

# **Ionic Strength Response of Zwitterionic Polymer Membranes**

By

YANGMING KOU

An honors thesis submitted in partial fulfillment  
of the requirements for the completion of

Bachelor of Science in Chemical Engineering

Department of Chemical and Biological Engineering  
Tufts University  
Medford, Massachusetts

May 2016

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Yangming Kou

*Department of Chemical and Biological Engineering  
Tufts University, Medford, MA 02155, USA*

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# Abstract

Amphiphilic zwitterionic copolymer membranes exhibit high flux, sharp selectivity and high surface hydrophilicity and have potential uses in various industrial separation processes. However, zwitterions can respond to changes in ionic strength and undergo conformation changes due to anti-polyelectrolyte effect in aqueous environments. In this study, we investigate whether varying ionic strength conditions can affect the material properties of these amphiphilic zwitterionic copolymer, therefore changing membrane performance in different feed ionic strength. We found that these membranes are stable in water permeance and solute rejection over a wide range of feed ionic strength because the rigid hydrophobic domains of the copolymer restrict the zwitterionic copolymer domains to respond to varying ionic strength in solution. We also show that annealing these zwitterionic copolymer membranes in different ionic strength solutions can improve the mobility of hydrophobic domains and allow the zwitterionic domains to rearrange in response to higher ionic strength in solution. This leads to significant increase in membrane permeance but only a slight increase in solute rejection. Hence, membrane annealing in different ionic strength solutions may be used to tune and improve the performance of these zwitterionic polymer membranes for high-throughput industrial separation processes.

## 1 Introduction

Water scarcity is a global challenge recognized by international organizations such as the United Nations. Currently, around 2.8 billion people, or a third of the world’s population, are affected by water scarcity daily.<sup>23</sup> Furthermore, water is the most fundamental and heavily required component in modern businesses such as textile manufacturing, beverage breweries and pharmaceutical industry. For example, the textile industry in India alone uses around 425,000,000 gallons of water every day,<sup>10,18</sup> which is enough water for the daily use by more than one million average American families.<sup>22</sup> Since water is commonly used as a solvent, improving industrial separation processes by recycling water streams and reducing the amount of water required for industrial production can help tackle the problem of water scarcity.

Membrane filtration has recently risen in prominence as a green separation method widely applicable to waste water treatment, food and beverage industry, and the production of pharmaceuticals. Membranes are energy efficient, environmentally friendly, and scalable for industrial operations, giving them clear advantages in comparison with traditional energy and material intensive separation methods such as distillation or chromatography. Good filtration membranes need to exhibit certain properties such as sharp selectivity, high flux and fouling-resistance to be suited for practical use. Sharp selectivity allows the membrane to retain as much solute to be removed as possible based on the membrane’s pore size cut-off and diffusivity. High transmembrane flux allows a fast permeate flow rate through the membrane during filtration processes. Finally, an ideal membrane should not be prone to fouling, a process described as the loss of membrane permeability due to the adhesion of feed components on the membrane surface.<sup>7,8</sup>

During previous studies, we have found that promising filtration membranes exhibiting size-based selectivity of small molecules ( $<1500$  g/mol) can be made from a class of zwitterionic amphiphilic random copolymers.<sup>9</sup> Zwitterions, defined as neutral molecules with equal numbers of positively and negatively charged functional groups, have a high degree of hydration and resistance to biomolecular fouling.<sup>11,13–15,19,24</sup> Random copolymerization of a zwitterionic monomer with a hydrophobic monomer can further result in a bicontinuous network of channel-like domains of zwitterions,<sup>12</sup> formed through electrostatic interactions of locally charged functional groups and held together by the hydrophobic “channel walls”.<sup>2,3,5,16</sup> Hydrophobic domains of the copolymer are selected to be rigid and glassy in order to prevent swelling of the zwitterionic domains, preventing potential loss of selectivity during filtration processes. Figure 1 shows both the self-assembly schematic of zwitterionic copolymers and a representative transmission electron microscopy image of a zwitterionic amphiphilic copolymer thin film that provides direct evidence for copolymer self-assembly.<sup>9</sup>

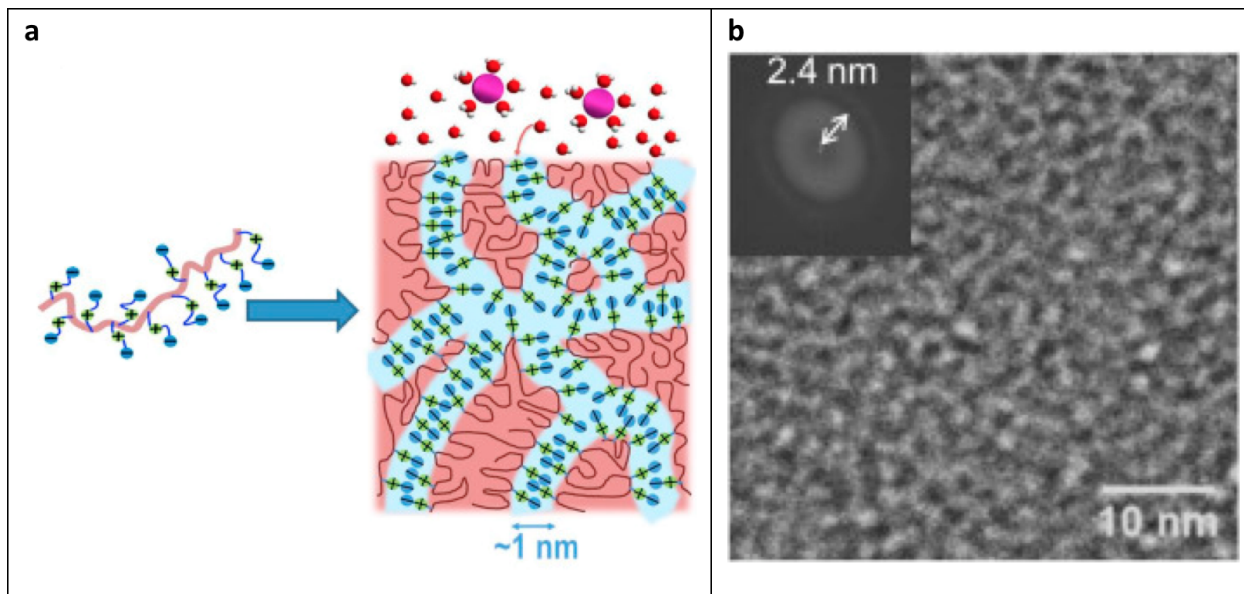


Figure 1: (a) Schematic of the self-assembly of zwitterionic copolymers into bicontinuous networks of zwitterionic (indicated by green and blue charged groups) and hydrophobic (pink) domains. The zwitterionic domains act as a network of hydrophilic nanochannels  $\sim 1$  nm in diameter, held together by the glassy hydrophobic domains. (b) The self-assembled morphology of zwitterionic copolymer poly(2,2,2-trifluoroethyl methacrylate-*random*-sulfobetaine methacrylate) (PTFEMA-*r*-SBMA), documented by transmission electron microscopy (TEM). Zwitterionic SBMA domains were stained with  $\text{Cu}^{2+}$  ions and appear dark, while PTFEMA phase forms the lighter regions. The TEM image shows interconnected SBMA domains with a characteristic period of  $\sim 2.4$  nm, yielding an estimated channel size of around 1.2 nm.<sup>9</sup>

Literature shows that polyelectrolytes, polymers that contain zwitterionic groups at each repeat unit, can undergo conformation changes in an aqueous solution by the addition of a low-mass salt (LMS), termed as the anti-polyelectrolyte effect. As seen in Figure 2, in the presence of a salt, dipole-dipole interactions between zwitterions are shielded by counterions from the dissolved salt in water. This results in increased hydration of the zwitterions, thus allowing the bulk polyelectrolyte to exhibit a higher degree of mobility and an increased affinity to water.<sup>13</sup> Several other studies have indicated that the presence of dissolved small ions like salt can also influence the interaction of various zwitterion-containing polymers in water and increase overall polymer hydrophilicity.<sup>21, 25, 28</sup> However, the effect of ionic strength on our amphiphilic statistical copolymers containing both zwitterionic and hydrophobic domains is yet to be understood. While the zwitterionic domains of the copolymer would tend to respond to ionic strength in the aforementioned fashion, their movement may be restricted by the more rigid and glassy hydrophobic domains of the copolymer.

