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RPPR Final Report

as of 12-Jun-2018

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Final Report for Period Beginning 01-Jun-2014 and Ending 30-Nov-2017

Title: 7.3 Polymer Chemistry. Understanding the Novel Stimuli Responsive Transport Properties of Multifunctional, Nanostructured Block Polymer Membranes

Begin Performance Period: 01-Jun-2014

End Performance Period: 30-Nov-2017

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STEM Degrees: 2

STEM Participants: 5

Major Goals: We will be able to determine: 1) how block polymer architecture affects the membrane nanostructure, 2) how the membrane nanostructure and functionality affects the rate of solvent flow and solute permeation through the membrane, and 3) how these transport properties influence the kinetic response of the membrane to specific external stimuli. In this way, clear relationships between polymer chemistry, transport properties, and membrane performance in response to external stimuli will be established.

Accomplishments: Please see attachment.

Training Opportunities: Over its lifetime, this project has helped to support the training of 3 graduate students at the University of Notre Dame. All of these graduate students interact with each other on a frequent basis in order to foster a deeper appreciation of how different aspects of the project work synergistically to develop fundamental scientific knowledge that guides future generations of polymeric membrane devices. Additionally, the Notre Dame graduate students coordinated a visit with the graduate student from Purdue University. During that visit the student from Purdue learned how the block polymer materials are cast into membranes and how the membranes are then tested. By seeing all parts of the process, it is anticipated that the student will have a more robust understanding of how her portion of the project impacts the overall goals of the team.

Finally, the graduate students have presented their work at poster sessions on the campus of the University of Notre Dame, at a joint symposium between Purdue and Notre Dame regarding soft materials, at the American Institute of Chemical Engineering National Conference (including an Invited Talk as part of the DSM Science and Technology Award Session in November 2016), and at the American Chemical Society Annual Meeting. Having these opportunities to present their work and engage in scientific discussions has both increased the student's knowledge on the subject and also inspired them to continue to produce excellent work.

Results Dissemination: The results of this work have been published in field leading, peer reviewed journals and have been presented by junior and senior researchers at meetings of leading societies in the field. Thus, we believe that the academic and industrial communities are familiar with our work.

Honors and Awards: DSM Science and Technology Award Session - November 2016 (Jacob Weidman)
DuPont Young Professor Award - May 2015
ACS PRF Doctoral New Investigator Award - September 2014
North American Membrane Society Young Membrane Scientist Award - June 2014

RPPR Final Report
as of 12-Jun-2018

Protocol Activity Status:

Technology Transfer: The work detailed in this proposal has led to a patent being licensed by a start-up company (Anfiro, Inc) focused on the development of membranes for water treatment.

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)

Participant: Jacob Logan Weidman

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Siyi Qu

Person Months Worked: 6.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Yizhou Zhang

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Theodore J Dilenschneider

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Joseph Vallin

Person Months Worked: 3.00

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Other Collaborators:

RPPR Final Report
as of 12-Jun-2018

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Grant Agreement #:W911NF-14-1-0229
June 01, 2014 to November 30, 2017

Lead Organization: University of Notre Dame
Technical Point of Contact: Professor William A. Phillip

**Understanding the Novel Stimuli Responsive Transport Properties of Multifunctional,
Nanostructured Block Polymer Membranes**

ARO Program Manager: Dr. Dawanne Poree

Foreword

Nanoporous membranes based on self-assembled block polymer precursors are an emerging class of promising separations, controlled release, and sensing devices due to the tunable nanostructure and chemistry of the multifunctional materials that constitute these devices. These nanoporous membranes offer a novel platform for applications that require high throughput, high surface area, a well-defined pore size, and varying material functionality. And, with their readily tunable properties, block polymer membranes will allow for significant improvements in myriad applications. In order to realize the potential of this novel membrane platform, numerous fundamental questions regarding how to process these materials into functional devices and how the nanoscale structure and chemistry of the devices affect their performance must be addressed. Here, we summarize our efforts to address some of these questions over the lifetime of this research project. Three specific fronts on which significant research progress has been made are discussed in this report. First, we have made use of the chemical versatility purposefully built into our block polymer platform to fix heavy metal binding ligands within the nanopores of the membranes and demonstrated the use of these functionalized thin films in water treatment applications. Additionally, we have begun to identify the molecular interactions that generate a unique, long-lived hysteretic response to solution pH that emerges in our block polymer membranes. Finally, we have combined the self-assembly and non-solvent induced phase separation (SNIPS) fabrication technique with the dip coating archetype in order to produce high performance block polymer membranes in the hollow fiber configuration. Moreover, through a detailed understanding of how polyelectrolyte brushes respond to external stimuli, we were able to develop resilient nanofiltration membranes with robust performance profiles from the block polymer materials. These exceptionally-selective membranes have a pore diameter of 2 nm and are capable of resolving molecules with only a 0.8 nm difference in size. As such, over the course of this research project we were able to make significant progress toward elucidating the structure-response relationships for block polymer membranes that offer enhanced throughput and improved selectivity in traditional and emerging membrane applications.

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Statement of Problem Studied

Responsive polymeric materials offer the promise of coatings and devices that change their physical and chemical properties dramatically in response to small changes in external stimuli. As such, research into these materials for military and civilian applications has grown significantly in the past 30 years. However, to date, the majority of studies that have developed stimuli-responsive membranes have focused on modifying the surface chemistry of pre-existing commercial membranes. Unfortunately, because existing membranes are hindered by a broad pore size distribution, it has been difficult to develop a rigorous link between the responsive polymer microstructure and functionality and the macroscopic transport properties of the resulting membrane. Furthermore, there is strong evidence to suggest that, using traditional polymers and membrane processing methodologies, the pore size distribution of commercial membranes cannot be reduced without sacrificing membrane throughput. Therefore, this research project sought to address the critical need for a stimuli-responsive polymer membrane platform that contained a high density of singly-sized pores through the use of self-assembled block polymers as membrane precursors. *In this way, clear relationships between polymer chemistry, transport properties, and membrane performance in response to external stimuli could be established.*

Current filtration membranes are hindered by a wide pore size distribution. This wide distribution, which can be seen in Figure 1, is a direct result of the non-solvent induced phase separation (NIPS) process used to fabricate commercial membranes. Despite efforts to reduce the spread of this distribution by modifying the NIPS process, it remains a major hindrance to the deployment of membranes in advanced applications. Therefore, new methods and materials need to be developed in order to produce nanoporous membranes with a high density of pores that all possess a single, well-defined size. As demonstrated in Figure 1, membranes made from self-assembled block polymers possess a high density of singly-sized pores whose diameter can be tuned between 2 to 50 nm and whose chemical functionality can be easily and rationally tailored. We sought to exploit this unique control over the structure and chemistry of the membrane to initiate systematic studies that elucidated the effects that various physical and chemical properties (e.g., polymer chemistry and membrane pore size) have on the characteristic transport properties (e.g, hydraulic permeability and solute permeability) of stimuli responsive block polymer membranes. Through the strongly coupled interplay of polymer synthesis, membrane fabrication, materials characterization, and transport testing, the research efforts supported by

this funding were able *to establish fundamental structure-property-performance relationships for these highly selective membranes that exhibit unique transport mechanisms*. Ultimately, this fundamental information will enable the development of membranes for a large number of established and emerging applications, including water purification, sensing, and drug delivery, that provide the Soldier with new and improved capabilities on the battlefield.

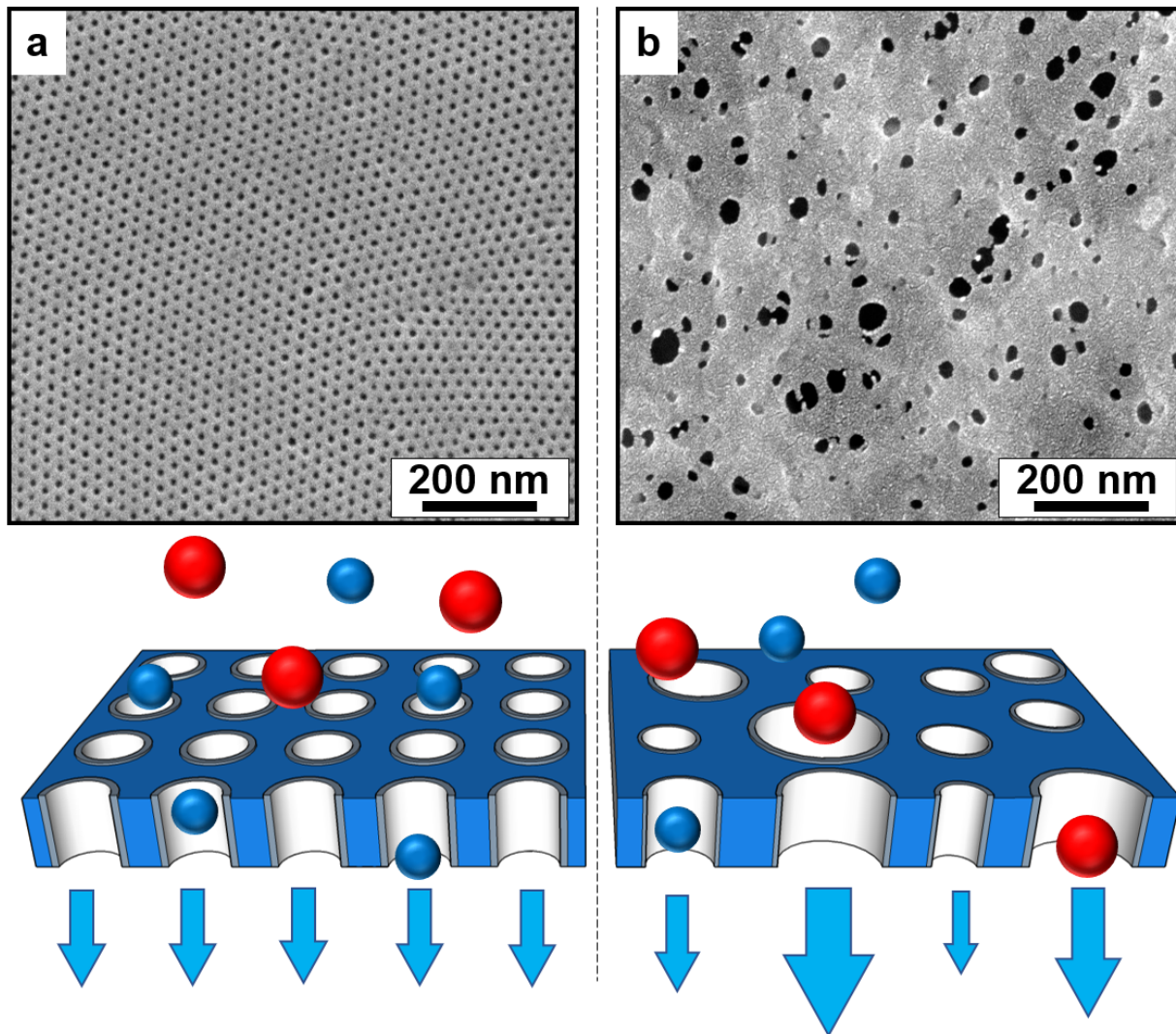


Figure 1. Scanning electron micrographs of (a) a self-assembled block polymer membrane and (b) a commercial membrane made using a standard non-solvent induced phase separation process. The highly-ordered nanostructure of the self-assembled membrane offers the potential for higher performance (i.e., higher throughput and more selective) separations relative to commercial membranes because the well-defined, narrow pore size distribution produces highly-selective filters, and generates a uniform flow distribution through each pore. The blue and red spheres represent solutes of varied size being filtered from solution. The width of the blue arrows is proportional to the volumetric flow through the associated pore. Solute selectivity and a uniform residence time for fluid flowing through the membrane pores are essential in the development of functional membranes for advanced applications.

Summary of the Most Important Results

Highlights Related to Block Polymer Synthesis and Membrane Fabrication

1. For the first reported time, we were able to fabricate a membrane from a self-assembled block polymer precursor that was synthesized via a reversible addition-fragmentation chain transfer (RAFT) polymerization mechanism. The polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) (PI-PS-PDMA) triblock polymer precursor resulted in a pore-lining block (i.e., PDMA) that can be functionalized using straightforward schemes post-assembly. Critically, the conversion of the PDMA moieties to poly(acrylic acid) (PAA) occurred *without* disrupting the well-defined nanostructure of the block polymer membrane.
2. Hydraulic permeability and solute rejection tests were conducted on the parent PDMA-functionalized membrane and the PAA-functionalized membrane. The PDMA-functionalized membrane demonstrates a pH-independent permeability while the PAA-functionalized membrane demonstrates a pH-dependent permeability providing evidence of successful functionalization. Moreover, both membranes demonstrate a sharp molecular weight cut-off (MWCO), which is consistent with a well-defined pore size and narrow pore size distribution.

Highlights Regarding to Block Polymers as Adsorptive Membranes for Metal Ion Capture

3. The performance of the PAA-functionalized membrane as a high capacity copper adsorbent capable of separating two solutes by chemical, and not physical, means was demonstrated. The capacity of the membrane adsorber was the highest measured to-date and was consistent with the PAA content of the material, which could enable the directed design of these sorbents applications based on rigorous scientific principles.
4. We demonstrated that the PAA groups that lined the pore walls of these block polymer membranes can be easily reacted to other functionalities that are molecularly-designed for target applications. For example, upon reaction with cysteamine at room temperature, the pore-lining groups are converted to *N*-(2-ethanethiol) polyacrylamide (PASH) moieties that act as high capacity binding sites for heavy metal ions, including lead, gold, cadmium, and silver cations.
5. The PASH-functionalized membrane is able to adsorb up to 1.4 mmol Pb²⁺ per gram of membrane, which compares favorably with other state-of-the-art lead adsorbers in the field (1.3-1.5 mmol g⁻¹). Furthermore, in dynamic uptake experiments, we demonstrated that mass transfer limitations in the PASH-functionalized membrane were minimal such that in single-pass flow through experiments, more than 98% of the lead in 10 mL of a feed solution containing 50 ppm could be removed by 15 mg of membrane material.
6. The high capacity for lead removal was retained in the presence of several competing and background ions (e.g., 50 ppm Cd²⁺, 10 mM NaCl, 10 mM MgCl₂, and a synthetic groundwater formulation). Once saturated, the high density of selective binding sites could be repeatedly (over at least 20 cycles) and fully regenerated through the addition of a mildly acidic solution.

Highlights Related to Molecular Origins of an Unusually-Stable Hysteric Response to pH

7. For the first reported time, we were able to demonstrate that poly(acrylic acid) (PAA) chains at extremely high grafting densities and confined in nanoscale pores of self-assembled block polymer membranes displayed a unique long-lived hysteretic behavior. Hydraulic permeability measurements demonstrated that different effective pore diameters arose in a pH range of 3 to 8, as determined by the pH of the previous environment. Further studies using Fourier transform infrared (FTIR) spectroscopy demonstrated that the fraction of ionized PAA moieties depended on the thin film history; this was corroborated by metal adsorption capacity, which demonstrated the same pH dependence.
8. We established that this hysteresis was persistent, enduring for weeks, in a manner unlike most other systems. Furthermore, we identified that this unique behavior was caused by the ability of the PAA chains to form a metastable hydrogen bond network within the pores of block polymer membranes.

Highlights Regarding the Fabrication of Highly-Selective Hollow Fiber Membranes

9. We introduced the facile dip-coating archetype to the self-assembly and non-solvent induced phase separation (SNIPS) nanomanufacturing process in order to produce ultra-thin polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) (PI-PS-PDMA) membranes on a hollow fiber support. By exploiting the flexibility of this membrane fabrication archetype, hollow fiber membranes fabricated in this manner demonstrated both a high-throughput and highly selective pores in the nanofiltration regime. Namely, a hollow fiber membrane with a 40-nm-thick active layer, pores with a well-defined diameter of 5.1 nm, and a hydraulic permeability of 27 L m⁻² h⁻¹ bar⁻¹ was fabricated.
10. Fundamental knowledge generated by comparing the nanostructures and transport performance of a hollow fiber membrane and its flat-sheet analog fabricated using identical SNIPS conditions enabled the systematic control of the nanoscale architecture of the membrane at the interface between the hollow fiber support and self-assembled active layer. This was crucial to the generation of the high-performance hollow fiber nanofiltration membranes.
11. The generation of exceptionally-selective nanofiltration membranes was demonstrated through the use of a distinct functionalization protocol that allowed for the introduction of sulphonic acid moieties within the pores of block polymer membranes. Hollow fiber membranes with a pore diameter of 2 nm and the ability to selectively distinguish between molecules with a 0.8 nm difference in diameter were generated based on fundamental knowledge related to the behavior of polyelectrolyte brushes.
12. The block polymer nanofiltration membranes are capable of selectively removing dissolved ions from solution using a Donnan exclusion mechanism. The extent of multivalent ion and monovalent ion removal is comparable with commercial nanofiltration membranes.

Facile Fabrication of Chemically-Tailored Block Polymer Membranes Using the SNIPS Method
Because we were implementing a relatively new class of materials in order to design and fabricate next-generation membranes, many fundamental questions regarding how to transform

these materials into high performance as mass transfer devices needed be addressed. As such, our initial efforts focused on the advancement of self-assembled block polymers as membrane precursors that could be modified rationally post-assembly. The key findings related to the polymerization of the polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) (PI-PS-PDMA) block polymer precursors as well as the initial efforts to cast membranes from these materials are presented in greater detail in the published articles:

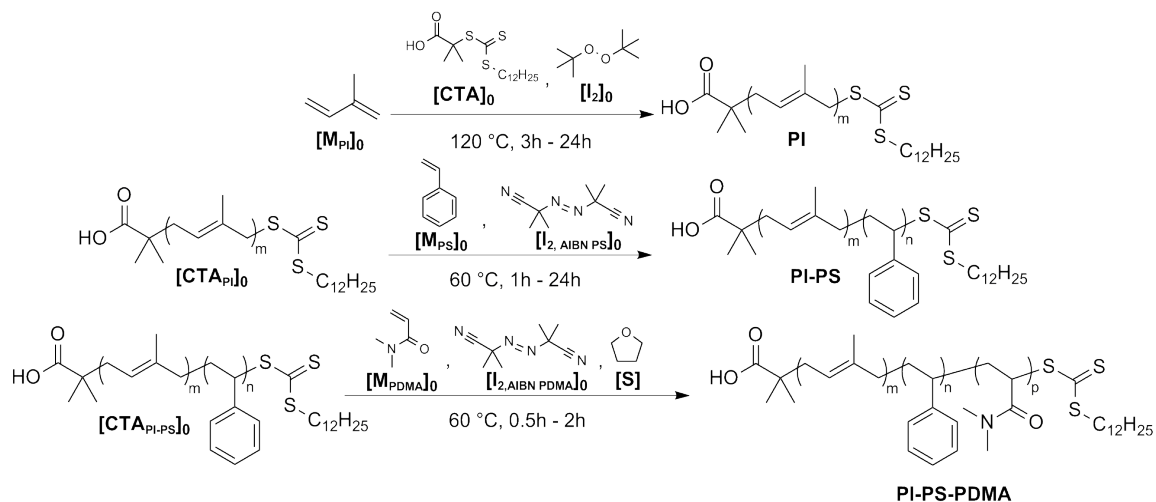
“Tunable Nanoporous Membranes with Chemically-Tailored Pore Walls from Triblock Terpolymer Templates,” Mulvenna, R. A.; Weidman, J. L.; Jing, B.; Pople, J. A.; Zhu, Y.; Boudouris, B. W.; Phillip, W. A. 2014, *J. Membr. Sci.*, 470, 246–256.

