( (J) \) is the flow of matter through the membrane per unit area of membrane. Permeability of a mixture component is typically derived from measurement of the component’s flux,

\[ J = -A \frac{dX}{dx}, \quad (5) \]

where \( A \) is the phenomenological permeability coefficient and \( \frac{dX}{dx} \) is the gradient driving permeation (i.e., concentration, temperature, pressure). The phenomenological
coefficients and gradients are listed for a variety of transport types in Table 1-1. For example, in the pressure-driven reverse osmosis application described above the driving force is the pressure drop \((dP = P_f - P_p)\) across the membrane thickness \((dx)\) and flux is dictated by the permeability coefficient \((k)\) of the membrane material to a given species \((i.e., \text{salt or water})\). Other coefficients dictating flux are the diffusion coefficient \((D)\), thermal diffusivity \((\lambda)\), dynamic viscosity \((\mu)\), and electrical conductance \((G)\).

<table>
<thead>
<tr>
<th>Governing Relation</th>
<th>Type of Transport</th>
<th>Flux</th>
<th>Coefficient</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fick’s law</td>
<td>mass flux</td>
<td>(J_m) ((\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}))</td>
<td>(-D) ((\text{m}^2 \cdot \text{s}^{-1}))</td>
<td>(\frac{dc}{dx})</td>
</tr>
<tr>
<td>Darcy’s law</td>
<td>volume flux</td>
<td>(J_v) ((\text{m}^3 \cdot \text{m}^{-1} \cdot \text{s}^{-1}))</td>
<td>(-L_p = \frac{k}{\mu}) ((\text{m}^2 \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}))</td>
<td>(\frac{dP}{dx})</td>
</tr>
<tr>
<td>Fourier’s law</td>
<td>heat flux</td>
<td>(J_h) ((\text{J} \cdot \text{m}^{-2} \cdot \text{s}^{-1}))</td>
<td>(-\lambda) ((\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}))</td>
<td>(\frac{dT}{dx})</td>
</tr>
<tr>
<td>Newton’s law</td>
<td>momentum flux</td>
<td>(J_n) ((\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}))</td>
<td>(-\mu) ((\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}))</td>
<td>(\frac{dv}{dx})</td>
</tr>
<tr>
<td>Ohm’s law</td>
<td>electrical flux</td>
<td>(J_i) ((\text{C} \cdot \text{m}^{-2} \cdot \text{s}^{-1}))</td>
<td>(-G) ((\text{S}))</td>
<td>(\frac{dE}{dx})</td>
</tr>
</tbody>
</table>

1.2.2. Historical Developments

Membrane science has benefited from the fundamental contributions of multiple fields, including chemistry, biology, physics, and engineering. As early as 1748, traces of membrane science can be found; one example is Nollet’s studies of water permeation through a diaphragm that led him to coin the term “osmosis” [6]. Work through the early 1900’s was focused on understanding the phenomena involved in barrier and interfacial
Membranes were employed as model systems to study transport processes, such as diffusion, osmosis, and dialysis. Later work focused more on understanding membrane transport and on developing membranes as a technology [15-21]. Major scientific developments are outlined in Figure 1-4.

**Figure 1-4.** Timeline of major scientific developments that have enabled membrane science.
Membrane technology has evolved dramatically over the last century (Figure 1-5). Collodion (nitro cellulose) ultrafiltration and microfiltration membranes—described by Fick as early as 1855 [9]—were produced commercially for laboratory separations in the early 1900’s [22-23]. The 1940’s saw the rise of commercial ion exchange membranes, which were previously employed exclusively in fundamental studies [24-26]. This was followed by the opening of the first successful electrodialysis facility in 1952 and the first sea salt production facility in 1961 [27]. Around this time, cellulose acetate membranes emerged. Cellulose acetate films were first shown to be capable of desalinating water in 1959 [28]. In 1963, Loeb and Sourirajan demonstrated the phase separation technique, used widely to this day, for the formation of integrally-skinned asymmetric cellulose acetate membranes for seawater desalination [29]. About a decade later, Cadotte developed interfacial (thin film) composite membranes [30]. By 1979, the first reverse osmosis seawater desalination facility opened [31] and in 1982 the first pervaporation facility opened.
Essentially all life forms require membranes for critical biological functions. Biological membranes serve as a protective layer for genetic and metabolic materials. They selectively transmit water, ions, and organic compounds in and out of cells and organs. Passive diffusion of carbon dioxide, oxygen, and water across cellular membranes ensures biological equilibrium is maintained. Transmembrane protein channels, such as aquaporins, actively regulate the passage of specific species, such as sugars and amino acids to aid in metabolism. Much works has gone into understanding the structure and function of biological membranes, leading to the creation of biomimetic membranes and processes.

Membrane separations have traditionally played an important role in biotechnology and medicine [32-33]. For almost 70 years now, since Kolff formed his...
model of an artificial kidney—not an exact replica, but a functional dialyser for medical treatment—scientists have tried to replicate the intricate structures and functions of the body [34]. Artificial cells, organs, and liposomes all rely on the ability to mimic biological membranes by controlling the permeation of certain chemical species. Today, membranes are used in controlled drug delivery in order to allow for slow release of a pharmaceutical from a reservoir into the blood stream of a patient. Microfiltration and ultrafiltration have long been used for sterile filtrations of fermentation media, protein concentration, and buffer exchange, where high-throughput is needed, but extreme selectivity is not. More precise size separations required for protein purification and protein-virus separations are currently being aided by advances in membrane materials and high-performance tangential flow filtration systems.

Growth of the field of membrane science and technology took off following World War II, following in the steps of rapid developments in polymer science [35]. A large demand for advanced technologies in water quality analysis and treatment was also spurred at that time, as drinking water sources in Europe had become severely polluted during the war and rapid population growth in arid regions, such as California, prompted interest in “saline water conversion” in the US [35]. Since Hassler, McCutcheon, and others theorized on the ability to desalinate water with synthetic membranes at UCLA, as early as 1950, researchers have sought to use membranes to produce potable water from alternative sources [36]. Today, research continues on membrane-based methods of purifying alternate water sources such as seawater, brackish water, and wastewater to drinking water standards to relieve water stress. Currently, membrane technology is widely applied for pre-treatment (microfiltration and ultrafiltration), for softening and
removal of dissolved metals and organic molecules (nanofiltration), and for desalination (reverse osmosis). Reverse osmosis is also used in the high technology sector for ultrapure water production. Membrane separations are favored over many other treatment options because, in principle, they require no chemical additives, thermal inputs, or spent media disposal; however, this is rarely achieved in practice due to fouling.

Gas separations are widely applied in industry. The earliest large-scale application of gas separations was for hydrogen recovery from ammonia purge gases starting in the 1970’s [37]. The use of this technology has since increased as the need for pure hydrogen gas increased in applications such as hydrotreating, hydrocracking, and hydrodesulfurization due to new environmental regulations. Today, gas separations are broadly used to treat flue gas, syngas, and other off gases for emissions control and carbon dioxide capture. Other industrial applications of gas separations include air separation for nitrogen production, carbon dioxide separation for power production, recovery of organics in mixed gas streams, and natural gas dehydration.

While membrane technologies are most widely applied in the realm of medicine and water treatment, other applications exist and continue to grow. Membrane processes are incorporated in various energy applications, including batteries, fuel cells, and osmotic energy recovery (e.g., pressure retarded osmosis). The food and beverage industry relies on membranes for the production of pure water, filtration of fluid streams, meat packaging materials, and production of carbon dioxide. Membranes are also applied in textiles, for example with high performance clothing like Gore-Tex. Environmental applications constitute a large demand for membrane technology. Pervaporation, nanofiltration, reverse osmosis, and gas separations are applied in environmental
remediation applications to treat and remove regulated chemical and microbial contaminants.

Membranes are favored over other technologies for water treatment, such as disinfection, distillation, or media filtration because, in principle, they require no chemical additives, thermal inputs, or require regeneration of spent media. Although such an ideal membrane has not yet been realized in the 150 years since Maxwell theorized his magical ‘sorting demon,’ commercial membrane technologies can perform efficient, selective, and reliable separations [5]. While the use of gas separation, pervaporation, and electrochemical membrane processes for industrial and environmental separations has increased dramatically in the past few decades, pressure-driven membrane processes remain the most widely used membrane technologies for water treatment applications [38].
Typically, pressure-driven membranes are classified according to characteristic pore size or their intended application (Table 1-2) [5, 38-39]. Currently, membrane technology is commercially available for suspended solids, protozoa, and bacteria removal (microfiltration, MF), for virus and colloid removal (ultrafiltration, UF), for hardness, heavy metals, and dissolved organic matter removal (nanofiltration, NF), and for desalination, water reuse, and ultrapure water production (reverse osmosis, RO) [37-38]. While commercially available membranes perform well in many applications, the drive to protect existing water resources and to produce new water resources demands membranes with improved productivity, selectivity, fouling resistance, and stability.
available at lower cost and with fewer manufacturing defects. Better membranes require better materials.

1.3.0. Conventional Membrane Materials

1.3.1. Mesoporous Ceramic Membranes

As early as the 1940’s inorganic membranes were developed for the enrichment of uranium. In the 1980’s, the knowledge gained was applied for the formation of ceramic MF and UF membranes for industrial separations [40]. Generally, ceramic membranes are asymmetric in structure with a dense upper region atop a porous support (Figure 1-6). The mechanically stable support materials include, but are not limited to, alumina, silica, zirconia, mullite, oxide mixtures, and sintered metals [41]. Typical ceramic membranes are formed via the sol-gel process, in which particle dispersions are forced to agglomerate [40, 42]. The asymmetric structure is achieved by depositing particles of decreasing size and sintering at high temperature in order to achieve continuous, porous layers [42]. Pore size and characteristics of the upper selective region may be tuned based upon the grain size and particle type selected [40].
Post treatments are applied to alter the porosity of ceramic membranes. Mullite (3Al$_2$O$_3$·2SiO$_2$) ceramic supports—formed through high temperature calcinations of kaoline clay—are desirable due to their enhanced mechanical strength. The extreme temperatures required for the formation of mullite allow for strong inter-crystalline bonds to form during the crystallization process. Free silica can be leached with a post treatment of strong alkali solution. The porosity of the resulting structure can be controlled by the leaching factors: time of leaching, concentration of leaching solution, and temperature at which leaching occurs [43]. Coatings (of porous metals, metal oxides, and zeolites) can also be applied to ceramic membranes to further control performance with coating thickness, pore structure, and surface characteristics [44].

With their enhanced mechanical, thermal, and chemical stability ceramic materials are well suited for challenging water purification processes, such as industrial wastewater, oil/water separations, and hazardous waste treatment [43]. Flux through ceramic membranes is more easily recovered after fouling because ceramics can withstand harsh chemical and thermal cleaning methods [45]. Ceramics pose the
opportunity for extended membrane lifetimes even under extreme fouling and cleaning conditions, which would destroy their polymeric counterparts. However, ceramics are typically considered too expensive for large-scale membrane applications, such as municipal drinking water production and wastewater treatment, so their application has been historically limited to relatively small-scale industrial separations not suitable for polymeric membranes [42, 45-46].

1.3.2. Integrally-Skinned Membranes

Porous polymeric membranes (i.e., MF/UF) have been applied to various water treatment processes, including water and wastewater filtration and as pretreatment for NF or RO membranes [38-39]. These membranes have an integrally skinned, often asymmetric structure consisting of an open porous support layer beneath a relatively thin, less porous skin layer of the same material (Figure 1-7) [5, 39, 47-48]. The separation occurs at the skin layer while the support provides a nearly resistance-free path for water (and unrejected solutes carried in the permeating water) to exit the membrane. The highly selective top layer of MF/UF membranes, having pores ranging from ~0.01 to ~0.2 µm, is considered the active region of the membrane [5, 39].

Flat sheet forms of MF/UF membranes are formed through nonsolvent induced phase inversion of preformed polymers over a nonwoven support fabric, which provides mechanical strength to the membrane. Alternatively, the phase inversion reaction can be carried out to form hollow fiber forms of MF/UF membranes. The phase inversion technique relies upon the controlled interaction of solvent and nonsolvent solutions to induce a phase separation transitioning a polymer from a liquid dispersion into a solid
state [5, 39, 49]. A recent review elucidates the details of this process [50]. A homogeneous polymer solution, containing polymer and solvent, is immersed into a nonsolvent coagulation bath and polymer solidification occurs during the miscible solvent and nonsolvent exchange [5, 49]. Membrane characteristics vary with casting conditions, polymer selection, polymer concentration, the solvent/nonsolvent system and additives, and coagulation bath conditions [5, 51-52].

Figure 1-7. Conceptual cross-section of an asymmetric, integrally skinned membrane.

Cellulose acetate (CA) was one of the first polymers employed in aqueous membranes, with the invention of the Loeb-Sourirajan asymmetric membrane in the 1950’s, and continues to be employed to form membranes with properties ranging from MF to RO [47, 53]. Other cellulosic derivatives include cellulose diacetate, triacetate, and regenerated cellulose. Cellulose acetate is obtained from cellulose – a naturally occurring
linear compound found in wood pulp and cotton linters – via acetylation; CA is hydrophilic and produces smooth membrane surfaces with low fouling propensity [54-55]. Cellulosic membranes are also relatively easy to manufacture with a wide range of pore sizes and are relatively inexpensive [53]. Disadvantages of CA include limited temperature range (less than 30 °C) and pH range (approximately 4-6) [5]. Higher temperatures and more alkaline conditions accelerate the rate of hydrolysis causing degradation of the polymer. A further operational limitation of CA membranes is their chlorine intolerance; continuous exposure of less than 1 mg·L⁻¹ of free chlorine will oxidize CA membranes opening the pores and causing a loss of selectivity [56]. Also, due to the cellulose backbone, CA membranes are biodegradable and can, in fact, be consumed by organisms growing in biofilms.

Other more widely applied MF/UF membrane polymers include polysulfone (PSf), polyethersulfone (PES), sulfonated PSf or PES, polyacrylonitrile (PAN), polypropylene (PP), polytetrafluoroethylene (PTFE, a.k.a., Teflon), and polyvinylidine fluoride (PVDF) [42]. These materials exhibit excellent permeability, selectivity, and stability in water treatment applications. Polysulfone and PES membranes are among the most popular materials for UF membranes, as well as the standard support substrates used in formation of NF and RO composite membranes, while PP and PVDF are more popular materials for MF membranes.

1.3.3. **Thin Film Composite Membranes**

A major breakthrough in the field of membrane separations was the development of thin film composite membranes, which comprise an ultra-thin “barrier” layer
polymerized \textit{in situ} over a porous polymeric support membrane \cite{5, 57}. These membranes are often referred to generically as “interfacial composite,” “composite,” or “TFC” membranes, although TFC\textregistered is registered trademark of Koch Membrane Systems, Inc. in the US and other countries. The major advantage of TFC membranes over integrally skinned asymmetric membranes is that the chemistry, and hence, performance of the upper selective layer and the porous support layer can be independently selected to optimize composite membrane performance \cite{58}. In addition, more expensive monomers can be used to form the selective layer without dramatically increasing cost because this region only accounts for a small portion of the total material. The key factors driving the development of TFC membrane materials over the past 40-50 years was the pursuit of high flux, high selectivity RO membranes for seawater desalination. Along the way, low-pressure RO membranes for desalting brackish water and for reclaiming wastewater to nearly ultrapure levels were developed along with NF membranes now used predominantly for water softening and dissolved organic removal.

Thin film composite membranes are born out of conventional asymmetric polymeric membranes and, thus, are structurally similar to those discussed above; however, in TFC membranes the support and active layers are composed of two distinct polymers. The porous layer is generally formed through phase inversion and the dense layer is applied through interfacial polymerization or coating (dip, spray, spin) followed by cross-linking \cite{5, 57}. Curing (heat, UV, chemical) is frequently applied to further of the extent of polymer cross-linking, which significantly impacts the stability, permeability, and selectivity of the thin film \cite{5, 52}. Thin film composite RO/NF
membranes are most often formed on the surface of a microporous support membrane via interfacial polymerization (i.e., in situ polycondensation).

A large number of TFC membranes have been successfully developed from different polymers such as polyurea, polyamide (PA), polyurea-amide, polyether-amide, and others [57, 59-61], most of which have shown excellent selectivity, in particular high salt selectivity and relatively high water permeability for RO applications. Polyamide chemistry, developed by Cadotte and others, was first applied in the 1960’s when DuPont and Monsanto developed asymmetric, integrally-skinned hollow fibers for RO seawater desalination [62]. Polyamide TFC membranes continue to be employed because they yield good salt rejection, while overcoming the relatively low flux of their integrally skinned counterparts. While PA can be used in greater temperature and pH ranges than CA membranes it is even less chlorine tolerant, which is a particular concern for seawater desalination applications.

Microporous supports for TFCs may be prepared from PSf, PES, sulfonated PSf and PES, polyether ketones, PVDF, sulfonated PVDF, or PAN through any number of casting procedures cited in the literature [56, 59, 63-64]. Polysulfone is the most widely used polymer for RO support membranes [5, 65]. Additives such as poly(ethylene glycol) and polyvinylpyrrolidone (PVP) have been made to PSf support membrane casting solutions to increase porosity of the support membrane skin layer, and thus, the composite membrane permeability [66-68]. Presumably, the de facto commercial TFC membrane is an interfacially polymerized PA thin film formed over a PSf membrane with molecular weight cutoff of about 60 kDa; [56, 59-60, 63-64, 69-72] however, the exact chemistry of commercial TFC membrane supports and coating films are proprietary.
Interfacial polymerization of TFC membranes is accomplished as follows [59-60, 63, 73]. The microporous support membrane is immersed in an aqueous solution containing the first reactant (e.g., a diamine monomer). The substrate is placed in contact with an organic solution containing the second reactant (e.g., a triacyl halide). The organic solution is chosen to be immiscible with the aqueous solution so that the reaction proceeds at the interface of the two solutions. A dense but very thin polymer layer forms over the support membrane surface, which inhibits further polyamide formation and stops the reaction. The selective layer formed is very thin, which provides high water permeability, but densely cross-linked, which provides high salt rejection. The most common TFC coating film chemistry explored in the open literature is based on the amine monomer 1,3-diaminobenzene or \textit{m}-phenylenediamine (MPD) polymerized with 1,3,5-tricarbonyl chloride or trimesoyl chloride (TMC), other di/tri-acid chlorides, or combinations thereof. The standard NF membrane derives from piperazine or polypiperazine derivatives polymerized with TMC, other di/tri-acid chlorides, or combinations thereof. It is suspected that most differences in commercial TFC NF/RO membranes result from the use of different support membranes, interfacial polymerization additives, and physical/chemical post-treatments [70-81].

One common goal of post-treatments is to reduce a TFC membrane’s propensity for surface fouling. This can be achieved through surface modifications via graft polymerization induced by methods such as plasma exposure [82-83], UV-photoinitiation [84], or redox initiation [73]. Recently, Kim \textit{et al.} produced nanostructured RO membranes through plasma induced graft polymerization, in which a PSf supported PA RO membrane is exposed to plasma at atmospheric pressure to prime the surface and then
free-radical graft polymerization of a small, hydrophilic, water soluble monomer, poly(methacrylic acid) (PMAA), is applied [83]. The nanostructured surface roughness of the PMAA film (5.2-7.1 nm thickness) is nearly three times that of the unmodified TFC membrane. Membrane permeability doubled, with negligible changes in salt rejection. The modified membranes appeared to resist gypsum scaling 2-5 times longer than a low-fouling commercial RO membrane. This appears to be the first appearance in the open literature of a plasma-induced graft polymerization process at atmospheric conditions, which makes it potentially compatible with conventional membrane manufacturing infrastructure.