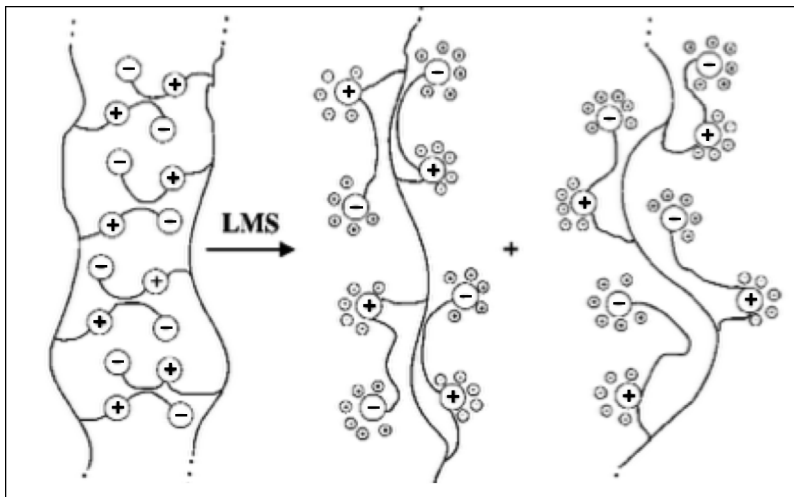


Figure 2: Schematic diagram showing that the dipole-dipole self-assembly of polyelectrolytes may be disrupted by the addition of a low-mass salt (LMS) into aqueous solutions due to the anti-polyelectrolyte effect. The addition of salt can result in the formation of individual zwitterionic groups surrounded with a counterion atmosphere of hydrated salt ions around each zwitterion. Polyelectrolytes are also expected to swell and exhibit higher hydration under high ionic strength in solutions.<sup>13</sup>

Because our amphiphilic copolymers make up the selective layer of our filtration membrane, it would be particularly interesting to characterize the degree of change to our zwitterionic copolymer’s self-assembled structure as well as the resulting membrane performance parameters under varying ionic strength. Knowing how the performance of the zwitterionic membrane would change in response to ionic strength during filtration is important because the ionic strength in filtration feed streams during industrial operation can greatly vary. Furthermore, we can also seek ways to actively tune the performance of our membranes by changing the self-assembled structure of our copolymer using water solutions with different ionic strength, taking advantage of this responsive behavior of zwitterionic groups.

In this work, we first investigated the ionic strength response of zwitterionic copolymer membranes to changing feed ionic strength. We characterized the water affinity and surface hydrophilicity of the bulk copolymer in various ionic strength conditions, and the membrane permeance and size-based selectivity when filtering solutions at varying ionic strengths. Second, we sought ways to tune membrane performance by annealing our membranes in solutions of various ionic strength. We compared the resulting membrane permeance and size-based selectivity before and after membrane annealing, and aimed to correlate any changes in pore size and permeance with expected behavior of the polymer.

## 2 Experimental

### 2.1 Materials

Sulfobetaine methacrylate (SBMA), 2-methacryloyloxyethyl phosphorylcholine (MPC), azobisisobutyronitrile (AIBN) and 4-methoxyphenol (MEHQ) were obtained from Sigma-Aldrich (St. Louis, MO). Monomer 2,2,2-trifluoroethyl methacrylate (TFEMA) was obtained from Scientific Polymer Products Inc (Ontario, NY). Trifluoroethanol (TFE), dimethyl sulfoxide (DMSO), methanol (MeOH), ethanol (EtOH), isopropanol (IPA), tetrahydrofuran (THF), hexane, and basic activated alumina were obtained from VWR (West Chester, PA). NMR solvent deuterated dimethyl sulfoxide (DMSO- $d_6$ ) was obtained from Cambridge Isotopes Laboratory (Tewksbury, MA). All chemicals were used as received, except for TFEMA, which was purified by passing through a basic alumina column to remove inhibitors. PVDF 400R ultrafiltration base membranes were purchased from Sepro Membranes Inc (Oceanside, CA) and were used as base membranes for polymer coating. Ultrapure deionized water generated by Biolab 3300 RO, a building-wide RO/deionized water purification unit by Mar Cor Purification, was used for all experiments.

## 2.2 Synthesis of zwitterionic copolymer

### 2.2.1 Synthesis of PTFEMA-*r*-SBMA copolymer

Four grams of SBMA was first dissolved using approximately 20 ml of DMSO per gram of SBMA in a round-bottomed flask. Six grams of TFEMA was passed through a column of basic activated alumina to remove the inhibitor and added to the flask, totaling 10 g of monomer mixture, followed by 0.01 g of free-radical initiator AIBN. The flask was sealed with a rubber septum, purged with nitrogen gas for 15 min, and placed in an oil bath at 70 °C. The free-radical polymerization reaction was allowed for at least 20 h. Reaction was terminated by adding 0.5 g of MEHQ to the flask. Copolymers were precipitated in a 1:1 EtOH/hexane mixture, vacuum filtered, and twice extracted with MeOH for at least 8 h to remove remaining solvent and monomers. The final product was dried *in vacuo* at 50 °C overnight. The copolymer composition was determined by <sup>1</sup>H-NMR spectroscopy.

### 2.2.2 Synthesis of PTFEMA-*r*-MPC copolymer

Four grams of MPC was first dissolved in approximately 20 ml of EtOH per gram of MPC in a round-bottomed flask. Then, six grams of TFEMA was passed through a column of basic activated alumina to remove the inhibitor and added to the flask, totaling 10 g of monomer mixture, followed by 0.01 g of free-radical initiator AIBN. The flask was sealed with a rubber septum, purged with nitrogen gas for 15 min, and placed in an oil bath at 70 °C. The free-radical polymerization reaction was allowed for at least 20 h. Reaction was terminated by adding 0.5 g of MEHQ to the flask. Copolymers were precipitated in THF, vacuum filtered, and twice extracted with THF for at least 8 h to remove remaining solvent and monomers. The final product was dried *in vacuo* at 50 °C overnight. The copolymer composition was determined by <sup>1</sup>H-NMR spectroscopy.

## 2.3 Preparation of thin film composite membranes

Copolymers were dissolved in TFE at 50 °C to make a 10 % w/v solution. The solution was passed through a 1 µm glass fiber syringe filter (Whatman) and degassed by heating at 50 °C in a sealed vial for at least 1 h until no gas bubbles were visible. The polymer solution was then allowed to cool down to room temperature. Thin film composite membranes were prepared by coating a thin layer of polymer solution onto PVDF 400R ultrafiltration membranes using either a doctor blade with gate size of 25 µm, or a steel rod with nominal coating thickness of 6 µm. The coated membrane was then immediately immersed into an IPA bath for 20 min, followed by a deionized water bath for at least overnight.

## 2.4 Characterization of membrane morphology

Membrane thickness and morphology was characterized by using a Phenom G2 Pure Tabletop Scanning Electron Microscope (SEM) operating at 5 kV. Membrane samples were freeze-fractured using liquid nitrogen for cross-sectional examination, and sputter coated with gold-palladium before imaging.

Membrane surface hydrophilicity was characterized by measuring its contact angle using the sessile drop technique on a goniometer (ramé-hart). A small piece of membrane was affixed to a flat platform, and droplets of deionized water or aqueous NaCl solution were deposited onto the sample membrane surface. The resulting image was captured by a digital camera. Contact angle was determined by the instrument's computer software.

## 2.5 Characterization of membrane performance

Filtration experiments were performed on 25 mm diameter membranes using a 10 mL Amicon 8010 stirred, dead-end filtration cell (Millipore) with an effective filtration area of 4.1 cm<sup>2</sup>, attached to a 1 gal reservoir. All filtration experiments were performed by applying a transmembrane pressure of 20 psi (1.4 bar) with house compressed air. Filtration cells were stirred continuously to minimize concentration polarization. Deionized water was first passed through the membrane until the flux remained stable over at least 30 min. Upon stabilization, permeate was continuously collected and weighed to determine the transmembrane flux, the mass or volumetric flow rate through the membrane per unit of membrane area. The membrane

permeance, a membrane property defined as the membrane flux normalized by the transmembrane pressure difference, is calculated by

$$L_p = \frac{J}{\Delta p} \quad (1)$$

where  $L_p$  is the membrane permeance ( $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ),  $J$  is the volumetric flux across the membrane ( $\text{L m}^{-2} \text{ h}^{-1}$ ) and  $\Delta p$  the transmembrane pressure difference (bar).

Membrane selectivity was characterized by filtering various small molecules of known structure and size, typically organic dyes or vitamins. In all cases, an aqueous solution containing  $100 \text{ mg L}^{-1}$  of the small molecules was filtered through the membrane. During filtration experiments, the first milliliter of filtrate was discarded to allow stabilization. The subsequent 1–2 mL of filtrate was used to measure solute rejection by the membrane. Rejection measures the membrane’s ability to separate given solutes from the feed solution, and is defined as

$$\mathbb{R} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where  $\mathbb{R}$  is rejection,  $C_f$  is the feed solute concentration ( $\text{mg L}^{-1}$ ) and  $C_p$  is the permeate solute concentration ( $\text{mg L}^{-1}$ ).<sup>8</sup> Solute concentration in the feed and permeate were measured by UV-Vis spectrophotometry (Thermo Scientific Genesys 10S).