“Kinetic Analysis for the Polymerization of High Molecular Weight A-B-C Triblock Polymers via a Reversible Addition-Fragmentation Chain Transfer (RAFT) Mechanism,” Mulvenna, R. A.; Prato, R. A.; Phillip, W. A.; Boudouris, B. W. 2015, *Macromolecular Chemistry and Physics*, 216, 1831-1840, DOI: 10.1002/macp.201500201

Synthesis of Block Polymers Using a Controlled Radical Polymerization Mechanism.

Our initial efforts focused on the design and synthesis of a triblock polymer that would self-assembled into well-defined structures upon membrane fabrication. Furthermore, the pore-lining block of the polymer was designed such that the pore chemistry of the membrane could be altered in the solid-state (i.e., after membrane fabrication) in a straightforward manner without disrupting the exquisite self-assembled structure. To accomplish these aims, each block of the polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) (PI-PS-PDMA) triblock was designed to serve a specific purpose. The hydrophobic PS block forms the matrix of the membrane; the PI block increases the toughness of the membrane relative to the diblock analog, which makes the membranes easier to handle; and the PDMA block causes the pore walls to be lined with moieties that can be functionalized in the solid-state using straightforward approaches. As detailed throughout the report, this end block functionality allowed new chemistries designed for fundamental studies that elucidate how the nanoscale structure and chemistry of these devices affect their properties to be incorporated into the membrane.

Scheme 1. Synthesis and nomenclature of the polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) (PI-PS-PDMA) triblock polymers.



In order to generate a well-defined nanostructure using the combined self-assembly and non-solvent induced phase separation, or SNIPS, membrane fabrication method, the melt phase self-assembly of the block polymer precursor utilized in the process is critical. In particular, we have found that the fabrication of well-ordered membranes requires that: (1) the overall molecular weight of the triblock polymer is relatively high ($\geq 40 \text{ kg mol}^{-1}$); (2) the molecular weight distribution of the macromolecule is relatively narrow ($\text{Đ} \leq 1.5$); and (3) the composition of the block polymer is held within a relatively tight window with respect to the volume fractions of the three constituent moieties. Upon proper control of molecular weight, dispersity, and composition of the triblock polymer, the structure of the resulting membranes may be tuned for targeted applications. Due to the importance of controlling macromolecular architecture and composition, we utilized the RAFT polymerization mechanism such that the PI-PS-PDMA membrane precursors can be synthesized in a predictable and reproducible manner (Scheme 1).

Fabrication of PI-PS-PDMA Block Polymer Membranes using the SNIPS Method.

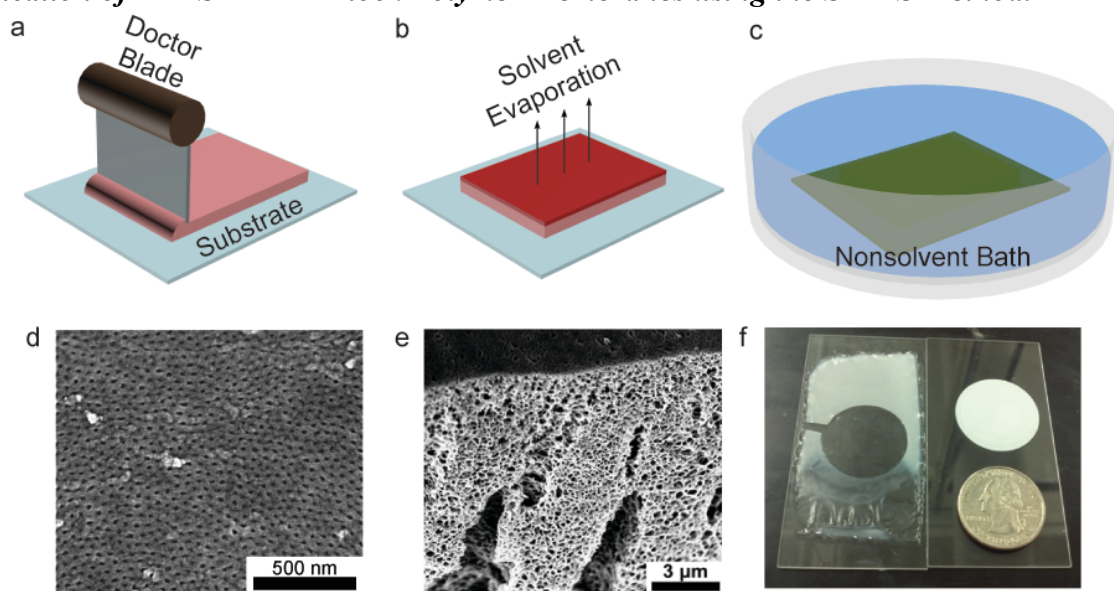


Figure 2. A schematic of the self-assembly and non-solvent induced phase separation (SNIPS) membrane fabrication technique, and the resulting membrane. (a) A polymer solution is prepared by dissolving a block polymer in a solvent or mixture of solvents. The solution is then drawn into a thin film through simple casting techniques (*e.g.*, using a doctor blade). (b) Solvent is allowed to evaporate from the thin film in a controlled manner for a predetermined period of time. (c) Then, the thin film is plunged into a non-solvent bath. The non-solvent causes the polymer to precipitate, which traps the nanostructure of the membrane. The result is a nanoporous membrane with an asymmetric structure that comprises a highly-selective active layer situated on top of a gutter layer with a high porosity. (d) and (e) SEM micrographs of the top and cross section of membranes made using the SNIPS process. (f) The fabricated membrane next to a US quarter showing the laboratory-scale of the membrane. However, the size of the membranes made via the SNIPS technique are limited simply by the dimensions of the casting substrate.

After obtaining the PI-PS-PDMA block polymers, they were processed into membranes using the SNIPS technique. Membranes were fabricated from a solution of 15% (by weight) polymer in a mixed solvent of dioxane-tetrahydrofuran (70-30 by weight). The solution was spread evenly on a glass substrate using a doctor blade (Figure 2). Solvent was allowed to evaporate from the film for a short period of time. During this time, the polymer concentration at the air-film interface increased, which resulted in the self-assembly of the block polymer into distinct nanoscale domains. Subsequently, the film was plunged into a non-solvent bath to precipitate the polymer, which trapped the self-assembled structure of the block polymer. A micrograph of the top surface of the parent membrane shows an average of 9.4×10^{13} pores m^{-2} with an average pore diameter of 53 nm and a standard deviation of 20 nm (Figure 3a).

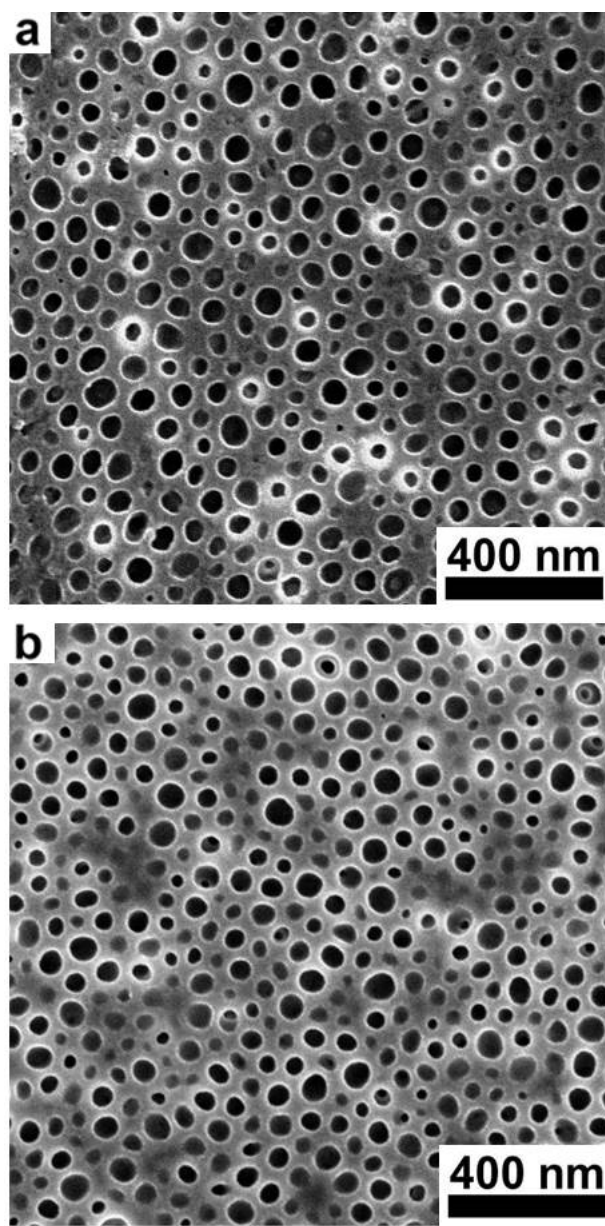


Figure 3. SEM micrographs of the top surface of the block polymer-derived membranes.
(a) The active layer surface of the PI-PS-PDMA parent membrane that was cast using the SNIPS

process. (b) The active layer surface of a refunctionalized PI-PS-PAA membrane. This membrane is produced by soaking a parent membrane in a 6 M hydrochloric acid solution. Note that the features of both surfaces are approximately the same despite the chemical treatment used.

The as-cast membrane performed well as a size-selective filter (*vida infra*). However, the conversion of the pore walls to a variety of specific functionality is of utility in the production of chemically-selective, fouling resistant, and stimuli responsive membranes. This had not been demonstrated prior to our efforts. *We established that the PDMA moiety of the triblock polymer lines the pore walls of the membrane and that it can be converted to a poly(acrylic acid) (PAA) moiety through simple base-catalyzed hydrolysis. The PAA is a robust platform for the additional of any number of chemistries to the membrane walls through carbodiimide coupling reactions.* Furthermore, because this functionalization occurs after the well-ordered structure of the membrane is fixed in place, many different responsive chemistries can be utilized to line the pores of the membrane.

The conversion of the PDMA moiety to PAA was performed by immersing the as-cast membrane in an aqueous 6 M HCl solution at elevated temperature. Figure 3b shows an SEM micrograph of the membrane following the conversion of the PDMA moiety to the PAA moiety. The structure of the PAA-functionalized membrane has the same characteristic surface features as that of the PDMA-functionalized membrane. Furthermore, the porosity, average pore size, and pore density of the PAA-lined membrane were estimated, and their values were found to be within 4% of the values reported for the parent membrane.

Following the conversion to PAA, the hydraulic permeability of the membrane was determined over a pH range between 1 and 12. These data are represented by the red diamonds in Figure 4a. The permeability of the membrane remained low ($\sim 0.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) as the pH of the feed solution was decreased from pH 12.0 down to 4.0. At pH 3.5, there was a sharp increase in permeability. As the pH was decreased further, the permeability continued to increase. This dependence of the permeability on pH is due to the extension and contraction of the PAA chains lining the walls of the pores in the membrane. At high pH ($\text{pH} > \text{pK}_a$ of PAA), the deprotonated PAA is negatively charged, which causes the PAA chains to extend into the open pores. Because the deprotonated PAA chains contain negative charges that repel each other, the PAA brushes extend farther into the pores of the membrane, which results in a lower permeability for $\text{pH} > \text{pK}_a$ of PAA. In an acidic environment ($\text{pH} < \text{pK}_a$ of PAA), the PAA is protonated. These uncharged polymer chains are able to collapse back, in part, toward the pore wall. This increases the effective diameter of the pores, which results in higher permeabilities. The neutral PDMA brushes exhibit no protonation in this pH range. As such, no pH-permeability dependence was observed in the parent membrane (blue rectangles in Figure 4a). This provides direct transport-based evidence, which corroborates Fourier transform infrared spectroscopy analysis (not shown), that the chemical nature of the membrane pores has been modified

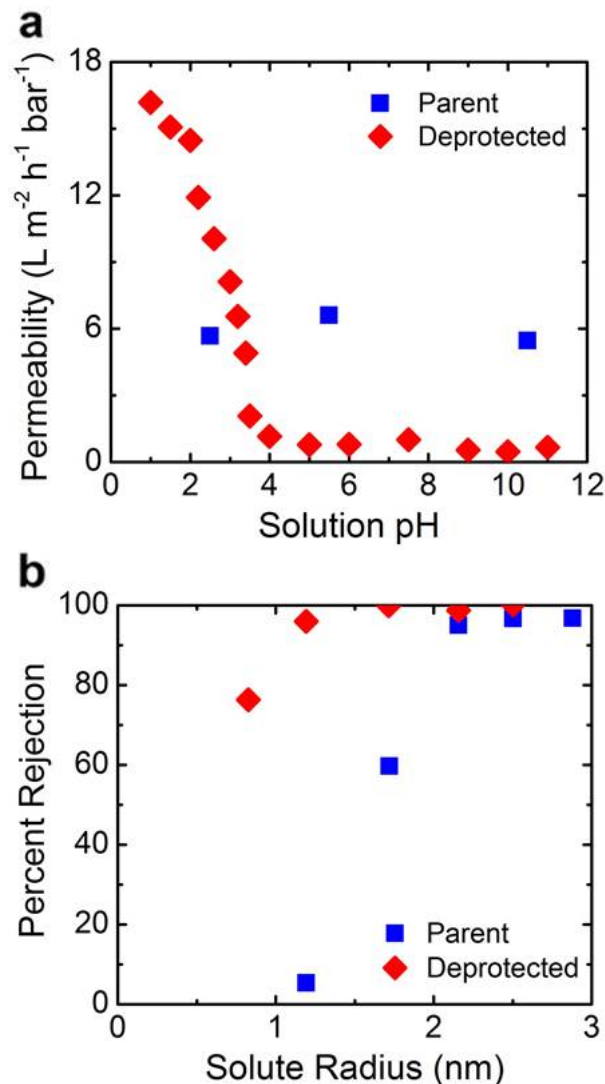


Figure 4. Transport properties of PDMA and PAA functionalized block polymer membranes. (a) Hydraulic permeabilities of the parent and deprotected (*i.e.*, PAA-functionalized) block polymer membranes plotted vs. solution pH. For pH values ranging from 2-11, the parent membrane had a constant hydraulic permeability of $6 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$. The PI-PS-PAA membrane had a permeability of $0.6 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ from pH 4-12. Below pH 4, the permeability of the PI-PS-PAA membrane increased monotonically; reaching a permeability of $16 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ at pH 1. (b) Solute rejection curves for the parent and deprotected (*i.e.*, PAA-functionalized) membranes were generated using solutions that contained polyethylene oxide (PEO) molecules as model solutes of known size. PEO molecular weights of 1.1, 2.1, 4.0, 6.0, 7.8, and 10.0 kDa were used. The percent rejection was determined by taking the ratio of the PEO concentration in the permeate to the 1 g L^{-1} feed.

Nanoporous Block Polymer Thin Films Functionalized with Binding Ligands for the Efficient Capture of Heavy Metal Ions from Water

The key findings related to the use of block polymer membranes as high capacity sorbents for heavy metal contaminants are presented in greater detail in the published articles:

“Nanostructured Membranes from Triblock Polymer Precursors as High Capacity Copper Adsorbents,” Weidman, J. L.; Mulvenna, R. A.; Boudouris, B. W.; Phillip, W.A. 2015, *Langmuir*, 31, pp 11113-11123.

“Nanoporous Block Polymer Thin Films Functionalized with Bio-Inspired Ligands for the Efficient Capture of Heavy Metal Ions from Water,” Weidman, J. L.; Mulvenna, R. A.; Boudouris, B. W.; and Phillip, W.A., *ACS Applied Materials & Interfaces*, 9, pp 19152–19160.

Fundamental Studies of Adsorptive Block Polymers Capable of Binding Copper Ions

The PAA-functionalized membrane provides a platform for initiating several fundamental studies regarding chemically-tailored membranes. As one example the conversion of the pore walls to poly(acrylic acid) (PAA) produced a membrane that is capable of capturing copper selectively. The copper binding capacity of PAA-functionalized membranes was evaluated using permeation tests and prolonged soaking experiments (Figure 5a). The vertical axis represents the binding capacity and the horizontal axis represents the copper concentration in solution at equilibrium. The experimental data for the two methods of determining capacity demonstrate strong agreement. The highest capacity determined from transport tests, 4.1 mmol Cu²⁺ g⁻¹ membrane slightly exceeded the capacity calculated using the PDMA-content of the triblock polymer material, 4.0 mmol Cu²⁺ g⁻¹ membrane, which is represented by the horizontal dashed line in Figure 5a. This theoretical value was calculated by assuming complete conversion of PDMA to PAA and that each PAA repeat unit binds one copper ion. The strong agreement between the experimental and calculated saturation capacities suggests that a one to one ratio of PAA repeat unit to copper ion is a more accurate reflection of the binding stoichiometry than the more commonly observed ratio of two carboxylic acid moieties to one copper ion. This may be driven by the high concentration of dissolved copper ions at saturation. Prior studies have demonstrated that at high concentrations of copper ions a single carboxylic acid group interacting with a single copper ion is a viable binding mechanism because the anions in solution can help to stabilize the complex.

More importantly, the agreement between the experimental and theoretical saturation capacities suggests that the copper makes use of all of the available binding sites throughout the entire membrane. This allows us to estimate the binding capacity of the membrane accurately based on the PDMA weight fraction incorporated into the triblock polymer precursor. Or, perhaps more importantly, a membrane with a specific binding capacity can be designed systematically by selecting the triblock polymer compositions wisely. This control over active site density during the precursor synthesis and membrane functionalization stages provide block polymer materials with advantage over other adsorbents, where capacities are often only determined experimentally after synthesis.