### 1.3.4. Mixed Matrix Membranes

Mixed matrix membranes seek to take advantage of both the low cost and ease of fabrication of organic polymeric membranes and the mechanical strength and functional properties of inorganic materials. Zimmerman et al. first discussed mixed matrix membranes in the 1990’s as a way to push the limitations of polymeric membranes for gas separations [85]. Mixed matrix membranes including inorganic molecular sieves, such as zeolites and silicalite, embedded within a polymer matrix are employed to provide preferential flow paths for the target species to pass through [86-89]. The formation of continuous pathways of fast diffusion molecular sieves is theorized to occur at a volume fraction of filler material known as the ‘percolation threshold’. At this point, target molecules can traverse the entire membrane cross-section through the filler [85] [90-91] [92]. Above certain high volume fractions, defects tend to occur at the polymer-filler interface limiting selectivity [85]. Mixed matrix membranes present an opportunity
for tunable water treatment membranes as well, through increased selectivity, targeted functionalities, and improved thermal, chemical and mechanical stability. The interplay between enhanced properties and defect formation must be balanced to derive positive benefits without compromising the integrity of the membrane.

Micron-sized inorganic particles are added to typical porous water treatment membranes to achieve enhanced selectivity, as well as other functional properties [93-97]. Inorganic fillers in porous membranes are shown to inhibit macrovoid formation, increase pore interconnectivity, and improve mechanical strength [94]. Such morphological and mechanical changes are desirable to avoid compaction of membranes during high-pressure separations. One example of this is the Zirfon® UF membrane, composed of an asymmetric PSf membrane with zirconia (ZrO$_2$) particles [94, 96]. These membranes exhibit elevated permeability without compromise of particle retention [94, 96]. The increased permeability is due to grain disturbances that occur when zirconia content is sufficiently high (~40 wt.%) during phase inversion formation of the top layer and increase pore distribution preferentially at the particle-matrix interface [93, 96]. Aerts et al. report that as zirconia particle (~0.9 µm) content increases, elastic strain in Zirfon® UF membranes decreases, producing a more mechanically robust membrane [93]. Wara et al. dispersed ceramic alumina particles (~0.34 µm) in CA membranes during phase inversion, observing reduced macrovoids and, thus, increased selectivity [95].
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CHAPTER 2

NANOTECHNOLOGY-ENABLED
WATER TREATMENT MEMBRANES
2.1.0. Nanotechnology for Water Treatment

Over the past decade, nanotechnology has rapidly changed from an academic pursuit to commercial reality. Nanotechnology promises to dramatically enhance many water purification technologies such as adsorption, ion exchange, oxidation, reduction, filtration, membranes, and disinfection processes [1]; however, one key issue related to nanotechnology is the question of how to best apply it. Specifically, it is not clear how to interface nanoparticles with contaminants. At present, many expensive nanoparticles cannot be added to water like commodity chemicals and some nanoparticles could present new hazards to human health and the environment [2]. Thus, additional separation processes are required to recover nano-materials for risk avoidance and reuse. A promising approach is to immobilize nanomaterials on or within a solid matrix, such as a membrane. The resulting membrane may exhibit improved separation performance, chemical, thermal or mechanical stability, interfacial properties, or advanced functionality depending on the nano-material selected.

Already nanotechnology concepts have led to new water treatment membranes that exceed state-of-the-art performance and enable new functionality, such as high permeability, catalytic reactivity, and fouling resistance. Herein, we present a brief overview of conventional materials used to prepare “state-of-the-art” pressure-driven membranes [3]. This is followed by a critical review of current literature on nanotechnology-enabled water treatment membrane materials. Finally, we compare the “present day” merits and limitations of each water treatment membrane nanotechnology.
2.2.0. Nanostructured Inorganic Materials

2.2.1. Zeolite-Coated Ceramic Membranes

A current thrust in ceramic membrane development is to form membranes with water permeability on the range of UF membranes, but solute selectivity like that of NF or RO membranes [4]. In 2001, molecular dynamics simulations showed that zeolite membranes—previously applied solely for gas separations—may be applicable for aqueous osmotic separations [5]. Since then, thin zeolite membranes have been studied for RO desalination of brackish water as well as a variety of wastewaters [6-12]. For RO applications, ceramic alternatives offer the clear advantage of mechanical stability under high pressures and chemical stability to withstand disinfectants. In many wastewater treatment applications, ceramic membranes are more fouling-resistant and chemically stable than current polymeric membranes.

Zeolites are naturally occurring aluminosilicate minerals with highly uniform sub-nanometer and nanometer scale crystalline structures. Typical zeolite membranes are amorphous silicate, aluminosilicate or aluminophosphate crystalline structures formed via hydrothermal synthesis [13-14]. Other synthesis methods include in situ layer-by-layer crystallization and dry gel conversion in the presence of a template-water vapor [15]. Aluminosilicate crystals are intrinsically inert, imbuing these membranes with extreme thermal and chemical stability [12]. Zeolite crystals consist of a three-dimensional cross-linked (Si/Al)O₄ tetrahedral framework, in which each Al or Si atom occupies the vertex of a network connecting four oxygen atoms. The framework structure contains cavities that allow for the movement and containment of ions and water molecules [16]. The containment of molecules in a given zeolite framework is a function of temperature,
water content, ion type, and the ratio of Si to Al atoms in the matrix [17]. Cronstedt, a Swedish mineralogist, first characterized these structures in 1756, terming them zeolites, a term with Greek roots meaning ‘boiling stones’, because of their inherent ability to give up water upon heating [17]. Many natural zeolites can be produced synthetically, while additional structures, with no natural occurrence, have been synthesized and are characterized as zeolites based on their structures, such as zeolite-A produced by Linde Corporation [17].

A few common zeolite materials employed in membranes include MFI-type, sodalite (SOD), and Linde Type A (LTA). Zeolite ZSM-5 (MFI)—the most commonly applied zeolite in membranes—is composed of a unit cell with the chemical formula $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}\sim16\text{H}_2\text{O}(n\sim3)$ [17]. The MFI structure contains straight channels in one direction and perpendicular sinusoidal channels that are not interconnected [12]. The drawback of employing MFI-type zeolites in porous membranes is that the crystals must be oriented with respect to the permeation direction. The hydrated form of SOD, referred to as hydroxyl sodalite [17], has also been applied in membrane materials [13]. This mineral has the chemical formula $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}·8\text{H}_2\text{O}$ [17]. Sodalites are not mineralogically defined as zeolites, but felspathoids because in nature salt molecules are contained in their frameworks. The SOD cage, often referred to as the $\beta$-cage, is quite common to zeolite structures and when crystalline networks are created with this cage structure zeolitic properties are exhibited. One common example is the zeolite-A (LTA) unit cell, defined by the chemical formula $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}·27\text{H}_2\text{O}$ [17]. The LTA structure is composed of SOD cages ($\beta$-cages) connected by truncated cubo-octahedron ($\alpha$-cages), forming an interconnected cage structure. The interconnected inner channel in
LTA offers the opportunity for simplified membrane fabrication since crystal alignment is unnecessary.

Pore size and framework density are the primary factors of concern when considering zeolites for water separations; pore size determines ion selectivity and framework density determines water permeability. Atoms other than Si and Al can be substituted into the cage structures of zeolites via ion exchange to imbue alternate charge and structural properties. Since the ability to act as a molecular sieve is due to the channel widths, changing the atoms in the framework, and thus the channel widths, will change the sieve properties [18]. Additionally, both the ion and water molecule mobility through a zeolite depend upon the relative density of the framework structure; open porous structures will facilitate less hindered transport [17]. This is indicated by the framework density, defined as the number of Si or Al atoms per 1000 Å. Framework densities (normalized for ideal Si frameworks) are 18.4, 16.7, and 14.2 for MFI, SOD, and LTA, respectively [19], implying that LTA would be expected to have the largest water mobility.

The Si:Al ratio of a zeolite cage is the most important factor affecting chemical stability, hydrophilic properties, and occurrence of inter-crystalline defects [17] – all primary factors of concern when engineering selective and robust water treatment membranes. An increase in Si:Al ratio implies a decrease in the overall surface charge on the framework. The MFI-type zeolites are capable of a large range of Si:Al ratios, from approximately 30 in the ZSM-5 form to nearly pure Si for the isomorphous silicate type MFI. Noack et al. find that as the Si:Al ratio decreases in MFI-type zeolites water
permeability and selectivity for water increase; however, defects simultaneously increase until a point where selectivity is compromised [15].

Separations in zeolitic materials occur primarily through molecular sieving, competitive adsorption or ion exchange [13]. Ions with small hydrated radii diffuse more quickly through zeolite pore structures. Cationic adsorption occurs onto the negatively charged surface of zeolite membranes, and may enhance diffusion by establishing a charge gradient. Initially, adsorption occurs onto the pore walls. Inter-crystalline molecular sieving occurs when the electrical double layers of these adsorbed ions overlap and inhibit the passage of charged ions [6-7]. Hydrophilic zeolite membranes previously applied for gas separations are composed of a loose, thick zeolite film through which separation occurs [20-23]. However, the new RO membranes being developed require an ultra-thin, dense layer and so pains must be taken to form nanoscale zeolite coatings to produce membranes with permeability on par with polymeric RO membranes.

Li et al. apply MFI-type zeolite membranes (thickness ~3 µm) for RO desalination (with 0.1 M NaCl feed solution at 2.07 MPa) [6]. Water flux is 0.112 kg·m⁻²·h⁻¹ with 76.7% Na⁺ rejection. The membrane is also challenged with a complex solution, more reminiscent of real RO feed waters, and the resulting water flux and rejection are lower (0.058 kg·m⁻²·h⁻¹ with Na⁺ rejection of 58.1%). The reduced rejection is attributed to double layer compression within intercrystal pores of the zeolite material due to the high ionic strength of the feed solution. Another study with similar MFI membranes reports higher flux and rejection values (>95% of Na⁺ ions) [7]. Higher trans-membrane pressure increases water permeation and observed ion rejection, resulting in better separation performance. Higher operating temperature increases both water and salt
permeation, but having a larger impact on salt permeation. This is due to the reduced viscosity of the feed solution and increased diffusivity of water molecules and salt ions [6]. The effect of temperature is consistent with that observed for traditional polymeric RO membranes, absent the effects of polymer swelling at higher temperatures [24]. While these membranes served as a proof of concept, higher water flux and salt rejection are both needed for MFI-based RO membranes to be commercially viable.

Duke et al. prepare MFI-type membranes for seawater desalination via template-free secondary growth [8]. Zeolite films are formed over alumina supports by dip coating in a silicalite suspension and grown under hydrothermal conditions. This method improves control over membrane formation and produces fewer defects by decoupling the deposition and crystal growth steps. Alumina content should influence surface hydrophobicity and charge [15]; however, in this study surface charge did not vary with Si:Al ratio [8]. In RO mode (with 0.5 wt.% sea salts at 700 kPa) rejection is highest (50%) in an alumina-free silicate membrane due to strong electrostatic shielding of Na\(^+\) ions by the monopolar surface, which maintains the ideal double layer for this application. Because the Si:Al ratio allows for tuning of the surface properties and the resultant electrostatic double layer such membranes could also be tuned for specific ion-selective applications, but further work is needed to fully understand the connection between zeolite chemistry and membrane performance.

Liu et al. form an \(\alpha\)-alumina supported MFI-type zeolite membrane via in situ crystallization on the inner surface of tubular ceramic membranes for the removal of organics from produced water [12]. In RO (with 0.1 M NaCl solution at 2.76 MPa) the membranes produce a water flux of 0.35 kg·m\(^{-2}\)·h\(^{-1}\) with Na\(^+\) rejection of 99.4%. Ion
separation occurs via size exclusion of hydrated ions as well as Donnan exclusion at pore entries. When tested for produced water treatment the coated membranes exhibit a water flux of 0.33 kg·m⁻²·h⁻¹ with an organics rejection of 96.5%. With non-electrolyte solutions zeolite membrane selectivity is dominated by molecular sieving and so very different rejections are seen for high and low dynamic molecular size compounds. This work produced high salt rejections, but higher permeability must concurrently be achieved for practical application of these zeolite membranes.

Kumakiri et al. synthesize A-type zeolite membranes via hydrothermal synthesis atop a porous α-alumina substrate [14]. The substrate is seeded with crystals, dipped in an alumina-silica solution, and crystallized at 80°C for 5 hours. This process is repeated multiple times until reasonable separation performance is achieved. The membranes tested for performance in RO (with 10 wt.% ethanol feed solution at 1.47 MPa and 30 °C) have pure water flux of 0.14 kg·m⁻²·h⁻¹. The membrane selectivity for the ethanol/water mixture is 44%. Flux varies linearly with applied pressure, while selectivity is not significantly influenced. Most significantly, the membrane is mechanically stable up to pressures as high as 50 kgf·cm⁻² (4.90 MPa). If performance of these membranes can be made competitive, their mechanical strength will make them ideal in high-pressure applications.

Kazemimoghadam formed composite polycrystalline hydroxyl SOD membranes atop high porosity tubular mullite supports [13]. The active SOD layer was formed through hydrothermal growth by coating the ceramic support with crystal seeds (~0.4 nm diameter), dipping it in a homogeneous aluminate-silicate gel, and treating it at 100°C to allow crystal growth. The zeolitic membrane was tested for performance as an RO
membrane for water treatment at variable trans-membrane pressures (100 to 300 kPa), feed temperatures (20 to 60 ºC), and feed rates (0.5 to 3 L·min⁻¹). Flux increased with trans-membrane pressure, temperature (due to resulting lower viscosity), and feed rates (due to enhanced turbulence and hydrodynamic effects). High permeability was achieved (∼10⁻¹² m·Pa⁻¹·s⁻¹), on the order of current polymeric seawater RO membranes; however, no salt rejection data was published. If competitive selectivity can also be achieved, these materials may offer new opportunities for RO membranes in high temperature, pressure, and fouling applications.

Here we normalized zeolite membrane water permeability (from each paper reviewed above) by zeolite film thickness and performed the same calculation for permeabilities typically reported for commercial polymeric RO membranes to produce a Darcy permeability—defined as ‘specific water permeability’ in Table 2-1 [25]. While the permeability of the relatively thick (~3-50 μm) zeolite films formed to date do not compare to ultra-thin (~50-250 nm) TFC RO membranes, the specific water permeability compares favorably in some cases. Specifically, the SOD membranes produced by Kazemimoghadam et al. [13] appear to have specific water permeability 3 orders of magnitude lower than commercial seawater RO membranes. If defect free zeolite films could be formed with thickness of 0.2 μm, the resultant membrane would have a water permeability of ∼0.5×10⁻¹⁰, which is equivalent to a tight polymeric UF membrane. Obviously, this could make zeolite-based RO membranes a viable alternative material for high flux RO membranes, but with dramatically enhanced thermal, mechanical, and chemical stability. The challenge remains improving control over crystal nucleation and
growth to ensure defect free ultra-thin zeolite films, which may require abandoning or substantially modifying traditional hydrothermal synthesis methods [14].

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Test Temp (°C)</th>
<th>Film Thickness (μm)</th>
<th>Solute Type</th>
<th>Solute Rejection (%)</th>
<th>Solute Permeability (m·s⁻¹)</th>
<th>Water Permeability (m·Pa⁻¹·s⁻¹)</th>
<th>Specific Water Permeability (m²·Pa⁻¹·s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWRO*</td>
<td>20</td>
<td>~0.2</td>
<td>NaCl (32 g/l)</td>
<td>99.7</td>
<td>~2×10⁻⁸</td>
<td>~3×10⁻¹²</td>
<td>~0.6×10⁻¹⁸</td>
<td>25</td>
</tr>
<tr>
<td>BWRO</td>
<td>20</td>
<td>~0.1</td>
<td>NaCl (2 g/l)</td>
<td>98.5</td>
<td>~7×10⁻⁸</td>
<td>~10⁻¹²</td>
<td>~1×10⁻¹⁸</td>
<td>25</td>
</tr>
<tr>
<td>HFRO</td>
<td>20</td>
<td>~0.1</td>
<td>NaCl (0.5–1.5 g/l)</td>
<td>97.5</td>
<td>~1×10⁻⁷</td>
<td>~20⁻¹²</td>
<td>~2×10⁻¹⁸</td>
<td>25</td>
</tr>
<tr>
<td>NF</td>
<td>20</td>
<td>~0.05</td>
<td>MgSO₄ (0.5 g/l)</td>
<td>98.0</td>
<td>~10⁻⁷</td>
<td>~40⁻¹²</td>
<td>~2×10⁻¹⁸</td>
<td>25</td>
</tr>
<tr>
<td>MFI</td>
<td>20</td>
<td>~3</td>
<td>NaCl (0.1 M)</td>
<td>76.7</td>
<td>7×10⁻⁷</td>
<td>~0.01⁻¹²</td>
<td>~0.04⁻¹⁸</td>
<td>6</td>
</tr>
<tr>
<td>MFI</td>
<td>30</td>
<td>~3</td>
<td>NaCl (0.1 M)</td>
<td>98.0</td>
<td>2×10⁻⁷</td>
<td>~0.03⁻¹²</td>
<td>~0.1⁻¹⁸</td>
<td>7</td>
</tr>
<tr>
<td>MFI</td>
<td>20</td>
<td>~1.2</td>
<td>NaCl (0.1 M)</td>
<td>99.4</td>
<td>0.6×10⁻⁷</td>
<td>~0.03⁻¹²</td>
<td>~0.04⁻¹⁸</td>
<td>12</td>
</tr>
<tr>
<td>SOD</td>
<td>20</td>
<td>~50</td>
<td>none tested</td>
<td>99.4</td>
<td>~2×10⁻¹²</td>
<td>~10⁻¹⁸</td>
<td>~10⁻¹⁸</td>
<td>13</td>
</tr>
<tr>
<td>LTA</td>
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<td>none tested</td>
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<td>~0.03⁻¹²</td>
<td>~0.1⁻¹⁸</td>
<td>~10⁻¹⁸</td>
<td>14</td>
</tr>
</tbody>
</table>

*Commercial polymeric seawater RO (SWRO), brackish water RO (BWRO), high-flux RO (HFRO)

Perhaps other fields should be examined for insight into new fabrication approaches. For example, Öztürk and Akata present a method for the oriented assembly of zeolite-A monolayers for nanoelectronics applications [26]. E-beam lithography is combined with direct attachment to form patterned mono and double layers of zeolite-A nanocrystals (~250 nm) atop silicon wafers. A dilute PMMA solution is spun onto silicon wafer surfaces to form resist films (~400 and 850 nm thick). The films are pre-baked and then patterns are defined with e-beam lithography. Direct attachment is achieved by applying a zeolite powder to the silicon wafer, pressing the zeolites, and heating. The direct attachment method results in >90% coverage of the silicon surface, strong binding
to the wafer, and strong organization with a cube face of each zeolite oriented parallel to the silicon surface. Coverage is limited by the degree of homogeneity of the synthesized nanocrystals and pattern resolution is limited by the size of the nanocrystal, implying further tunability of the procedure. While this method is likely too expensive for large-scale membrane fabrication, alternative low-cost direct attachment methods could be sought by examining the rich knowledge of inorganic thin films in other fields.