### 2.5.1 Membrane performance with different feed ionic strength

In order to characterize the effect of ionic strength in feed solution on membrane performance, filtration experiments were performed by alternating water and aqueous dye solutions with increasing NaCl concentrations in exponential increments (0 M,  $10^{-3}$  M,  $10^{-2}$  M,  $10^{-1}$  M and 1 M) as feed solutions for the membrane. In some cases, solutions with decreasing NaCl concentrations were also used as feed solutions for the membrane during filtration experiments to characterize the reversibility of the membrane’s response to ionic strength changes. Membrane permeance and solute rejection values were measured for each filtration experiment.

### 2.5.2 Membrane performance after annealing in different ionic strength solutions

Thin film composite membranes can be further treated by annealing to alter membrane performance. In each annealing cycle, the membrane swatch was immersed in deionized water or an aqueous NaCl solution at  $50^\circ \text{C}$  for 24 h. Filtration experiments were performed on the membrane after being annealed in aqueous solutions of increasing NaCl concentrations (0 M, 0.1 M, 0.5 M) by filtering water and various dye solutions. Finally, the membrane was annealed in deionized water to investigate the possible reversibility of membrane annealing under various ionic strength. Membrane permeance and solute rejection values were measured for each filtration experiment. This complete series of experiments were performed on the same membrane swatch, to avoid the effects of sample-to-sample variation.

## 3 Results and Discussion

### 3.1 Synthesis and characterization of zwitterionic copolymer

#### 3.1.1 Reaction chemistry and chemical composition

Statistical copolymers of hydrophobic monomer 2,2,2-trifluoroethyl methacrylate (TFEMA) with hydrophilic, zwitterionic monomer sulfobetaine methacrylate (SBMA) or 2-methacryloyloxyethyl phosphorylcholine (MPC) were synthesized via free radical polymerization. The reaction scheme for the synthesis of PTFEMA-*r*-SBMA is given in Figure 3. PTFEMA-*r*-MPC was synthesized using analogous methods by Prity Bengani. Free radical polymerization was used due to its robustness and scalability for copolymer synthesis. TFEMA was chosen because it is hydrophobic and does not swell in water, and because the glass transition temperature of its homopolymer, PTFEMA, was significantly above room temperature ( $T_g = 74^\circ \text{C}$ ) so that the copolymer would remain rigid even when the zwitterionic groups are hydrated. SBMA and MPC were chosen because both zwitterions exhibited high levels of copolymer hydrophilicity as compared to other potential zwitterionic monomer candidates such as 3-(2-vinylpyridinium-1-yl) propane-1-sulfonate (SB2VP) and 3-(4-vinylpyridinium-1-yl) propane-1-sulfonate (SB4VP). These observations were based on

preliminary data from polymer water uptake, contact angle, water permeance and fouling resistance of polymer thin film composite membrane filtration tests.

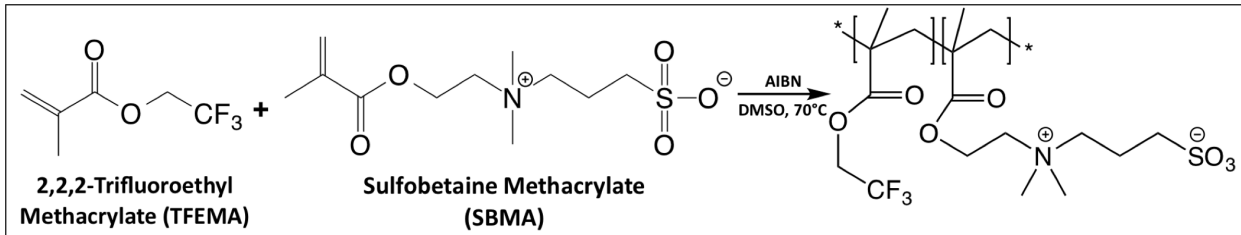


Figure 3: Reaction schematic showing the synthesis of PTFEMA-*r*-SBMA copolymer using free radical copolymerization of TFEMA and SBMA monomers.

Both copolymers were synthesized successfully. PTFEMA-*r*-SBMA copolymer with 40 wt% SBMA content was synthesized because the resulting copolymer exhibits both high water permeance and stability under high ionic strength feed solutions when made into thin film composite water filtration membranes.<sup>9</sup> The conversion at the end of the reaction period was  $\sim 70\%$ . Copolymer composition was characterized by  $^1\text{H-NMR}$  spectroscopy (Bruker Avance III 500 MHz) using 1 % LiCl in DMSO- $d_6$ . Sample spectra and peak assignments are given in Figure 4. From multiple batches of PTFEMA-*r*-SBMA syntheses,  $^1\text{H-NMR}$  spectroscopy showed that copolymer compositions were within 5 % of monomer composition in the reaction mixture, indicating that large blocks of SBMA were likely not present, and that copolymerization was essentially random.<sup>26</sup> Similar observations were also seen for the synthesis of PTFEMA-*r*-MPC copolymer.

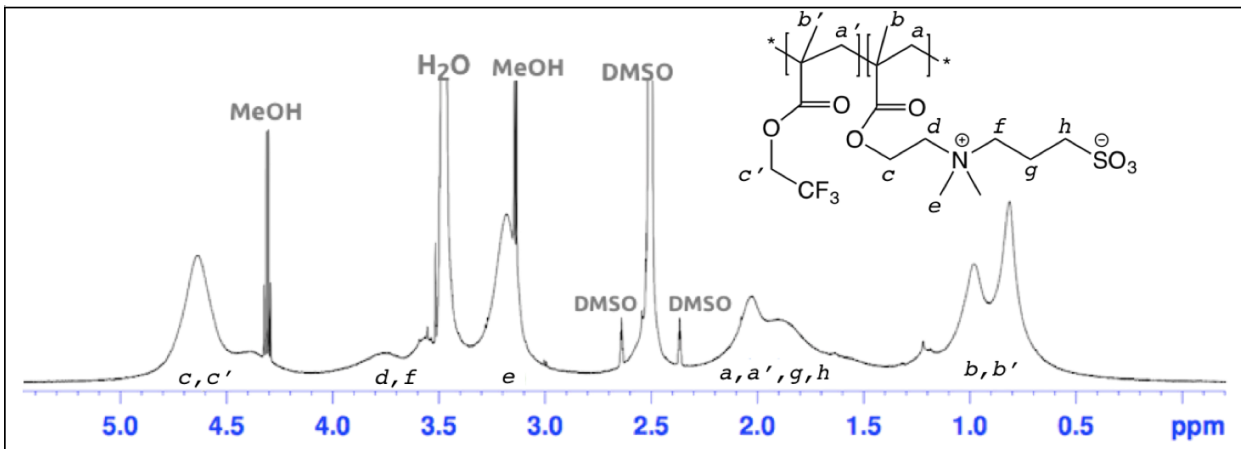


Figure 4:  $^1\text{H-NMR}$  spectra of amphiphilic zwitterionic copolymer PTFEMA-*r*-SBMA with an SBMA content of 39 wt%, indicating successful random copolymerization of the two monomers.

### 3.1.2 Polymer water uptake under varying ionic strength aqueous solutions

Water uptake of the amphiphilic copolymer PTFEMA-*r*-SBMA was measured to further study how different ionic strength conditions can influence the polymer's hydrophilicity. Previous studies on zwitterionic homopolymers have shown that, in the presence of a low-mass salt in aqueous environments, each charged functionality in the zwitterion starts to interact with the hydrated salt ions instead of being bound by intramolecular forces within the polymer. As a result, the zwitterionic groups are more swollen, being surrounded by larger hydration shells.<sup>13</sup> Based on this, in a statistical copolymer, we would expect the hydrophilicity and hydration of zwitterionic groups to also increase upon the addition of salt ions. Therefore, we hypothesize that under higher ionic strength conditions, our zwitterionic copolymer should exhibit a higher degree of water uptake. However, PTFEMA, the hydrophobic domain of the copolymer, has a glass transition temperature much higher than room temperature. This makes the hydrophobic domains of this microphase-separated structure is set, even upon immersion in salt solutions. Thus, the copolymers discussed here may be less susceptible to the anti-polyelectrolyte effect in response to varying ionic strength of the immersion



solution.

Water uptake of PTFEMA-*r*-SBMA copolymer was measured by immersing small pieces of copolymer into deionized water or aqueous NaCl solutions of varying ionic strength at room temperature for 72 hours, and the results are summarized in Figure 5. In all cases, the copolymer exhibited an average water uptake of  $19 \pm 5$  %. While the copolymer exhibited a slight increase in water uptake in higher ionic strength solutions by around five percentage points, this was within the error margin of the measurements. Overall, the copolymer did not show a significant change in water uptake with varying ionic strength at room temperature. This observation is most likely attributed to the rigidity of the TFEMA domain reducing movement of the copolymer’s zwitterionic domain in response to changes in ionic strength.