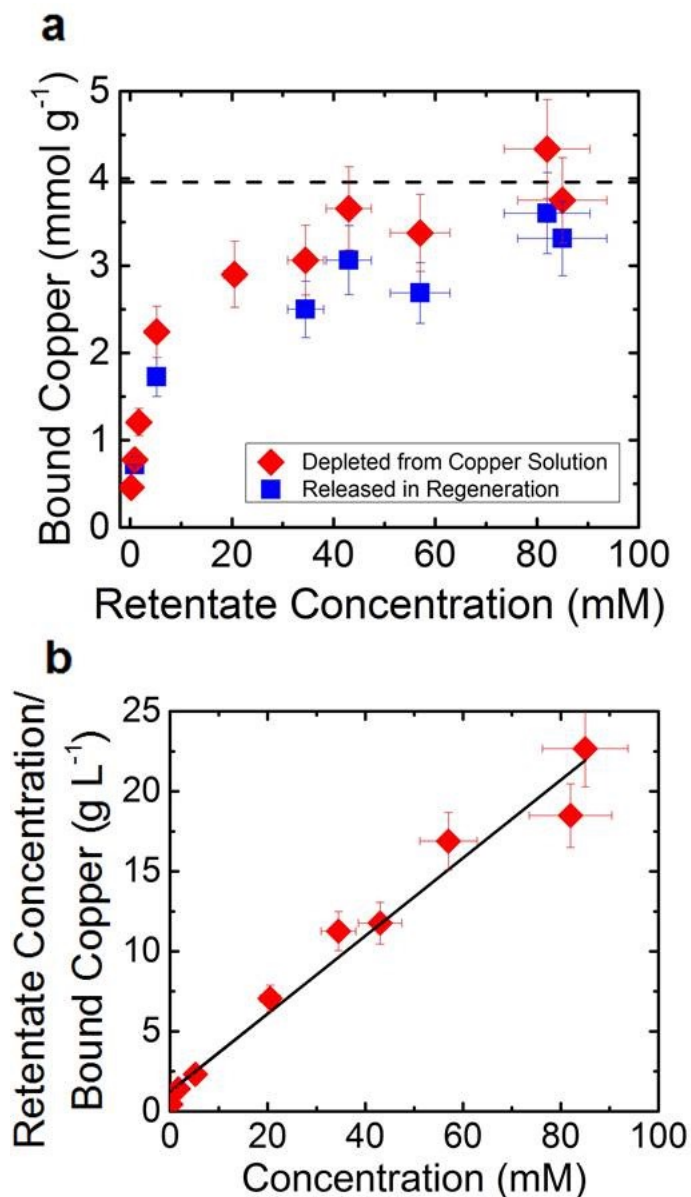


Figure 5. Copper binding isotherm. (a) Copper uptake capacity as a function of CuCl_2 concentration in solution at pH between 4 and 5. The copper capacities were determined by analyzing the concentrations of the permeate and retentate solutions during breakthrough experiments. These data are marked by red diamonds. Copper capacity was also determined by amount of copper released after exposing a PAA-functionalized membrane to a pH 1 solution. These data are shown by blue squares. The black dotted line at 3.98 mmol g^{-1} represents the theoretical copper capacity calculated using the moles of poly(acrylic acid) (PAA) groups in the block polymer precursor. (b) A comparison of the experimental capacity to a Langmuir isotherm, with a solid black line shown as a best fit curve of the data. The inverse of the value of the slope suggests a saturation capacity of $4.1 \pm 0.3 \text{ mmol g}^{-1}$ for this section of membrane.

The binding of copper ions to PAA is pH-dependent and reversible (Figure 6). We have demonstrated, for the first time that functional self-assembled block polymer membranes show strong potential as a platform for future membrane adsorption devices. As such, these results demonstrate the future ability of these types of membranes to have tailored functional groups such that specific adsorption of metal ions or other small molecules of interest can occur in a selective and straightforward manner.

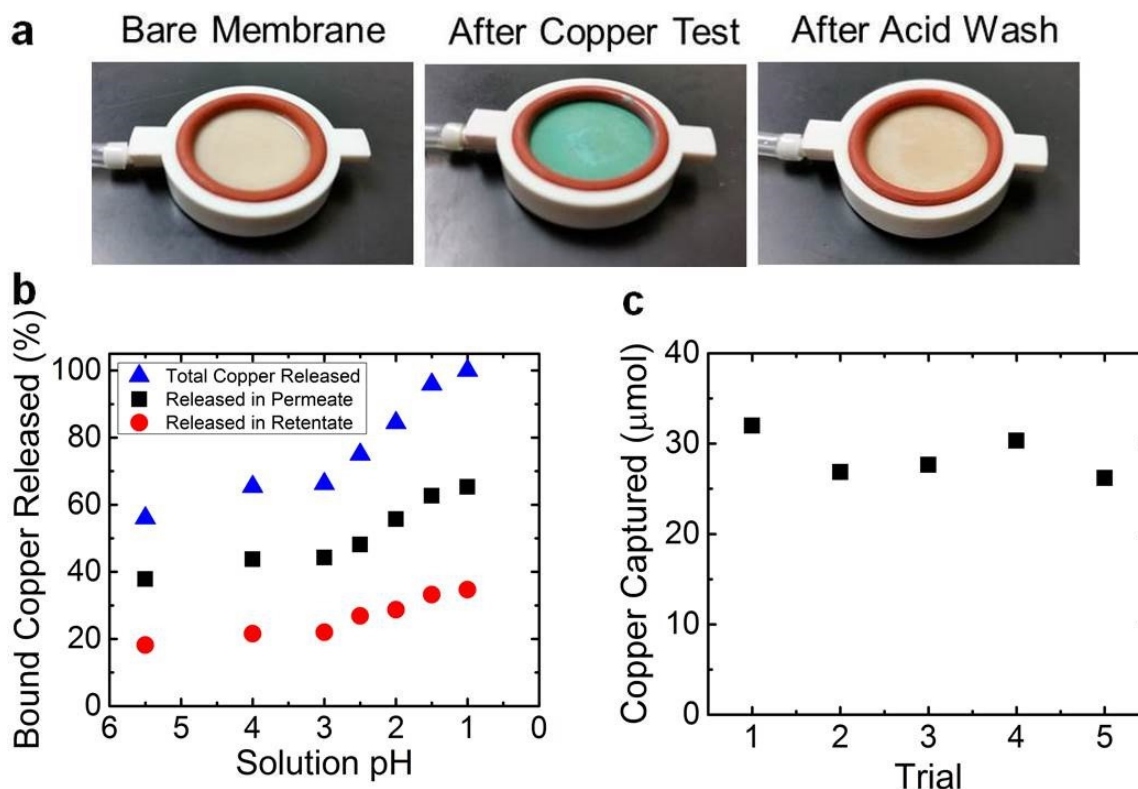


Figure 6. Demonstration of repeated copper adsorption and desorption. (a) Photographs of the PI-PS-PAA membrane before (left) and after (center) a copper capture experiment. The copper adsorbs through the membrane, giving it a blue-green color. After washing the membrane with an acidic solution (right), the membrane returns to its original off-white color. (b) Increasingly more acidic solutions (moving left to right) were added to the membrane loaded with copper, with the amount released into solution was determined. At each pH, 4 mL of acid were added and after stirring for 10 minutes, the solution permeated through the membrane, until 2 mL was collected downstream. The copper concentration in the upstream side of the membrane shows the ions released in the red circles, while the black squares show the ions collected in the permeated solution. The combined total is shown by the blue triangles. (c) Saturation capacity over the course of multiple adsorption experiments at 8 mM CuCl_2 feed concentration. The capacity of the first experiment was determined to be 32 μmol , and the concentration of the acid wash solutions

Adsorptive Block Polymer Membranes Capable of Binding Lead and Cadmium Ions

The functionalization of the PAA moieties with glutathione, a naturally-occurring peptide that captures heavy metal ions in many living systems, was carried out via ethylcarbodiimide

(EDC) coupling reactions. The results of heavy metal ion removal tests (not shown) using the glutathione-functionalized membranes clearly demonstrated their ability to adsorb heavy metal ions that are considered significant human health threats, namely, cadmium (II) and lead (II). Glutathione possesses a thiol moiety that is crucial to its ability to capture heavy metal ions effectively. Therefore, we hypothesized that more effective metal capture (on a per mass basis) could be realized by eschewing the extraneous functional groups within glutathione in order to more efficiently incorporate the thiol moiety. This hypothesis was tested through the introduction of cysteamine to the pores of the thin film as shown by the magenta structure in Figure 7a. Cysteamine consists of the binding thiol moiety at one end and a primary amine, which enables direct coupling to the PAA repeat units using the straightforward EDC carbodiimide coupling reaction, at the other end. The PI-PS-PAA and polyisoprene-*b*-polystyrene-*b*-poly(*N*-2-ethanethiol acrylamide) (PI-PS-PASH) spectra before and after reaction with cysteamine, respectively, are displayed in Figure 7b. As can be seen in the spectra, the 1720 cm⁻¹ carboxylic acid peak of the PI-PS-PAA film, shown in the black spectrum, decreases in intensity while the amide peak at 1640 cm⁻¹ grows in intensity as shown in the spectrum of PI-PS-PASH, represented in magenta. Combined, these observations confirm successful introduction of cysteamine within the nanopores of the PI-PS-PASH thin film.

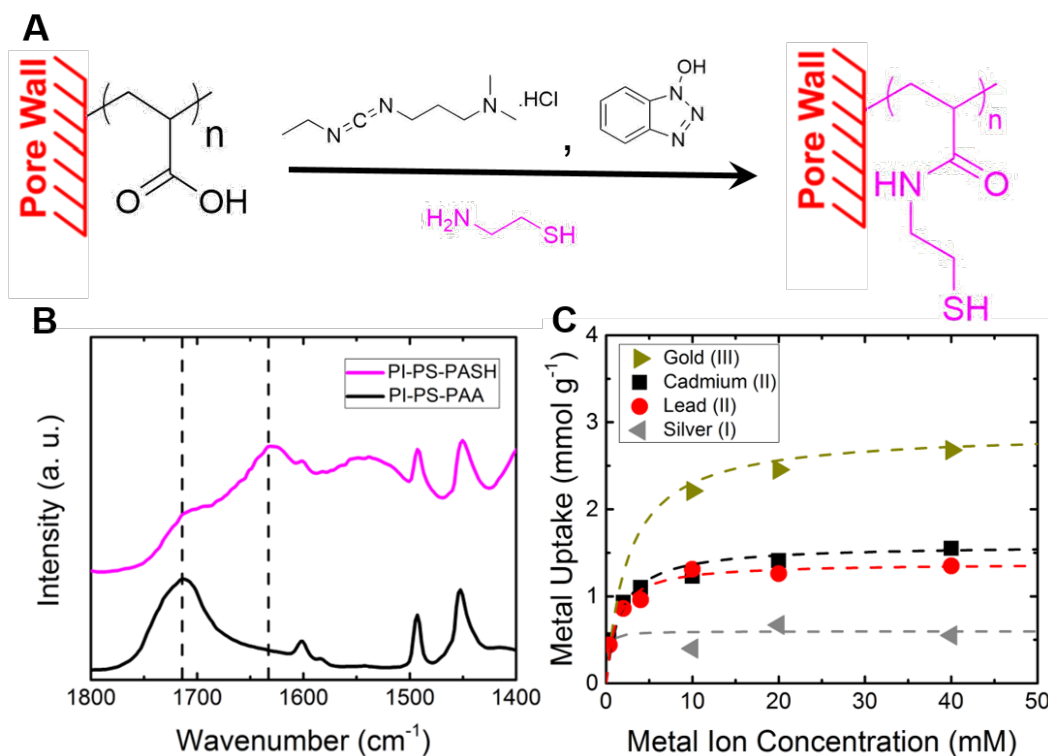


Figure 7. Coupling cysteamine to PI-PS-PAA membranes. (A) Reaction scheme showing the conversion of the pore wall lining PAA groups to bio-inspired PASH groups. (B) Comparison of FTIR spectra of the membrane before (black) and after (magenta) the conversion reaction. The decrease of the carboxylic acid peak (~1720 cm⁻¹) and rise of the amide peak (1650 cm⁻¹) suggest functionalization by the cysteamine molecule. (C) Uptake capacity calculated from metal adsorption experiments as measured by ICP as a function of metal ion concentration. The ions captured by the membrane include gold (III) (yellow arrows), cadmium (II) (black squares), lead (II) (red circles), and silver (I) (gray arrows). The uptake capacity values were calculated based

on both the depletion of ions from the retentate and the concentration of ions in the acid wash solution. Dashed lines represent best fit Langmuir isotherms for each metals ion.

The metal binding isotherms of the PI-PS-PASH thin films were established using solutions at higher ion concentrations in order to fully elucidate the salient features of the binding isotherms displayed in Figure 7c. The cadmium (II) and lead (II) adsorption rises sharply as a function of ion concentration at values less than 5 mM before approaching maxima near 1.55 and 1.35 mmol g⁻¹ membrane, respectively. These adsorption capacities compete with the highest reported capacities for state-of-the-art lead and cadmium adsorbers.

The execution of the batch uptake experiments also highlighted the rapid mass transfer in this adsorptive membrane platform. The data presented in Figure 8, which shows the temporal evolution of the bulk concentration, can be fit to a model for a generalized rate process that is first order in the solute concentration.

$$V_s \frac{dc}{dt} = -kcA_m \quad (1)$$

$$c = c_0 \exp\left(-\frac{kA_m t}{V_s}\right) \quad (2)$$

Here, c is the concentration of solute at time t , c_0 is the initial concentration of solute at $t = 0$, V_s is the volume of the solution, A_m is the area of the membrane, and k is the rate constant based on the membrane area. Based on this model, the experimental rate constant extracted from Figure 8 is equal to $1.5 \times 10^{-3} \text{ cm s}^{-1}$. This rate constant is an average of the mass transfer coefficient characteristic of lead transport to the thiol binding moieties and reaction rate constant for binding. Using the diffusion coefficient of lead in water, $9.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, normalized by the membrane thickness, 50 μm , the mass transfer coefficient can be estimated as $1.9 \times 10^{-3} \text{ cm s}^{-1}$, which despite the approximate nature of the estimate compares favorably with the experimental value of the rate constant. This favorable comparison indicates that solute uptake is likely limited by mass transfer to the binding sites not the binding reaction.

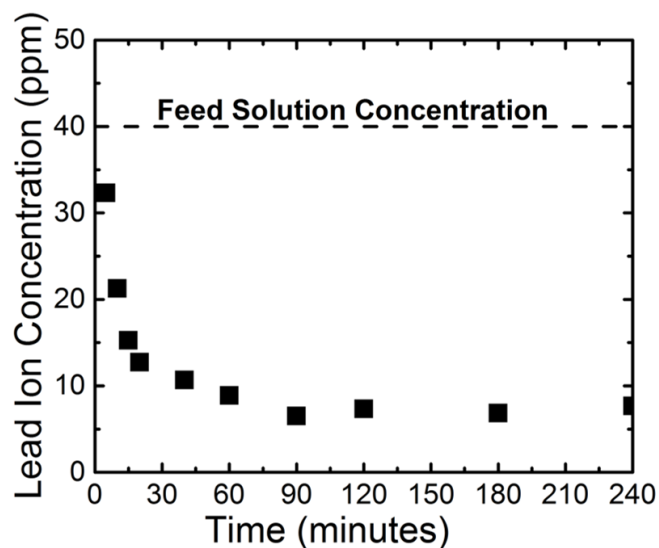


Figure 8. Temporal variation in retentate concentration during batch adsorption experiment. A ~ 36 mg (8.5 cm^2) PASH-functionalized membrane was added to a 10 mL solution containing a 40 ppm lead (II) nitrate solution. Aliquots were drawn as a function of time, and analyzed in ICP-OES for lead ion concentration.

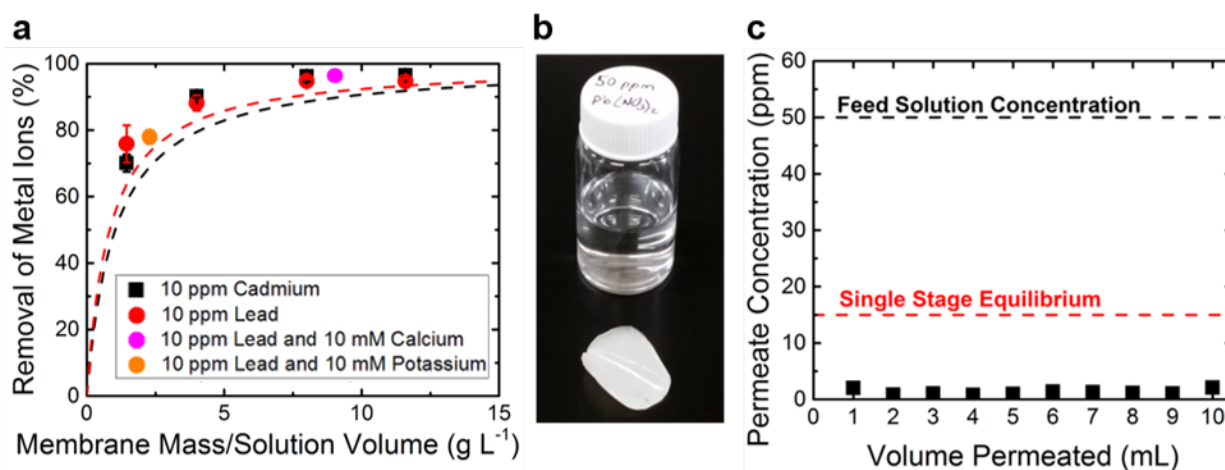


Figure 9. Heavy Metal Uptake by PI-PS-PASH Membranes. (a) Comparison of the removal of metal ions from solution by the ratio of membrane mass to solution volume. The percent of ions removed by the cysteamine-functionalized membrane is plotted as a function of the ratio of membrane mass to solution volume. Membranes were placed in solutions containing 10, 20, and 40 ppm (0.05 to 0.4 mM) concentrations of the metal ions. The removal of cadmium is shown by the black squares, and the removal of lead is shown by the red circles. The theoretical values for these data are also plotted by the dashed lines (cadmium (II) in black and lead (II) in red) based on the isotherms reported in Figure 7c. The magenta and orange data points represent the removal of lead (II) cations in the presence of a 10 mM solution of the competing salts, calcium chloride and potassium chloride, respectively. (b) Photograph of a 1-inch circle of membrane on a scale showing its mass of ~ 20 mg compared to a vial containing a 10 mL solution of 50 ppm (0.25 mM) lead (II) nitrate. This membrane is able to treat an amount of contaminated solution

roughly 500 times its own weight in a one-stage equilibrium adsorption, reducing its concentration by 70%. (c) The results of the separation in a membrane configuration of the materials in panel B show the permeate concentration of lead (II) ions as a function of permeated volume. The black dashed line represents the feed concentration, while the red dashed line represents the predicted concentration after a one-stage equilibrium adsorption.