2.2.2. Reactive/Catalytic Ceramic Membranes

Reactive surfaces are applied in water treatment as semiconductor-based (e.g., titania, zinc oxide, ferric oxide) membranes activated by UV or sunlight to engage in redox processes for the degradation of organic compounds [27-30]. The application of photocatalysis to water treatment was first discussed by Carey et al. in 1976 when they recognized the ability to degrade polychlorobiphenyls (PCBs) [31]. Semiconductor electronic properties are defined by having a filled valence band and an empty conduction band. In photocatalysis, semiconductors function by absorbing a photon of energy greater than their own bandgap energy, and creating an electron-hole pair via excitation of electrons from the conductive to the valence band [27, 32]. Photocatalysis occurs when a semi-conductor nanoparticle is irradiated with an amount of energy, $hv$, greater than its own bandgap energy, $\Delta E$. These electron-hole pairs will either recombine (in a matter of nanoseconds) or react with the surrounding media. The latter is only possible if the electron and/or hole can be trapped in a surface defect or captured by an appropriate scavenger in the bulk media [33].
In bulk semiconductor materials, only the hole or electron is normally available for interaction; however, in nanoscale materials both are available at the surface allowing for high efficiency interactions. The mechanism by which oxidation of organic molecules in water is initiated at the particle surface is not yet fully understood, but theories include direct oxidation by the electron hole (positron), indirect oxidation via hydroxyl radicals produced on the surface or in the solution, or some combination thereof [27]. Suspended nano-photocatalysts are applied for remediation of contaminants; the suspended state provides maximum surface area and activity [34-36]. The key drawbacks of suspended processes are nanocatalyst recovery and regeneration (or disposal) of spent material. A clever approach is catalyst coated magnetic iron oxide nanoparticles, which would enable magnetic recovery of nanoparticles [37-38].

Catalysts coatings have been formed on polymeric membranes to create reactive surfaces for enhanced separations while eliminating the complexity of catalyst recovery [39-44]. Titania nanoparticles are highly photoactive and exhibit antimicrobial activity under UV light [32, 45]. Water purification systems based on photolytic disinfection are currently available. Inactivation of pathogens occurs by DNA damage from UV irradiation and through the production of reactive oxygen species, in particular hydroxyl radicals, which damage the cell wall of organisms (inactivation by cell lysis). Molinari et al. altered commercially available porous polymeric membranes with a titania layer, by filtering a nanoparticle suspension through and applying UV/vis irradiation and show elevated (4-Nitrophenol) photodegradation [39]. Madaeni and Ghaemi form “self-cleaning” RO membranes with the addition of titania nanoparticles; the cleaning, as well as elevated flux, witnessed upon UV application are attributed to two concurrent
phenomena: photocatalysis and ultra-hydrophilicity [41]. To curtail the inevitable titania-catalyzed UV degradation of the organic parts of the conventional membranes, Mo et al. prepare PSf-supported self-cleaning PA/titania membranes through interfacial polymerization, which contain a layer of silicon dioxide between layers of cross-linked PA and titania [40]. Flux recovery after 15 h of operation (with water cleansing and UV exposure every 3 h) is greater than 98% for these photocatalytic membranes, significantly higher than standard water treatment membranes.

Titania nanopowders are also applied to ceramic membrane surfaces, such as silica [46-47], alumina [48], zeolites [49], and activated carbon [50], which are more stable than polymers under UV light and in the presence of reactive oxygen species. Choi et al. report on reactive membranes with titania coatings atop alumina supports [48]. Acid and surfactant are employed in the sol-gel process to tailor the resulting membrane morphology and produce high efficiency films and composites. XRD analysis reveals anatase crystals throughout the thin film with crystalline size of 8-10 nm. This size range is known to produce the optimum catalytic activity because it is the point where the blue shift occurs favoring surface recombination of electron-hole pairs and allowing for the maximum number of active sites per mass of catalyst [51]. The structure of these films is highly porous and interconnected, enabling a high surface area for both adsorption and photocatalytic activity on the titania surface. Three dip-coatings are sufficient to create a defect-free skin layer (~0.9 µm thick); while more layers may be desirable to provide more active area, each layer also increases processing time and cost [48]. The resulting membrane has water permeability of 6.71 L·m⁻²·bar⁻¹·h⁻¹ and molecular weight cut-off of ~12 kDa. The overall permeability is high considering that the Al₂O₃ substrate has a
relatively low permeability (11.0 \text{ L \cdot m}^{-2} \cdot \text{bar}^{-1} \cdot \text{h}^{-1}); even higher permeability may be achieved with more permeable ceramic supports (e.g., mullite).

Catalytic ozonation is used for natural organic matter and organic compound removal in water and wastewater treatment; when combined with a catalytic metal oxide other substances can be degraded such as phenols, aromatic hydrocarbons, and humic substances [52-55]. Karnik et al. exhibit the potential for catalytic membranes in combined ozonation/UF for disinfection byproduct removal [56]. Commercially available ceramic membranes (composed of a mixture of alumina, zirconia, and titania) are coated via the layer-by-layer technique with iron oxide nanoparticles (4-6 nm diameter). The coating layer has negligible resistance, witnessed by unchanged membrane permeability. The membranes serve as catalysts in the ozone degradation of natural organic matter and disinfection by-products. Specifically, total trihalomethanes and halogenic acetic acids, are removed up to 90 and 85%, respectively. The proposed mechanism by which this degradation occurs is the decomposition of ozone on the iron oxide coating surfaces, enhancing hydroxyl radical production and, thus, degradation [57-58].

The major limitation of photocatalysis is the fast recombination of the produced electron-hole pairs. This limits degradation of organics and inactivation of organisms with complex, dense cell wall structures, such as bacterial endospores that require longer exposure times [32, 59]. When immobilized in membranes or in reactive surfaces, the active area is reduced, further limiting the photoactivity [38]. Research shows that doping the particles with ions increases the photoactivity by separating the photo-induced charges and enhancing surface availability [59-61]. For disinfection applications, reactive oxygen species production that ultimately leads to cell wall compromise and cell demise
is limited by the ability for the nanoparticle to maintain electron-hole pairs [32, 62]. Krishna et al. coat multi-walled carbon nanotubes (CNTs) (known to have large surface area and substantial photon-generated electron trapping capacity) with titania in order to delay recombination [32]. Titania-coated CNTs display two times the inactivation rate of commercially available titania alone when tested on *B. cereus* spores.

**Table 2-2.** Comparison of applications and advantages demonstrated by organic, hybrid, and inorganic membranes

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Applications and Advantages Demonstrated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MF</td>
</tr>
<tr>
<td>Polymeric</td>
<td>✓</td>
</tr>
<tr>
<td>Mixed Matrix</td>
<td>✓</td>
</tr>
<tr>
<td>Catalytic/Reactive</td>
<td>✓</td>
</tr>
<tr>
<td>Ceramic</td>
<td>✓</td>
</tr>
</tbody>
</table>

Both zeolite and catalyst-coated membranes face similar challenges as have always faced ceramic water treatment membranes, that is, high manufacturing cost and low packing density relative to polymeric membranes. A comparison of the advantages each novel inorganic material brings to the membrane landscape is presented in **Table 2-2**. Reactive and catalytic membranes are not introduced as a way to enhance performance over current membrane technologies, but rather to introduce new capabilities to ceramic membrane materials. An additional hindrance of photocatalytic water treatment is the energy demand for irradiating the surfaces. To minimize this, solar induced
photocatalytic surfaces have been investigated and applied [44, 63]. Reactive surface-mediated photocatalysis for water treatment shows promise, particularly for the purpose of small-scale production where solar energy can be utilized.

2.3.0. Nanomaterial-Based Composite Materials

2.3.1. Nanocomposite Mixed Matrix Membranes

Today, mixed matrix membranes comprising nanoparticle fillers are emerging. These membranes are also referred to as polymer-nanocomposite membranes. Isodimensional nanoparticles are commonly used as nanocomposite fillers as they provide the highest surface area per unit volume. Nanoparticles for membrane applications are most often prepared through the sol-gel process, which yields high purity samples and allows for control over size, composition, and surface chemistry [64-65]. Additional formation processes include: inert gas condensation, pulsed laser ablation, spark discharge generation, ion sputtering, spray pyrolysis, laser pyrolysis, photothermal synthesis, thermal plasma synthesis, flame synthesis, low-temperature reactive synthesis, flame spray pyrolysis, mechanical alloying/milling, mechano-chemical synthesis, and electrodeposition [64]. The favorable characteristics of nanoparticles can be exploited, similar to micron-scale inorganic particles, by directly including these particles in the casting solution.

Attention to nanoparticles for environmental applications has grown as their ability to preferentially disinfect, adsorb, and degrade pollutants in aqueous solutions is realized [1, 64, 66-68]. Metal oxide nanoparticles, specifically magnesium oxide (MgO) particles, inactivate Gram-positive bacteria, Gram-negative bacteria, and spore cells [66].
Alumina nanoparticles are useful as an adsorbent for nickel [Ni(II)] in aqueous solutions [69]. Iron oxide, aluminum oxide, and titanium oxide nanoparticles adsorb heavy metals [64]. Zero-valent iron nanoparticles have been applied for the removal of halogenated hydrocarbons, radionuclides, and organic compounds [70-72]. Such nanoparticles pose an efficient alternative to activated carbon for water and wastewater treatment, with increased surface area and activity due to their nanoscale characteristics [64]. Nanocomposite membranes have been researched for a variety of goals, including targeted degradation, enhanced flux and selectivity, decreased fouling propensity, and increased thermal and mechanical stability [73-82], while maintaining the ease of fabrication and low cost of their fully polymeric counterparts.

Targeted degradation can be achieved with addition of nanoparticles to polymeric membranes, particularly for reductive dechlorination processes [83-85]. Bi-metallic nanoparticles (e.g., Fe/Pd, Fe/Ni, Mg/Pd) are applied for pollutant degradation, wherein the first zero-valent metal, often iron, serves as an electron donor and is actually responsible for degrading the target compound while the second metal serves as a catalyst to promote the reaction through hydrogenation [85-90]. Wu et al. employ CA supported palladium-coated iron nanoparticles (~10 nm; 1.9 wt.% Pd) formed through microemulsion to facilitate trichloroethylene decomposition and find that dechlorination is significantly enhanced [83-84]. Smuleac et al. show elevated degradation of 2,2’-dichlorobiphenyl with PVDF membranes containing similar Fe/Pd nanoparticles (~20-30 nm) formed through in situ polymerization [85]. In the latter case, nanoparticles are formed within the polymeric matrix through an ion exchange with Fe²⁺, followed by reduction to Fe⁰, and deposition of Pd. In situ formation of nanoparticles inhibits
agglomerate formation, a common issue when nanoparticles are dispersed in membrane casting solutions [91]. Good dispersion of nanoparticles is required to reap benefits for mixed matrix membranes; in some cases, membranes containing nanoparticle agglomerates perform worse than the unmodified membranes with no fillers at all [92].

Particles that alter the surface properties of membranes can change separation performance and fouling behavior [74, 93-94]. Yan et al. add alumina nanoparticles (~10 nm; 19 wt.%) to casting solution during phase inversion of PVDF to form mixed matrix UF membranes [74]. While pore density and size are not altered, hydrophilicity, water permeability, fouling resistance, flux recovery, and mechanical stability increase [74]. Maximous and Nakhla prepare PES UF membranes with alumina nanoparticles (~0.48 nm; 0.01-0.05 wt.%) and find that membrane fouling and flux decline are reduced [75]. Fan et al. add polyaniline (PANI) nanofibers to commercial UF membranes (1-15 wt.%) and find increases in water permeability, selectivity, and surface wettability [76-77]. Antifouling nature improves and flux recovery increases (to as high as 90%) with particle additions in the blended membranes [76]. Furthermore, flux recovery could be achieved with a simply water cleanse, implying that adsorption to these improved surfaces is much weaker than to unmodified membranes [77].

Reduced fouling via enhanced hydrophilicity is a goal of many nanocomposite studies. Luo et al. produce PES UF membranes dip-coated with titania nanoparticles and find contact angle reduction from 39.6 to 19.2 degrees [95]. The same group cast films with controlled titania contents (5, 10, and 15 wt.%) and find the largest reduction in contact angle at 10 wt.% (from 79.6 to 41.2°); at the higher 15 wt.% contact angle reduction dropped off (to 73.8°) possibly because of nanoparticle agglomeration [96].
This beneficial breakpoint points toward the existence of optimum particle loading depending on starting materials. Bae et al. form titania nanocomposite polymer membranes through electrostatic self-assembly and find reductions in cake layer formation, including reductions in initial sharp flux decline and eventual irreversible fouling [97]. It is found that pore size and water permeability slightly decrease [97], but depending on application the anti-fouling capacity may outweigh this loss.

Particles with antimicrobial properties can help reduce biofouling of membranes [98]. Silver nanoparticles are excellent bacteriocides [78, 99-101]. Silver nanoparticle coatings are now widely applied as antibacterial safeguards in many consumer products [101]. Morones et al. study the activity of nanoscale silver particles embedded in a carbon matrix towards four types of Gram-negative bacteria and find that all four are inactivated due to interaction with the silver nanoparticles [78]; however, only those particles freed from the carbon matrix are able to interact with the cell membranes, enter the cells, and effectively inactivate them. Biofilm formation is successfully reduced in nano-silver containing membranes due to the successive release of ionic silver over the lifetime of a membrane [73].

In order to ensure sustained ion release, silver nanoparticles incorporated in membranes must be fully reduced to the zero-valent state [102]. Taurozzi et al. find that when PSf membranes are formed with silver nanoparticles included in the casting solution—both following ex situ reduction of the nanoparticles prior to addition to the casting solution and with in situ reduction during casting—water permeability increased, with slight reductions in solute rejection [73]. Enhanced performance is attributed to macrovoid broadening and increased pore size and pore density due to the presence of
nanoparticles. Because nanosilver dissolves rapidly in water, long-term testing is needed to quantify the lifetime of these membranes and to understand the impacts of defect formation due silver dissolution.

Mixed matrix membranes have been formed with the addition of nanotubes [103-105]. Carbon nanotubes exhibit antimicrobial activity [106]; thus, presenting an opportunity for improved disinfection or antifouling membranes. Bundling is often an issue, especially with single-walled CNTs, due to the van der Waals interactions between nanotubes and the fact that they are insoluble in water and organic solvents; this hinders the application for large scale fabrication of membrane materials [107]. Lin et al. recommend functionalizing CNTs with polymer groups that are structurally similar to the bulk polymer matrix to aid nanotube dispersion and homogenous membrane properties [105].

Choi et al. cast multi-walled CNT/PSf mixed matrix membranes by nonsolvent induced phase inversion [103]. Nanotubes are pretreated with acid to aid in dispersion throughout the solvent. Surface hydrophilicity of the membranes increases with the presence of CNTs due to the carboxylic acid groups that form on CNT surfaces during acid pretreatment. Pore size increases with nanotube additions up to 1.5 wt.% and then decreases, becoming smaller than pure PSf at 4 wt.%. Water permeability and rejection increased with nanotube additions as high as 2 wt.%, likely because the improved hydrophilicity and resulting anti-fouling ability plays the dominant role in membrane performance. At 4 wt. % the permeability begins to drop and the rejection increases. This may be an example where the blended membrane structure is being defected at low additions, and pores are being blocked at high additions, based on the results seen. Brunet
et al. formed nanotube/polymer membranes by dispersing multi-walled CNTs (4 wt.%) throughout a PSf/PVP polymer matrix via phase inversion [104]. PVP seemed to aid in the dispersion of CNTs throughout the membrane casting solution. Mechanical stability (indicated by the degree of elongation to failure) is only slightly enhanced in the mixed matrices with well-dispersed nanotubes; however, if dispersion could be better achieved this should increase since the presence of CNT aggregates reduces stability. The blended membranes did not display the desired antimicrobial activity because the contact between organisms and the CNTs stabilized in the polymer matrix is not sufficient to enable inactivation. Future applications may attempt to expose CNTs to solution for antimicrobial applications.

Inorganic fillers additionally enhance the thermal and mechanical stability of polymeric membranes by reducing the impacts of heating and membrane compaction. Compaction occurs during the initial stages of membrane operation, resulting in irrecoverable flux decline [108]. The majority of compaction is known to occur in the bulk macrovoid region of asymmetric membranes [109] and so adding mechanically strong fillers to this region is thought to assist in reduced structural losses. Ebert et al. demonstrate increased stability of poly(vinylidene fluoride) (PVDF) membranes when titania nanoparticles are included as inorganic fillers in the phase inversion casting solution [110]. Filled membranes exhibit higher thermal stability (as witnessed by minimal change in pore distribution following heat treatment) and less compaction (as seen by minimal structural changes after pressure application in the filled membranes). Calculations show an 83% decrease in pore volume in pure PVDF membranes, but only a 17% decrease in PVDF/titania membranes following compaction [110]. In another study,
silica and zeolite nanocomposite-PSf supported RO membranes are shown to experience less compaction than pure PSf supported membranes [111]. In general, the nanocomposite-PSf supported membranes have higher initial water permeation and less flux decline during compaction. Electron microscopy images verify that the nanocomposite-PSf supports resist the deleterious impacts of compaction by maintaining open surface pores better than the pure PSf supported RO membrane.

Mixed matrix membranes can also be formed by dispersing polymeric structures within inorganic matrices. Arkas et al. synthesized organo-silicon dendritic networks within a porous ceramic membrane and showed the resultant filter was effective at removing toxic polycyclic aromatic compounds from water [112]. Dendrimers are polymers with a high level of branching and symmetric structure of central core, repeating polymer units, and terminal functional groups. While dendritic polymer synthesis is more tedious than conventional polymers, the tunable functional groups and tendency to form nanocavities make them desirable for functional membrane applications. The filters are capable of reducing polycyclic aromatics in water to a few ppb. The filters are also regenerated by acetonitrile washing thanks to the chemical stability of the ceramic backbone.