Next, polymer water uptake was measured by immersing similar pieces of copolymer into a same set of solutions at a higher temperature of 50 °C. While this temperature is still below the  $T_g$  of PTFEMA, it is likely to impart better chain mobility, thus enabling the polymer chains to rearrange. The polymer was soaked in solutions for a reduced time of 24 hours. The increased temperature resulted in a significant two-fold increase in water uptake across every ionic strength as compared to those tests performed at room temperature. The increased water uptake result is most likely due to the increased temperature and hence polymer chain mobility, which allowed the copolymer’s zwitterionic and hydrophobic domains to exhibit more movement. Furthermore, the water uptake by the copolymer at 50 °C was 7–10 % higher in the high ionic strength solutions. This further suggests that at higher temperatures, the amphiphilic copolymer can better respond the changes in the hydrophilicity of its zwitterionic groups in response to increased ionic strength. This is likely due to higher mobility of the hydrophobic domains containing the zwitterionic groups.

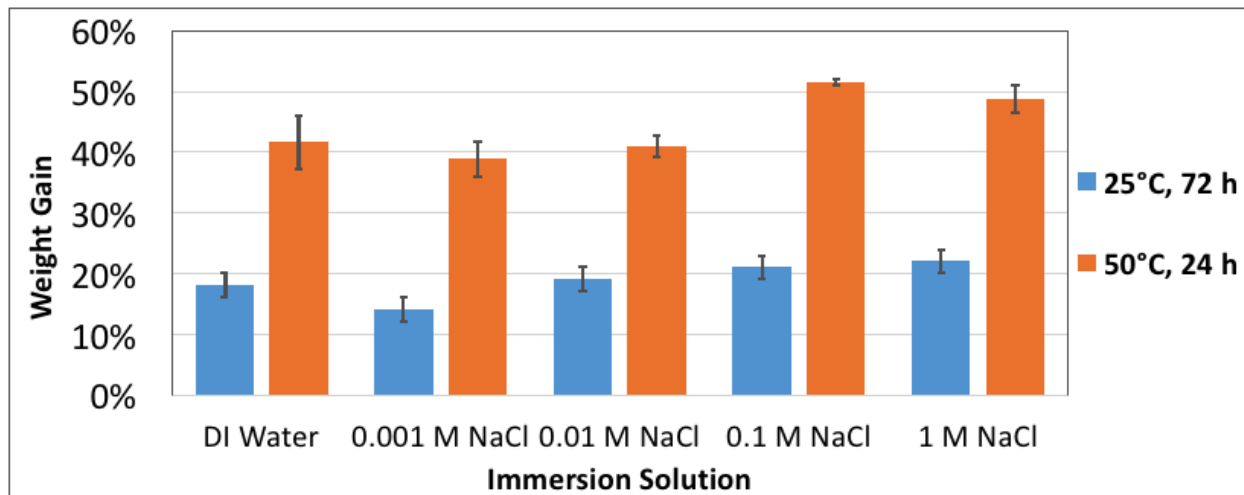


Figure 5: Water uptake of PTFEMA-*r*-SBMA copolymer in different ionic strength solutions at 25 °C for 72 h, and at 50 °C for 24 h.

## 3.2 Characterization of membrane morphology and surface properties

### 3.2.1 Preparation of thin film composite membranes

After successful synthesis of amphiphilic copolymers, thin film composite (TFC) water filtration membranes were prepared where the synthesized copolymers served as the membrane’s selective layer. A thin polymer layer was coated onto a commercially available PVDF 400R base membrane. A 10 wt% polymer solution in TFE was spread onto the base membrane using either a doctor blade sate to a gate size of 0.01”/25  $\mu$ m, or a steel coating rod with a nominal coating thickness of 6  $\mu$ m in a well ventilated open space. The coated membrane was then immediately immersed into IPA to precipitate the polymer into a thin film on top of the support layer. When the amphiphilic copolymer solidifies into a dense thin film, it microphase separates into hydrophobic and hydrophilic domains due to the high incompatibility between the hydrophobic and zwitterionic groups. The morphology of this microphase-separated microstructure is a bicontinuous network of each domain. The hydrophilic/zwitterionic domains act as a network of “channel”

like nanostructures favorable for water filtration.<sup>9</sup>

Figure 6 shows representative cross-sectional SEM images of uncoated PVDF 400R support membrane TFC membranes coated with a PTFEMA-*r*-SBMA selective layer. SEM images verified that TFC membranes we prepared resulted in a dense layer of PTFEMA-*r*-SBMA coating with  $\sim 1\ \mu\text{m}$  thickness. Membranes with PTFEMA-*r*-MPC copolymers were prepared in a similar fashion and had similar morphologies.

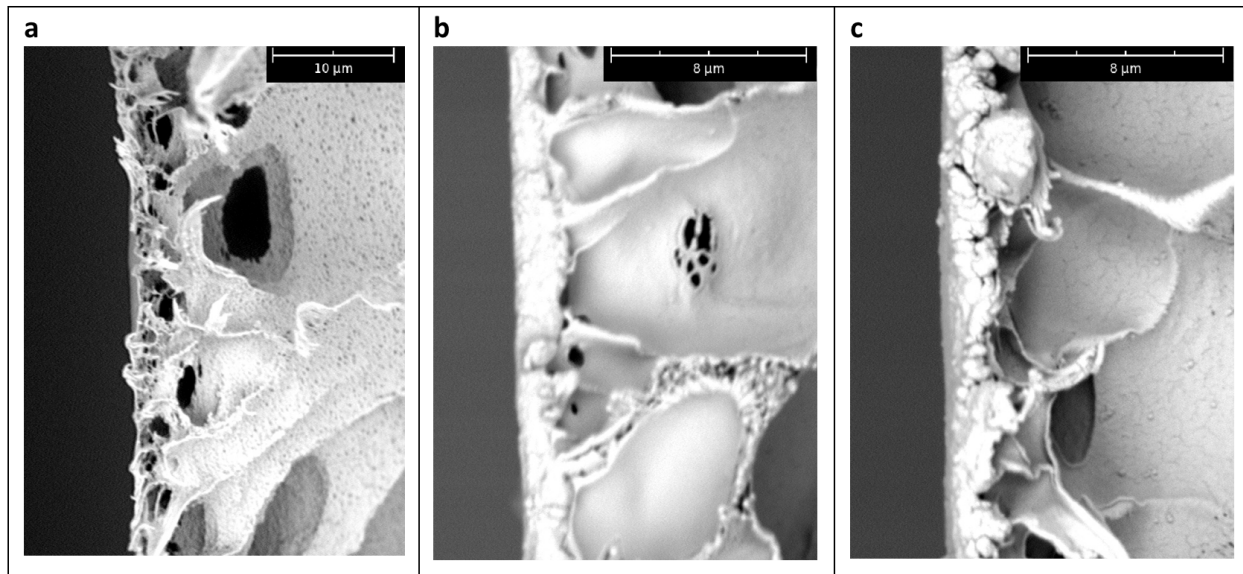


Figure 6: Cross-sectional SEM images of uncoated PVDF 400R support membrane and thin film composite (TFC) membranes with PTFEMA-*r*-SBMA selective layers. (a) Uncoated supported membrane. (b,c) TFC membranes made by coating the support membrane with PTFEMA-*r*-SBMA using (b) doctor blade with a thickness of 0.01"/25  $\mu\text{m}$  and (c) stainless steel rod with a thickness of 6  $\mu\text{m}$ . (a) at 5000 $\times$  magnification; (b,c) at 10,000 $\times$  magnification.

### 3.2.2 Contact angle

Contact angle measurements were used to characterize the surface hydrophilicity of the TFC membranes in response to varying ionic strength. The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface, as shown in Figure 7. Generally, a contact angle less than  $90^\circ$  indicates that wetting of the surface is favorable, and that the liquid tends to spread over a large area on the surface. Conversely, contact angles greater than  $90^\circ$  imply that wetting of the surface is unfavorable and the fluid will minimize its contact with the surface to form a compact liquid droplet.<sup>27</sup> When water is used as the wetting fluid, lower contact angles indicate a more hydrophilic surface, whereas higher contact angles indicate a more hydrophobic surface.

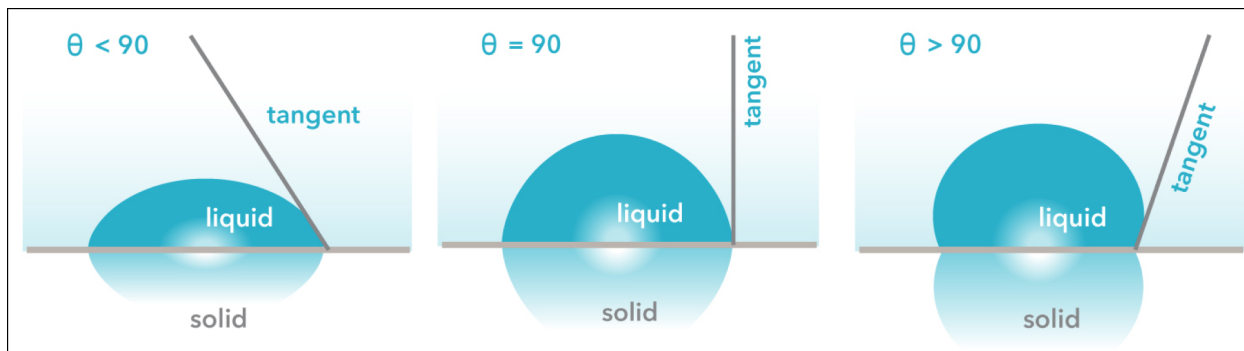


Figure 7: Illustration of various contact angles formed by sessile liquid drops on a smooth homogeneous solid surface.

