

NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: Ion-Rejecting Membranes with Polyelectrolytic Layers Produced through Surface-Initiated Atom Transfer Radical Polymerization

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Background and Introduction

Overview. Previously, nanofiltration and reverse osmosis membranes for the removal of charged dyes and ions have been produced through layer-by-layer (LbL) deposition of polyelectrolytes. LbL-assembled layers are synthesized by dipping a charged surface in solutions of alternately-charged polyelectrolytes, which are electrostatically attracted to the previous, oppositely-charged layer (Figure 1A-C). LbL-assembled membranes have shown promising performance, rejecting as much as 93.5 and 98.5% of NaCl and Na₂SO₄, respectively (Jin, Toutianoush et al. 2003). However, this technology has not been implemented in industry because the membrane is not stable at varying pH's, and the electrostatic "bonds" easily break over time under high pressure. This research explores a new method of producing a covalently-bonded polyelectrolyte membrane through highly-controlled surface-initiated atom transfer radical polymerization (SI-ATRP) (Figure 1D).

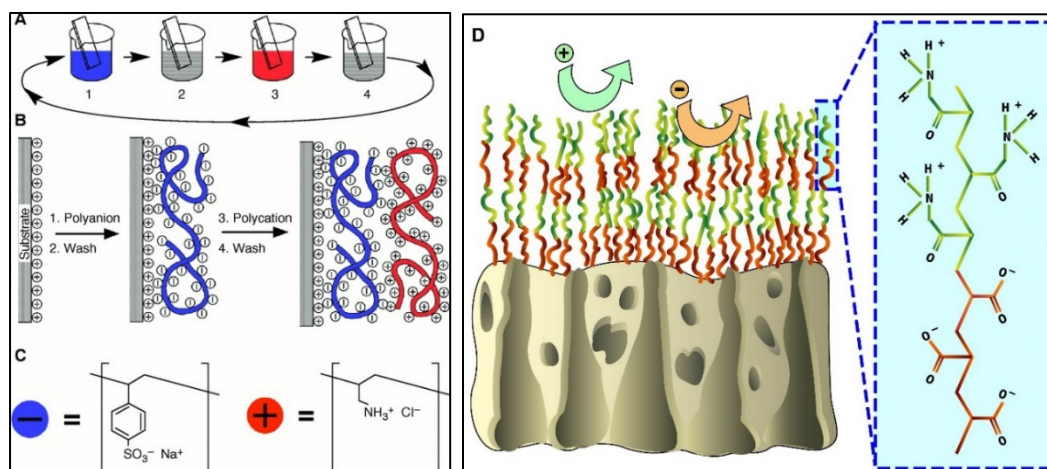


Figure 1. (A-C) Dip-coating methods for LbL-assembly of poly(styrene sulfonate) and poly(allylamine hydrochloride) to produce polyelectrolytic layers on glass slides. Image from reference (Decher 1997). (D) Possible covalently-bonded version of charged layers comprising poly(acrylic acid) and poly(allylamine), produced through SI-ATRP. Layers reject like-charge ions.

Hypothesis. SI-ATRP atop a porous substrate may be used to produce an effective polyelectrolytic-brush layer for high rejection of salt ions.

Study Goals. (1) Explore how brush density affects membrane performance. (2) Explore the effects of the thickness and quantity of each polyelectrolyte layer. (3) Compare performance of distinct charged bands versus randomly-mixed charged repeat units. (4) Exploit the ease of SI-ATRP to add additional layers to enhance membrane lifespan, such as a hydrophilic layer to reduce organic fouling.

Objectives of Research. (1) To develop a fundamental understanding of SI-ATRP on membrane substrates to control and verify brush density, length, and location. (2) To apply fundamental understanding to the production of a charged polyelectrolytic brush-layer membrane with high salt-rejection and sufficient permeability.

Needs Served by this Research. The methods developed during fundamental studies of SI-ATRP on membrane substrates will be helpful for any application of SI-ATRP. Because the mechanisms of LbL-assembly are not fully understood, optimizing the system and reproducing results have proven difficult. By utilizing the more controlled method of SI-ATRP, polyelectrolytic membranes could be stabilized and their mechanism of ion rejection may be better elucidated.

Progress to Date: Fundamental Study of SI-ATRP on Membrane Substrates

Objectives. The components of this fundamental study comprise identifying and stabilizing an appropriate porous substrate upon which SI-ATRP may be conducted and controlling and verifying brush density, length, and location. Finally, for better control, methods to grow uncharged brushes and subsequently cleave sidechains to produce charged polymers must be developed. In the previous report, methods and results for substrate stabilization and density control and verification were discussed. Here, I present progress on polymer length determination and a proof of concept as well as wrapping up the project with polymer brush location control.