Nanoparticle-containing mixed matrix membranes, a.k.a., nanocomposite membranes, have the potential to provide novel functionalities, enhanced performance, and heightened stability while maintaining the ease of membrane fabrication. Table 2-3 summarizes the major advantages of several novel materials discussed in this section. While nanoparticle mixed matrix membranes are not yet commercially available, the micron-scale predecessors would seem to have paved the way for advances in this
technology. As industrial-scale nanoparticle production grows, costs of these materials will come down and many of the research level innovations may make their way into the marketplace.
### Table 2-3. Summary of characteristics demonstrated for mixed matrix membranes

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Particle Diameter (nm) [Length (µm)]</th>
<th>Particle Amount (wt. %)</th>
<th>Membrane Properties Altered and Novel Characteristics Shown with Particle Additions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina/PES</td>
<td>~ 0.48</td>
<td>0.01-0.05</td>
<td>Decreased rate of membrane fouling Decreased flux with increased particle amount Decreased flux decline due to fouling over time</td>
<td>75</td>
</tr>
<tr>
<td>Alumina/PVDF</td>
<td>~ 10</td>
<td>19</td>
<td>Increased hydrophilicity Increased mechanical stability Increased flux over 40%</td>
<td>74</td>
</tr>
<tr>
<td>CNT/PSf</td>
<td>~ 10-40 (~ 50)</td>
<td>4</td>
<td>Increased surface roughness Increased surface hydrophilicity Increased mechanical stability</td>
<td>104</td>
</tr>
<tr>
<td>CNT/PSf</td>
<td>~ 10-20 (~ 10-50)</td>
<td>0.5-4</td>
<td>Increased hydrophilicity Increased permeability, up to 2 wt. % Decreased rejection, up to 2 wt. % Decreased permeability and increased rejection at 4 wt. %</td>
<td>103</td>
</tr>
<tr>
<td>Fe-Pd/PVDF</td>
<td>~ 20-30</td>
<td>2</td>
<td>Targeted dechlorination In-situ formation of nanoparticles at pore walls Decreased pure water flux over 90%</td>
<td>85</td>
</tr>
<tr>
<td>PANI/PSf</td>
<td>~ 43 (~ .259)</td>
<td>10</td>
<td>Increased hydrophilicity and surface roughness Decreased fouling propensity Increased pore size (~5 to 7 nm) and porosity Increased mechanical stability Increased flux 2-fold</td>
<td>77</td>
</tr>
<tr>
<td>Silica/PSf</td>
<td>~ 34-130 (~ 250-300)</td>
<td>17</td>
<td>Increased mechanical stability Decreased compaction under applied pressure Decreased flux decline</td>
<td>111</td>
</tr>
<tr>
<td>Zeolite/PSf</td>
<td>~ 34-130 (~ 250-300)</td>
<td>17</td>
<td>Increased mechanical stability Decreased compaction under applied pressure Decreased flux decline</td>
<td>111</td>
</tr>
<tr>
<td>Ag/PSf</td>
<td>~ 20-50</td>
<td>4</td>
<td>Increased permeability 90% Decreased rejection from ~82 to 70% Introduced antibacterial properties Reduced biofilm growth</td>
<td>73</td>
</tr>
<tr>
<td>Titania/PES</td>
<td>~ 5-24 (~ 40 nm coating on surface)</td>
<td>~ 5-20</td>
<td>Increased hydrophilicity Increased flux nearly 50% Decreased rejection from ~78 to 65%</td>
<td>95</td>
</tr>
<tr>
<td>Titania/SPES</td>
<td>not reported</td>
<td>~ 5-20</td>
<td>Increased hydrophilicity Increased thermal stability Increased mechanical stability</td>
<td>96</td>
</tr>
<tr>
<td>Titania/PVDF</td>
<td>~27</td>
<td>40</td>
<td>Increased thermal stability Decreased compaction under applied pressure Increased water flux</td>
<td>110</td>
</tr>
</tbody>
</table>
2.3.2. Thin Film Nanocomposite Membranes

Nanoparticle additions have been made to the thin films of TFC RO membranes in order to take advantage of the properties of the nanomaterials. Addition of nanoparticles to interfacial polymerization processes or surface attachment via self-assembly has introduced the concept of thin film nanocomposite (TFN) membranes, which offer potential benefits of enhanced separation performance, reduced fouling, antimicrobial activity, and other novel functionality [96-97, 113-116]. As with TFC membranes, TFN membrane performance can be fine-tuned with nanoparticle additions to the support membrane, the coating film, or both.

Zeolite nanoparticle-based TFN RO membranes attempt to leverage the molecular sieving properties of zeolites [113, 116]. By casting molecular sieves in the thin film of an RO membrane, where diffusion controls the transport process, the goal is to essentially reach the percolation threshold in the dense selective layer with an individual particle (Figure 2-1). Jeong et al. cast zeolite-polyamide thin films atop PSf support membranes by dispersing zeolite nanoparticles in the TMC solution prior to interfacial polymerization [113]. Water permeability of zeolite TFN membranes increases as much as 80% over identically cast TFC membranes at the highest TFN particle loading (0.4 wt.%), with rejections consistently above 90%. Pure water permeability increases even for pore-filled zeolites, although permeability increases more for pore-opened zeolites supporting the role of molecular sieving. These results appear to imply a combination of effects contribute to the permeability enhancement born out of zeolite fillers.
Lind et al. similarly cast TFN membranes also containing LTA nanoparticles (0.2 wt.%) in the thin film through interfacial polymerization and characterized membrane structure, morphology, and separation characteristics [114]. The presence of zeolite nanoparticles results in higher permeability, greater negative surface charge, and thicker membranes regardless of particle size used (97, 212, and 286 nm). Larger nanoparticles produce membranes with highly favorable surface properties, while smaller nanoparticles increased permeability more by increasing the characteristic pore size. All TFN membranes reported are less cross-linked than pure polyamide TFC counterparts, suggesting another potential mechanism by which TFN membrane permeability is enhanced. This work implies that the addition of nanoparticles can be tailored to particular membrane applications with the selection of nanoparticle size and type.

Later, TFN membranes were cast by Lind et al. by including sodium- and silver-exchanged LTA nanoparticles (~140 nm; 0.4 wt.%) in the PA polymerization reaction [116]. Increased pure water permeation is found in both TFNs, with more significant increases, as much as 66%, with silver zeolites; rejection (tested with NaCl and PEG) is not affected. Silver-zeolites not only provided more hydrophilic surfaces, but also...
actively inhibit biofouling due to the antimicrobial nature of nanosilver. Lee et al. prepared composite PA thin film NF membranes with titania (∼60 nm) nanoparticles in the skin layer through interfacial polymerization [115]. As titania concentration increases towards 5 wt.%, water flux increases and salt rejection decreases, suggesting significant defects formed in the nanocomposite coating film. TFN membranes capable of single-pass seawater desalination were achieved by Lind et al. including LTA nanoparticles (∼250 nm; 0.4 wt.%) in the interfacial polymerization of PA atop PSf membranes [117]. The nanocomposite membranes showed higher flux and higher rejection (> 99.4%) than neat hand-casted TFC membranes.

Carbon nanotubes have attracted attention for novel environmental applications. Brady-Estévez et al. demonstrate the use of CNTs for the removal of viral and bacterial pathogens from water at low pressure inputs [118]. A thin coating of bundled single-walled CNTs (maximum gap ∼0.3 µm) is overlaid on the surface of a PVDF microporous membrane (5 µm pore size). After passing water through the filter all E. coli cells (∼2 µm) are removed, likely due to size exclusion. More importantly, a fluorescence-based viability test proves that nearly 80% of the bacteria are inactivated after 20 min contact time (an 8-fold increase over the uncoated microporous membrane). This result is confirmed with a metabolic activity test that finds only 6% of the E. coli cells are metabolically active following interaction with the filter. Viral pathogen removal is exhibited by passing a suspension containing a model virus, MS2 bacteriophage (∼27 nm), through the filter. Size exclusion is not enough to explain the virus removal seen, even with the presence of the nanoporous coating. Results of viral inactivation by the CNT-coated filter are conclusive, yet vary with CNT layer thickness indicating a lower
limit of contact time required for inactivation. Full virus removal (5-7 log removal) is observed with a 6 µm skin layer; 3.2-log removal is seen with a thin 2 µm layer. Such uses of CNTs offer an exciting opportunity for use in disinfection and water filtration.

**Table 2-4. Summary of thin film nanocomposite membranes formed**

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Particle Diameter (nm) [Length (µm)]</th>
<th>Particle Amount (wt. %)</th>
<th>Membrane Properties Altered and Novel Characteristics Shown with Particle Additions</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Ag-Zeolite/PA-PSf        | ~ 140                                | 0.4                      | Increased hydrophilicity
Increased water permeability by 66%
Decreased propensity for biofouling | 116       |
| Titania/PA-PES           | ~ 60                                 | 1-9                      | Decreased permeability and increased rejection at low particle additions
Increased permeability and decreased salt rejection above 5 wt.% | 115       |
| Zeolite/PA-PSf           | ~ 250                                | 0.4                      | Increased hydrophilicity and surface charge
Decreased surface roughness
Increased water permeability by 80% | 113       |
| Zeolite/PA-PSf           | ~ 250                                | 0.2                      | Increased hydrophilicity
Increased water permeability
Increased salt rejection in RO testing | 117       |

A summary of the major TFN membranes and advantages discussed is presented in **Table 2-4**. While several researchers have attempted to alter the performance of composite membranes by adding nanoparticles to the thin film, it appears that only molecular sieving particles have the ability to enhance flux, while maintaining selectivity. Here, we predict the performance of nanocomposite thin films using a Maxwell mixing model and the relative permeabilities of the filler nanoparticle and thin film polymer coupled with the fractional content of each. Theoretically, the permeability of TFNs
containing impermeable nanoparticles (e.g., titania nanoparticles) decreases, while the permeability of TFNs employing permeable nanoparticles (e.g., SOD-zeolite nanoparticles) increases (Figure 2-2). Any nanoparticle with water permeability higher than that of the polymer matrix can increase the permeability of the resulting nanocomposite membrane by providing preferential flow paths through the cross-section. The filler fraction required for reasonable enhancements will depend upon the intrinsic permeabilities of both phases. Conversely, impermeable nanoparticles can only reduce the water permeability of a membrane because they reducing the area available for permeation through the polymer film. However, impermeable fillers can increase membrane permeability through defect formation, which may also compromise solute rejection. This is a simple analysis, but the concept must be kept in mind as research continues on nanocomposite materials. For certain applications, a loss in permeability may be overcome by the benefits of super-hydrophilic or antimicrobial nanoparticles that significantly reduce membrane fouling, but in general reduced permeability is not a desirable feature. Cost considerations are also important, while antimicrobial and zeolite nanoparticles are expensive, zeolite TFNs have shown higher flux at extremely low loadings such that the cost increase may be minimal.
2.4.0. Biologically-Inspired Materials

2.4.1. Aquaporin Membranes

Aquaporins are the protein channels that control water flux across biological membranes. Agre et al. won a Nobel prize for discovering the first of these proteins, which they named Aquaporin-1 (AQP1), in 1993 [119]. This first characterized aquaporin is found widely in human tissues with the purpose of rapid, passive transport of water across cell membranes. Such transport channels exist in the cells of species in all three domains of life. A single trans-membrane protein is ~120 kDa in size, with a
tetramer structure composed of four channels [120]. These channels are responsible for
the physiological plumbing of our bodies, including our red blood cells, our brain, and
our kidneys. Water movement in aquaporins is mediated by selective, rapid diffusion
caused by osmotic gradients [121-122]. The hourglass shape of AQP1, with selective
extracellular and intracellular vestibules at each end, allows water molecules to pass
rapidly in a single-file line, while excluding proteins [121, 123].

Figure 2-3. Molecular ordering of water molecules being transported through nanoscale
channels (aquaporins and carbon nanotubes) as predicted by molecular dynamics
simulations. Adapted from [124].

Zhu et al. produced a fundamental study to simulate water permeation in AQP1
[125]. Two factors involved in water transport are defined: osmotic permeability, $p_f$,
molecular movement due to concentration differences resulting in net mass transfer, and
diffusion permeability, $p_d$, random movement of molecules resulting in no net transfer. In the theory, water molecules transport in single-file through a narrow aquaporin channel; a constant number of molecules are assumed to occupy the channel at all times and the water molecules are assumed to move together in discrete translocations, or hops (Figure 2-3). In the case of diffusion permeability dominated movement, a “permeation event” involves the movement of two molecules between opposite reservoirs. This requires that a molecule moves all the way through a channel and is different than a hop. The ratio of $p/p_d$ is, in fact, the number of effective steps a water molecule must move in order to permeate a channel.

The highly selective water permeability of aquaporin channels is an interesting concept when considering water treatment membranes. Biological lipid bilayers containing aquaporins transport water and maintain selectivity that far surpasses all commercial RO membranes. Single aquaporins transfer water molecules at rates of 2-8×10⁹ molecules per second [120]. Kaufman et al. predict that a membrane with 75% coverage of aquaporins could have a hydraulic permeability in the range of 2.5×10⁻¹¹ m·Pa⁻¹·s⁻¹, an order of magnitude higher than commercial seawater RO membranes [120].

Kumar et al. include Aquaporin-Z from E. coli bacterial cells in a polymeric membrane [126]. This aquaporin is selected based on the ability for high water permeation and high selectivity. In addition, it is easy to purify and multiply using a recombinant E. coli strain. A symmetric triblock copolymer with a high hydrophobic to hydrophilic block ratio is selected, reminiscent of a lipid-bilayer membrane. The resulting protein-polymer membrane demonstrates over an order of magnitude increase in water permeability over a purely polymeric membrane, as well as full rejection of glucose,
glycerol, salt, and urea. These results demonstrate that aquaporins are functional for synthetic applications.

Figure 2-4. Conceptual cross-sectional image of a semi-permeable lipid bi-layer membrane cast atop a nanofiltration-type support membrane. Adapted from [120].

The transport across biological membranes is driven by an osmotic pressure (or salt concentration) gradient, rather than a mechanical applied pressure gradient as in industrial filtration processes. Kaufman et al. demonstrate supported lipid bilayers formed atop dense water permeable NF membranes that can be operated under a mechanical driving force as RO membranes (Figure 2-4) [120]. NF membranes are chosen as the support because of their high permeability and low surface roughness that allowed for minimal distortion of the lipid bilayer. Aquaporin solutions (of protein PM28, the integral protein of a spinach leaf plasma membrane) are deposited onto commercially available NF membranes (NF-270 and NTR-7450) via vesicle fusion. Electrostatic
interactions are tailored to optimize surface coverage with the lipid bilayer; formation on NTR-7450 at pH 2 with a low ionic strength solution and with the NF membrane surface and the protein vesicles having opposite charges produces the best results. Full, defect-free coverage is implied by the decrease in permeability of the composite membrane (from ~30 to ~2×10^{-12} m·Pa⁻¹·s⁻¹).

**Figure 2-5.** Aquaporin-containing proteoliposomes are incorporated into the polyamide thin film during the interfacial polymerization process and act as preferential flow paths through the selective layer of the RO membrane. Image adapted from Zhao et al.[127]

Currently, scale-up is the primary concern for biomimetic membrane development. Some fabrication methods form free-standing lipid/polymer membranes and hydrogel-supported lipid layers.[128-132] Others, following the lead of Kaufman et al.,[120] demonstrate approaches to form aquaporin films atop robust conventional supports.[133-135] A recent approach has been shown by Zhao et al.[127] in which aquaporins are first incorporated into proteoliposomes and the resulting structures are included in a cross-linked polyamide coating film (**Figure 2-5**). Similar to the zeolitic TFN membranes discussed above, here, the proteoliposomes form highly selective preferential flow paths for water passage through the selective layer. These membranes were shown to produce
~40% higher permeability than commercial brackish water RO membranes with similar or greater salt rejection. In addition, these membranes have been produced in 200 cm² sheets and hold promise for further scale-up thanks to their utilization of the conventional interfacial polymerization method.

Further work must be done to further optimize the formation of such structures and their resulting permeability and selectivity; however, this work demonstrates the potential for incorporation of biological aquaporins into pressure-driven RO membranes in the future. At this time, aquaporin-based membranes are not commercially available due to the difficulties of attaining large quantities of proteins and producing large areas of membrane material, but research continues in this area. A synthetic approach to producing and purifying aquaporin samples in large quantities might improve practical implementation. Furthermore, techniques to simplify the fabrication and produce mechanically robust membranes will bring the promise of these materials to reality.

2.4.2. Vertically Aligned Nanotube Membranes

Nanotubes have attracted attention because of their many unique properties [136-137]. Carbon nanotubes exhibit a fast mass transport reminiscent of aquaporin water transport in which water transport is 2-5 times higher than theoretical predictions by the Hagen-Poiseuille equation [138-139], and gas transport is over an order of magnitude larger than Knudsen diffusion predictions [139]. The striking flow rate has been studied with molecular dynamic simulations and attributed to atomic smoothness and molecular ordering, in which water molecules are passed through CNTs in a one dimensional single-file procession [124, 140]. This finding implies significant advantages of aligned
CNT membranes over conventional membranes through reduced hydraulic driving pressure, and therefore, lower energy costs; however, this will not be the case in desalination applications where productivity is limited by osmotic pressure via the ‘thermodynamic restriction’[141]. Carbon nanotube-based membranes may also have longer lifetimes than conventional membrane materials due to the excellent mechanical properties that CNTs exhibit [142-143].

When CNTs act as the selective layer they can form an array of high flux molecular sieves within a polymer matrix ([Figure 2-6]) at the surface of a membrane. Kim et al. fabricate aligned CNT/polymer membranes that allow for efficient gas separation processing; CNTs allow for increased selectivity and gas flux due to their intrinsic properties [144]. Highly selective, high flux membranes provide a more efficient, lower energy option [145]. It is the hope that water treatment analogues to these membranes will be produced with similar materials.

![Figure 2-6. Conceptual image of an array of aligned nanotubes embedded in a nonporous polymeric matrix.](image)
Most uniform, aligned nanotube arrays to date are produced through chemical vapor deposition (CVD) [146-151]. Fornasiero et al. attempted to model and study biological porin ion transport with sub-2 nm diameter CNTs as surrogates [151]. Aligned CNTs are grown through CVD on a silicon surface and then encapsulated through conformal deposition of silicon nitride to form composite membrane structures. The CNTs are adapted by fixing negatively charged functional groups at the ends in order to mimic porin structure and the selectivity region at the openings, which dictates ion transport. Pressure-driven NF is coupled with capillary electrophoresis for ion concentration analysis in the filtrate. Ion exclusion is found to be as high as 98%. The results show ion transport is dominated by Donnan type rejection based on electrostatic interactions between membrane surface charge and particle charge rather than steric effect [151].

Gao et al. grow dense arrays of titanium carbide crystal-filled, aligned CNTs (inner diameter 10-100 nm) atop a titanium substrate through CVD with a simultaneous solid state reaction [146]. Choi et al. produce uniform (10 nm diameter) aligned CNTs atop nickel deposited silicon substrates through microwave plasma-enhanced CVD; it is found that the nickel thin film characteristics largely control the growth rate and resulting diameter and density of CNTs [147]. Mauron et al. produce aligned CNT films (20-28 nm diameter; 20-35 μm thick) atop silicon chips through CVD with gaseous acetylene and nitrogen [150]. Overall perpendicular alignment of multi-wall CNTs on the preformed substrate is seen and attributed to high nanotube density, although the individual nanotubes are curved. Yoshikawa et al. produce thin, narrow, uniform,
vertically aligned CNTs (2.5-6.0 nm diameter; 20-90 µm length) atop commercial aluminum foil using catalyst-supported CVD [149].

Holt et al. produce gap-free sub-2 nm diameter aligned double-walled CNT membranes (1.3-2 nm pores determined by size exclusion) through an automated and reproducible microelectromechanical system fabrication, using catalytic CVD [139]. Pore densities are as high as 0.25×10^{12} pores per cm^2 [139], the highest example to date. Water flux through these CNT membranes is found to be at least 3 orders of magnitude higher than theoretical, Hagan-Poiseuille predictions [139]. These nanoporous membranes offer opportunities for extreme selectivity, without compromising water permeation. While aligned CNT membranes show promise, alignment via CVD is expensive, sensitive, and not yet applicable for large-scale fabrication.