Since SBMA was the most hydrophilic zwitterion used for copolymer synthesis, TFC membranes coated with PTFEMA-*r*-SBMA selective layers were used to perform contact angle measurements. The results are summarized in Figure 8. Static contact angle results suggest that the surface hydrophilicity of TFC membranes coated with PTFEMA-*r*-SBMA does not change in response to different ionic strength in the water droplet. Thus, we did not observe the implications of the anti-polyelectrolyte effect in this experiment. This observation may be attributed to the fact that the copolymer selective layer was deposited onto the membrane by immersion-precipitation method in a non-aqueous non-solvent such as IPA. During this process, the hydrophobic domains of the amphiphilic copolymer may align more readily towards the interface between the non-solvent and the polymer solution as polymer precipitation takes place. The resulting membrane interface therefore becomes hydrophobic and insensitive to varying ionic strength due to the rigidity of the hydrophobic domains of the copolymer. Furthermore, the membranes tested were dried prior to testing. This process can lead to a more hydrophobic membrane surface due to polymer rearrangement at the surface to minimize surface energy. For more accurate measurements, captive air bubble contact angle measurements may provide more insight. Indeed, this was the case in recent work by Prity Bengani on related polymers.

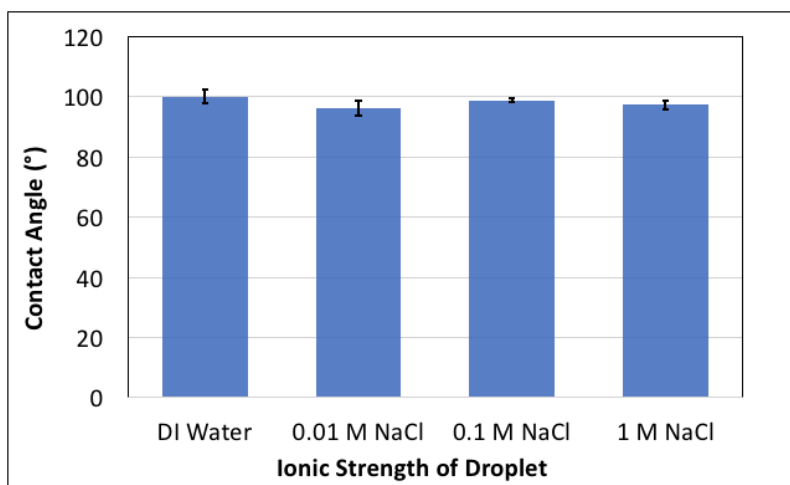


Figure 8: Static contact angle of droplets of deionized water or NaCl aqueous solutions of varying ionic strength on unannealed PTFEMA-*r*-SBMA TFC membranes. The large static contact angles of  $\sim 100^\circ$  across all measurements indicate that the TFC membrane surface is relatively hydrophobic. In addition, surface hydrophilicity does not exhibit significant change in response to increasing ionic strength in contacting droplet.

The water uptake results indicated that annealing in saline solutions may change the hydrophilicity of these copolymer. To determine if this also leads to a more hydrophilic surface, we annealed membranes in different concentrations of NaCl(aq) at  $50^\circ\text{C}$  for 24 hours, dried them and measured the contact angle. Static contact angle measurements were taken on dried membrane surfaces, and results are summarized in Figure 9. In all cases, the surface contact angle remained around  $90\text{--}100^\circ$ . This indicates that the hydrophilicity of the membrane surfaces does not exhibit significant change despite annealing at high ionic strength solutions.

While these results seem to contradict with previous findings from the water uptake measurements, factors such as membrane drying can also influence surface properties and contribute to the contact angle results. When amphiphilic copolymer membranes are dried in air, the hydrophobic domains of the copolymer rich in fluorinated groups may orient towards the polymer-air interface, thereby decreasing the surface hydrophilicity of the membrane. In order to further validate this claim, future wet contact angle measurements using the captive bubble method can be made to study the effect of membrane surface hydrophilicity without having to dry the membranes prior to contact angle measurements.

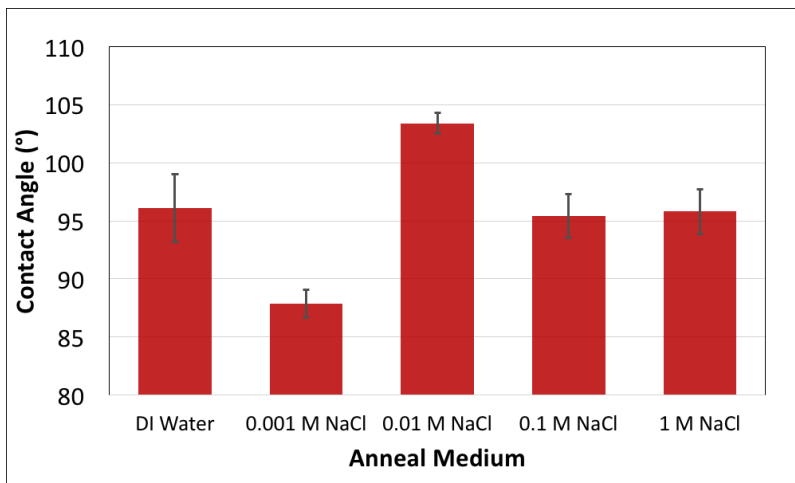


Figure 9: Static contact angle of water droplets on air-dried PTFEMA-*r*-SBMA coated TFC membranes annealed at various ionic strength solutions. Static contact angles were consistently in the range of  $95 \pm 5^\circ$ , indicating that the surface hydrophilicity of TFC membrane after annealing in water or aqueous solutions of NaCl does not exhibit significant change as compared to unannealed membranes regardless of the NaCl ionic strength in the annealing solution.

### 3.2.3 Fourier transform infrared (FTIR) spectroscopy

While previous findings have shown that polyzwitterions can undergo conformation changes in response to varying ionic strength environments due to the anti-polyelectrolyte effect,<sup>13</sup> water uptake results by our amphiphilic copolymer suggest that their zwitterionic domains only exhibited a higher degree of hydrophilicity at 50 °C due to improved polymer chain mobility at elevated temperatures. Therefore, we hypothesize that the zwitterionic domains of these copolymers are more likely to rearrange towards the polymer-water interface when they are annealed in higher ionic strength water solutions, thereby exhibiting greater anti-polyelectrolyte effect. Since FTIR spectroscopy can determine the type and amount of a wide range of chemical functional groups and observe some intermolecular interactions such as hydration and hydrogen bonding on material surfaces, we hoped to observe characteristic peak shifts on the surfaces of these copolymer membranes after annealing them in different ionic strength environments, thereby indicating the possible changes to the interactions experienced by the hydrophilic functional groups of the amphiphilic copolymer.

Previously, other researchers have used FTIR spectroscopy to observe changes in the surface chemical properties of poly(acrylonitrile-*random*-sulfobetaine methacrylate) (PAN-*r*-SBMA), a similar amphiphilic zwitterionic copolymer, when its polymer thin film was immersed in aqueous solutions containing different ionic strength. The symmetric stretch vibration of PAN-*r*-SBMA's hydrated sulfonate groups in free-standing polymer thin films shifted from 1037 cm<sup>-1</sup> to 1042 cm<sup>-1</sup> when the polymer thin film was immersed into NaCl(*aq*) with concentration higher than 0.1 M. The peak occurring at the lower wavenumber of 1037 cm<sup>-1</sup> was assigned as the undissociated sulfonate groups of the zwitterionic copolymer domain of SBMA, while the peak occurring at higher wavenumber of 1042 cm<sup>-1</sup> was assigned as the dissociated and hydrated sulfonate groups that were surrounded by an atmosphere of dissolved NaCl ions in water.<sup>21</sup>