Operating these thin films in a flow-through configuration would make better usage of the thiol binding moieties within the nanoporous materials due to the implicit staging of the configuration. In order to test the material capabilities in this configuration, a flow-through experiment was performed using a 10 mL stirred cell. As shown in Figure 9b, a membrane only 5 cm² in area (~18 mg) was used to treat 10 mL of contaminated solution, which is roughly 500 times its own weight. A 50 ppm (0.25 mM) lead (II) nitrate solution was pressurized to permeate through a thin films sample 1-inch in diameter, and the downstream concentration was measured as a function of permeated volume, as displayed in Figure 9c. The dashed black line represents the concentration of the 10 mL of feed solution and the red dashed line is the final concentration that is predicted for a single-stage equilibrium process based on the results of Figure 9a. The concentration of the permeate solution, represented by the black squares, remains steady at a value around 1 ppm lead ions throughout the entire 10 mL of solution processed. This removal of nearly 98% percent is significantly higher than the single stage equilibrium prediction, confirming the expected advantage of multiple equilibrium stages, characteristic of the flow-through configuration. A control experiment using magnesium as the cation in solution resulted in less than 5% of the magnesium being rejected, suggesting that the lead separation mechanism occurs through adsorption within the membrane rather than electrostatic rejection at the membrane-solution interface.

The ability of this material to be operated in this manner with such efficient performance displays its potential for implementation in water treatment systems, achieving near complete removal of toxins while also allowing high throughput of treated water. For the block polymer thin films to advance as a water treatment platform, it must be possible for the active thiol ligand to be regenerated once the thin film is saturated with bound metal ions. Because thin film adsorbers often experience a significant decrease in capacity as the material is cycled through loading and unloading phases, the PI-PS-PAG and PI-PS-PASH thin films were tested for their uptake over multiple cycles. For the reversible complexation reaction between the thiol moiety and lead (II) or cadmium (II) complexation, the presence of a mild acid is sufficient to release the bound ions and regenerate the free thiol groups. Therefore, the membranes were soaked in 40 ppm (0.4 mM cadmium and 0.2 mM lead) solutions to adsorb ions, then placed in a pH 1 solution to regenerate the binding sites. The uptake values measured during four consecutive cycles are shown in Figure 10. In all cases, the measured uptake of the metal ions remained high and demonstrated no noticeable decrease in capacity, suggesting that the acid rinse successfully regenerates the binding sites without deactivating them, which indicates that membranes made from this material could provide efficient separations to produce a clean water stream during a loading stage, then be rinsed with a mild acid during a brief unloading stage to allow the membrane to serve as a continuous separator whose performance profile does not deteriorate.

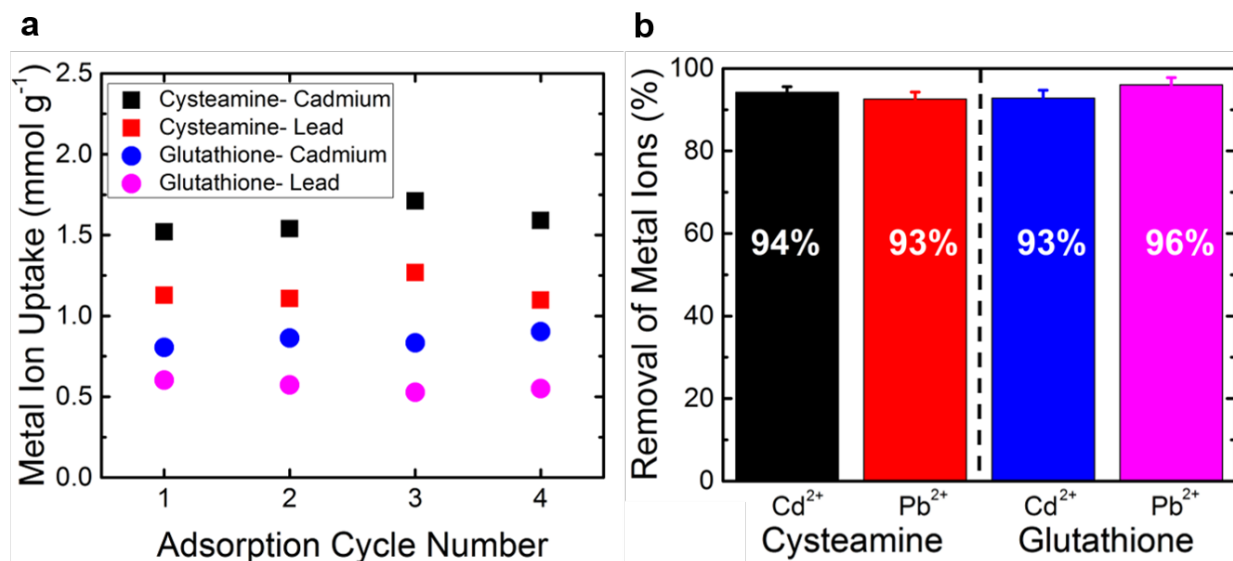


Figure 10. Consistent membrane performance after regeneration and in the presence of competing ions. (a) Membrane sections functionalized by cysteamine or glutathione were placed in solutions containing cadmium (II) or lead (II) cations at a concentration of 40 mM (4000 ppm cadmium and 8000 ppm lead). Following metal ion uptake, the membranes were placed in acid baths to release the bound ions and regenerate the binding sites. This cycle was repeated four times for each of the four binding group-cation combinations, with the metal uptake plotted as a function of the number of cycles. (b) Membranes were soaked in mixed metal solutions of cadmium (II) and lead (II) at concentrations of 10 ppm (0.1 mM cadmium and 0.05 mM lead) and 20 ppm (0.2 mM cadmium and 0.1 mM lead). The two left bars represent the percent of metal removed in the solution containing cysteamine-functionalized membranes, with the black bar representing cadmium (II) removal and the red bar representing lead (II) removal. The two right bars represent the amount of metal removed in the solution containing glutathione-functionalized membranes, with the blue bar representing cadmium (II) removal and the magenta bar representing lead (II) removal.

While the nanoporous block polymer thin films displayed desirable properties in their high adsorption capacities, efficient removal of contaminants in flow configurations, and consistent performance upon regeneration, they must also be able to maintain this high performance in the presence of competing salts, which occur naturally in polluted water systems. This was tested by adding 3.3 cm² of a PI-PS-PASH membrane (12 mg) to solutions containing a mixture of lead (II) and cadmium (II) ions. Here, the metal concentrations were 10 and 20 ppm (0.05 to 0.20 mM) for each metal with the final percent removals for both experiments shown in Figure 10b. The PASH-functionalized thin films removed 93-94% of the lead ions (shown by the red and magenta bars, respectively) using only a single equilibrium stage, in good agreement with its reported removal in the single metal ion experiments shown in Figure 9a. The uptake of cadmium ions by PASH-functionalized (black bar) thin films showed similar performance to its single cation experiments as well (Figure 9a), suggesting that the presence of the competing lead cations does not disrupt the capture of cadmium in this concentration regime. Additional experiments in the presence of other common cations were executed using a competing cation concentration of 10 mM, and the results are plotted as the magenta (Ca²⁺) and orange (K⁺) data

points in Figure 9a. The heavy metal ion removal remained near the same values as those achieved in single cation experiments. This is a promising result, as it suggests that the efficient capture of a target heavy metal ion is relatively unaffected by the presence of other ions, which makes it a viable option for implementation in systems where multiple competing cations will be present in solution. Furthermore, the thin films are capable of capturing several heavy metals simultaneously, making the block polymer thin film platform an effective option for potential utilization in water treatment processes across a broad variety of water quality conditions

Hydrogen Bonds Between Poly(acrylic acid) Repeat Units Generate Unusually Stable Hysteresis in the pH Response of Self-Assembled Block Polymer Membranes

The key findings related to the hysteretic response of block polymer membranes to external stimuli are presented in greater detail in the recently-published article: “Unusually Stable Hysteresis in the pH-Response of Poly(Acrylic Acid) Brushes Confined within Nanoporous Block Polymer Thin Films,” Weidman, J. L.; Mulvenna, R. A.; Boudouris, B. W.; and Phillip, W.A., 2016, J. Am. Chem. Soc., 138 (22), pp 7030–7039, DOI: 10.1021/jacs.6b01618

Hysteresis in the Physical Properties of Nanoporous Block Polymer Membranes.

Stimuli-responsive soft materials are a highly-studied field due to their wide-ranging applications; however, only a small group of these materials display hysteretic responses to stimuli. Moreover, previous reports of this behavior have typically shown it to be short-lived. In our efforts, poly(acrylic acid) (PAA) chains at extremely high grafting densities and confined in nanoscale pores displayed a unique long-lived hysteretic behavior caused by their ability to form a metastable hydrogen bond network. An enhanced understanding of the polymer chemistry and physics governing this hysteresis gives insight into the design and manipulation of next-generation sensors and gating materials in nanoscale applications.

Because the PDMA moieties, which are subsequently converted to PAA moieties, are introduced during the block polymer synthesis we can confine PAA brushes within the nanopores of the result thin films at higher densities than can be achieved using standard methodologies. Estimates of this density suggest it is ~2.5 times larger than the densities reported for other methods of introducing polymers onto surfaces. It is likely that this high surface density of polymer chains is critical to the hysteretic behavior.

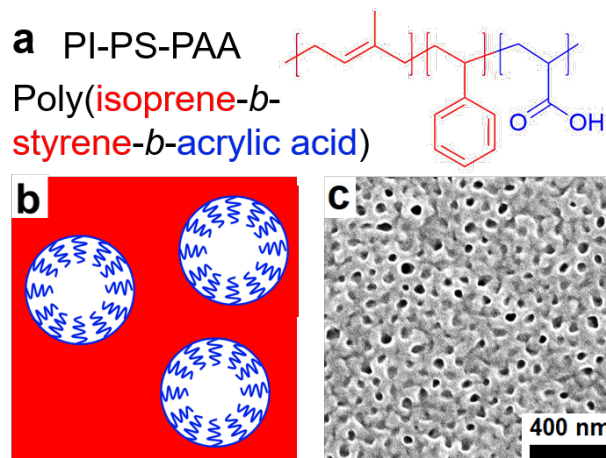


Figure 11. Membranes Fabricated from a PI-PS-PAA Block Polymer with PAA-lined Pore Walls. (a) The membranes are generated from polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-

dimethylacrylamide) (PI-PS-PDMA) block polymer precursors and then converted to polyisoprene-*b*-polystyrene-*b*-poly(acrylic acid) (PI-PS-PAA) after casting. (b) Schematic depicting the locations of the polymer blocks after membrane fabrication via the SNIPS method and functionalization reaction. The polyisoprene and polystyrene moieties form the matrix, and they are depicted as red. The self-assembled pores of the membrane are lined by brushes of the poly(acrylic acid) block, which are represented in blue. (c) An SEM micrograph of the surface of the PI-PS-PAA membrane depicting the true pore structure of the membrane. Note that the PAA domain is not visible in this SEM image as the polymer contracts to the pore walls under the vacuum conditions used in the SEM imaging.

The flux of solution through the membrane is a function of the applied pressure and the hydraulic permeability. The permeability depends on a characteristic size, in this case pore diameter at the upper surface, to the fourth power. Thus, changes in the pore diameter modify the overall permeability of the membrane, or alternatively, observed changes in membrane permeability suggest corresponding changes in the pore diameter.

The permeabilities of PI-PS-PAA membranes were measured in stirred cell experiments. Solutions of varying pH were added to a cell containing a membrane sample. The volumetric flux of water through the membrane was determined by dividing the slope of the accumulated mass versus time data by the area of the membrane and the density of water. Dividing this measured flux by the pressure applied yielded the permeabilities displayed in Figure 12a.

At the beginning of the experiment, with the membrane exposed to a pH 2.0 solution (corresponding to Point 1 in Figure 12), the membrane permeability was $10.9 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. Following this, solutions of incrementally higher pH were added to the stirred cell, and left to equilibrate with the membrane for ~20 minutes. The experiments began and permeated a total of ~2 mL for each data point over a timespan ranging from 0.5 to 12 hours, and the corresponding permeabilities were measured. The results of these measurements, which are denoted by the red triangles in Figure 12, were executed with the solution pH changing as shown (*i.e.*, moving from left to right in Figure 12). The permeability decreased between pH 3.0 and pH 4.0, then remained constant at $\sim 6.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ in DI water at pH 5.5 (Point 2, Figure 12). Further increasing the pH resulted in a gentle decrease in permeability until the solution pH was around pH 9.5 where the permeability neared its lowest value of $0.9 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$.

Beginning from a pH 13.0 solution (Point 3, Figure 12) and decreasing the pH, the permeability values matched that of the increasing pH experiments through a pH of 9.5. However, the permeability values showed clear hysteresis beyond this point, as the permeabilities below this pH remained near $1.3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ through to a pH of 4.0, including DI water at pH 5.5 (Point 4). Below pH 4.0, the permeability began to rise sharply. At a solution acidity of pH ~3.2, the permeability value for the experiments executed with solutions of decreasing pH rejoined the permeability values from the curve for experiments conducted with increasing pH. For solutions with a pH below this value through a solution pH of 2.0, the measured permeabilities matched. It is noted that between the pH values of 3.2 and 8.3, the permeabilities did not match between the two curves. This clear hysteresis in the permeability with respect to pH is of significant interest as controlling the previous pH conditions of the solution to which the membrane was exposed will impact the permeability in the near DI water (*i.e.*, typical operating) conditions. Continued experiments in both directions showed the trend was repeatable and consistent.

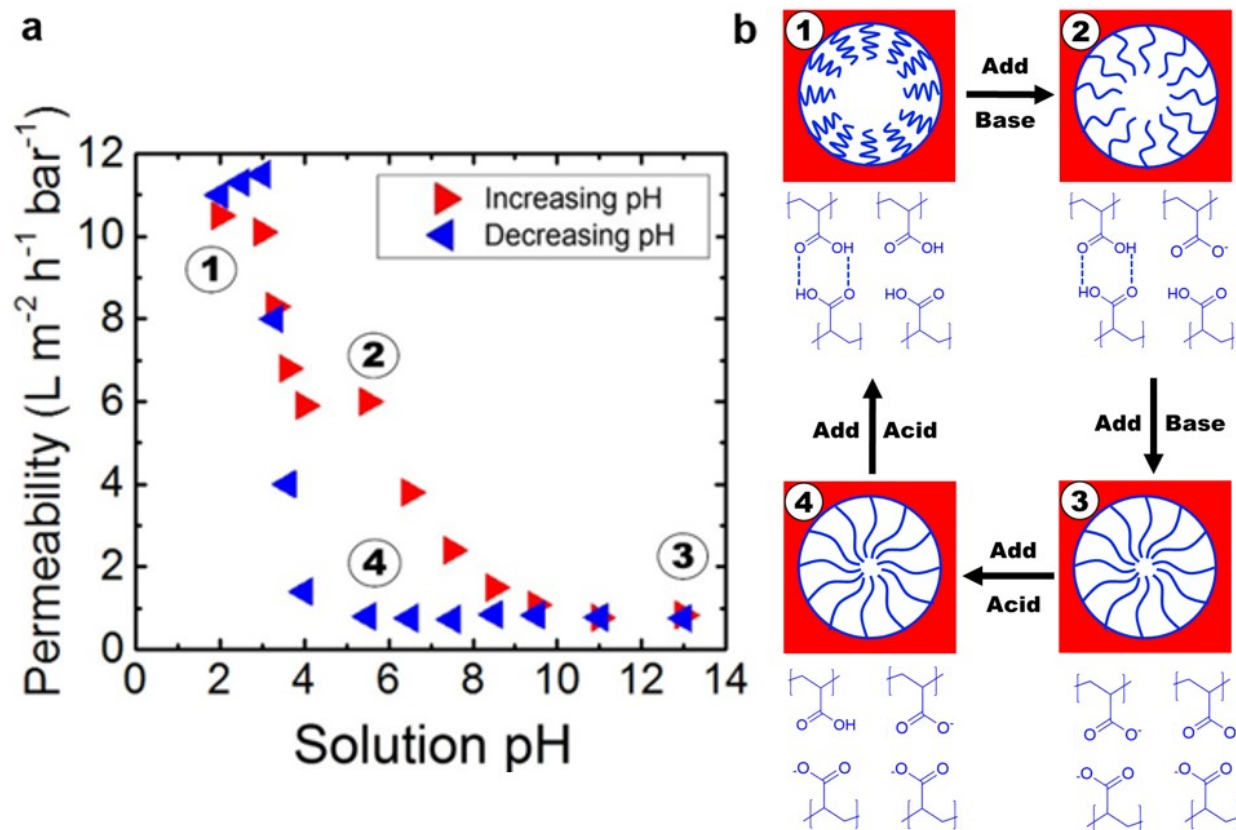


Figure 12. Membrane Permeability Displays a Hysteretic Dependence on pH. (a) The hydraulic permeability of a PI-PS-PAA block polymer-based membrane as a function of the solution pH. The membrane was fabricated from the PI-PS-PDMA-44 block polymer sample. Two series of experiments were implemented. First, a membrane began in a pH = 1.0 solution and its permeability was measured as the membrane was exposed to solutions of incrementally higher pH (red symbols); this is referred to as increasing pH. Second, a membrane began in a pH = 13.0 solution and the permeability was measured as the membrane was exposed to solutions of incrementally lower pH (blue symbols); this is referred to as decreasing pH. (b) Schematic diagrams of the pore structure and PAA conformation corresponding to the four points noted in Figure 12a. The PI and PS block segments form the matrix of the membrane, and are represented as the red region surrounding the pore in the illustration. The PAA chains that line the pore walls are represented in blue. (1) In a pH 2.0 solution, the PAA chains are not extended, resulting in a pore with a relatively large diameter. The carboxylic acid groups of the PAA are protonated and are capable of forming hydrogen bonds with another PAA moiety. (2) After addition of a base to increase to a pH 5.5 solution, some of the PAA repeat units are deprotonated resulting in the PAA chains extending slightly and decreasing the pore size. Some of the PAA repeat units remain hydrogen bonded to their counterparts, which prevents the full extension of the PAA brushes. (3) In a pH 13.0 solution, most of the PAA repeat units are deprotonated and electrostatically repel one another, which results in highly extended chain conformation that reduces the pore diameters. (4) In DI water (pH = 5.5) after exposure to a basic solution, most of the PAA groups remain deprotonated, and the pores retain a very small diameter. The process is repeatable and reversible.