Films of aligned CNTs have also been produced through self-assembly approaches [144, 152-153]. Heer et al. accomplish this by drawing aqueous suspension of CNTs (~10 nm diameter; 1-5 µm length) through a 0.2 µm pore ceramic filter and then transferring the deposit to a Teflon surface [152]. After rubbing the surface with Teflon or aluminum foil the tubes reorient perpendicular to the surface. The vertically aligned structure is confirmed by electron microscopy images. A magnetic alignment approach for macroscopic film formation, involving high pressure filtration of suspended single-walled CNTs in a magnetic field, is applied by Casavant et al. to produce (125 cm^2 of 10 µm thick) aligned CNT membranes [153]. Theoretical calculations are confirmed to show that the magnetic alignment was primarily a function of tube diameter, rather than magnetic field. Kim et al. prepare CNT/polymer composite membranes, having similar gas transport properties to nanotube composites prepared through CVD, by passing a
single-walled CNT suspended solution through a PTFE filter in order to align nanotubes; a PSf coating is applied in order to maintain perpendicular orientation and impart mechanical strength [144].

Srivastava et al. exhibit the potential for CNT filters in two important environmental applications: the separation of heavy hydrocarbons from petroleum during crude oil post-distillation and the removal of microbial contaminants from drinking water [154]. Macroscale hollow carbon cylinders are produced with densely packed, radially aligned, micron-length multi-walled CNTs through the continuous spray pyrolysis method. To confirm the bio-adsorption of contaminants, namely *E. coli* (2-5 μm), *Staphylococcus aureus* (~1 μm), and the poliovirus (~25 nm), from drinking water, unfiltered biological suspension and post-treatment filtrate are incubated in both solid and liquid media and then plated; biological growth is seen in the unfiltered samples, but none is found in the filtrate. These biofilters offer not only an efficient means for treatment, but also an economical means. Due to the strong mechanical and thermal stability, CNT filters can be cleaned (by ultrasonication and autoclaving) and reused, whereas conventional water filtration membranes are typically disposed off at the end of one use due to permanent damage from biofouling and inability to withstand cleaning.

A 2007 molecular dynamics simulation by Corry points out the importance of the type of CNT selected for membrane production [155]. Results show that narrow CNTs with an “armchair” structure – those classified as (5,5) and (6,6)-type nanotubes – might completely reject ions due to the large energy barrier at the nanotube openings created by stable hydrogen bond formation. Larger (7,7)- and (8,8)-type nanotubes will not select against ions in this way. Water on the other hand, forms no stable hydrogen bonds with
any CNT types and permeates rapidly. While extreme permeation enhancements are often predicted (as much as 3 orders of magnitude over current membranes), these predictions have been made assuming maximum coverage of CNTs per unit area, but it is not clear that such high packing densities are practically possible. Using the results of this simulation and assuming the CNT packing density achieved experimentally to date (with double-walled CNTs) by Holt et al. [139], Corry projects flux enhancements of 2-fold and 4-fold over a commercially available seawater RO membrane with (5,5) and (6,6) aligned CNT membranes, respectively, [155].

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Salt Rejection (%)</th>
<th>Water Permeability (m·Pa⁻¹·s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial SWRO</td>
<td>99.7</td>
<td>~ 3×10⁻¹²</td>
<td>25</td>
</tr>
<tr>
<td>Zeolite TFN</td>
<td>99.4</td>
<td>~ 6×10⁻¹²</td>
<td>117</td>
</tr>
<tr>
<td>Aquaporin Biomimetic</td>
<td>99.0</td>
<td>~ 2×10⁻⁹</td>
<td>126</td>
</tr>
<tr>
<td>CNT Biomimetic</td>
<td>none tested</td>
<td>~ 7×10⁻⁷</td>
<td>139</td>
</tr>
<tr>
<td>CNT Biomimetic (projected)</td>
<td>95.0</td>
<td>~ 2×10⁻¹¹</td>
<td>155</td>
</tr>
</tbody>
</table>
A comparison of novel seawater RO materials (i.e., zeolite TFN, aquaporins, aligned nanotubes) currently prepared at the laboratory scale and summarized in the previous sections is presented in Table 2-5. Based on the highest achieved performance of aligned nanotube membranes to date, projections were made for this material versus current polymeric seawater RO membranes (Figure 2-7) using permeability projections compiled by Corry [155] and the maximum CNT density demonstrated by Holt et al. [139]. At a fractional content of 0.03% in an impermeable matrix, a CNT membrane will exceed the commercially available SWRO standard. This limit is within the previously achieved range, but thus far no large-scale aligned CNT membranes have been fabricated. Carbon nanotubes promise mimicry of biological aquaporin channels, with a material producible in large quantities; however, fabrication of large areas of these materials is a key step to enable commercial application. Both aquaporin and CNT based membranes will likely be limited by their cost and lack of scalability. We note this was also the case for polymeric RO membranes 50 years ago, so the scale-up issues may be resolved over time if performance enhancements prove practically achievable.
2.4.3. *Isoporous Block Copolymer Membranes*

One advance aimed at solving the issue of scale up and manufacturing of membranes with uniform, aligned nanopores involves block copolymer self-assembly [156]. In 1994, François and his research team formulated an emulsion method whereby water droplets condense on a rapidly cooled polymer surface in a humid environment to create porous structures [157-158]. Water molecules arrange themselves on the surface and polymer precipitates around them. Finally, evaporation of the water droplets occurs, leaving a honeycomb pore structure. This idea is widely applied [159-162], yet a full understanding of the molecular level activity has yet to be reached. Self-assembly,
defined as the “autonomous organization of components into patterns or structures without human intervention [156],” of block copolymers show promise for translating ‘bottom-up’ synthesis methods into large-scale manufacturing processes, which is needed for practical water treatment membranes.

Block copolymers are macromolecules composed of multiple block polymeric species with the ability to self-assemble into highly ordered structures when placed in a selective solvent [161, 163-165]. Block copolymer self-assembly provides the opportunity for narrow pore size distributions and high porosities, as well as sharp molecular weight cut-off. In self-assembly, the characteristic differences between blocks will cause separation into microphases during polymerization. An analogy can be drawn to the hydrophobic effect in which natural amphiphilic molecules, such as phospholipids, become ordered in water with a compact hydrophobic region surrounded by dispersed hydrophilic segments in order to reach a thermodynamically favorable arrangement [165]. Similarly, when water is added to a system of block copolymers dissolved in an aqueous solution, the blocks will align with the hydrophobic ends precipitating and the hydrophilic ends remaining extended in solution [161]. Furthermore, when any selective solvent is added to a solvent-nonsolvent system consisting of macromolecules of two distinct regions – one soluble, the other insoluble – a predictable arrangement will form based on the respective interactions of each polymer with the solvent [165].

The geometry of block copolymer nanostructures is determined by the molecular weights of the blocks and the ordering depends upon the concentrations of the blocks and the insoluble to soluble ratio [163, 165]. At a certain point, known as the critical aggregation concentration (CAC), the blocks will go from dispersed unimers to self-
assembled isotropic structures [165]. The ratio of the insoluble volume to the total volume occupied by the copolymer can generally determine the resultant structure the macromolecule will attain in solvent. If the insoluble volume is less than 33% of the total volume, spherical micelles (hydrophobic core with a hydrophilic corona) will form (Figure 2-8), between 33 and 50% cylindrical micelles form, and then up to the theoretical point of 100% insoluble fraction a membrane (composed of two monolayers) will form [163, 165]. Reverse micelles can also be formed with a hydrophilic inner core when nonsolvent, rather than a solvent, is added to the system [166-167]. Additionally, these same ideas can be expanded beyond diblock copolymers to multi-block systems [165]. By varying the concentrations and conditions under which self-assembly occurs various structures can be formed, including densely packed cylindrical pores ideal for water separation membranes [168]. Techniques for producing such membranes involve phase inversion (which is successful, but expensive as the block copolymer is used for both the support and the selective layers), shear aligning (which typically produces thicker than desired films), and controlled substrate-polymer interactions (which are effective, but difficult to control in large-scale production) [169]. In theory, aligned cylinders formed through nanostructuring of block copolymers could enable a fully polymeric analog to aquaporin or aligned CNT membranes, providing an opportunity to take advantage of nanopore performance, while maintaining ease and economy of large-scale polymeric membrane fabrication.
Figure 2-8. Di-block copolymer micelle formation upon reaching the critical micelle concentration. Adapted from [170].

Self-assembly for bottom-up structure formation can result in membranes containing defects due to the various factors [171]. One particularly interesting characteristic of copolymers is that they are “soft” meaning that they tolerate a large amount of such imperfections and still assemble relatively homogenously. While imperfections may be seen as a major limitation in some applications, for aqueous membrane materials where total homogeneity is not a requirement this soft nature poses processing and manufacturing advantages. Dove points out that while micellar assemblies are soft and may be reverted to unimers with a change in conditions, there is the opportunity to cause selective crosslinking [163], which enhances the mechanical, thermal, and chemical stability of the membranes [160, 172]. The soft nature also means that minimal external fields – electrical or shear – will impact the arrangement [165]. This could have implications for auto-arranging of materials on demand and an opportunity for self-cleaning membranes.
Peinemann et al. demonstrate the ability to combine block copolymer self-assembly with conventional phase inversion to achieve highly ordered, asymmetric porous membranes composed solely of block copolymer materials [164]. This process is very complex involving both thermodynamic and kinetic factors: during fabrication, block copolymers will align in order to obtain a thermodynamically favorable, low energy arrangement. However, perpendicular arrangement is difficult to guarantee throughout the thickness of copolymer membranes. Predictions of arrangement must take into account the factors of solvent composition, selectivity, and concentration [164, 171]. In their one step process, Peinemann’s group achieves a non-ordered porous structure—typical of polymeric membranes—overlaid with a 200-300 nm thick dense layer of aligned nanocylinders, with a pore density of $240 \times 10^{12}$ and an effective pore diameter of 8 nm [164]. Water flux through these membranes is $20 \text{ l}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 0.5 bar with 82% rejection of ~7 nm albumin [164]. A similar UF membrane was formed with effective pore size ~ 25 nm, pore density $\sim 2.3 \times 10^{10}$ pores cm$^{-2}$, and water permeability of 890 L $\cdot$ m$^{-2}$ $\cdot$ h$^{-1}$ $\cdot$ bar$^{-1}$ [173]. It was shown that these pores were pH-sensitive, with flux being cut by nearly 99% with feeds of pH 3 and lower. One-step fabrication holds promise for large-scale production. Peinmann holds a patent for the process of block (di- and tri-) copolymer membranes for separation applications, including UF and NF [174].

Phillip et al. report fabrication of a 100 $\mu$m thick, nanoporous block copolymer membrane with tunable selectivity, narrow pore size distribution (~14 nm), and a 40% void fraction [175]. Membranes are formed using the “doubly reactive” block polymer [175] combined with selective etching of a single block [176]. The process allows for simplified alignment because the block polymer acts as a structural template during
crosslinking [175]. Water permeability was lower than predicted, but did increase linearly with applied pressure. If the membrane thickness is decreased to 0.5 µm, the membrane would become competitive (at 5600 gal·ft\(^2\)·day\(^{-1}\) with a 200 kPa pressure drop) with typical membranes formed through phase inversion. Flux was found to decrease with pH of permeate by as much as 60% (from pH 2 to 12). The molecular weight cut-off of the membrane was found to correlate with the molecular weight of the etchable block employed, implying further tuning of such membranes for target separation applications is possible.

Another route for employing block copolymers is to form a thin layer atop a sacrificial substrate and then transfer it to a functional support layer. Using copolymers for upper layer alone provides large cost savings and may pose an advantage for large-scale production [177]. This is fiscally appealing as block copolymers are more costly than typical polymers used in membrane formation. Yang et al. created a NF membrane, with an 80 nm thick top layer of 15 nm diameter cylindrical pores atop a (250 µm) conventional support, capable of filtering viruses [178]. This approach holds benefits of a highly tunable top layer, with pores ranging from 10 to 40 nm, and the reliability of conventional supports. The process is limited in its scalability because of the difficulty of transferring films without damage to the porous structure.

To avoid complications in the transfer step, self-assembly of block copolymers directly atop functional supports has been attempted. Here, separate tailoring of the support and selective layers allow for novel membrane fabrication. Fierro et al. employ block copolymer membranes in direct formation atop a conventional porous support and study the impact of polymer selection on physical characteristics [159].
assembly outcome the affinity of the substrate for each block employed must be considered, as the substrate tends to be selective towards one of the block units. Orientation of the self-assembly is strongly impacted by the surface composition and roughness on which assembly is initiated [159, 179]. Phillip et al. fabricate membranes with a 4 µm thin film of monodisperse, 24 nm diameter vertically aligned, hexagonally-packed cylinders directly atop a commercially available microporous support membrane in a single step of controlled evaporation [169]. Ultraviolet light (254 nm) is applied to ensure full adhesion between the copolymer film and commercial support layer. UV also promotes crosslinking between micelles. A single block is selectively etched to form the open pores. Water permeability in UF testing is lower than expected likely because the pores were not aligned or etched through the full length of the thin film. Membrane rejection of 100 kDa polyethylene oxide is over 93%. This evaporative self-assembly method provides an opportunity for economical scalability by using a simple fabrication process and selecting a commercially available, mechanically robust support layer. In addition, the dual material membrane means that characteristics of support structure and thin film selectivity can be independently fine-tuned with respect to applications.

Li et al. employ a homopolymer (i.e., polyacrylic acid) to guide self-assembly of their diblock copolymer system. Ordered nanoporous films are formed directly atop various polymeric and ceramic porous supports via spin coating followed by solvent evaporation [180]. The addition of the homopolymer allowed for the desired pore structure to be achieved under various casting conditions (humidity, substrate, solvent, film thickness) with no need for thermal or solvent treatments. The homopolymer is then selectively removed. In NF tests, liquid permeability ranges from 1.2-1.6 L·m⁻²·bar⁻¹·h⁻¹,
increasing with homopolymer content. Molecular weight cut-off of the membranes is
determined to be 400-500 Da (defined for 90% rejection of polyethylene glycol).
Interestingly, while the homopolymer is necessary to attain self-assembly of cylindrical
pores, it can be removed with a simple water soak without changing the pore structure
implying that it is not chemically stable in the self-assembled structure. The use of such
homopolymer additives presents an opportunity for simple and scalable fabrication of
membranes with highly tunable performance characteristics.

Multiblock or star copolymers enable more predictable alignment atop
commercial substrates by compensating for the discrepancy in substrate affinity between
blocks with a symmetric arrangement. It is predicted that more complex structures result
in a reduced thermodynamic loss due to conformational entropy and provide an
opportunity for more specific nanoscale tuning of structures [157, 159, 181]. Stratford et
al. simulate a method for producing what they termed Bijels (bicontinuous interfacially
jammed emulsion gels), which are self-assembled three dimensional structures formed
through liquid-liquid interfacial sequestering of particles to form a matrix [181].
Stratford’s predicted kinetic path is applied, using the emulsion technique first presented
by François’ group [157], by Chen’s group to prepare tunable porous structures with self-
assembling ABA triblock amphiphilic copolymers into a highly ordered honeycomb film
[170]. With honeycomb structures it is consistently found that the hydrophobic-
hydrophilic ratio of the blocks determines the ordering and size of pores; namely, the
regularity of pores decreases with increasing hydrophilic block content and pore diameter
increased with increasing hydrophobic block length [158, 161, 170]. The ability to tune
pore size with hydrophobic block selection and water content [161] is intuitive based on
the proposed formation path in the emulsion technique [157]. Beattie et al. form similar matrices through reversible addition-fragmentation chain transfer [158, 182]. Kabuto et al. experiment with honeycomb formation using a commercially available polymer and create an asymmetric membrane with a top layer of ordered 3 nm pores [160]. Upon cross-linking the honeycomb surface inverts from hydrophobic to hydrophilic, allowing for filtration through the pores [160]. As a further understanding of the mechanisms at play in formation is reached, this highly ordered and predictable membrane formation process will gain exposure in the membrane field.

**Table 2-6. Summary of block copolymer-based membranes demonstrated performance**

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Pore Diameter (nm)</th>
<th>Pore Length (µm)</th>
<th>Molecular Weight Cut-Off (kDa)</th>
<th>Water Permeability (m·Pa⁻¹·s⁻¹)</th>
<th>Reported Enhancement Over Commercial Standard</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Block Copolymer Composite</td>
<td>not reported</td>
<td>~ 0.2</td>
<td>~ 0.5</td>
<td>~ 4×10⁻¹²</td>
<td>Competitive permeability with sharp NF-range MWCO Added pore tunability with addition and selective etching of homopolymer</td>
<td>180</td>
</tr>
<tr>
<td>Pure Block Copolymer Membrane</td>
<td>~ 14</td>
<td>~ 100</td>
<td>~ 35</td>
<td>~ 5×10⁻¹²</td>
<td>Permeability predicted to be 1-2 orders of magnitude higher than commercial if pore length/film thickness cut in half</td>
<td>175</td>
</tr>
<tr>
<td>Pure Block Copolymer Membrane</td>
<td>~ 15</td>
<td>~ 0.2-0.3</td>
<td>~ 50</td>
<td>~ 5×10⁻¹¹</td>
<td>Permeability does not exceed commercial standards Phase inversion method shows promise for scale-up</td>
<td>164</td>
</tr>
<tr>
<td>Block Copolymer Composite</td>
<td>~ 24</td>
<td>~ 0.5</td>
<td>~ 100</td>
<td>~ 3×10⁻¹²</td>
<td>Permeability will surpass commercial if pore length/film thickness can be reduced to ~ 100 nm</td>
<td>169</td>
</tr>
<tr>
<td>Pure Block Copolymer Membrane</td>
<td>~ 30</td>
<td>~ 0.4</td>
<td>none tested</td>
<td>~ 2×10⁻⁹</td>
<td>Increased permeability over an order of magnitude Added pH sensitivity to pores</td>
<td>173</td>
</tr>
</tbody>
</table>

Membranes with aligned nanopores formed by self-assembly of block copolymers during phase inversion offer a significant promise as fully polymeric analogs to aquaporin and aligned CNT membranes. A summary of the materials discussed is
provided in Table 2-6. While current permeabilities are not higher than current filtration membranes, the sharp molecular weight cut-off, high porosity, and simple fabrication of these materials offers promise for the future. Additionally, predictions of permeability for these membranes once morphology is fine-tuned (e.g., films are made thinner, pores are opened throughout the film layer) shows promise that these will easily overcome current standards. In principle, these structures could be fine-tuned for water filtration applications, but may also serve as more ideal support substrates for high-flux, high-selectivity forward and reverse osmosis membranes for desalination and osmotic power production.

2.5.0. Comparison of Nanotechnology-Enabled Materials

The aims of nanotechnology-enabled water treatment membranes encompass many different goals and performance enhancements. Chemically stable ceramic membranes have been modified for high selectivity NF and potentially RO membranes with zeolite thin film coatings. Self-cleaning and catalytic membranes have been formed with antimicrobial and photocatalytic nanoparticle coatings. Mixed matrix membranes offer enhanced separation performance, fouling resistance, and mechanical stability for filtration applications and as support membranes for TFC or TFN membranes. Thin film nanocomposites seek to produce compaction resistant membranes with silica, self-cleaning photocatalytic membranes with titania nanoparticles, or highly permeable and selective membranes with molecular sieve zeolites. Biologically inspired membranes—aquaporins, aligned CNTs, and block copolymers—seek to simultaneously improve selectivity and permeability. Each of these innovative materials concepts promises unique
performance enhancements and each has unique hurdles to overcome before it is commercially viable.