We performed FTIR spectroscopy on PTFEMA-*r*-SBMA coated TFC membranes, which were annealed at 50 °C for 24 hours in deionized water or NaCl(*aq*) containing varying ionic strength. All membranes were kept wet in their respective annealing solutions during FTIR spectroscopy measurements to prevent changes to polymer surface properties due to drying in air. The FTIR spectra of various swatches of PTFEMA-*r*-SBMA copolymer membranes are given in Figure 10. While the full-spectrum surface FTIR spectra of the annealed membranes suggest no significant peak changes in the copolymer coating after varying the ionic strength of the annealing solution (Figure 10a), this is likely due to the low resolution of the spectral data when FTIR spectroscopy is performed over a wider range of wavenumbers. In high resolution FTIR scans, we observed that a peak occurring at 1080 cm<sup>-1</sup> when the membrane was annealed in deionized water was shifted to 1076 cm<sup>-1</sup> after the membrane was annealed in saline water (Figure 10b). This peak was consistent between samples. Since an online FTIR spectra database<sup>20</sup> suggests that the symmetric stretching of hydrated sulfonate groups can result in peak absorbance ranging from 1025 cm<sup>-1</sup> up to 1120 cm<sup>-1</sup>, we believe this peak is to be associated with the sulfonate groups that are part of the zwitterionic functionality. In contrast with our findings, FTIR peaks corresponding to the sulfonate groups in previous studies are observed to shift to lower, not higher, wavenumbers with increasing ionic strength in solution. We still need to confirm reproducibility, gather better evidence for this peak assignment, and understand the exact causes of this reverse shift. But this data may indicate the association/dissociation of sulfonate groups as our PTFEMA-*r*-SBMA copolymer experiences the anti-polyelectrolyte effect, as a result of the different ionic strength present in the membrane annealing solution.

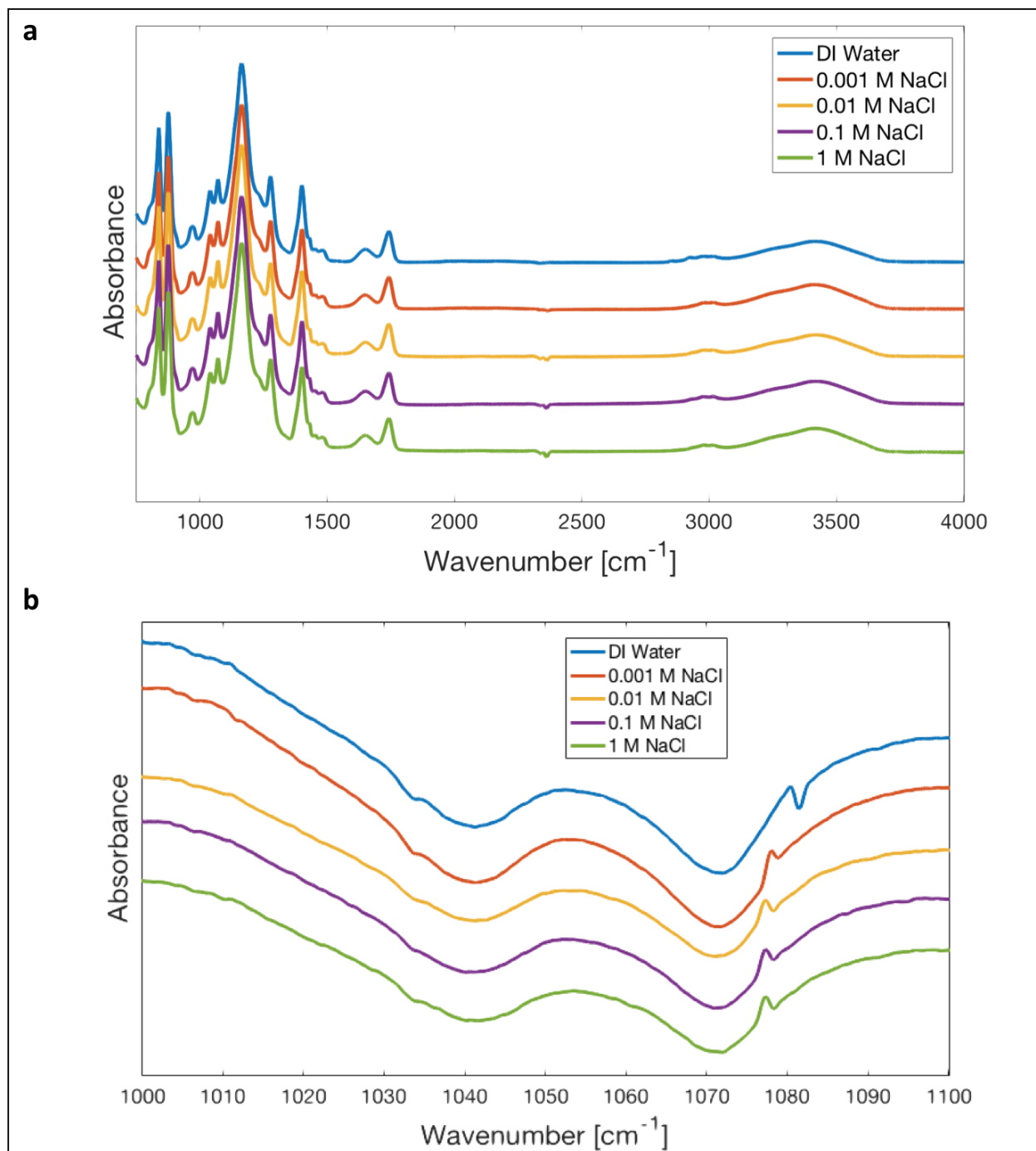


Figure 10: FTIR absorbance spectra of PTFEMA-*r*-SBMA coated TFC membranes annealed in deionized water or NaCl(*aq*) of varying ionic strength, given as (a) full spectrum, obtained in the range of 600–4000  $\text{cm}^{-1}$  by 4  $\text{cm}^{-1}$  increment and (b) high resolution spectrum focusing in the range of 1000–1100  $\text{cm}^{-1}$  by 1  $\text{cm}^{-1}$  increment.

### 3.3 Performance of PTFEMA-*r*-SBMA TFC membranes with feeds of varying ionic strength

#### 3.3.1 Membrane permeance with deionized water

To record the baseline membrane performance, we performed dead-end filtration experiments in stirred cells with deionized water and applying a transmembrane pressure of 20 psi (1.4 bar). We then calculated membrane permeance, defined as the volumetric flux of water through the membrane normalized by the transmembrane pressure difference (Equation 1). PTFEMA-*r*-SBMA coated TFC membranes showed high water permeances, up to  $6.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . PTFEMA-*r*-MPC coated TFC membranes also showed moderate water permeances of up to  $4.75 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . Both TFC membranes exhibit significantly higher water permeance as compared to a commercially available poly(ether sulfone) (PES) membrane that has similar molecular weight cut-off of 1 kDa (Santorius), which shows a water permeance of  $2.55 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ .

#### 3.3.2 Rejection of organic solutes at low ionic strength

A crucial property of membranes is their selectivity. Previous studies have found that our amphiphilic copolymer based TFC membranes exhibit size-based selectivity derived from the self-assembled structure of the copolymer, with an effective pore size of  $\sim 1 \text{ nm}$ , which corresponds to a molecular weight cut-off on the order of  $1000 \text{ g/mol}$ .<sup>17</sup> The effective pore size was further verified by transmission electron microscopy (TEM) on polymer thin films of PTFEMA-*r*-SBMA.<sup>9</sup> In this project, we aimed to verify the separation properties of the membranes manufactured recently, and gather baseline rejection data on selected solutes for analyzing any changes in selectivity with ionic strength.

To characterize membrane selectivity, we performed dead-end stirred cell filtration experiments with a series of small organic molecules, and measured solute rejection through our amphiphilic copolymer based TFC membrane. Solute rejection, previously defined by Equation 2, is a measure of the membrane’s ability to separate the target solute from the feed solution during filtration. Solute rejection was determined by measuring the filtrate absorbance using ultraviolet-visible spectrophotometry (UV/Vis) at the maximum absorbance wavelength of each solute. The concentration of the filtrate was made by correlating the measured filtrate absorbance to a calibrated absorbance-concentration curve, following the Beer-Lambert law. PTFEMA-*r*-SBMA was selected as the copolymer primarily used in this study, because TFC membranes coated with this copolymer exhibited the highest water permeance. We selected negatively charged and neutral dyes because they are rigid molecules with sizes comparable to the measured domain size of  $\sim 1 \text{ nm}$ . Molecular diameters were calculated by determining the molecular volume of the solute using Molecular Modeling Pro (ChemSW) and calculating the diameter of a sphere of equivalent volume<sup>3,4,6</sup> (Table 1).

Table 1: Chemical name, size, charge per unit, and maximum absorbance wavelength of small molecule probes used in filtration experiments.