The observed changes in permeability result from changes in the diameters of the pores within the active layer of the membrane, as we have demonstrated previously. These are, in turn, determined by the physical and chemical interactions between the repeat units of the PAA chains that line the pore walls. Because these repeat units contain a carboxylic acid moiety, their interactions with the surrounding solution may cause them to protonate or deprotonate, depending on the solution pH. At pH 1, the chains are highly protonated, as depicted in Figure 12b. Protonated carboxylic acids, including PAA, have the ability to form hydrogen bonds with other carboxylic acids (*e.g.*, repeat units along the same chain or with units on neighboring PAA chains). This results in the possibility of some PAA units forming a hydrogen-bonded network, as shown schematically in the top left panel of Figure 12b. In turn, the resulting pore has a relatively large diameter due to the collapsed state of the uncharged PAA chains, which corresponds to the highest permeabilities observed in Figure 12a. Increasing the solution pH by adding a DI water solution deprotonates some PAA repeat units that are not involved in hydrogen bonds, as shown in the top right panel of Figure 12b. Many hydrogen bonds remain intact, while the partial charging of the free (*i.e.*, repeat units not associated with hydrogen bonds) PAA units results in the extension of the PAA chains toward the center of the pore, decreasing the observed permeability to nearly half of that of the acidic state.

Adding a basic solution (pH 13.0) results in the deprotonation of almost all of the PAA units, inducing a greater extension of the PAA chains toward the center of the pore due to electrostatic repulsion between the repeat units of like charges. The electrostatic repulsion between PAA units is strong enough to disrupt the hydrogen bonded network. The ionized PAA chains swell to the point that the pores are nearly closed off in the base state, as shown by the bottom right panel of Figure 12b, which is plausible given the radius of gyration of the PAA block is ~ 25 nm and the dry state radius of the pores is ~ 20 nm. This, combined with the high surface density of PAA (between 0.5 to 1 chains nm^{-2}) along the pore walls, results in the pore volume being nearly completely occupied by PAA chains and a near zero permeability. Adding a more acidic DI water solution to the membrane results in the re-protonation of some PAA units, though still only a small fraction. The electrostatic interactions that are still present dominate the PAA chain response and cause the pore to retain its nearly closed state, as displayed in the bottom left of Figure 12b. Addition of the original acidic solution re-protonates the chains and induces hydrogen bonding, returning the system to the state shown schematically in the top left panel of Figure 12b. This cycle can be repeated with the same states achieved in a consistently reproducible manner.

Hysteretic events have been observed in the pH response of some membranes and other polymeric materials. However, it is extremely rare for a material to display long-lived hysteretic swelling; for instance, this has been reported in a gel that contained both positively and negatively charged moieties, but not in a porous membrane. Rather, almost all experiments with hysteretic films or membranes demonstrated that the hysteresis was kinetic in nature and, given sufficient time, would disappear. The kinetic limitations could be associated with polymer chain relaxation or lack of solvent access to all of the chains within the membrane pores. By allowing sufficient time for polymer chain relaxation, the chains were able to reach equilibrium conformations that are not achieved immediately after changing pH conditions. Alternatively, the residual behavior could be a result of needing sufficient permeation of a solution to allow the system to return to equilibrium. The return to equilibrium could be achieved in these cases within seconds to hours of being left to equilibrate. For this reason, permeability experiments on long time scales with DI water solutions were performed on the membranes.

Specifically, membranes were exposed to a pH 1.0 solution, 5 mL of which was permeated through the membrane to ensure that the pore walls throughout the active layer of the membrane achieved equilibrium with the solution. Then the cell was washed several times with DI water and left to soak for 1 h before adding a fresh 10 mL of DI water, and the membrane permeability was measured as a function of time. After 4 mL had permeated, the cell was emptied and a fresh 10 mL of DI water was added. This was repeated until a total of 12 mL had permeated through the membrane. The measured permeabilities are displayed by the red squares in Figure 13. Initially, the permeability decreased over the first 3 mL in the presence of the DI water solution. The pore-lining PAA groups swelled partially during this time as the DI water deprotonated more of the carboxylic acid units as the water permeated through the pores. This value then leveled after 3 mL and remained at the relatively high value of $8.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ during the rest of the experiment, which lasted several hours. A similar experiment was performed after the membrane had been exposed to a pH 13.0 solution, with the measured permeabilities shown by the blue circles in Figure 13. The permeability did not change significantly throughout the permeation of 12 mL of DI water over a period of 10 hours. This suggests that the hysteresis is neither kinetically-trapped by insufficient relaxation time, nor limited by lack of access of the bulk solution to PAA repeat units within the pores. Rather the membrane remains in long-lived metastable states that have different pore sizes at the same pH.

The approximated pore diameters shown by the cartoons in Figure 12b are based on the observed permeabilities in Figure 12a. These are assumed to be affected greatly by the differences in electrostatic repulsion in the different pH conditions, which is determined by how many of the PAA units are charged. One straightforward way to establish the degree of ionization is through FTIR spectroscopy, which has been shown to display different absorption peaks for the different states of PAA. Protonated carboxylic acid units absorb at wavenumbers of $\sim 1720 \text{ cm}^{-1}$. This is true for both hydrogen-bonded PAA (1729 cm^{-1}) and free protonated PAA (1712 cm^{-1}), though the observed peaks may be difficult to deconvolute. The deprotonated form of PAA has several absorption peaks, one of which occurs around 1550 cm^{-1} . The relative areas of these characteristic peaks can be used to determine the relative ionization of PAA in membranes under different experimental conditions. Thus, membrane pieces were prepared by soaking them in pH 1.0 or pH 13.0 solutions for at least 1 h, followed by soaking the membranes in a solution prepared at another pH. The solutions used were prepared in the same manner as described above for the permeability experiments. The membranes were left to soak in the solutions of various pH values for 4 h, then pulled from the solution, dabbed with a porous cloth to visual dryness, and vacuum-dried for 20 m.

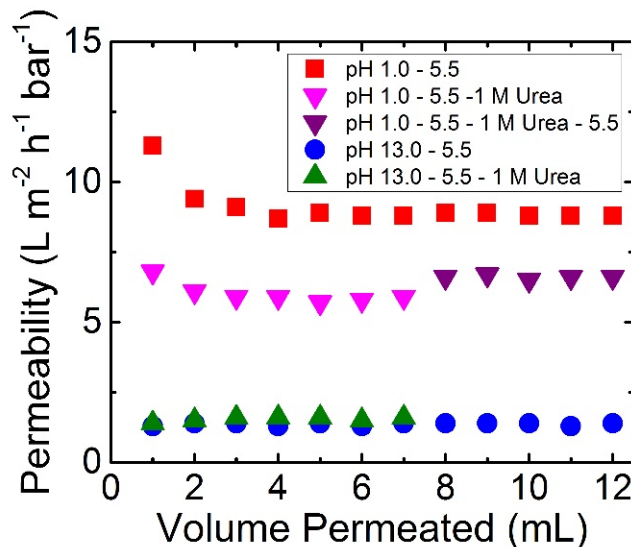


Figure 13. Hysteretic States are Long-lived and are affected by the Addition of Urea. The hydraulic permeability of a PI-PS-PAA block polymer membrane as a function of the volume of DI water permeated. The membrane was fabricated from the PI-PS-PDMA-97 block polymer sample. All measurements were collected using a solution at pH 5.5. Data points represent the average value for each 1 mL of permeate collected. The history of the solution passing across the membrane is summarized in the legend with the terminal entry being the condition used during permeability measurements. A membrane was rinsed with DI water after being exposed to a pH 1.0 solution, then the DI water permeability was measured (red squares). A 1 M urea solution was then added to the stirred cell and the permeability was evaluated (magenta triangles). The cell was then filled with DI water again and the permeability was measured (purple triangles). A membrane that was exposed to a pH 13.0 solution was rinsed with DI water and measured for its DI water permeability (blue circles). This was followed immediately by permeability measurements of a 1 M urea solution (green triangles).

Four representative FTIR spectra are shown in Figure 14a, and these are labeled 1–4 in order to correspond with the preparation conditions shown in Figure 12. After exposure to a pH 1.0 solution, the resulting FTIR spectrum shown in the red curve and labeled with a 1 displayed a broad peak near the 1720 cm^{-1} wavenumber, suggesting the presence of protonated PAA groups. A membrane that was soaked in pH 1.0 solution followed by DI water, shown by the magenta curve (Trace 2), provided a similar peak in the 1720 cm^{-1} region. This suggests that the PAA chains in these two states are mostly protonated, as was depicted in Figure 12b. Note that it is difficult to determine if the PAA forms hydrogen bonds using this experimental technique due to the potential for overlap of the hydrogen-bonded and free PAA signals. Upon exposure to pH 13.0 solution, the resulting FTIR spectrum shown in blue (Trace 3) displayed a peak near 1550 cm^{-1} , and the acquired FTIR spectrum of a membrane soaked in DI water following the soak in basic solution showed similar absorption, as shown by the green curve with the label 4. This suggests that the PAA groups were mostly deprotonated, as was depicted in Figure 12b. Similar to the permeability measurements in DI water, there was a significant difference in the FTIR spectra of the membranes soaked in DI water after exposure to highly acidic and basic solutions, (magenta and green curves), respectively. This difference demonstrates that the ionization of

PAA units in DI water is strongly dependent on the previous solution conditions surrounding the membrane.

Additional FTIR spectra were collected for pieces of membranes over a range of pH values, using solutions prepared in the same manner as those described for the permeability experiments. The degree of ionization was observed as the solution pH changed incrementally between the four states shown in Figure 14a. A comparison between the permeability and the percent ionization shows a strong correlation between the two metrics. This backs the hypothesis that the observed hysteresis that arises in the physical properties of the block polymer membrane is correlated with the discontinuous change in the electrostatic interactions between the repeat units of the polymer chains. This discontinuous change in the electrostatic interactions is caused by hydrogen bonds between the PAA repeat units preventing some of the repeat units from deprotonating.

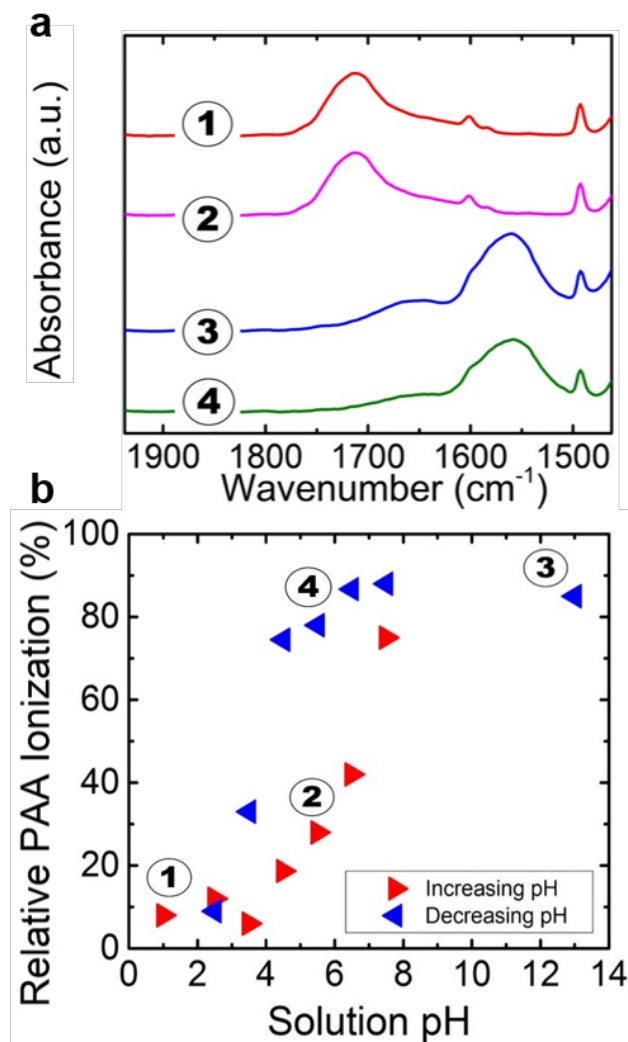


Figure 14. Degree of Ionization of PAA Shows a Hysteretic Dependence on pH. (a) FTIR spectra of vacuum-dried membranes after exposure to the four pH conditions labeled in Figure 12a. These conditions are the membrane: (1) exposed to a pH 1.0 solution (red line); (2) soaked in a pH 5.5 solution (magenta line), after exposure to a pH 1.0 solution; (3) exposed to a pH 13.0 solution (blue line); and (4) soaked in a pH 5.5 solution, after exposure to a pH 13.0 solution (green line). The peak at $\sim 1712\text{ cm}^{-1}$ in the red and magenta curves corresponds to protonated carboxylic acids, and the peak at $\sim 1560\text{ cm}^{-1}$ in the blue and green curves corresponds to deprotonated carboxylic acids. (b) The relative degree of ionization of the PAA chains as a function of solution pH. The pH was increased following exposure to a pH 1.0 solution (red triangles) or decreased following exposure to a pH 13.0 solution (blue triangles). The values of percent ionization were determined from the peak areas in the normalized FTIR spectra.

Hysteresis in Chemical Properties of Membrane.

In addition to controlling the physical properties of the membrane, the ionization of the PAA groups controls the chemical properties of the membranes. One property that relies on ionized PAA repeat units is the adsorption of copper ions, which has been discussed above. In the study mentioned above, membranes that were exposed to a basic solution, and thus had

mostly ionized PAA groups, were soaked in CuCl_2 solutions in DI water. Copper ions were reversibly adsorbed by the negatively-charged PAA units, and the membranes were regenerated with the addition of a pH 1 solution, which shifted the equilibrium to favor protonated PAA repeat units and released the copper ions back into solution. The concentration of copper in the retentate solution and the pH 1 copper regeneration solution were determined via ultraviolet-visible (UV-Vis) light spectroscopy, resulting in measured copper uptakes for the membrane under different conditions. In this study, the hysteretic behavior of the copper uptake was assessed in a similar manner.

The amount of copper bound to the membrane in these experiments was determined from the depletion of copper from the retentate solution and the concentration of the acid wash solution by the characteristic absorption of copper ions at $\lambda = 930 \text{ nm}$. These data are plotted in Figure 15a as a function of the pH of the copper solution. The red data points indicate the membrane pieces that were initially soaked in pH 1 solutions, while the blue data points are membranes initially in pH 13.0 solutions.

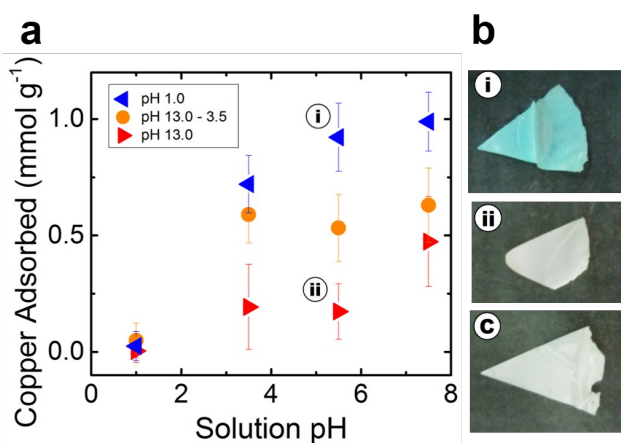


Figure 15. Copper Binding in Membranes is Hysteretic and Tunable. (a) The amount of copper adsorbed by membranes exposed to solutions of varying pH. After the membrane was soaked in a copper-free solution of pH-adjusted water [pH 1.0 (red arrows), pH 13.0 (blue arrows), or pH 13.0 followed by pH 3.5 (orange circles)], it was placed in a 8 mM CuCl_2 solution at the pH values indicated on the horizontal axis. (b) Photographs of the membrane samples after soaking in an 8 mM CuCl_2 solution at pH 5.5. Prior to submerging the membrane in the copper chloride solution, they were (i) soaked in a pH 13.0 solution and (ii) soaked in pH 1.0 solution. Sample (C) is a control membrane that was not exposed to a copper-containing solution.

This can also be observed visually, as shown in Figure 15b, as two pieces of membrane that were soaked in a (i) basic or (ii) acidic solution were added to an 8 mM CuCl_2 solution at pH 5.5, then removed and photographed after adsorbing copper. The membrane after exposure to the basic solution appeared blue, while the membrane that was soaked in acidic solution had a similar hue to the membrane not placed in a copper solution (c).

A final copper uptake experiment was performed, in which membranes that had previously soaked in acidic (pH 1.0) or basic (pH 13.0) solutions were added to scintillation vials containing DI water as before, but left for ~150 h instead of ~3 h. The membranes were then removed from the DI water solutions and added to vials of 8 mM CuCl_2 to determine the copper uptake. Based on both the depletion of the copper from the feed solution and the amount released

in the acid wash, values for the copper uptake were determined. The membrane that was initially soaked in basic solution had a resulting uptake of 0.72 ± 0.05 mmol g⁻¹ membrane, while the membrane initially soaked in acidic solution had a resulting uptake of 0.35 ± 0.06 mmol g⁻¹. These values fall just outside the range of the error of the short soak time experiments, but remain distinct from one another. This suggests that unlike other materials that show a short-lived hysteresis on the order of minutes to hours, the PI-PS-PAA membrane displays a hysteresis that endures up to a week in solution, and possibly longer.

Hysteresis Arises from the Hydrogen Bonding of PAA.