Here, we ranked the aforementioned membrane nanotechnologies based on two categories: (1) performance enhancement and (2) state of commercial readiness and three sub-categories within each category. Performance sub-categories considered potential enhancements in membrane (a) permeability, (b) selectivity, and (c) robustness over the current state-of-the-art. Robustness encompasses chemical, mechanical, and thermal stability as well as fouling resistance and enhanced cleanability. Commercial readiness sub-categories included (1) anticipated material costs, (2) manufacturing scalability, and (3) apparent time to commercialization. Those membrane nanotechnologies that promise significant performance improvements over current industry standard membranes were ranked positive, those that offer lower performance were ranked negative, and those that did not change the performance (or if no information was available) were given a neutral score. Membrane nanotechnologies close to commercial reality, cheaper than the state-of-the-art, and capable of being produced using existing membrane manufacturing infrastructure were ranked positive, those judged oppositely were ranked negative, and those not promising change in the specific metric (or if no information was available) were given a neutral score. The scores given to each membrane nanotechnology reviewed above are shown in Table 2-7 [3].
Table 2-7. Comparison of nanotechnology-enabled technologies

<table>
<thead>
<tr>
<th>Nanotechnology-Enabled Membrane Concept</th>
<th>Potential Performance Enhancement</th>
<th>Potential Commercial Viability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Productivity</td>
<td>Selectivity</td>
</tr>
<tr>
<td>Reactive/Catalytic Surfaces</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>Zeolitic Coatings</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Mixed Matrices</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Nanoparticle TFNs</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Zeolite TFNs</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Aquaporins</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>Aligned Nanotubes</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Block Copolymers</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Reactive/catalytic and zeolite coated ceramic membranes promise improved performance with marginal changes in current inorganic membrane fabrication methods (i.e., low cost impact). However, these innovations are not out of the laboratory yet and will most likely be limited by the same factors that have always limited ceramic membranes—high capital cost and low membrane area density relative to polymeric membrane equivalents. Ceramic membranes with reactive surfaces have been proven effective in laboratory studies, but more research needs to be done to produce commercially viable systems. While negligible improvement to productivity for such membranes has been shown, selectivity can be increased with catalyzed degradation of target compounds. Additionally, reactive surfaces have been shown to be biofouling resistant and so an enhancement in robustness is promised. For these reasons, the ratings of 0 (no improvement) to productivity and +1 (slight improvement) to both selectivity and robustness are assigned. These membranes show no major changes in commercial
viability when compared to current ceramic membranes and so neutral ratings are applied in all categories of time to commercialization. The materials and production cost roughly the same amount as current ceramics and the materials discussed here are between laboratory and pilot-scale testing, but none are known to be commercially available as of yet.

Zeolitic coatings promise the ability to tune the molecular selectivity of ceramic membranes. Thanks to the extreme stability of inorganic materials, these membranes may have a future in desalination and purification of challenging wastewaters (needs currently met primarily by polymeric membranes); however, the synthesis of zeolite films must be improved to obtain thinner layers and achieve competitive water permeability without sacrificing selectivity. In terms of potential performance enhancements, zeolitic coatings are given a –1 rating for productivity because currently these achieve lower flux than commercially available materials. These were rated neutral in terms of selectivity since rejections comparable to current membranes have been shown. These materials were given a +1 rating for robustness, however, because they pose a more chemically and thermally stable alternative to current membranes typically applied for high pressure and complex water separations. Similar to reactive/catalytic surfaces, zeolitic coatings are given neutral scores for commercial viability, with the exception of cost effectiveness. The materials to produce fully zeolitic coatings made presumably cost more than typical polymer membrane materials and ceramic materials and so a –1 rating is assigned.

Mixed matrix membranes and TFNs offer significant performance enhancements with minimal changes to current manufacturing processes. All inorganic-organic materials evaluated offer a significant productivity enhancement when tested against
current state-of-the-art membranes. Mixed matrices and zeolite TFNs show no significant change to membrane selectivity; however, nanoparticle TFNs do show some decrease in selectivity due to defect formation and so these are given a −1 rating for selectivity. All inorganic-organic materials also show an enhancement in robustness, through either compaction resistance or hydrophilic, anti-fouling surfaces due to the presence of filler materials, earning them a +1 rating for robustness. Mixed matrix membranes and nanoparticle TFNs both receive ratings of −1 for cost effectiveness due to the added cost of filler materials. Thin film nanocomposites containing zeolites, however, have been shown in the literature to improve on all aspects of performance using only small amounts of relatively inexpensive filler materials and so were rated neutral for cost effectiveness. All materials in this category are given a +1 rating for scalability since all can be produced through current polymeric membrane processes by simply adding nanoparticles to the casting or coating solutions. While mixed matrices have been seen at the laboratory scale only, earning them a neutral score for time to commercialization, early stages of TFN membranes are now commercially available, earning them a +1 score.

Biologically-inspired membranes all promise extremely high performance enhancements, but are currently far from commercial reality. Aquaporin-based membranes promise to revolutionize membranes with at least an order of magnitude increase in flux over the current membranes available, earning them a rating of +3 for productivity. Aligned nanotubes and isoporous block copolymer membranes have also been predicted and shown to reach extreme flux enhancements, earning them +2 and +1 ratings for productivity, respectively. All biologically inspired membranes promise to alter the bounds of membrane selectivity with extremely narrow pore distributions. The
nearly monodisperse morphology of these membrane materials earns them a +2 for selectivity. Neither aquaporin, nanotube-based, nor block copolymer membranes show significant changes in membrane robustness if cast within or atop polymeric matrices and so all received a neutral rating in that category. Both aquaporins and nanotubes are expensive to purify and have not yet been formed in large membrane areas and so both receive a –1 rating for cost effectiveness and scalability. Aquaporins are difficult to attain in large quantities and few studies have shown the ability to form uniform coatings of protein membranes for industrial applications. Aligned CNT films have been produced uniformly, but only over small surfaces. At this point, both materials are in the laboratory production phase and so earn neutral scores for time to commercialization. Block copolymer materials are not significantly more costly than current polymeric membranes, particularly since research is moving towards using the specialized polymers for the selective layers only and so these receive a neutral score for cost. Because self-assembled block copolymer membranes can be formed through typical membrane fabrication processes with current infrastructure they earn a +1 for scalability. Aligned block copolymer membranes are in stages of early development and ideal polymer systems must still be found to achieve the outcomes promised, earning them a –1 for time to commercialization. However, if the polymerization conditions can be mastered so that fabrication of these structures can occur reliably and at large scales with minor changes to infrastructure, they will pose a promising, low-cost, fully polymeric counterpart to high performance aquaporin and CNT membranes. Biologically-inspired membranes promise the greatest separation performance enhancements; however, their cost and robustness are unproven and they appear most challenging to produce for large commercial applications.
However, this was also the case for polymeric membranes 40-50 years ago and these scale-up issues can be resolved if the performance enhancements promised by these exiting materials prove practically achievable.

![Figure 2-9. Comparison of the potential performance and commercial viability of nanotechnology-enabled membrane advances based on review of current literature. Performance enhancement relates to permeability, selectivity, and robustness, while commercial viability relates to material cost, scalability, and compatibility with existing manufacturing infrastructure.](image)

While each technology clearly has its own merits, an overall ranking is proposed here by summing the three scores from each category and plotting the total scores for performance enhancement against commercial viability (Figure 2-9) [3]. The ideal
technology offers both revolutionary performance enhancements and is already commercially available (upper right quadrant). Biologically-inspired membranes promise the greatest potential performance enhancements and are farthest from commercial reality, while zeolite TFN membranes offer moderate performance enhancement and appear nearest to commercial viability. The other materials offer noteworthy performance enhancement while remaining far from commercial reality. None of the membrane nanotechnologies fell in the optimal (upper right) quadrant of the chart, but this could change over time as biologically inspired membrane technology matures.

Readers should note that we propose this ranking methodology as a means to provoke critical thought rather than as an endorsement or indictment of any specific membrane nanotechnology. We realize limitations are inherent to any such ranking system. The most obvious limitation is that our assessment represents a ‘snapshot in time’ of the technology landscape, which is ever changing. While our intent is to provide an objective evaluation of the technologies, we realize that our ranking may be somewhat subjective. Regardless of the current ranking, each membrane nanotechnology concept described has the potential to revolutionize water treatment to varying degrees, but each material must be developed, matched to the ideal application, and fine-tuned to produce commercially available membranes.
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CHAPTER 3

FABRICATION AND OPTIMIZATION OF
SELF-ASSEMBLED MEMBRANES
3.1.0. Introduction

Block copolymers are macromolecules composed of distinct polymeric species with the ability to self-assemble into highly ordered structures [1-4]. Due to the seemingly endless combinations of physical properties, molecular weights, and architectures, block copolymer containing materials have attracted attention for a variety of applications [5]. By varying the conditions under which self-assembly occurs various structures can be formed, including a high density of cylindrical nanopores ideal for macromolecular separations, hemodialysis, micro/nano-fluidics devices, and water filtration [6-7]. It has already been shown that membranes formed through self-assembly of block copolymers can produce “ultrafiltration-like” membranes with enhanced selectivity and permeability, while maintaining the ease and economy of large-scale polymeric membrane fabrication [8-11].

The regular morphologies produced by block copolymer self-assembly provide the opportunity for narrow pore size distributions (i.e., sharp molecular weight cut-offs) and high porosities, potentially generating breakthrough selectivity and permeability. Techniques for producing membranes from these polymers involve shear aligning (which often produces thicker than desired selective layers), controlled substrate-polymer interactions (which is effective, but difficult to scale-up), and self-assembly/nonsolvent induced phase separation (S-NIPS) (which is both effective and scalable) [12]. To imbue the membranes with mechanical stability, a support layer is typically included. One option is to employ a sacrificial substrate [12-15]. The selective layer can be formed atop a compatible surface, typically an oxide layer (that can later be dissolved with acid) or a glass plate (from which the film will easily delaminate). Then the self-assembled layer
can be transferred to a porous support material. A major advantage of this type of process is that neither chemical compatibility (with the casting solution) nor physical limitations (i.e., morphology) of the support substrate impact self-assembly, allowing reliable predictions of the resulting structure from thermodynamic models. Additionally, using block copolymers for the selective layer only is attractive since it allows cheaper, conventional materials to be used for the bulk volume of the membrane [16]. A potential disadvantage is the lack of strong bonding between the membrane and support, which may result in weaker mechanical stability relative to membranes cast directly onto porous supports.

An important factor to consider when applying self-assembled materials for membrane filtration applications is the pore formation technique. Promising results have been shown using a single etchable component either as one of the copolymer segments or as an additional homopolymer included in the casting solution [13, 17-19]. This method results in highly regular and tunable membrane structures since the size of the pores is primarily dependent on the molecular weight and volume fraction of the etchable component [18]. When controlled evaporation is used to induce phase separation, however, there is concern of the segregated features failing to span the entire thickness of the membrane, in which case the wash step may not result in fully open pores [12].

Peinemann et al. first demonstrated the ability of a diblock copolymer employing a water compatible block (i.e., poly 4-vinyl pyridine, P4VP) and a water incompatible block (polystyrene, PS) to generate asymmetric membrane structures, in which the selective skin layer and porous support are made up of a single copolymeric material, via a hybrid S-NIPS process, eliminating the additional transfer and etching steps [3]. In the
case of the diblock copolymer PS-b-P4VP, the P4VP block resides within the pore walls as an anchored chain and controls the pore size based on its acid-base sensitivity [4, 8]. The major advantage of the water compatible vinyl pyridine block is that no phase needs to be removed in a post-treatment and the asymmetric structure can be formed directly, with the self-assembled mesoporous selective layer atop a macroporous phase inverted substructure. Various casting solution additives have been shown to assist in templating the cylindrical structure and enforcing the membrane, including metal salts, carbon nanotubes, and carbohydrates [20-23]. Phillip et al. employed the same water compatible P4VP block, but used a PI-b-PS-b-P4VP triblock terpolymer architecture to improve mechanical stability of the resulting membranes [15]. The addition of polyisoprene (PI) in triblock films nearly tripled toughness over the diblock films; thus, making the concept more viable for large-scale membrane fabrication and application, also enabling the use of lower molar mass polymers to create smaller pore sizes. Jung et al. have also shown it is possible to take advantage of the water compatible block as the middle segment in other triblock systems, opening up even more opportunities in this area [24].

Triblock terpolymers are exciting materials to explore for membrane applications because of their extended tunability and more reliable self-assembly, compared to their diblock copolymer counterparts [24]; however, little work has been done in this area to date. Herein, the formation of novel triblock terpolymer membranes is explored by varying polymer concentration, ratio of nonvolatile to volatile solvent in the casting solution, and the length of the solvent evaporation period.
3.2.0. Materials and Methods

3.2.1. Triblock Terpolymer Synthesis and Properties

A novel triblock terpolymer poly(isoprene-b-styrene-b-4 vinyl pyridine) (PS-b-PS-b-P4VP), referred to hereafter as ISV, was synthesized as the starting material for these membranes using a sequential anionic polymerization technique [15]. The concentration of the polymer was kept under 10 wt% throughout the procedure. Approximately 500 mL of benzene was distilled into a 1 L reactor and the anionic initiator sec-BuLi was added to the reactor in a glove box via syringe. Distilled isoprene was added to the reactor and allowed to polymerize for a minimum of 8 hours before a 5 mL aliquot was terminated with methanol for gel permeation chromatography analysis. Distilled styrene was then added to the reactor in a glove box via syringe. The styrene polymerized onto the polyisoprene block for 36 h, after which a small aliquot was terminated with methanol for gel permeation chromatography and nuclear magnetic resonance spectroscopy analysis. The benzene was subsequently removed from the reactor and a 10× molar excess of diphenylethylene was added relative to the sec-BuLi. Approximately 500 mL of THF was distilled directly into the reactor, which was then cooled to -78 °C and distilled 4-vinylpyridine was added. The 4-vinylpyridine polymerized onto the poly(isoprene-b-styrene) for 1.5 h, after which the triblock terpolymer was terminated with degassed methanol. The final terpolymer was dissolved in chloroform and twice precipitated into methanol. The primary polymer in this study has an overall molecular weight of 59 kDa and a polydispersity of 1.19. The relative fractions of each component are listed in Table 3-1.
Table 3.1. Composition of ISV-59 used in this study

<table>
<thead>
<tr>
<th>Component</th>
<th>Density [25] (g·ml⁻¹)</th>
<th>Molar Mass (kDa)</th>
<th>Volume Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(isoprene), PI</td>
<td>0.93</td>
<td>14.5</td>
<td>27.3</td>
</tr>
<tr>
<td>poly(styrene), PS</td>
<td>1.05</td>
<td>32.7</td>
<td>54.7</td>
</tr>
<tr>
<td>poly(4 vinyl pyridine), P4VP</td>
<td>1.15</td>
<td>11.8</td>
<td>17.9</td>
</tr>
</tbody>
</table>

The chemical structure of the terpolymer is depicted along with the functionality of each component (Figure 3-1). Poly(styrene) (PS), which makes up the majority (54.7%) of the overall terpolymer volume, provides a strong, high modulus backbone for the material. Poly(4 vinyl pyridine) (P4VP) is a water compatible (hydrophilic) component, which becomes protonated at low pH and de-protonated at high pH. This characteristic has been previously exploited in structured materials as a pH-valve [22]. The poly(isoprene) (PI) provides the terpolymer with toughness. The presence of rubbery, low $T_g$, PI is shown to nearly triple total toughness (9.0 versus 3.20 GJ·m⁻³) over a similar diblock of PS-b-P4VP [15, 26] (Figure 3-2).
Figure 3-1. Structure of the ISV terpolymer, indicating the PI provides toughness, PS delivers a high modulus and P4VP allows for the water compatible nature.

Figure 3-2. Stress-strain curves of the bulk triblock PI-b-PS-b-P4VP terpolymer and diblock PS-b-P4VP copolymer films. The area under the curve indicates total toughness of the material. Used with permission [15].
Bulk films of ISV-59 are cast from chloroform and slowly solvent annealed to allow the triblock terpolymer to achieve its equilibrium structure. The films are characterized following a previously described procedure [15]. Both the transmission electron microscopy (TEM) micrographs and small-angle X-ray scattering (SAXS) trace are consistent with a core-shell hexagonal structure (Figure 3-3).

Figure 3-3. TEM images of bulk films of the ISV-59 terpolymer (a) with the PI selectively stained with OsO₄ and (b) the P4VP with I₂. (c) SAXS trace of the bulk terpolymer, with dashed lines corresponding to \((q/q^*)^2 = 1, 3, 4, 7, 9, 12, 13\), consistent with a two-dimensional hexagonal morphology. Both TEM and SAXS are consistent with a core-shell hexagonal bulk structure.
3.2.2. Membrane Fabrication

Casting solutions were prepared by dissolving ISV-59 in solutions of 1,4-dioxane (DOX) and tetrahydrofuran (THF) (Sigma-Aldrich, St. Louis, Missouri, USA) via mechanical stirring at room temperature for ~2 h and then left overnight at room temperature to allow any dissolved gas to dissipate. A large parameter space was explored in order to optimize ISV-59 membrane performance via the S-NIPS process. Polymer concentrations of 12, 15, and 18 wt% in solvent mixtures with compositions of 70:30, 60:40, and 50:50 wt:wt% DOX:THF were used to give a total of nine different casting solutions. The casting solutions were drawn across a glass substrate with a casting knife set at 229 μm blade height. Solvent was allowed to partially evaporate for a defined time period (between 20-70 s). The glass plate was then immersed into a coagulation bath of 18 MΩ laboratory deionized water to induce polymer precipitation. After 1 h the membrane was removed from the water bath, separated from the glass plate, washed thoroughly, and stored in deionized water.

3.2.3. Membrane Characterizations

Contact angles were measured on membrane samples in a captive bubble chamber filled with deionized water (DSA10, KRÜSS GmbH, Hamburg, Germany). The equilibrium values were taken as steady-state averages of left and right angles with an average of 12 contact angles measured per sample and discarding the high and low values before averaging. Surface area difference (SAD) and root-mean-squared (RMS) roughness values were measured with atomic force microscopy (AFM) (Bruker Dimension 5000 Scanning Probe Microscope, Santa Barbara, California, USA). Pore
radii were determined using scanning electron microscope (SEM) micrographs (JEOL JSM-6700F FE-SEM, Tokyo, Japan). Pore lengths were estimated using cross-sectional SEM micrographs (Nova 230, FEI, Hillsboro, Oregon, USA). Samples were prepared for SEM by soaking in ethanol for 15 s, drying in air, mounting on carbon tape, and sputter coating with Au for 30 s. Cross-sections were freeze-fractured in liquid nitrogen prior to mounting. Pore structure and porosity characterizations on SEM micrographs were performed with the NIH ImageJ software according to a previously described method [27].