Chemical Name	Calculated Diameter (Å)	Net Charge	$\lambda_{\text{max}}$ (nm)
Ethyl Orange	8.23	−1	472
Acid Blue 45	8.41	−2	596
Chicago Sky Blue 6B	8.79	−4	593
Acid Red 1	8.80	−2	532
Brilliant Blue R	11.08	−1	553
Riboflavin (Vitamin B2)	8.49	0	445
Vitamin B12	13.14	0	361

Figure 11 shows the relationship between solute rejection and calculated dye diameter of PTFEMA-*r*-SBMA coated TFC membrane of negatively charged and neutral dyes. The data indicates that our TFC membranes exhibit a size-based cut-off around  $9\text{--}10 \text{ Å}$  for anionic dyes. The rejection of both neutral dyes appears to be lower. The selectivity of these membranes should not be affected by solute charge: the selective layer of those membranes consists of our amphiphilic copolymers, which are overall electrostatically neutral. One possible cause of the difference in solute rejection between negatively charged dyes and neutral dyes

is the effect of hydration shells. Negatively charged dyes in their aqueous solutions have larger hydration shells. This results in a positive deviation of the actual effective solute diameter from the calculated value for negatively charged solutes. Furthermore, multiple molecules of the same dye can also form larger dye aggregates through different types of intermolecular forces, thereby resulting in further increases effective diameter of the dye from the calculated value. Finally, past results obtained from membranes with PTFEMA-*r*-SBMA selective layers have shown higher rejection values for Vitamin B12, the larger neutral solute (90–95 % in other studies, vs. 80 % in this study). We are currently seeking to identify the cause of this difference. Preliminary work by Will Lind and Prity Bengani indicates that Vitamin B12 rejection is especially sensitive to changes in casting conditions. In any case, the measured rejections for this membrane swatch were used as the comparison point for successive experiments.

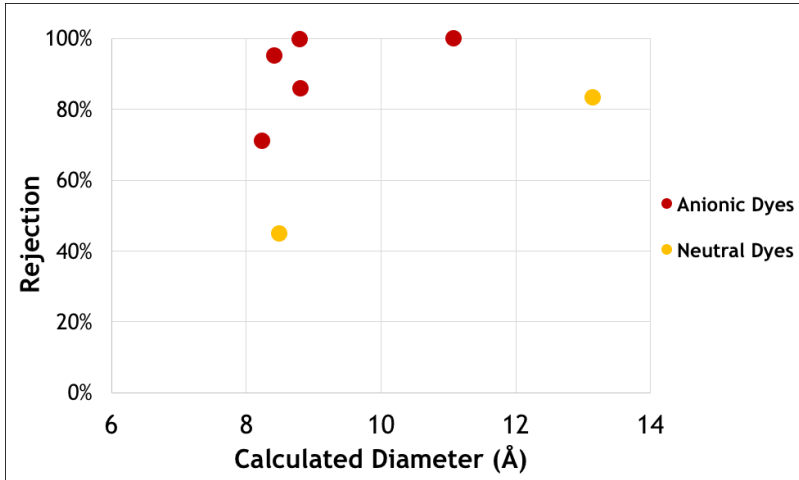


Figure 11: Rejection of dyes with overall anionic or neutral charge by PTFEMA-*r*-SBMA TFC membranes. The membrane shows a sharp size-based cut-off at 9–10 Å (0.9–1 nm) when using negatively charged dyes.

### 3.3.3 Change in permeance and rejection with varying feed ionic strength

#### 3.3.3.1 Effect of feed ionic strength on membrane permeance

In order to investigate how feed ionic strength may affect the performance of our zwitterionic amphiphilic copolymer TFC membranes during filtration, filtration experiments were performed by feeding  $\text{NaCl}(aq)$  of varying ionic strength through our membranes. While polyelectrolytes are known to swell and undergo conformation changes under higher ionic strength due to anti-polyelectrolyte effect, the water uptake measurements indicated that the hydrophobic glassy domains of PTFEMA prevent the deformation of the zwitterionic “nanochannels”, thus curtailing any changes in effective pore size and permeability. Based on this, we hypothesize that the performance of our amphiphilic zwitterionic membranes will remain relatively stable against changes in feed ionic strength. The zwitterionic domains of our copolymer are tightly connected to PTFEMA domains by covalent bonds, which decreases the copolymer’s tendency to undergo overall conformation change in response to ionic strength in solution during filtration.

Figure 12a shows that a significant drop in the permeance of PTFEMA-*r*-SBMA TFC membrane is not observed when filtering  $\text{NaCl}$  aqueous solutions with ionic strength as high as 1 M. The slight decrease in membrane permeance at high ionic strength (*i.e.* 1 M) may be due to the progressive deposition of the organic dye filtered in between water and salt solution runs to track membrane selectivity. This was noted by the membrane becoming tinted blue (the color of the dye used) as the experiment progressed. As the solubility of most organic dyes depends on salinity, this may lead to higher potential for crystallization on the membrane surface, where the local concentration is higher due to concentration polarization.

To check reproducibility and reversibility of the change, filtration experiments were run on another swatch of the TFC membranes where the concentration of  $\text{NaCl}$  in feed solutions was first increased from 0 to 1 M and then decreased back to 0 in approximately exponential increments. Membrane permeance results in Figure 12b also suggest that our copolymer TFC membranes can maintain consistently steady water



permeances against variations in feed ionic strength conditions over a wide range. A similar behavior was observed for the PTFEMA-*r*-MPC membranes (Figure 12c). Both amphiphilic copolymers are structurally similar, so they are expected to respond to changes in feed ionic strength similarly.

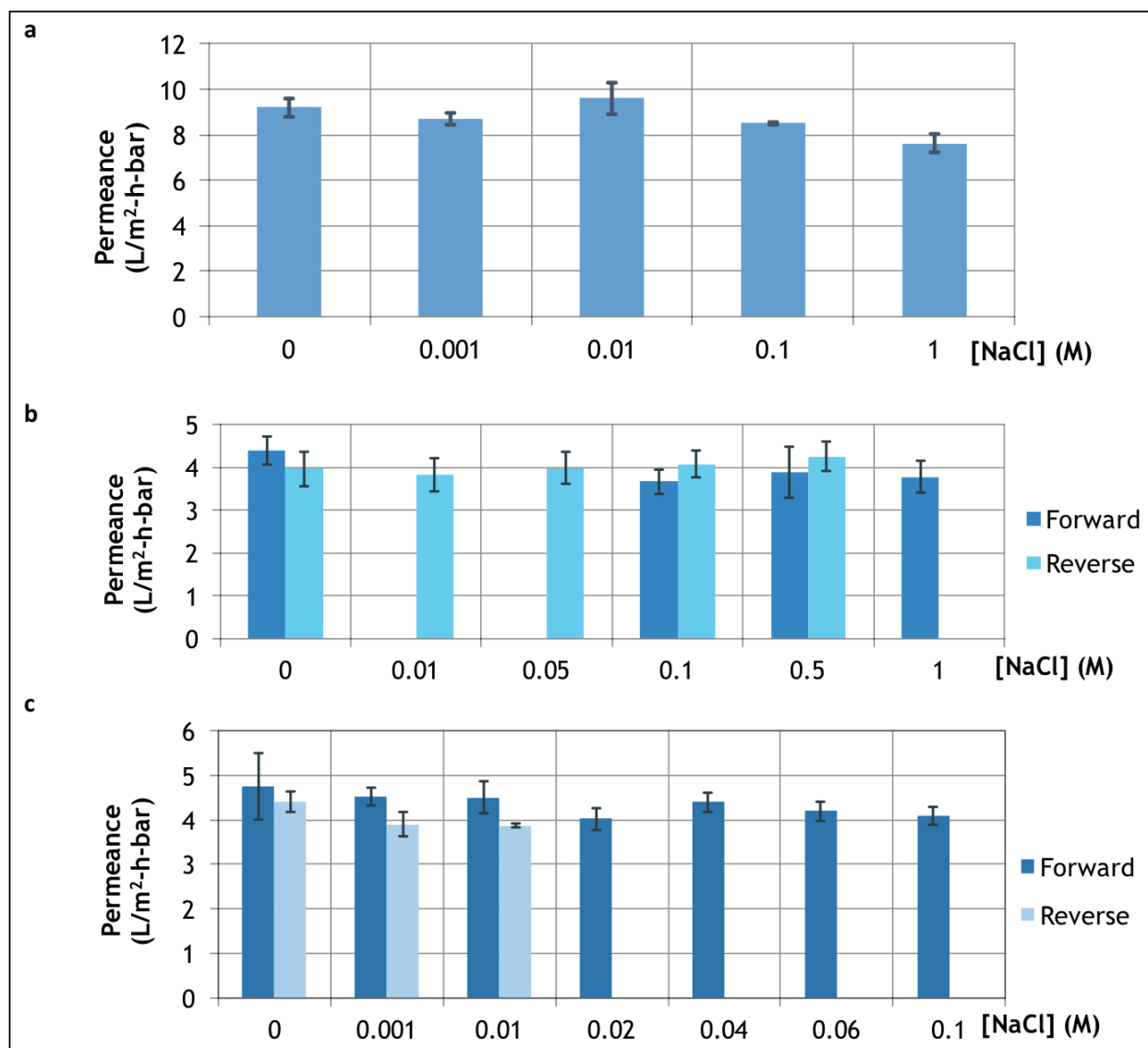


Figure 12: Water permeances of zwitterionic copolymer membranes under varying feed ionic strength. Two different swatches of PTFEMA-*r*-SBMA membranes were used in (a) and (b), while a swatch of PTFEMA-*r*-MPC membrane was used in (c). In (b) and (c), feed ionic strength was first increased then decreased during each set of filtration experiments. No significant drop in water permeance was observed in these experiments.