The pores of the nanoporous block polymer thin film show hysteretic and tunable behavior in both physical (*i.e.*, pore size) and chemical (*i.e.*, copper binding) properties, but the cause of the hysteresis is not elucidated merely by the presence of these properties. If the state of the PAA chains that line the pore walls in DI water after exposure to either acidic or basic solution is the local minimum in free energy, a disturbance of the PAA chains from the metastable state may drive the PAA conformation toward to the global minimum in free energy. It has been noted that PAA has the ability to form hydrogen bonds with itself when it is placed in acidic conditions that cause the carboxylic acid moieties to protonate. It is possible that a network of hydrogen bonds may persist in DI water after the membrane was initially exposed to acidic conditions, as shown in Figure 12b. In this case, the DI water does not deprotonate enough PAA repeat units to perturb the system sufficiently to break the network of hydrogen bonds. This results in a metastable state, where the ionization level would be higher if all of the PAA units were free rather than some of them being locked in hydrogen bonds. This keeps the PAA in a more collapsed conformation, resulting in larger pores with less ionization of the PAA units. Because the difference between hydrogen-bonded and free PAA in FTIR spectroscopy is not easily measured, experiments were performed that introduced urea, which can be used as a hydrogen bond disruptor in solution, to the nanopores. That is, two membrane pieces were placed in DI water following exposure to an acidic (red) or basic (blue) solution, and they were then evaluated using FTIR spectroscopy (Figure 16a). Similarly, two more pieces were placed in the same conditions followed by soaking in 300 mM urea for 2 h, and then they were evaluated using FTIR spectroscopy. The spectra for the urea-soaked membranes after initially soaking in an acidic solution are displayed in Figure 16a as the magenta curve, with membranes initially soaked in a basic solution shown by the green curve. For membranes initially soaked in a basic solution, the change of the spectra before and after the addition of urea is minimal. However, the change in spectrum for the membrane that was initially soaked in an acidic solution is significant, with a large increase in the degree of ionization. This was further supported by copper uptake experiments shown in Figure 16b, where the amount of copper uptake is plotted against the concentration of urea in the soaking solution before being added to the copper solution. The membranes that had been exposed to urea after exposure to acid showed an increase in copper uptake above 100 mM of urea. This demonstrates that the presence of urea disrupts hydrogen bonds between PAA repeat units, and results in an increase in the degree of ionization of the PAA repeat units.

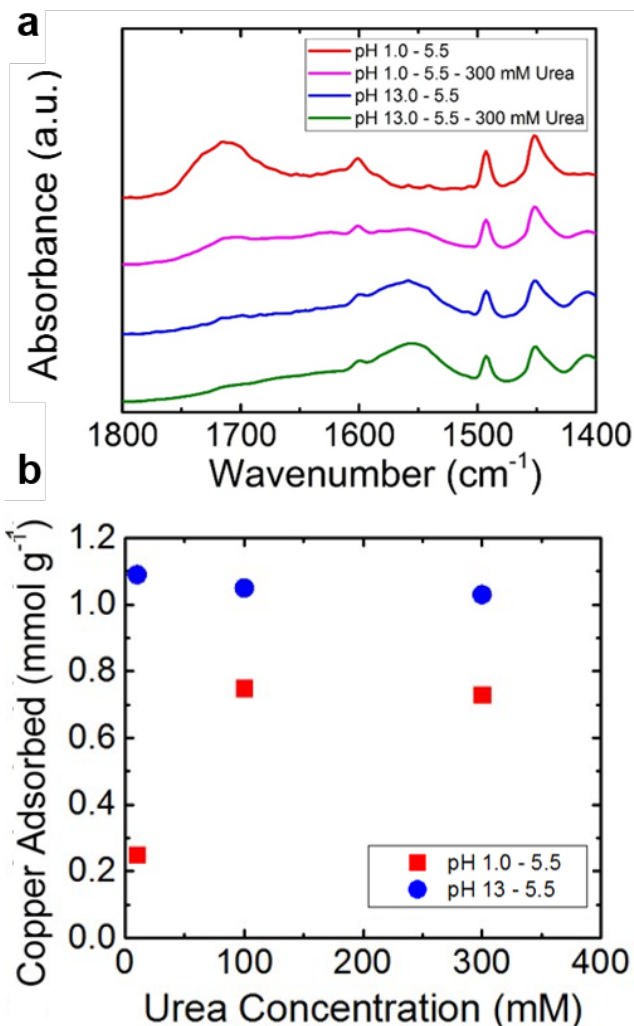


Figure 16. Urea Disrupts Hydrogen-Bonded PAA Network. (a) FTIR spectra of membranes exposed to a solution containing urea. After exposure to either an acidic (pH 1.0) or a basic (pH 13.0) solution and subsequent soaking in DI water or DI water then a 300 mM aqueous solution of urea, the membranes were dried under vacuum and analyzed. (b) Copper uptake of membranes after soaking the membranes in solutions of varying urea concentrations (10 mM, 100 mM, 300 mM) after an initial exposure to pH 1.0 (red squares) or pH 13.0 (blue circles). The membranes were removed from the urea solutions and placed in copper solutions at pH 5.5 and left to adsorb copper overnight. A subsequent soak in pH 1 acid released the copper ions, and the copper concentrations of both the retentate and acid solutions were used to determine the amount of copper adsorbed in the membrane.

Urea disrupts the hydrogen bonds between PAA repeat units, which allows more acrylic acid groups to equilibrate with the surrounding solution, resulting in an increase in the ionized form of PAA. This, in turn, increases the magnitude of the repulsive electrostatic interactions between PAA chains, which is expected to cause chain extension, further decreasing pore size, and therefore, the permeability of the membrane. This was established in permeability experiments, immediately following the DI water permeability tests in Figure 13. After the

membrane was exposed to acid, followed by DI water, the permeability leveled to a value near $9.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, as shown by the red squares. After the addition of a 1 M urea solution to the cell, the permeability decreased and achieved a steady-state value $6.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ after 2-3 mL had permeated, as shown by the magenta triangles in Figure 13, which held steady through 8 mL of permeate. To test if the urea solution had only temporarily disrupted the state of the pores, the cell was washed and an additional 10 mL of DI water was added to the cell. The addition of urea after the membrane was exposed to DI water after basic solution resulted in no noticeable change in permeability, as shown by the green triangles. This suggests that the pore size decreases after addition of urea, due to both the breaking of hydrogen bonds that limit the extension of the PAA and the increase in ionization. Breaking hydrogen bonds perturbs the membrane to a state with smaller pores, suggesting that the presence of hydrogen bonds drives the observed hysteretic behavior in the PI-PS-PAA membranes.

The chemistry and confined geometry of the weak electrolyte polymer evaluated in this study demonstrates that control over these crucial nanoscale properties leads to tunable behavior of a nanoscale material that has a memory of the previous environment. This hysteretic behavior, which is rarely reported in membrane systems, is possible due to the uniquely high density of PAA chains that line the pore walls of membranes fabricated using the SNIPS method. The effect of polymer-polymer hydrogen bonds within the confined nanopores is the most likely source of the hysteresis, with the bonds forming under acidic conditions that held the pores in a stable open state. This is because experiments with urea, which disrupts hydrogen bonds, showed a shift toward the equilibrium, highly ionized form of the confined PAA chains, supporting the mechanism of hydrogen bonding as the cause of the hysteresis. This new understanding regarding the underlying phenomena that control hysteretic behavior in these types of materials provides a unique outlook and a novel approach to macromolecular design of potential materials for sensors and gating processes.

Nanomanufacturing High Performance Nanofiltration Membranes Functionalized with Polyelectrolyte Brushes to Achieve Sub-Nanometer Selectivity

The key findings related to the generation of highly-selective nanofiltration membranes in the hollow fiber geometry from functionalized block polymer precursors are presented in greater detail in the published articles:

“Nanomanufacturing of High-Performance Hollow Fiber Nanofiltration Membranes by Coating Uniform Block Polymer Films from Solution”, Zhang, Y.; Mulvenna, R. A.; Boudouris, B. W.; and Phillip, W.A., 2017, *Journal of Materials Chemistry A*, 5, 3358-3370.

“Block Polymer Membranes Functionalized with Nanoconfined Polyelectrolyte Brushes Achieve Sub-Nanometer Selectivity,” Zhang, Y.; Mulvenna, R. A.; Qu, S.; Boudouris, B. W.; and Phillip, W.A., 2017, *ACS Macro Lett.*, 6 (7), pp 726–732, DOI: 10.1021/acsmacrolett.7b00278.

Nanomanufacturing High Performance Hollow Fiber Membranes by Dip-Coating.

To date, blade casting has been the primary method implemented for the fabrication of self-assembled block polymer membranes. The development of block polymer membranes in the hollow fiber geometry is crucial to expanding their utility to a broader range of applications (e.g., as high capacity membrane adsorber or an artificial kidney). When applied in full-scale modules, hollow fiber membranes are able to provide higher packing densities (i.e., active surface area per

module volume) and, in turn, a higher throughput of processed solution. However, to date, the production and performance of hollow fiber block polymer membranes have been hindered by excessive usage of costly block polymer materials and low throughputs. By introducing the facile dip-coating archetype to the self-assembly and non-solvent induced phase separation (SNIPS) technique, ultra-thin (thicknesses down to 200 nm) polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) (PI-PS-PDMA) membranes with highly-ordered, self-assembled nanostructures were coated onto the shell side of a hollow fiber support. With critical information generated by comparing the nanostructures and transport performance of a hollow fiber membrane and its flat-sheet analog fabricated using identical SNIPS conditions, a hollow fiber nanofiltration membrane with a 40-nm-thick active layer thickness and pores with a well-defined diameter of 5.1 nm was fabricated. For membranes with this small pore size, a relatively high hydraulic permeability = 27 m² h⁻¹ bar⁻¹ was measured. This high-performance hollow fiber nanofiltration membrane was generated by systematically controlling the nanoscale architecture of the block polymer membrane cross-section.

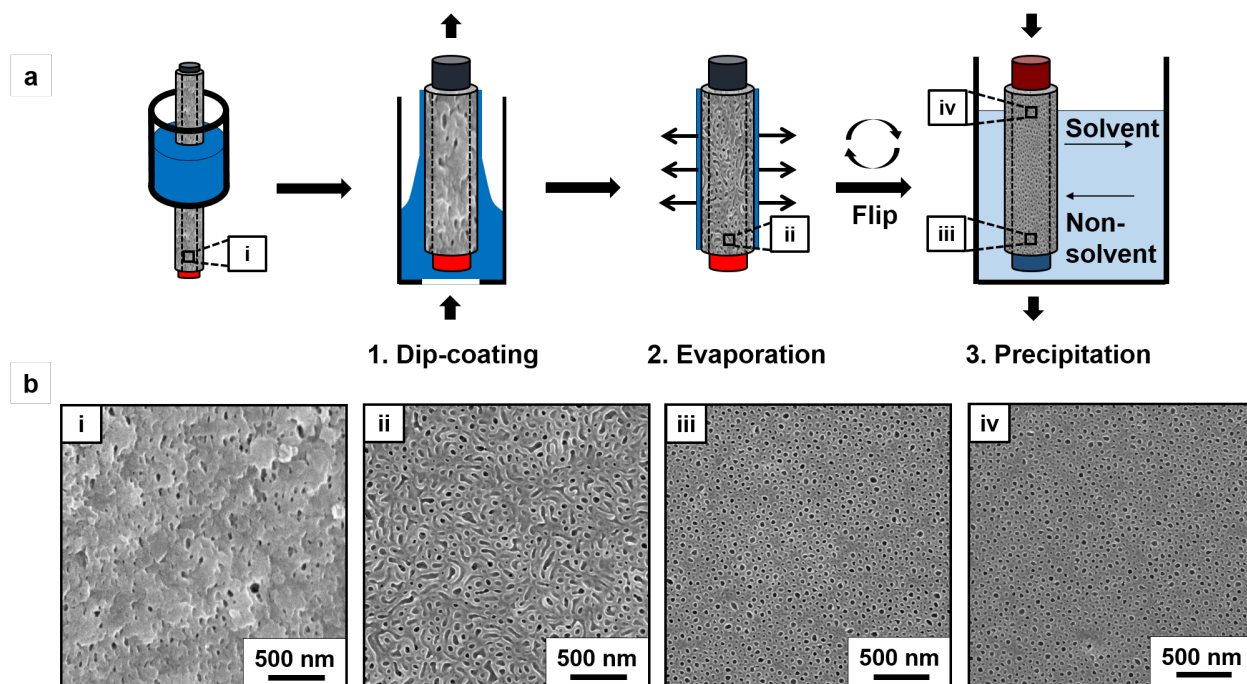


Figure 17. The PI-PS-PDMA block polymer was coated onto a PVDF hollow fiber using a customized coating reservoir with a small opening at the bottom. (a) A thin film of the polymer solution was coated onto the hollow fiber support by pulling the fiber continuously upward through the reservoir. Then, the solvent was allowed to evaporate (in part) from the thin film for a predetermined amount of time before the coated fiber was plunged into the non-solvent bath. (b) The nanostructure of the PVDF support is shown in the SEM micrograph (i) of panel (b). The nanostructure of the block polymer thin film formed using the SNIPS process is time dependent. Because the dip coating process requires ~25 s to complete, a gradient in evaporation time along the length of the fiber is created. Thus, solvent at the leading edge of the fiber, which passes through the reservoir first, has a longer solvent evaporation time than the trailing end of the fiber. As a result of this shorter evaporation time, incomplete assembly of the block polymer may result at the trailing end of the fiber. The nanostructure shown in the SEM micrograph (ii) in panel (b) is an example of this incomplete assembly. This issue was resolved by passing the

coated fiber into the non-solvent bath in the same path as it was pulled through the coating reservoir. In this way, the evaporation time along the length of the fiber was held constant such that the surface nanostructure at the trailing edge can evolve in a manner that is consistent with the leading edge. The SEM micrographs (iii) and (iv) in panel (b) demonstrate that a consistent nanostructure along the length of the fiber is generated. The blue and red poles on the hollow fiber are drawn for illustrative purposes only in order to indicate the orientation of the hollow fiber.

In our efforts, we reported the preparation of high performance self-assembled polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) (PI-PS-PDMA) hollow fiber membranes by combining dip-coating and the SNIPS methodology (Figure 17). By controlling the fabrication process to tailor the nanostructures of both the self-assembled active layer and cross-sectional substructure, hollow fiber membranes with coating thickness ranging from 200 nm to 2,000 nm were identified. Using electron microscopy analysis and transport experiments, critical information that guided the selection of optimized membrane fabrication conditions were identified by elucidating the impact of different nanoscale features of the membrane morphology on the membrane performance. Importantly, we identified that in order to produce a self-assembled block polymer membrane with both a high permeability and a high selectivity, it is not sufficient to just produce an active layer with a high density of well-defined nanoscale pores. Instead, the morphology of the cross-sectional substructure is also important (i.e., in order to realize a higher membrane permeability the substructure cannot contribute a significant resistance to flow).

The composite hollow fiber membranes were fabricated by pulling a PVDF hollow fiber support through the casting solution at a constant speed of 2.5 mm s^{-1} (Figure 17). Solvent was allowed to evaporate from this thin film for a period of 45 s prior to plunging the membranes into the non-solvent bath. SEM micrographs of the composite hollow fiber membrane cross-section and top surface are displayed in Figure 18. As demonstrated by Figure 18, the top active layer contains self-assembled nanoscale pores with an average dry-state pore diameter of $61 \pm 19 \text{ nm}$ and a porosity of $9.2 \times 10^{13} \text{ pores m}^{-2}$.

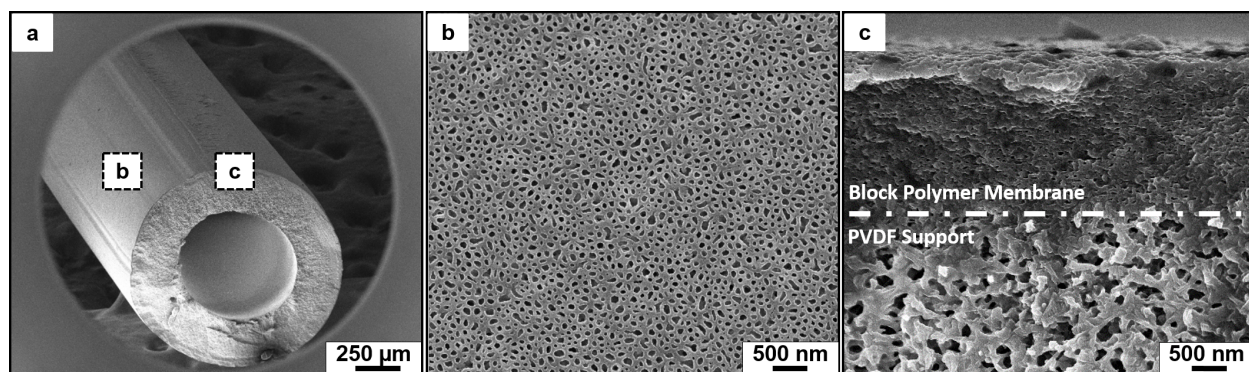


Figure 18. SEM micrographs of a composite hollow fiber block polymer membrane that was generated by coating a PVDF hollow fiber support with a 9% (by weight) PI-PS-PDMA-107 polymer solution. The PI-PS-PDMA block polymer was dissolved in 70/30 (w/w) mixture of 1,4-dioxane and tetrahydrofuran. (a) A lower magnification micrograph of the membrane cross-section with the regions marked that were used for the micrographs of panes (b)

and (c), respectively. (b) The self-assembled nanostructure observed on the active layer surface of the composite hollow fiber membrane. (c) A higher magnification micrograph of the membrane cross-section, which demonstrates that the composite membrane consists of a $\sim 2\ \mu\text{m}$ block polymer active layer on top of PVDF hollow fiber support.

Cross-sectional micrographs of the hollow fiber composite show a thin, spongy PI-PS-PDMA layer with a thickness of $\sim 2\ \mu\text{m}$. The homogenous, sponge-like structure of the hollow fiber could be a result of the smaller initial film thickness produced by dip-coating. The initial thickness would have affected the solvent concentration profile within the film prior to precipitation and vitrification of the block polymer in the non-solvent bath. In addition, the non-solvent exchange occurred only through one side of the PI-PS-PDMA membrane, because water was not able to penetrate through the lumen side of hollow fiber during the precipitation. It is likely that both of these factors contributed to the formation of a sponge-like cross-sectional morphology for the hollow fiber composite membrane. This dense cross-sectional morphology directly impacted the performance of the membrane as noted below.

Transport Properties of Hollow Fiber Block Polymer Membranes.

The hydraulic permeability of a membrane is a key factor in determining the utility of the membrane in various nanofiltration applications. The values of the permeability can also lend useful insights into the connection between the membrane nanostructure, functionality, and performance. The hydraulic permeability of the hollow fiber PI-PS-PDMA membrane was determined using applied pressures ranging from 5 to 30 psi. DI water at a pH of 5.5 was used in these experiments. The composite PI-PS-PDMA-107 hollow fiber membrane had a permeability of $1.4\ \text{L m}^{-2}\ \text{h}^{-1}\ \text{bar}^{-1}$.