3.2.4. Membrane Performance Evaluation

Membrane performance was evaluated in a dead-end stirred cell (Amicon 8010, EMD Millipore, Billerica, Maryland, USA) at 5 psi (0.34 bar) applied pressure. For all experiments, the feed cell was stirred at 600 rpm producing a Reynolds number of 9,798 in the stirred cell, as determined from

\[ Re_{SC} = \frac{\rho \cdot \omega \cdot r_{SC}^2}{\mu}, \]

where \( \rho \) is the density (kg·m\(^{-3}\)) and \( \mu \) the dynamic viscosity (kg·m\(^{-1}\)·s\(^{-1}\)) of the feed solution, which were assumed to be equal to the values for water at room temperature, \( \omega \) is the angular velocity (rad·s\(^{-1}\)), and \( r_{SC} \) is the radius of the stirred cell (1.25 × 10\(^{-3}\) m). The mass transfer coefficient, \( k_{SC} \), depends upon the diffusion coefficient, \( D \), of the feed solute and, therefore, varies slightly for each solute tested according to

\[ \frac{k_{SC} \cdot r_{SC}}{D} = 0.2 \, \text{Re}_{SC}^{0.567} \, S^{0.33}, \]

where \( S \) is a solute-dependent parameter.
with the Schmidt number being \( \text{Sc} = \mu \cdot \rho^{-1} \cdot D^{-1} \). In the case of bovine serum albumin, BSA, \((D = 5.9 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1})\) a mass transfer coefficient of \(5.8 \times 10^{-6} \text{ m} \cdot \text{s}^{-1}\) was produced [28].

Once a stable flow rate was attained (meaning no change for at least 10 min) permeate mass was measured every 30 s over a 30 min period. Solute rejection tests were performed using feed solutions of either 1 g·L\(^{-1}\) solution of BSA (Sigma-Aldrich) dissolved in a prepared phosphate buffered saline (PBS) solution, or 1.5 g·L\(^{-1}\) poly(ethylene glycol) (PEG) at 2, 10, 35, 50, 95, and 203 kDa (Polymer Source Inc., Dorval (Montreal), Quebec, Canada) dissolved in deionized water. BSA concentrations in the feed and permeate were determined by measuring the absorbance of 280 nm light with a UV-Vis spectrophotometer (Lambda 20, Perkin Elmer, Waltham, Massachusetts, USA). PEG concentrations were determined using a total organic carbon analyzer (Shimadzu TOC-V, Shimadzu Corp., Kyoto, Japan).

### 3.3.0. Results and Discussion

#### 3.3.1. Membrane Optimization

Solvent evaporation is a critical step in the S-NIPS process because it drives self-assembly of the block copolymer film. As evaporation time increases, the skin layer pore structure progresses from a disordered state to a more ordered, densely-packed state [29]. Here, polymer concentrations near, but just below, the concentration of ISV-59 required for ordering within the bulk solution were used [30]. Based on Flory-Huggins solvent-polymer interaction parameters—as calculated from solubility parameters [31]—it is assumed that the micelles were initially composed of poly(isoprene) (PI) cores and poly(4 vinyl pyridine) (P4VP) coronas because PI is the least soluble block (Table 3-2). After
the films were cast, solvent began to evaporate—with the more volatile THF evaporating more quickly—causing assembly of the micelles. As the solvents evaporated, we speculate that the degree of micelle interactions increased. The resulting membrane was composed of a PS matrix with spherical PI inclusion and P4VP-lined channels [15]. Based on this structure the overall void fraction in the selective layer of the ISV-59 membrane may be correlated with the P4VP fraction in the parent polymer.

Table 3-2. Solvent-polymer Flory-Huggins Chi Interaction Parameters [31]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$X_{\text{solvent-PI}}$</th>
<th>$X_{\text{solvent-PS}}$</th>
<th>$X_{\text{solvent-P4VP}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-dioxane, DOX (85.23)</td>
<td>2.55</td>
<td>0.20</td>
<td>0.23</td>
</tr>
<tr>
<td>tetrahydrofuran, THF (81.63)</td>
<td>2.61</td>
<td>0.35</td>
<td>0.11</td>
</tr>
<tr>
<td>deionized water (18.03)</td>
<td>13.8</td>
<td>10.2</td>
<td>7.84</td>
</tr>
</tbody>
</table>

During the evaporation period, the overall concentration of polymer increased, but the ratio of ISV:DOX also changed. Higher concentrations of both ISV-59 polymer and THF solvent in the casting solution reduced the evaporation time required to achieve the desired surface structure. However, because of the complexity of this system, these concentrations cannot be increased without restraint. While increased amounts of volatile THF shortened the required evaporation period to reach assembly, if evaporation occurred too rapidly self-assembly was unsuccessful and a disordered structure was trapped when the polymer was phase inverted. Care was taken to fine-tune the optimal
evaporation time for each solution to ensure self-assembled, water permeable structures were attained. In general, as evaporation length was increased for a given solution, a progression was seen from disordered structures, to increasingly ordered surfaces, and beyond to dense membranes. The latter transition from permeable membranes to dense membranes with negligible water flux correlated with a visual transition from opaque to transparent films. Evaporation time was increased up to the point that transparent films formed. This was a sign that the polymer precipitated prior to plunging into the coagulation bath forming a dense skin layer. Transparent films were also very brittle and broke apart during filtration tests, only filtration data for opaque films is presented.

SEM micrographs of the membrane selective layers fabricated from the casting solutions described in the experimental section are shown in Figure 3-4. Self-assembly successfully occurred for solutions of 12 wt% ISV-59 in solvent compositions of 70:30 and 60:40 wt% DOX:THF (by 70 and 45 s, respectively), but was unsuccessful in 50:50 wt%. It was also successful for 15 wt% solutions in solvent compositions of 70:30 and 60:40 wt% (by 45 and 40 s, respectively), but was unsuccessful at 50:50 wt%. We hypothesize that the disordered structures at 50:50 wt% occurred because the solvents evaporated so quickly that the surface structure was not able to equilibrate, and hence, was kinetically trapped before it reached an ordered state. At 12 wt% in the 50:50 wt% solvent system minimal assembly occurred before precipitation in the coagulation bath, while at 15 wt% assembly appears to have begun. At 18 wt% film formation was possible only at composition of 50:50 DOX:THF wt% and resulted in an overly dense membrane with negligible flux. The casting solutions of 18 wt% ISV-59 with lower concentrations
of THF resulted in viscous solutions due to a high degree of interactions between the polymer and solvent molecules and homogenous films could not be spread.

Figure 3-4. Surface SEM images of membranes cast from solutions as indicated. Membranes (a), (b), (d), and (e) were designated as successful because they self-assembled and gave rise to water permeation. Membranes (c) and (f) were unsuccessful, likely because the highly volatile solvent mixture evaporated fully before self-assembly could occur. Membrane (g) was able to assemble; however, it did not permeate water at the test conditions. Scale bar corresponds to 100 nm.

Of the solutions tested, four produced “successful” membranes—meaning 1) their SEM micrographs showed surface structures consistent with copolymer self-assembly, 2) they permeated water at 5 psi applied pressure, and 3) they rejected greater than 94% BSA. These were formed from solutions of 12 and 15 wt% ISV in 70:30 and 60:40 wt/wt% DOX:THF. Due to the fact that the structure was kinetically-trapped on its way to equilibrium by plunging it into the coagulation bath, a perfectly ordered structure was not
expected [6]. However, in each of these cases, a high density of monodisperse, highly ordered pores is seen at the surface. In each case, dry membrane thickness was ~50 µm. In all permeation tests, flux stabilized almost immediately and remained constant for the duration of testing. Permeation of PBS was slightly (<5%) lower than that of pure water, possibly due to changes in P4VP swelling [8] or the electroviscous effect [32] imposed by the buffer solution. Fouling occurred on the membrane surface and pore walls during BSA rejection tests (as witnessed by a flux reduction of ~40%); however, this was also nearly immediate and remained stable for >30 min.

**Figure 3-5.** Performance characteristics of four selected membranes, showing stable pure water permeability and observed rejection of 1 g·L⁻¹ bovine serum albumin (BSA) in phosphate buffered saline (PBS) solution. The highest permeability membrane is achieved with a low polymer concentration and a high THF concentration.
The most promising performance (380 LMH·bar$^{-1}$ and 95% BSA rejection) occurred in the membrane cast from a solution of 12 wt% ISV-59 and solvent composition of 60:40 DOX:THF wt%, with an evaporation period of 45 s (Figure 3-5). Separation performance of these membranes reveals the complexity of this system. When the evaporation period was reduced by increasing volatile solvent concentration the permeability increased; however, when it was reduced by increasing polymer concentration permeability did not increase. Additionally, when evaporation occurred too rapidly, assembly was unsuccessful. These factors must be balanced in each case to achieve a well-ordered and permeable membrane.

3.3.2. Membrane Surface Characterizations

Surface characterizations on the ISV membranes were also performed (Figure 3-6). A deionized water contact angle measurement on the ISV-59 membrane of 54° indicates a slightly more hydrophilic membrane than a commercial PES; therefore, elevated fouling would not be expected in comparison to the widely applied Biomax material [33-36]. The RMS roughness value is an indication of the standard deviation of pore sizes and, therefore, scales with polydispersity [37]. Measurements confirm the highly uniform nature of the self-assembled membranes with a value of 3 nm for ISV-59 versus 17 and 14 nm for the phase inverted and track-etched membranes, respectively. The large RMS value of the track-etched membrane is partly due to a less uniform pore structure compared to the self-assembled material, but may also reflect surface irregularities (i.e., low porosity) over the sample size used. The SAD is the ratio of the actual surface area to the flat projected area, indicating the number of roughness features
per unit area and scales with membrane surface porosity [37]. As expected, the SAD value for ISV-59 (10%) is larger than the other two membranes.

![Image](image.png)

**Figure 3-6.** Contact angle characterizations indicate that the self-assembled membrane has hydrophilicity in the range of typical commercial phase inverted membranes. Roughness measurements show that the ISV-59 self-assembled surface structure is highly uniform and porous represented by RMS and SAD values, respectively. *Inset shows AFM image of ISV-59 surface, scale bar corresponds to 100 nm.*

### 3.3.3. Comparison to Commercial Products

To further probe the performance of these membranes, we report a PEG molecular weight cut-off (MWCO) curve and compare it to that for commercially available phase inverted regenerated cellulose (RC) (Ultracel regenerated cellulose, 100
kDa MWCO, Millipore Corp.), phase inverted poly(ethersulfone) (PES) (Biomax 100 kDa MWCO, Millipore Corp.) and track-etched poly(carbonate) (PC) (Model No. PCT00320030, 30 nm nominal pore size, Sterlitech Inc., Kent, Washington, USA) membranes (Figure 3-7). The RC is considered a “conventional” phase inverted membrane, whereas Biomax membranes are known as the “state-of-the-art” for ultrafiltration, boasting a much sharper MWCO than conventional materials. The MWCO curve for the self-assembled membrane mirrored those of the track-etched and Biomax membranes. In addition, the pure water permeability was more than 6 times that of the track-etched membrane due to much higher porosity (Figure 3-8).

![Figure 3-7](image)

**Figure 3-7.** MWCO curves show that the self-assembled ISV-59 membrane has selectivity reminiscent of a PC track-etched membrane and the “state-of-the-art” Biomax PES phase inverted membrane. A conventional RC phase inverted membrane is included for comparison.
Figure 3-8. Surface SEM images of (a) PES Biomax 100 kDa MWCO phase inverted membrane, (b) PC 30 nm nominal pore size track-etched membrane, and (c) ISV-59 self-assembled block copolymer membrane, showing the marriage of high surface porosity and regular pore structure. Scale bar corresponds to 100 nm.

3.4.0. Conclusions

Nanoporous membranes represent a possible route towards more precise particle and macromolecular separations, which are of interest across many industries. Here, we explored membranes with vertically-aligned nanopores formed from a poly(isoprene-\textit{b}-styrene-\textit{b}-4 vinyl pyridine) (ISV) triblock terpolymer via a hybrid self-assembly/nonsolvent induced phase separation process (S-NIPS). Polymer concentration, solvent composition, and evaporation time in the S-NIPS process were varied to tailor ordering of the selective layer and produce enhanced water permeability. Here, water permeability was doubled over previous versions of ISV membranes. This was achieved by increasing volatile solvent concentration, thereby decreasing the evaporation period required for self-assembly. Fine-tuning was required, however, since overly-rapid evaporation did not yield the desired pore structure. It was shown that these vertically
aligned nanoporous membranes compare favorably with commercial UF membranes formed by NIPS and track-etching processes, which suggests there is practical value in further developing and optimizing these materials for specific industrial separations.

In the formation of self-assembled block copolymer membranes via the S-NIPS process three major factors influence membrane structure and separation performance: polymer concentration, solvent composition, and evaporation time. Our continued work with ISV membranes elucidates several features of ISV self-assembled porous materials.

- Self-assembled block copolymer ultrafiltration membranes, formed via the hybrid evaporative self-assembly/nonsolvent induced phase separation process offer densely-packed, regular pore structures and high porosities.
- Changes to the membrane fabrication conditions (i.e., casting solution composition and evaporation period length) strongly impact the resulting membranes.
- Increasing the volatile solvent concentration shortens the evaporation period required to reach the desired structure and leads to a more permeable membrane; however, if evaporation occurs too rapidly assembly is unsuccessful.
- In addition, increasing polymer concentration to reduce evaporation period does not increase permeability.
- Fine-tuning is required to achieve permeable, well-structured materials.
REFERENCES


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CHAPTER 4

RELATING STRUCTURE AND PERFORMANCE IN SELF-ASSEMBLED MEMBRANES
4.1.0. Introduction

An understanding of the mechanisms at play in membrane separations is crucial to further the field and intelligently tune materials to meet growing needs and applications [1]. Models are the tools used to understand membrane transport at a fundamental level. Models are used both to understand how a membrane performs and to relate its performance to physical and chemical factors. Two primary categories of transport models exist: phenomenological and mechanistic [2]. Phenomenological models treat the membrane as a “black box” and describe the separation process in terms of measureable parameters, such as solute passage and water flux. Empirical parameters (e.g., water and salt permeability coefficients) are used to represent the separation performance of a membrane by relating measured concentrations in the feed and the permeate streams. While these can be used to characterize performance they offer no mechanistic explanation of separation and are, therefore, difficult to compare between different material platforms. Mechanistic transport models have been developed to relate the separation performance observed in a membrane to the physical (e.g., pore structure, solute size) and chemical properties (e.g., energy of interaction) of the membrane and solute materials. Such structure-performance relationships allow for a more fundamental understanding of membrane transport.

Herein, we present a model approach to understanding porous membrane transport, which includes factors of both physical transport—accounting for convective and diffusive flow—and chemical affinity interactions between solutes and the membrane material. Chemical interactions are accounted for by a solute-membrane partitioning coefficient. This coefficient is determined experimentally through interfacial contact
angle analysis that allows for the characterization of surface tension components of both the solutes and the membrane material. These surface tension components are used to calculate the Gibbs free energy of interaction between the solute and membrane in the water phase. Additionally, long-range interactions are accounted for using aqueous phase energy decay relationships. Experimentally derived transport data is coupled with this model in order to characterize effective structural parameters for a given membrane, namely pore radius and thickness-to-porosity ratio. Combining the model with these characteristic structural parameters allows prediction of rejection for a variety of uncharged solutes by the given membrane. This model has previously been applied for commercially available nanofiltration and ultrafiltration membranes [3-4]. The forward predictions from this model agree well with experimental results, verifying its usefulness. This model poses a useful tool for characterizing membrane structure, predicting membrane performance, and understanding the impacts of chemical affinity on transport.

4.2.0. Improved Transport Model

4.2.1. Modeling Water Transport

The Hagen-Poiseuille pore flow model is used to relate membrane permeability ($L_p$), or pressure ($\Delta p$) normalized water flux ($J_v$), to structural parameters as

$$L_p = \frac{J_v}{\Delta p} = \frac{\varepsilon \cdot r_p^2}{8 \cdot \mu \cdot \tau \cdot l},$$

where $\varepsilon$ is the void fraction or porosity, $r_p$ is the pore radius, $\tau$ is the tortuosity, and $l$ is the thickness. The effective path length for permeation ($\Delta x = \tau \cdot l$) accounts for the actual
length traveled by solute and water molecules when pores are not perfectly aligned. The parameters can be grouped into a single term referred to as the structure factor, \( S = \tau \cdot l \cdot \varepsilon^{-1} \). In Figure 4-1, the water permeability is plotted for a range of geometries. For a given \( S \), such as 5 \( \mu \)m, it is clear that doubling of pore radius from 10 to 20 nm corresponds to an increase in water permeability from \( \sim1000 \) to \( \sim3500 \) LMH·bar\(^{-1} \), due to the fact that permeability scales with the square of the radius.

**Figure 4-1.** Water permeability \( (L_p) \) is plotted according to the Hagen-Poiseuille Pore Flow Model, which relates water transport to the geometry of modeled pores in the membrane selective layer. Pore radius \( (r_p) \) is varied along lines of constant structure factor \( (S = \tau \cdot l \cdot \varepsilon^{-1}) \).
4.2.2. Modeling Solute Transport

The observed rejection \((R_o)\), or observed separation factor \((S_o)\), is defined as

\[
R_o = 1 - S_o = 1 - \frac{c_p}{c_f},
\]

where \(c_p\) and \(c_f\) are the concentration of solute in the permeate and feed, respectively. Concentration polarization causes an elevated membrane surface feed concentration; hence, the actual rejection \((R_a)\) by a membrane can be determined from observed rejection, flux and mass transfer according to

\[
R_a = 1 - R_o + R_o \cdot \exp \left( \frac{J_v}{k_{SC}} \right).
\]

Mechanistic models of solute transport relate rejection to membrane structure. The actual rejection can be determined with the mechanical sieving (MS) model, developed by Zeman and Wales [5]

\[
R_{a, MS} = 1 - \left( 1 - \lambda \right)^2 \left[ 2 - (1 - \lambda)^2 \right] \exp(-0.7146\lambda^2),
\]

which relates rejection to physical properties only via the sieving coefficient \((\lambda = r_s / r_p)\), where \(r_s\) is the solute radius (6.75 nm for PEG-35). Alternately, the convection-diffusion-affinity (CDA) model can be applied [3] (Figure 4-2),

\[
R_{a, CDA} = 1 - \frac{\beta \cdot \phi \cdot K_c}{1 - \left( 1 - \phi \cdot K_c \right) \exp \left( -\frac{J_v \cdot K_c \Delta x}{K_d \cdot D \cdot \varepsilon} \right)}.
\]
Figure 4-2. Solute rejection plotted against sieving coefficient ($\lambda$) for different values of solute-membrane interfacial interaction energy ($\Delta G$) according to the convection-diffusion-affinity model. The black line corresponds to the case where the interaction is neutral and is, therefore, the case where the mechanical sieving (MS) and CDA models agree. For positive (repulsive) interaction energies the CDA model predicts higher rejection than the MS. For negative (attractive) interaction energies the CDA predicts lower rejection than the MS model.