Methods. *Investigation of Growth Rates.* Poly(*tert*-butyl acrylate) brushes are grown from the surface of cellulose membranes with 2-bromoisobutyral bromide initiator bonded. After cleavage of the brushes in highly basic conditions, the ester bonds that connect the *t*-butyl sidechains are also incidentally cleaved so polyacrylic acid (PAA) results. PAA can only be measured in an aqueous gel permeation chromatography (GPC) column, which is prone to inaccurate measurements due to the easy growth of bacteria within the column. Thus, the PAA is converted back to a measurable acrylate through an esterification reaction before passing through a GPC column with a polystyrene immobile phase. Direct comparison of growth rates on the nonideal cellulose film surfaces and the simultaneous homogeneous reaction was conducted.

Proof of Concept. To demonstrate the ability of SI-ATRP to produce distinct blocks of alternate functionality, a hydrophobic *t*-butyl acrylate brush at ~3000 Da was grown, followed by a layer of hydrophilic 2-hydroxyethyl acrylate brush at ~1000 Da. Changes in water contact angle throughout this layering process as well as changes in diffusion rates of solutes with different octanol/water partition coefficients—signifying different levels of hydrophobicity—prove the ability to produce distinct layers that change the selectivity and transport characteristics of a membrane.

Brush Location Control. A sealing wafer was developed to control the location of brush growth on commercial membranes of a small molecular weight cutoff (MWCO) of 30,000 Da as well as a larger MWCO of 100,000 Da by exploiting steric hindrance during the SI-ATRP reaction. *T*-butyl acrylate brushes will again be cleaved into PAA with carboxyl groups, where a heavier metal positive ion such as silver will then be bound to these functional groups. Cross-sections will be imaged in TEM.

Results and Discussion. Investigation of Growth Rates. For years, simultaneous homogeneous reactions of free-floating polymer conducted in the same environment as the heterogenous, surface-initiated polymerizations have been used as indicators for relative polydispersity and growth rates. However, more recent studies suggest surface topology highly affects brush growth behavior and rate during SI-ATRP. On a macroscopic scale, the topology of the membrane can be considered a flat surface, whereas on the microscale, it is a mixed morphology of concave and convex surfaces. Through direct cleavage and measurement of brushes, we found a unique growth pattern consisting of four distinct regions of growth behavior as well as diverging populations of length (Figure 2). Up until around 4000 Da, the brushes on the surface grow at nearly the same rate as in the bulk then slow significantly. When the bulk polymer has grown to around 15000 Da, the surface divides into two populations, a population which breaks free, accelerating rapidly, and a stifled population. These disparate populations then grow at a rate similar to the bulk.

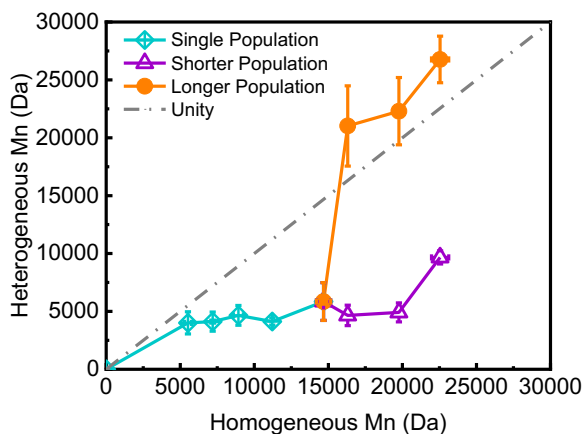


Figure 2. Simultaneous growth rates of heterogeneous versus homogeneous poly(*tert*-butyl acrylate) chains within the same environments. Heterogeneous growth is slowed at around 4000 Da, likely not due to radical-radical interaction because further growth is eventually observed for the shorter population. Rather, we hypothesize that a critical length is reached when brushes are long enough to entangle. Given enough time, a longer population breaks free, and the two populations continue to grow at close to the bulk rate.

Proof of Concept. I demonstrate here the ability to grow two layers, in succession, of differing functionality, verified through changes in water contact angles and diffusions rates (Figure 3). With a hydrophobic brush layer, the water contact angle is shown to increase whereas an added hydrophilic layer induces a lower contact angle. The drastic switching of diffusion, where sodium chloride initially passes through the bare cellulose membrane much faster than the hydrophobic solutes but then switches diffusion rate, indicates the ability to tailor membrane selectivity through strategic selection of brush type/functionality.