It is important to discuss the intrinsic separation efficacy of the nanoporous PI-PS-PDMA hollow fiber membrane prior to evaluating its overall performance. By correlating the effective pore size with the measured hydraulic permeability through the Hagen-Poiseuille equation, the performance of the membranes was evaluated, and the resistance to flow that impedes the performance of the hollow fiber membrane was identified. Through this systematic design archetype, a better block polymer-coated hollow fiber nanofiltration membrane was then nanomanufactured. The selectivity of the composite membranes was examined by executing molecular weight cut-off experiments. The PI-PS-PDMA membrane was challenged with solutions containing a single solute of a known size in order to characterize their separation selectivity and confirm the absence of defects. The results of the rejection measurements are displayed in Figure 19, where the solute percentage rejection was plotted as a function of hydrodynamic diameter of the solute. These curves confirmed the success of fabricating an intact block polymer layer on the hollow fiber support without pinhole defects and suggested the presence of a uniform nanoscale pore size.

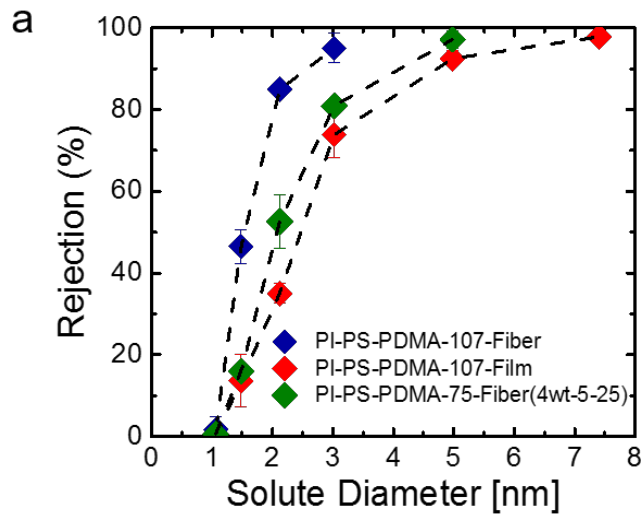


Figure 19. Solute rejection curves for the PI-PS-PDMA hollow fiber membranes. The membranes were challenged by feed solutions containing a single solute, with a known size, dissolved in water at a concentration of 1 g L⁻¹ and 0.5 g L⁻¹ for thin-film and hollow fiber rejection experiment respectively. All rejection experiments were conducted using solutions at pH 5.5. Sucrose and polyethylene oxide (PEO) with molecular weight of 1.1, 2.1, 4.0, 10 and 20 kg mol⁻¹ were used. The percentage rejection of solutes was plotted against their hydrodynamic diameter. (a) Percent rejection vs. solute size for three PI-PS-PDMA membranes in hollow fiber and flat sheet geometries.

Identifying the Dominant Hydraulic Resistances of the Hollow Fiber Membrane.

The effective pore sizes of the hollow fiber membrane was estimated by correlating the solute rejection data from Figure 19 with established theories for hindered transport. From this calculation, the effective pore diameter of PI-PS-PDMA membranes was estimated to be 3.5 nm for the hollow fiber. These nanometer scale pore sizes demonstrated the ability to fabricate nanofiltration devices with high permeability and selectivity without post membrane fabrication modifications. With experimentally determined pore diameters, the theoretical throughput of a membrane was evaluated. If the flow through the self-assembled active layer dominates transport, the Hagen-Poiseuille equation can be used to predict the hydraulic permeability (L_P) of the membrane using the structural features of the active layer, namely, the thickness (l), the number of surface pores per unit area (N), and the effective pore diameter (d_p).

$$L_P = N \frac{\pi d_p^4}{128 \mu l} \quad (3)$$

Here, μ is the solution viscosity. Ideally, flow through the self-assembled block polymer membranes will be challenged primarily by the resistance from the top active layer. For the PI-PS-PDMA-107 hollow fiber membrane using a pore density of 9.2×10^{13} pores m⁻², an effective pore diameter of 3.5 nm, and an active layer thickness 40 nm predicts a hydraulic permeability of 3.4 L m⁻² h⁻¹ bar⁻¹ should result. However, the experimental permeability 1.4 L m⁻² h⁻¹ bar⁻¹ was more than 50% lower than this calculated value, which suggests that the membrane supporting substructure contributes a significant resistance to transport and was responsible for lowered

permeability of the hollow fiber nanofiltration membrane. A detailed study of how to adjust the fabrication condition of the PI-PS-PDMA hollow fiber membranes in order to reduce the hydraulic resistance of the underlying gutter layer, by controlling its nanostructure, was executed and is summarized by the results presented in Figure 20.

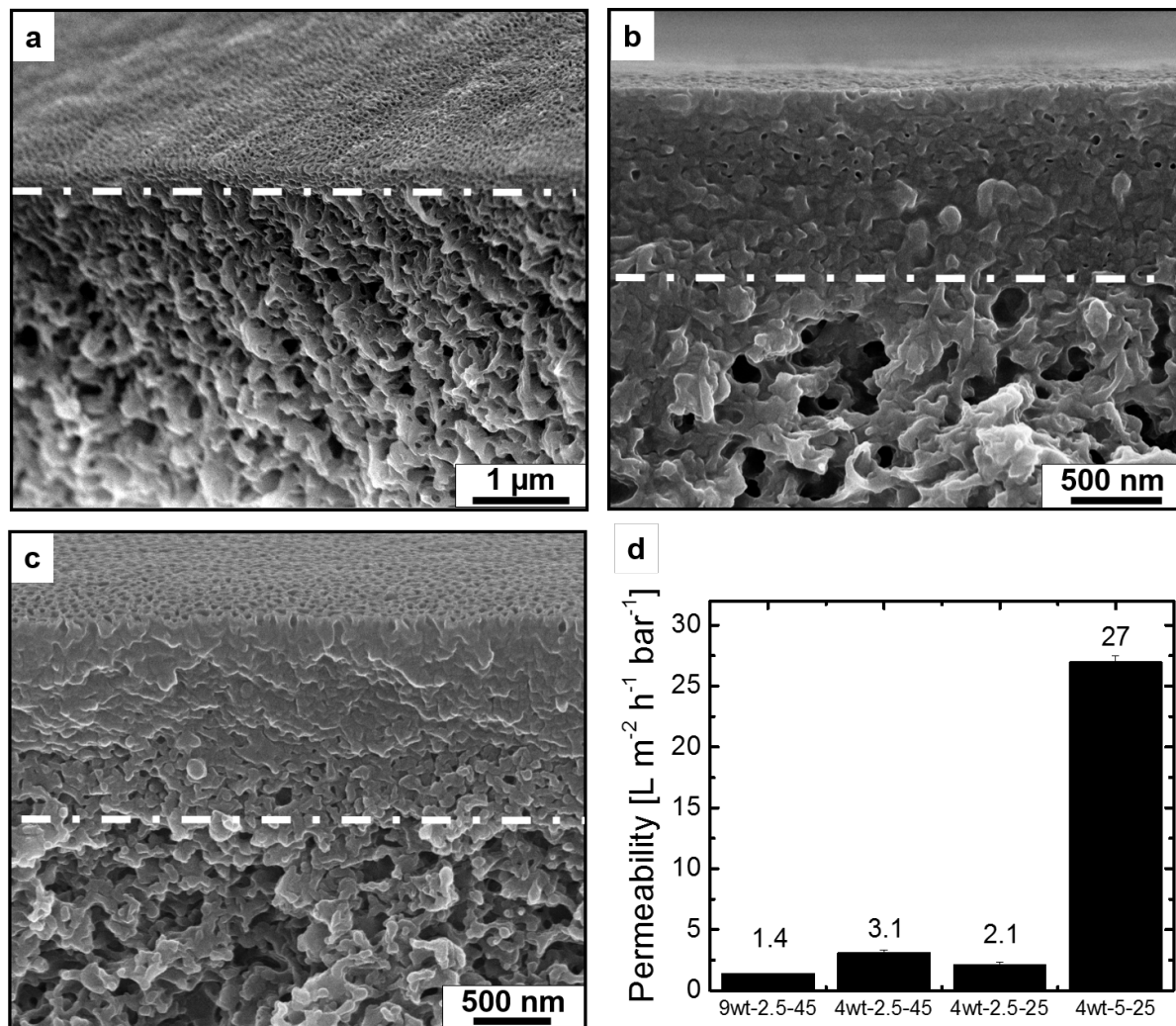


Figure 20. SEM micrographs of the membrane cross-section for hollow fiber membranes prepared from the same PI-PS-PDMA-75 block polymer precursor, but using different dip-coating and SNIPS conditions. All of the casting solutions were prepared by dissolving the PI-PS-PDMA polymer at 4% (by weight) in a solvent mixture of 7/3 (by weight) 1,4-dioxane to tetrahydrofuran. (a) The membrane was prepared with a dip-coating speed of 2.5 mm s^{-1} and a solvent evaporation time of 45 s. A uniform 200-nm-thick self-assembled active layer results. (b) The membrane was prepared using a dip-coating speed of 2.5 mm s^{-1} and an evaporation time of 25 s. A $\sim 1\text{-}\mu\text{m}$ -thick block polymer layer with a dense bottom results. (c) The membrane was prepared from a dip-coating speed of 5 mm s^{-1} and an evaporation time of 25 s. An asymmetric block polymer layer with a total thickness of $\sim 1.5 \text{ }\mu\text{m}$ with a porous bottom is produced. (d) A comparison of hydraulic permeability between different PI-PS-PDMA hollow fiber membranes.

A strategy, which combines dip-coating and the novel SNIPS techniques, has been demonstrated for tuning the nanoscale architecture of self-assembled PI-PS-PDMA hollow fiber nanofiltration membranes for optimal membrane performance. With critical information provided from elucidating the structure-property-performance relationship of PI-PS-PDMA flat-sheet and hollow fiber membranes fabricated from the same SNIPS conditions, higher performance hollow fiber membranes were generated by controlling easily-adjusted membrane casting parameters. In this way, a 1.5 μm thick PI-PS-PDMA composite on hollow fiber membrane was made with a pore diameter of 5.1 nm accompanied with a 40-nm-thick self-assembled layer without post-fabrication modification. This result suggests the self-assembled block polymer hollow fiber membrane can be prepared with high membrane throughput with minimum cost of block polymer material. Together with high porosity, well-defined pore sizes, tunable membrane nanostructure and tailored pore functionalities, self-assembled block polymer hollow fiber nanofiltration membrane is demonstrating its utility for versatile membrane applications that require a systematic control of solvent permeating through the nanoscale pores.

Extremely Selective Block Polymer Nanofiltration Membranes

The well-defined nanostructure of membranes manufactured from self-assembled block polymers enables highly selective separations; however, recent efforts to push the pore size of block polymer-based membranes to the lower end of the size spectrum have only been moderately successful for a variety of reasons. For instance, the conformational changes of the stimuli-responsive functional groups lining the pore walls of some block polymer membranes result in varied pore sizes that limit their applicable operational range. Here, we overcome this challenge through the directed design of the third moiety of an A-B-C triblock polymer. The use of this design paradigm allows for the preparation of a 500 nm-thick polyisoprene-*b*-polystyrene-*b*-poly(2-acrylamido-ethane-1-1-disulfonic acid) (PI-PS-PADSA) coating atop a hollow fiber membrane support. This nanoporous test bed, which exhibits an average pore radius of 1 nm, demonstrates an extremely high solute selectivity by fully gating solutes that have only an 8 Å size difference - a separation that is based solely on a sieving mechanism. Moreover, the successful demonstration of the test bed separation device offers a tangible means by which to manufacture next-generation nanofiltration membranes that require a robust performance profile over a dynamic range of conditions.

The development of robust block polymer membranes in the nanofiltration regime remains a challenge because phase separated domains with feature sizes below 5 nm are extremely difficult to access. This has led prior efforts to focus on realizing smaller pore sizes through the use of weak polyelectrolyte brushes that are confined within the nanopores of the block polymer materials, and that swell upon charging to constrict the pore diameter into the nanofiltration regime. For instance, block polymer membranes lined with poly(4-vinylpyridine) (P4VP) brushes exhibited pore diameters of 5 nm under well-controlled acidic conditions. This study demonstrated that the nanofiltration regime can be accessed by block polymer materials. However, due to the use of weak polyelectrolytes, the performance of these membranes as nanofiltration systems was restricted to a narrow window of operating conditions. In particular, conformational changes of the pore wall-lining polymer brushes in response to external stimuli (e.g., ionic strength, pH, and specific solutes) are directly correlated to reductions in the separation quality and consistency, which makes block polymer-based nanofiltration a less competitive candidate among other membrane technologies.

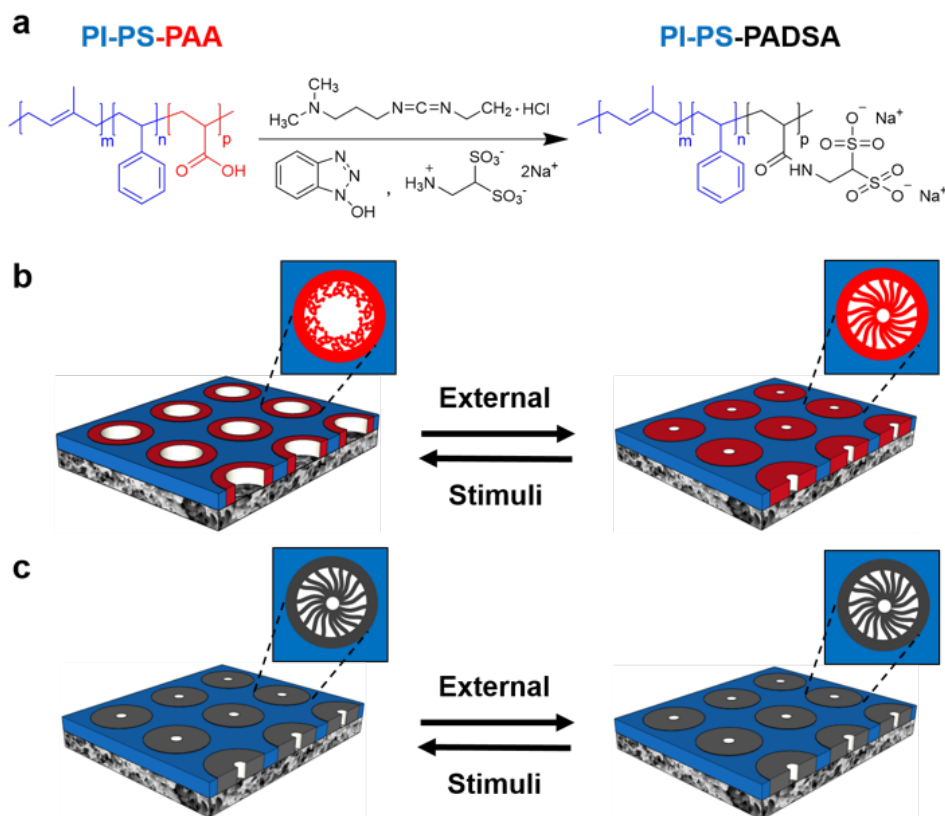


Figure 21. Schematic of PI-PS-PAA and PI-PS-PADSA Nanofiltration Membranes. (a) Macromolecular architectures of the polyisoprene-*b*-polystyrene-*b*-poly(acrylic acid) (PI-PS-PAA) and polyisoprene-*b*-polystyrene-*b*-poly(2-acrylamido-ethane-1-1-disulfonic acid) (PI-PS-PADSA) block polymer materials. Schematic diagrams demonstrating the pore size changes of (b) the PI-PS-PAA membrane and (c) the PI-PS-PADSA membrane in response to external stimuli.

In order to push self-assembled block polymer membranes firmly into the nanofiltration regime, we introduce a block polymer membrane that uses intrinsically-attached strong polyelectrolytes to produce a highly selective nanofiltration membrane that retains its performance over a dynamic range of solution conditions. Specifically, a polyisoprene-*b*-polystyrene-*b*-poly(*N,N*-dimethylacrylamide) (PI-PS-PDMA) precursor was the basis for this membrane design. The SNIPS methodology is used to fabricate composite hollow fiber membranes with a well-defined nanostructure. Subsequently, in order to access nanofiltration membranes with a robust performance profile, sulfonic acid moieties are introduced along the pore wall through simple chemical reactions associated with the uniquely high density of PDMA moieties that line the pore walls. The scheme shown in Figure 21a demonstrates the solid-state coupling reaction that enables the development of robust block polymer nanofiltration membranes. By using a combination of dip-coating and the SNIPS methodology above, composite hollow fiber membranes were generated from the PI-PS-PDMA material. Subsequently, selective hydrolysis of the pore-lining PDMA moieties, resulted in the production of a PI-PS-PAA membrane that was stimuli-responsive (Figure 21b). In order to develop a nanofiltration membrane that exhibited a constant separation quality over a broad range of

solution conditions, a carbodiimide coupling reaction was designed to covalently-attach sulfonic acid moieties onto the pore wall of the PI-PS-PAA membrane. The reaction occurred by placing the PI-PS-PAA membrane in an aqueous solution containing ammonium 2-aminoethane-1,1-disulfonic acid, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), and hydroxybenzotriazole (HOBt) at room temperature for 48 h. The introduction of a high density of poly(2-acrylamido-ethane-1,1-disulfonic acid) (PADSA) polymer brushes achieved the targeted goal of a robust (i.e., with respect to the stability window for practical operation) nanoporous thin film that allowed for the creation of a test bed device with high separation selectivity (Figure 21c)

The signatures of the chemical conversions that transformed the membrane from the PDMA-functionalized parent material to the PADSA-functionalized nanofiltration membrane are illustrated by the Fourier transform infrared (FTIR) spectra shown in Figure 22. Most significantly, the appearance of the peaks at $\sim 1030\text{ cm}^{-1}$ in the PI-PS-PADSA spectrum, which are characteristic of the sulfonate group, confirmed the successful covalent attachment of sulfonic acid moieties.