In this model, $K_c$ and $K_d$ are the convective and diffusive hindrance factors related to $\lambda$ [6],

$$K_c = \left(2 - (1 - \lambda)^2\right)\left(1 + 0.054\lambda - 0.998\lambda^2 + 0.441\lambda^3\right)$$  \hspace{1cm} (6)$$

and

$$K_d = \left(1 - 2.3\lambda + 1.154\lambda^2 + 0.224\lambda^3\right).$$  \hspace{1cm} (7)$$
When the solute-membrane partitioning coefficient accounts only for steric exclusion, i.e., \( \phi = (1 - \lambda)^2 \), eq 7 is equivalent to the size exclusion based convection-diffusion model [6-7]. However, in the CDA model \( \phi \) is a function of both physical (\( \lambda \)) and chemical (\( \Delta G \)) interaction parameters,

\[
\phi = 2 \int_0^{\frac{\rho}{r}} \rho \cdot g(\rho) \, d\rho = 2 \int_0^{\frac{\rho}{r}} \rho \cdot \exp\left(\frac{\Delta G(\rho)}{kT}\right) \, d\rho.
\]

(8)

Here, \( \rho \) is the dimensionless position in the pore (\( \rho = r/ r_p \)), \( r \) is the radial position, and \( g(\rho) \) is the radial distribution function, assumed to follow a Boltzmann distribution. For “small” pores, such as in nanofiltration and reverse osmosis systems, \( \Delta G(\rho) \) can be equated to the interfacial free energy at the pore wall; however, for “large” pores, such as those in microfiltration and ultrafiltration systems, the decay of \( \Delta G \) from the pore wall into the pore center must be considered. For the self-assembled ultrafiltration membranes in this study, we must account for the fact that the interaction energy decays at distances away from the pore wall interface. To do this we calculate a pore-averaged \( \phi \) by integrating across the pore radius [4, 8].

The total solute-membrane interaction energy (\( \Delta G \)) is equal to the sum of the apolar Lifshitz-van der Waals (\( \Delta G_{LW} \)) and the polar acid-base (\( \Delta G_{AB} \)) interactions. Here, electrostatic double layer repulsions are ignored because we are using an uncharged solute (i.e., PEG). The value of each interaction energy factor can be related to the surface tension components of the solute and membrane. These components are determined experimentally via the van Oss three liquid probe method [9-10]. Contact angles of two polar (deionized water and ethylene glycol) and one apolar (diiodomethane)
probe liquids are measured on the ISV-59 membrane surface. These measurements arise from the average of ten measurements per sample on three samples of each surface, to ensure accuracy. Surface tension values for the probe liquids and solute are taken from literature [11-12].

The van Oss equation can be applied three times with the three contact angle, $\theta$, measurements as inputs,

$$-\Delta G_{SL} = (1 + \cos \theta)\gamma_L^{\text{tot}} = 2\left(\sqrt{\gamma_M\gamma_L^{\text{LW}}} + \sqrt{\gamma_M^{+}\gamma_L^{-}} + \sqrt{\gamma_M^{-}\gamma_L^{+}}\right).$$  (9)

Surface tension components for the three probe liquids ($\gamma_L^{\text{LW}}, \gamma_L^{+}, \gamma_L^{-}$) are known so the system of three equations can be solved for the surface tension components of the membrane ($\gamma_M^{\text{LW}}, \gamma_M^{+}, \gamma_M^{-}$) phase (Table 4-1). The same process is repeated for the surface tension components of the solute by replacing the membrane terms with solute terms ($\gamma_S^{\text{LW}}, \gamma_S^{+}, \gamma_S^{-}$).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\gamma_L^{\text{LW}}$</th>
<th>$\gamma_L^{+}$</th>
<th>$\gamma_L^{-}$</th>
<th>$\gamma_L^{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISV-59</td>
<td>26.01</td>
<td>47.34</td>
<td>0.80</td>
<td>38.33</td>
</tr>
<tr>
<td>PEG-35 [7]</td>
<td>43</td>
<td>0</td>
<td>64</td>
<td>43</td>
</tr>
<tr>
<td>water [8]</td>
<td>21.8</td>
<td>25.5</td>
<td>25.5</td>
<td>72.8</td>
</tr>
<tr>
<td>ethylene glycol [8]</td>
<td>29.0</td>
<td>3.0</td>
<td>30.1</td>
<td>48.0</td>
</tr>
<tr>
<td>diiodomethane [8]</td>
<td>50.8</td>
<td>0.01</td>
<td>0.0</td>
<td>50.8</td>
</tr>
</tbody>
</table>
The Lifshitz-van der Waals interfacial interaction energy is related to the surface tension components according to [3]

\[ \Delta G_{o}^{LW} = 2A_s \left( \sqrt{\gamma_{S}^{LW}\gamma_{L}^{LW}} + \sqrt{\gamma_{M}^{LW}\gamma_{L}^{LW}} - \sqrt{\gamma_{S}^{LW}\gamma_{M}^{LW}} - \gamma_{L}^{LW} \right). \] (10)

The interaction energy is calculated in Joules, by multiplying by the membrane-solute interaction area \( A_s = \frac{1}{2} \pi r_s^2 \). The energy at any location in the pore is calculated from [4]

\[ \Delta G_{o}^{LW}(d) = -A_s \frac{A}{12 \pi d^2}, \] (11)

where \( A \) is the Hamaker energy constant \( (A = -12 \pi d_o^2 \cdot \Delta G_{o}^{LW}) \), \( d = 0 \) corresponds to the pore wall, and \( d_o \) is the minimum equilibrium separation distance (0.158 nm). The interfacial acid-base interaction energy can be written as [3]

\[ \Delta G_{o}^{AB} = 2A_s \left[ \sqrt{\gamma_{L}^{+}\left( \sqrt{\gamma_{S}^{+}} + \sqrt{\gamma_{M}^{+}} - \sqrt{\gamma_{L}^{+}} \right)} + \sqrt{\gamma_{L}^{-}\left( \sqrt{\gamma_{S}^{-}} + \sqrt{\gamma_{M}^{-}} - \sqrt{\gamma_{L}^{-}} \right)} - \sqrt{\gamma_{S}^{+}\gamma_{M}^{+} - \gamma_{S}^{LW}\gamma_{M}^{LW}} \right] \] (12)

and the local energy at \( d \) can be determined as [4]

\[ \Delta G_{o}^{AB}(d) = \Delta G_{o}^{AB} \exp \left( \frac{d_o - d}{j} \right), \] (13)

where \( j \) is the decay length of acid-base repulsions (0.6 nm).
4.3.0. Application of Model to Self-Assembled Membranes

4.3.1. Method

To further our understanding of ISV-59 membrane performance, the mechanical sieving (MS) and convection-diffusion-affinity (CDA) models of solute rejection were used to interpret structural properties of membrane selective layers. Using the MS model (eq 6) one can determine the effective pore size ($r_p$) from the experimentally determined PEG-35 rejection. Then the Hagen-Poiseuille model (eq 3) can be used to calculate the structure factor ($\Delta x/\varepsilon$) from the experimentally determined $L_p$. In the CDA model (eq 7) $R_a$ depends on two unknown parameters ($r_p$, $\Delta x/\varepsilon$). Here, we used experimentally determined $R_a$ for PEG-35 and pure water $L_p$ to solve the CDA and Hagen-Poiseuille equations simultaneously and determine the structural parameters of $r_p$ and $\Delta x/\varepsilon$. These modeled values are compared to those determined from SEM imaging to give us insight into how the membrane performs at a fundamental level.

4.3.2. Structural Insights

Measurements taken on SEM micrographs of dried samples indicated an apparent pore radius of ~11.3 nm and surface porosity of ~16.3% (Table 4-2). Pore were determined to be ~112 nm in length and assumed to be non-tortuous ($\tau = 1$). To gain insight into the in situ structure of the ISV-59 membrane, further interpretation of the structural parameters was necessary. Effective structural parameters, determined by inputting the measured performance values for PEG-35 rejection and pure water permeability into the MS and CDA models were compared to the apparent values obtained from SEM imaging. PEG-35 was chosen as an ideal tracer since it was
moderately rejected by and showed negligible fouling of the ISV-59 membranes. Results revealed that the effective pore size determined from the models was narrower and the effective structure factor was significantly larger than expected after visual inspection. Making the assumption of cubic packing (not completely accurate, but a good approximation for ISV-59 surfaces) the porosity could be related to the pore size and center-to-center spacing ($D$) by $\varepsilon = \pi r_p^2 \cdot D^2$. This showed the effective porosity was lower and the effective path length was higher than expected from SEM analysis. While the extent of these differences varied between the two models, the trends were consistent.

<table>
<thead>
<tr>
<th>Structural Parameters</th>
<th>SEM Imaging$^a$</th>
<th>Ferry Mechanical Sieving (MS) Model$^b$</th>
<th>Convection-Diffusion-Affinity (CDA) Model$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore radius, $r_p$ (nm)</td>
<td>11.3 ± 0.6</td>
<td>8.5</td>
<td>7.4</td>
</tr>
<tr>
<td>Porosity, $\varepsilon$ (%)</td>
<td>16.3 ± 0.4</td>
<td>9.3</td>
<td>6.9</td>
</tr>
<tr>
<td>Pathlength, $\Delta x = \tau l$ (nm)</td>
<td>112 ± 13</td>
<td>800</td>
<td>440</td>
</tr>
<tr>
<td>Structure factor, $\Delta x/\varepsilon$ (µm)</td>
<td>0.69</td>
<td>8.6</td>
<td>6.4</td>
</tr>
</tbody>
</table>

$^a$ Here, $r_p$, $\Delta x$, and $\varepsilon$ determined from ImageJ analysis of SEM images.

$^b$ Here, $r_p$ determined from fitting the MS model PEG-35 $R_a$, $\Delta x/\varepsilon$ determined from fitting experimental $L_p$ to Hagen-Poiseuille, while $\Delta x$ and $\varepsilon$, were then dissociated using the geometric assumption of cubic packing and constant center-to-center distance.

$^c$ Here, $r_p$ and $\Delta x/\varepsilon$ determined from fitting experimental $L_p$ and PEG-35 $R_a$ to the CDA model, while $\Delta x$ and $\varepsilon$ were then dissociated using the geometric assumptions above.
These results indicated two things. First, the *in-situ* pore size was narrower than seen in dried samples imaged under vacuum. Second, the self-assembled structure did not account for the majority of hydraulic resistance in the ISV-59 membrane. Rather, the region just below the pores caused significant resistance, likely through a combination of dead-ending of pores and increased tortuosity imparted by the immediate underlying non-ordered, phase inverted structure (Figure 6).

The narrower pore size can be explained primarily due to swelling of the polymer material. Images of membrane surfaces were taken on vacuum dried samples in an air environment. Swelling occurs in the aqueous environment during testing and would result in a shrinking of the open porous area relative to what is seen in imaging. In the case of ISV self-assembled membranes the swelling may be even more pronounced due to the fact that P4VP chains are anchored at the pore walls. We know that in different solutions the pores can open and close as a pH-sensitive valve. Similarly, going from dehydrated to swollen states the P4VP may fill more of the pore, resulting in a reduced effective pore size.

Typically with asymmetric membranes it is assumed that the majority of the resistance to flow and separation of solutes occurs in the uppermost selective region, in this case the aligned pores. The substructure is assumed to impart mechanical stability, but not much in the way of separation or resistance to flux. Here, we find that for these self-assembled membranes the transition region below the pores and possibly the macroporous substructure itself actually contribute to the overall resistance to flow through the membrane. The results do not imply that the aligned pores themselves are longer, but that the effective separation region extends beyond the pores.
Figure 4-3. (a) Cross-sectional image of the ISV-59 asymmetric membrane (left) showing dense, self-assembled structure atop macroporous structure. *Scale bar corresponds to 2 μm.* Inset shows a magnification of the upper region with ~112 nm aligned pores. *Inset scale bar corresponds to 200 nm.* (b) SEM image taken at a 38° angle to the surface at a crack in the membrane surface. While the fragile aligned pores are disrupted in this material imperfection, the substructure immediately underlying them can be seen. This dense region is thought to cause dead-ending of and resistance beneath the pores that appear open at the surface. *Scale bar corresponds to 200 nm.*
4.4.0. Conclusions

Discrepancies between the apparent aligned pore structure and the in-situ structure, determined by applying transport models to performance results, reveal that pores are narrowed and some are blocked by the dense region below the selective layer. Successful membrane structures consisted of a well-ordered, self-assembled selective layer atop an open macroporous substructure; however, these two layers did not form fully independently. Rather, a less porous layer appears to form between the skin layer and macrovoid substructure; perhaps, a partially ordered kinetically trapped layer forms as the membrane formation process transitions from evaporative self-assembly to nonsolvent induced phase separation. The result is some flow constriction beneath the ordered skin layer pores. Therefore, it seems important further optimize the evaporative self-assembly and nonsolvent phase separation so that the transitional layer thickness and density is minimized.
REFERENCES


CHAPTER 5

SUMMARY AND CONCLUSIONS
5.1.0. Chapter 1: Aquatic Membrane Separations

Today, we face a global water challenge. More than ever, existing fresh water resources need protection and new water resources must be developed in order to meet the world’s growing demand for clean water. This will require better water treatment technology. Membrane separations are one avenue towards ensuring our water safety and protecting our natural resources. Membrane technology has evolved dramatically over the last century. Today, research continues on membrane-based methods of purifying alternate water sources, such as seawater, brackish water, and wastewater, to drinking water standards to relieve water stress. Currently, membrane technology is widely applied for pre-treatment (microfiltration and ultrafiltration), for softening and removal of dissolved metals and organic molecules (nanofiltration), and for desalination (reverse osmosis). Reverse osmosis is also used in the technology sector for ultrapure water production. Membrane separations are favored over many other treatment options because, in principle, they require no chemical additives, thermal inputs, or spent media disposal. Chapter 1 presents an introduction to membrane science and technology and details the current industry standard membrane materials.

5.2.0. Chapter 2: Nanotechnology-Enabled Water Treatment Membranes

Over the past decade, nanotechnology has rapidly changed from an academic pursuit to commercial reality. Nanotechnology promises to dramatically enhance many water purification technologies such as adsorption, ion exchange, oxidation, reduction, filtration, disinfection, and membrane processes. Already nanotechnology concepts have led to new water treatment membranes that exceed state-of-the-art performance and
enable new functionality, such as high permeability, catalytic reactivity, and fouling resistance. Chapter 2 presents a critical review of current literature on nanotechnology-enabled water treatment membrane materials and a comparison of “present day” merits and limitations of each water treatment membrane nanotechnology. The final comparison provides a roadmap of where technologies are today and what is required to bring them to commercial reality.

- Zeolite coatings promise high selectivity, boasting separation capabilities only currently realized with polymeric materials. They also offer the chemical, thermal, and mechanical stability offered by conventional ceramic membranes; however, to date, practical fabrication has not been realized. Fabrication techniques must be fine-tuned to reduce the overall thickness of coatings in order to achieve the high fluxes needed to compete with current polymeric alternatives.

- Ceramic membranes offer increased selectivity with catalyzed degradation of target compounds. Additionally, reactive surfaces have been shown to be biofouling resistant and so an enhancement in robustness is promised. These materials have been proven effective in laboratory studies, but more research needs to be done to produce commercially viable membrane reactor systems.

- Mixed matrix membranes offer mechanically stable, compaction resistant filtration membranes and support structures for high-pressure applications and require no changes to current manufacturing techniques.
• Thin film nanocomposites seek to produce compaction resistant membranes with silica nanoparticles, fouling-resistant membranes with nano-silver, self-cleaning photo-reactive membranes with titania, or highly permeable and selective membranes with molecular sieve zeolites. The major advantage of these materials is the ability to fabricate them through standard practices and with available equipment since only an addition to the casting solutions is required.

• The most revolutionary performance enhancements are offered by biologically-inspired materials (aquaporin- and carbon nanotube-based membranes); however, these materials are also farther from commercial realization. Most performance projections to date are based on modeled results and initial laboratory-scale demonstrations. More work needs to be done to evaluate the scalability and long-term stability of these materials.

• Self-assembled block copolymer membranes present a fully polymeric alternative to biologically-inspired materials, offering significant performance enhancements as well as ease of scalability. While currently in early stages of development, activities are underway to bring these materials to a commercial reality.

5.3.0. Chapter 3: Fabrication and Optimization of Self-Assembled Membranes

Nanoporous membranes represent a possible route towards more precise particle and macromolecular separations, which are of interest across many industries. In Chapter 3, membranes with vertically-aligned nanopores formed from a poly(isoprene-\(b\)-styrene-\(b\)-4 vinyl pyridine) (ISV) triblock terpolymer via a hybrid self-assembly/nonsolvent induced phase separation process are explored. Polymer concentration, solvent
composition, and evaporation time in the fabrication process are varied to tailor ordering of the selective layer and produce enhanced water permeability. Water permeability is doubled over previous versions of these membranes by increasing volatile solvent concentration, thereby decreasing the evaporation period required for self-assembly. Fine-tuning is required, however, since overly-rapid evaporation does not yield the desired pore structure. It is shown that these vertically aligned nanoporous membranes compare favorably with commercial ultrafiltration membranes formed by conventional phase inversion and track-etching processes, which suggests there is practical value in further developing and optimizing these materials for specific industrial separations.

In the formation of self-assembled block copolymer membranes via the S-NIPS process three major factors influence membrane structure and separation performance: solvent composition, polymer concentration, and evaporation time. This work with ISV membranes elucidates several features of ISV self-assembled porous materials:

- Self-assembled block copolymer ultrafiltration membranes, formed via the hybrid evaporative self-assembly/nonsolvent induced phase separation process offer densely-packed, regular pore structures and high porosities.
- Changes to the membrane fabrication conditions (i.e., casting solution composition and evaporation period length) strongly impact the resulting membranes.
- Increasing the volatile solvent concentration shortens the evaporation period required to reach the desired structure and leads to a more permeable membrane; however, if evaporation occurs too rapidly assembly is unsuccessful.
• In addition, increasing polymer concentration to reduce evaporation period does not increase permeability.

• Fine-tuning is required to achieve permeable, well-structured materials.

5.4.0. Chapter 4:
Relating Structure and Performance in Self-Assembled Membranes

In Chapter 4, a model approach to understanding porous membrane transport is presented, which includes factors of both physical transport—accounting for convective and diffusive flow—and chemical affinity interactions between solutes and the membrane material. Chemical interactions are accounted for by a solute-membrane partitioning coefficient. This coefficient is determined experimentally through interfacial contact angle analysis that allows for the characterization of surface tension components of both the solutes and the membrane material. Experimentally derived transport data is coupled with this model in order to characterize effective structural parameters for a given membrane, namely pore radius and thickness-to-porosity ratio. This model poses a useful tool for characterizing membrane structure, predicting membrane performance, and understanding the impacts of chemical affinity on transport.

Structural parameters determined from this model approach are compared to those determined by SEM imaging. Discrepancies between the apparent aligned pore structure and the in-situ structure, determined by applying transport models to performance results, reveal that pores are narrowed and some are blocked by the dense region below the selective layer. Successful membrane structures consist of a well-ordered, self-assembled selective layer atop an open macroporous substructure; however, these two layers did not
form independently. Rather, a less porous layer appears to form between the skin layer and macrovoid substructure; perhaps, a partially ordered kinetically trapped layer forms as the membrane formation process transitions from evaporative self-assembly to nonsolvent induced phase separation. The result is some flow constriction beneath the ordered skin layer pores. Therefore, it seems important further optimize the evaporative self-assembly and nonsolvent phase separation so that the transitional layer thickness and density is minimized.