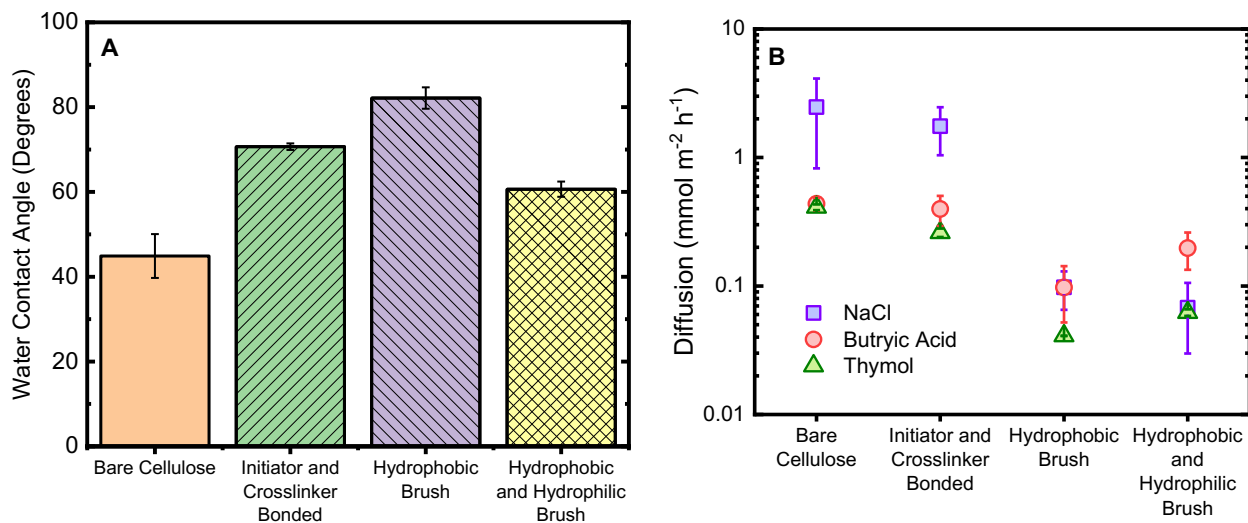


Figure 3. (A) Water contact angles throughout modification of a bare cellulose membrane, proving addition of hydrophobic and hydrophilic layers. (B) Changes in diffusion rates of solutes with varying octanol/water partition coefficients throughout addition of polymer layers.

Conclusions

Before SI-ATRP may be used to produce polyelectrolytic membranes, some basic understanding is necessary to develop methods to produce and reproduce these membranes as well as determine exactly what brush structures have formed. So far, as discussed in my first progress report, I have developed methods to control and verify brush length as well as produce the negatively-charged layers for the polyelectrolytic membranes. Importantly, I have elucidated the minimum crosslinker concentration necessary to stabilize the porous substrate. Through a new, more direct method of measuring brush density, I have demonstrated consistent control of this parameter as well.

Here, I have reported investigating growth rates on the nonideal surface of a cellulose membrane, elucidating a unique growth pattern and suggesting that any polyelectrolytic brushes must stay below 4000 Da total for full, uniform layering. I have proven the addition of distinct layers through changes in water contact angles and diffusion rates. I have developed a method to control brush location and a way to qualitatively verify this control through imaging techniques.

On a larger scale, the success of this polyelectrolytic membrane project could help alleviate water scarcity. Currently, a third of the world lives in areas with inadequate or unsafe water supply, with a projected shortage for two-thirds of the population by 2025 (Elimelech 2006). Although water conservation, repairing infrastructure, and improving water distribution systems can stretch current water resources, the only way to increase water supply is by reuse and desalination (Shannon, Bohn et al. 2008, Elimelech and Phillip 2011). With 97% of the Earth's water contained in the ocean, improving desalination technology could be a solution.

Next Steps

The final portion of the fundamental study includes imaging membranes and films in which my location control technique is utilized. This is important so polyelectrolytic layers reside only on the surface of the membrane in horizontal bands instead of clogging pores. Next, I will develop a polyelectrolytic polymer with alternately-charged layers and translate this polymer onto a porous support. Membranes with various numbers of polyelectrolyte bilayers at different densities will be synthesized and tested for water permeability and salt rejection.

References

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