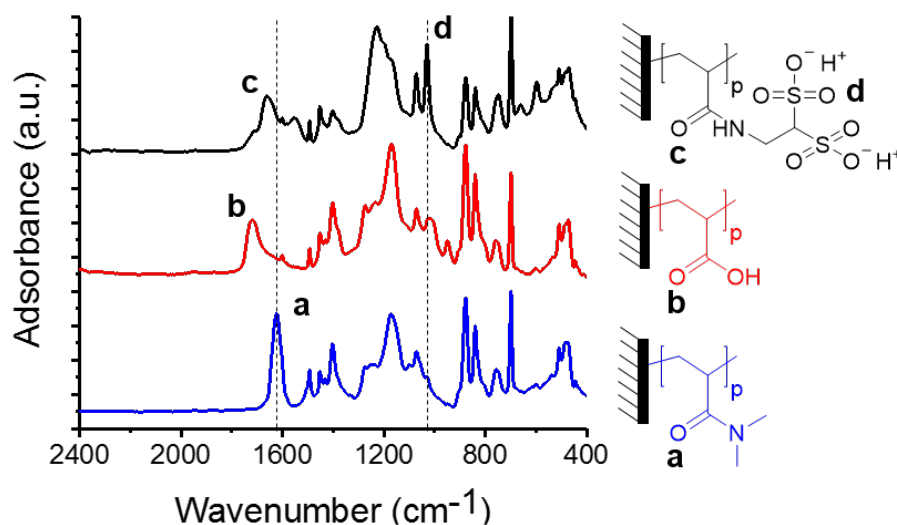


Figure 22. ATR-FTIR spectra confirmed the solid-state conversion of the pore wall lining functional groups from PDMA to PADSA. First, the parent PI-PS-PDMA membrane was immersed in an aqueous 6 M HCl solution at 80 °C for 28 h to convert PDMA to PAA. The disappearance of the amide carbonyl group at $\sim 1630\text{ cm}^{-1}$ (labeled as **a**) and the appearance of the carbonyl peak at $\sim 1720\text{ cm}^{-1}$ (labeled as **b**), which is associated with carboxylic acids, from the bottom to middle spectra are indicative of the successful conversion. The PI-PS-PAA membrane was then functionalized with 2-aminoethane-1,1-disulfonic acid at room temperature using a carbodiimide coupling reaction to produce the PI-PS-PADSA membrane in 48 h. The success of this coupling reaction was demonstrated by the shift of the carbonyl peak to $\sim 1660\text{ cm}^{-1}$ (labeled as **c**) and the appearance of two characteristic peaks associated with sulfonate at $\sim 1030\text{ cm}^{-1}$ (labeled as **d**) in the top spectrum. An estimation of percent conversion from PAA to PADSA is calculated from the relative characteristic peak areas collected prior and after the coupling reaction, which suggests the reaction achieves $\sim 90\%$ conversion within 48 h.

Because the self-assembled nanostructure of the block polymer membrane is critical to its performance, scanning electron microscopy (SEM) was used to ensure that the functionalization process did not distort the nanostructure produced by the SNIPS methodology. The micrograph in Figure 23a shows a cross-sectional view of the 500 nm-thick membrane that tapers from self-assembled nanopores at the top surface to macroporous material at bottom. This micrograph was obtained after the complete functionalization protocol to the PI-PS-PADSA membrane. Notably, only ~0.2 g of the PI-PS-PDMA was needed to produce a square meter of active surface area coated with the 500-nm-thick block polymer layer. The top surface of a membrane, which possessed a highly-ordered nanostructure, is displayed in Figure 23b. It is stressed that this highly-ordered structure was formed during the SNIPS casting procedure and persisted through the pore wall chemical conversion processes. Image analysis (using ImageJ software) of this micrograph indicated an average dry-state pore size of 34 ± 10 nm and a porosity of 1.6×10^{14} pores m^{-2} . It is important to note that, in the hydrated state, swelling of the polymer brushes (at extremely high grafting densities) that line the nanopores cause the operating pore sizes to be much smaller than the dry-state pore sizes that are imaged in SEM analysis. The energy-dispersive X-ray spectroscopy (EDS) elemental map presented in Figure 23c confirmed that the chemical modification is selective to the block polymer layer of the composite membrane. The green shading, which is indicative of oxygen, is confined within the 500 nm-thick PI-PS-PADSA layer while the red shading, which represents fluorine, is present in the underlying support.

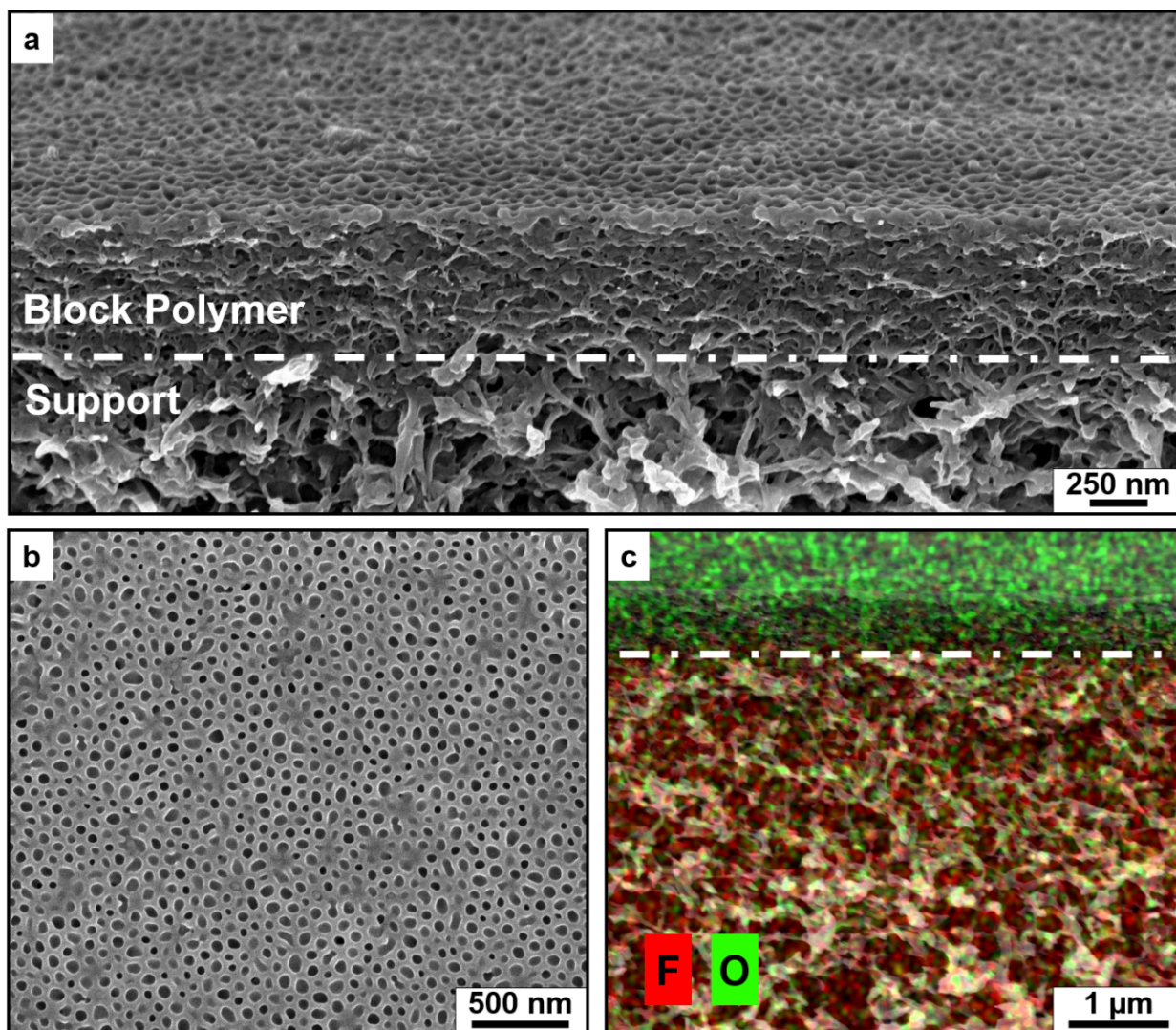


Figure 23. Micrographs of PI-PS-PADSA Nanofiltration Membranes. (a) A cross-sectional SEM micrograph demonstrates the 500 nm-thick block polymer layer of the membrane that tapers into a PVDF hollow fiber support. (b) An SEM micrograph of the self-assembled nanostructure on the top surface of the block polymer membrane after functionalization. Despite the changes in the chemistry of the pore-lining polymer brushes, the well-defined nanostructure is retained. (c) An energy-dispersive X-ray spectroscopy (EDS) elemental map of the PI-PS-PADSA membrane shows the oxygen-rich regions in green and the fluorine-rich regions in red.

The combination of the well-defined nanostructure and tailored chemical features of the PI-PS-PADSA nanoporous thin film resulted in a highly-selective nanofiltration device capable of performing over a broad range of operating conditions. Specifically, the stability of the PADSA brush conformation in response to external stimuli allowed for a nanoporous thin film that exhibited a well-defined diameter in solutions of varying pH and ionic strength. Moreover, the pore diameter and separation quality of the membrane were directly correlated with solute rejection experiments.

In these studies, the effects of increasing ionic strength on the rejection of neutral solutes by the PI-PS-PADSA membrane were examined through the development of the molecular weight cut-off (MWCO) curves shown in Figure 24. The performance of PI-PS-PAA membrane is displayed as a control. Because the separation efficacy of charged molecules (e.g., dyes) can be strongly affected by van der Waals and electrostatic interactions, neutral solutes were selected to evaluate the intrinsic size-selective separation capabilities of the PI-PS-PAA and PI-PS-PADSA membranes. The two samples were each challenged with single solute solutions that were prepared by dissolving sucrose or a polyethylene oxide (PEO) molecule of known molecular weight in: (1) DI water, (2) 10 mM NaCl, and (3) 10 mM MgCl₂ solutions. The solute rejection then was calculated by comparing the concentration of solute in the feed solution to that measured in the permeate solution. The hydrodynamic diameter of the solutes was retrieved from literature, which suggested that solute size was not affected strongly by the different background electrolyte conditions. The MWCO curves shown in Figure 24 highlight the robust nature and high selectivity of the PI-PS-PADSA nanoporous thin film in comparison to its PI-PS-PAA counterpart, and this highlights the critical nature of appropriate polymer chemical functionalization.

The PI-PS-PADSA membrane had an exceptionally high selectivity that was capable of fully gating solutes that are 8 Å different in terms of their hydrated size. This is characterized by the step function-like MWCO curve shown in Figure 24a. While the membrane almost completely rejected the 1.1 kg mol⁻¹ PEO (R = 94%), which is 1.8 nm in diameter, it allowed the free passage of sucrose (R = 6.5%), which has a diameter of 1.0 nm. As shown in Figure 24b, the PI-PS-PAA exhibited a relatively sharp MWCO at 2.1 kg mol⁻¹ PEO when the membrane was challenged in DI water or a 10 mM NaCl solution. The separation ability of the PI-PS-PAA membrane, however, was greatly compromised in the presence of 10 mM MgCl₂. It is likely that the association of magnesium cations with PAA repeat units lead to significant chain rearrangements in the nanoporous structure. This structural rearrangement of the polymer brushes resulted in a horizontal stretching of the MWCO curve, which was indicative of a reduced separation quality, and shifted the cut-off to larger PEO molecules with a molecular weight of 6.0 kg mol⁻¹.

The repulsive electrostatic interactions between the extremely high density of PAA and PADSA repeat units confined within the nanopores of the PI-PS-PAA and PI-PS-PADSA membranes resulted in highly-selective performance profiles. The strong repulsive forces induced chain swelling toward the center of the pore constricting the pore size to a diameter of ~2 nm and ~3 nm for the PI-PS-PADSA and PI-PS-PAA membranes, respectively. For both membranes in the solution containing NaCl and for the PADSA-functionalized membrane in the MgCl₂ solution, the pore diameters remained constant despite working in solutions of ionic strengths up to 3 M. This robust performance profile can be attributed to the uniquely high density of brushes grafted to the pore wall of the block polymer membranes, which causes the transition from the osmotic brush to salted brush regime to occur at high ionic strengths.

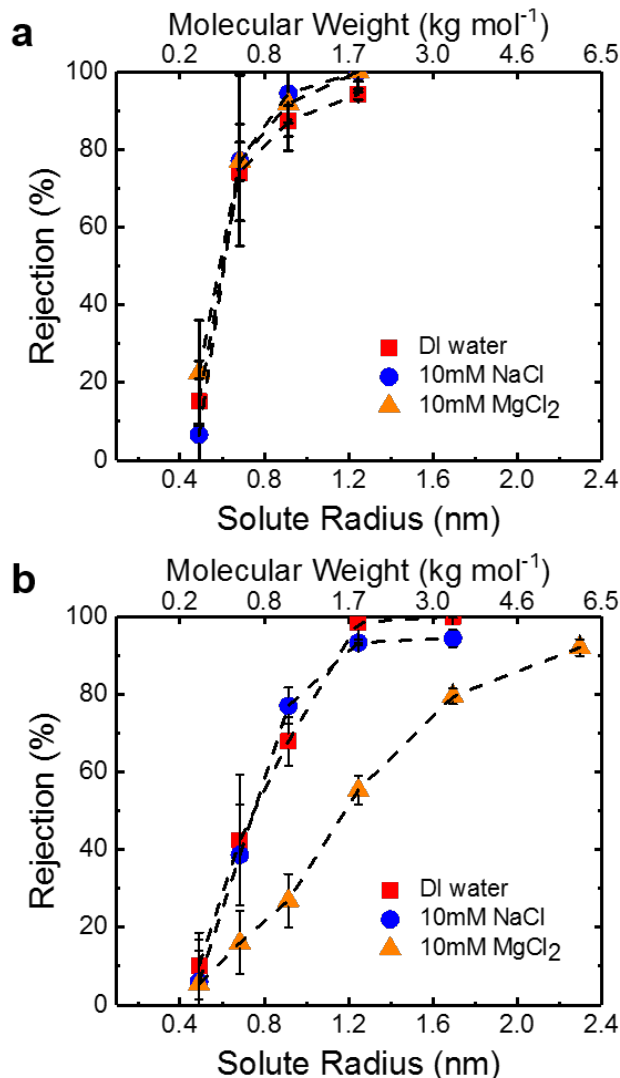


Figure 24. Size-selective solute rejection performance of (a) PI-PS-PADSA and (b) PI-PS-PAA hollow fiber membranes. The rejection of neutral PEO molecules was measured for DI water and feed solutions containing 10 mM NaCl or 10 mM MgCl₂ as a background electrolyte. The solute size and equivalent molecular weight of the PEO molecules are plotted on the bottom and top horizontal axes, respectively.

The response of polyelectrolyte brushes in solutions containing monovalent or multivalent cations is well-studied, and the transition of polymer brushes from the osmotic brush regime to salted brush regime has been probed experimentally in prior work. In the osmotic brush regime, the thickness of the extended brush does not depend on the concentration of ions in solution. In the salted brush regime, the brush thickness has a power law dependence on the concentration of ions in solution. It is likely that the high grafting density and high surface charge density of the materials demonstrated in this study shifts the transition between these two regimes towards higher ionic strengths. The response of the PAA chains in the presence of a salt containing a divalent cation, such as MgCl₂, is complicated by the ability of the PAA repeat units to complex with Mg²⁺, which can induce persistent screening of PAA and yield a relaxed

polymer chain packing at low ionic strength through a similar mechanism as the one described previously.

Finally, experiments have demonstrated that the PI-PS-PAA and PI-PS-PADSA membranes are capable of rejecting ionic solutes (NaCl, KCl, Na₂SO₄, and MgCl₂) at rates comparable with commercial membranes (Figure 25).

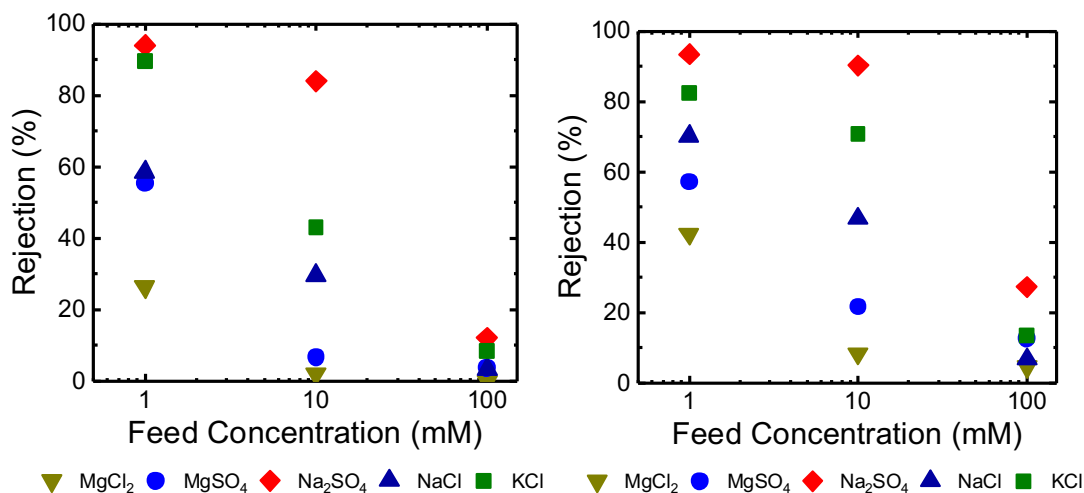


Figure 25. Salt Rejection by PI-PS-PAA and PI-PS-PADSA Block Polymer Nanofiltration Membranes.

In addition to the significant findings reported above, progress was made in other important areas related to the fundamental understanding and further development of self-assembled block polymer membranes.

Solution Self-Assembly Behavior of A-B-C Triblock Polymers and the Implications for Nanoporous Membrane Fabrication

The key findings related to the early-stage solution and assembly behavior of block polymer–solvent systems and their impact on membrane fabrication through SNIPS processing method are presented in greater detail in the published article: “Solution Self-Assembly Behavior of A-B-C Triblock Polymers and the Implications for Nanoporous Membrane Fabrication,” Sargent, J. L.; Hoss, D. J.; Phillip, W.A.; and Boudouris, B. W., 2017, J. Appl. Polym. Sci., 45531, DOI: 10.1002/app.45531.

Fit-for-Purpose Block Polymer Membranes Molecularly-Engineered for Water Treatment

The research team was asked to contribute two critical reviews on the possible application of block polymer membranes. One review focused on promising features, potential applications, and key technical challenges related to the development and implementation of these polymeric membranes.

“Nanoporous Membranes Generated from Self-Assembled Block Polymer Precursors: *Quo Vadis?*,” Zhang, Y.; Sargent, J. L.; Boudouris, B. W.; Phillip, W. A. J. Appl. Poly. Sci. 2015,

132, 41683.

The other focused on the application of these polymeric membranes to established and emerging water treatment processes.

“Fit-for-Purpose Block Polymer Membranes Molecularly-Engineered for Water Treatment,” Zhang, Y.; Almodovar Arbelo, N. E.; Weidman, J. L.; Corti, D. S.; Boudouris, B. W.; and Phillip, W.A., 2017, npj Clean Water, *accepted*.