### 3.3.3.2 Effect of feed ionic strength on solute rejection

In order to investigate the effect of feed ionic strength on membrane rejection, copolymer TFC membranes were used to filter aqueous dye solutions containing different concentrations of added sodium chloride. A negatively charged dye, Chicago Sky Blue 6B (CSB), and a neutral dye, Vitamin B12 (VB12), were selected for the experiments because both dyes have calculated molecular diameters similar to the measured membrane pore-size cut-off, and the rejections of both solutes were high when filtered in solutions with zero ionic strength (98 % and  $75 \pm 5$  % for CSB and VB12 respectively). Based on our hypothesis, our copolymer TFC membranes should not exhibit significant changes in solute rejection in response to higher ionic strength in feed solution, because PTFEMA domains of the copolymer are rigid and restrict the movement and conformation change of the zwitterionic domains. Solute rejection results summarized in Figure 13 further verifies our hypothesis. Rejection values are stable, with no significant change in a range of feed ionic strength up to 1 M NaCl(aq). Figure 13a and Figure 13b illustrate that the rejection behavior of PTFEMA-*r*-SBMA TFC membrane is stable under varying ionic strength conditions for both the negatively charged dye CSB and neutral dye VB12.

Similar trends were also found for the solute rejection of PTFEMA-*r*-MPC TFC membranes under different ionic strength (Figure 13c). While the rejection of CSB, the anionic dye, decreased slightly with increasing feed ionic strength, this observation is more likely attributed to the ionic strength (polyelectrolyte) effect on the hydration shell of the charged solute CSB. Since CSB carries four negative charges per molecule, electrostatic interaction with dissolved cations such as  $\text{Na}^+$  (aq) is favored than charge-dipole interaction with water molecules in solutions with high ionic strength. Therefore, a solution with high ionic strength decreases the shielding effect of water on charged dye molecules, reduces the radius of their hydration shells, and their effective molecular sizes in solution.<sup>1</sup> The observation of reduced rejection at high feed ionic strength is not seen during filtration of neutral dyes such as VB12 (Figure 13b). Preliminary data also suggest that PTFEMA-*r*-MPC membranes exhibit a lack of response in VB12 rejection under varying ionic strength.

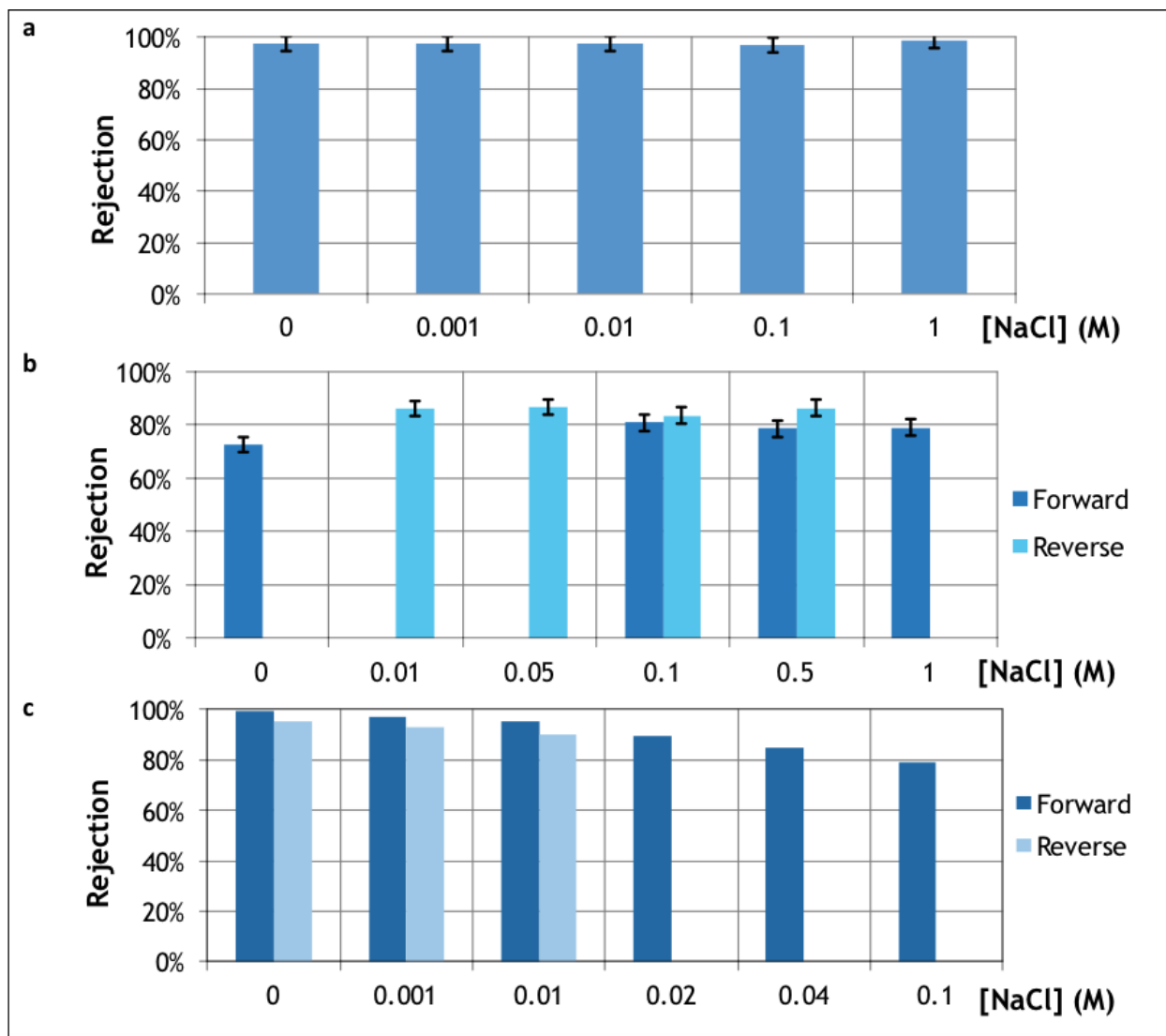


Figure 13: Solute rejection values of zwitterionic copolymer membranes under varying feed ionic strength, when filtering aqueous solutions of various solutes. The following combinations of copolymer and solutes are chosen for these experiments: (a) PTFEMA-*r*-SBMA membrane with Chicago Sky Blue, an anionic dye; (b) the same swatch of PTFEMA-*r*-SBMA membrane with Vitamin B12, a neutral dye; (c) PTFEMA-*r*-MPC membrane with Chicago Sky Blue.

### 3.4 Tuning membrane properties by annealing in aqueous solutions of varying ionic strength

Our first set of results indicate that the rigidity of hydrophobic domains of amphiphilic copolymers restrict the mobility of zwitterionic domains to rearrange spatially at room temperature in response to changes in ionic strength. As a result, these amphiphilic copolymer membranes do not exhibit response to varying ionic strength in feed during filtration. However, results from water uptake experiments (Figure 5) show that our amphiphilic copolymer had higher water uptake levels at a higher temperature of 50 °C. This suggests that the zwitterionic domains of the copolymer may be able to undergo rearrangement at higher temperatures. Therefore, we decided to anneal our membranes in saline aqueous solutions at higher temperatures for extended periods of time, to improve polymer mobility and enable the membrane selective layers to change in response to solutions of higher ionic strength. We hypothesize that when these membranes are kept in aqueous solutions of higher ionic strength at higher temperatures, the polymer can re-arrange to accommodate the increased hydrophilicity of the zwitterionic groups, and that this would reflect onto changes in membrane performance parameters (*e.g.* increased permeance and pore size).

### 3.4.1 Changes in permeance and pore size upon annealing in deionized water

To study the baseline changes in membrane performance upon annealing in aqueous solutions, we first annealed PTFEMA-*r*-SBMA TFC membranes in deionized water. This is because annealing can change several properties of membranes. It would enable the membrane selective layer to find its optimal, thermodynamically favored configuration when exposed to aqueous solution. This may include increased surface hydrophilicity and decreased surface roughness. Upon heating, the support membrane may also shrink, though the base membrane used here is rated for use at up to 60 °C. Therefore, this test will enable us to differentiate the effect of annealing from the effect of ionic strength.

Figure 14 compares the permeance and solute rejection of PTFEMA-*r*-SBMA membranes before and after annealing in deionized water. We found that annealing the membrane in deionized water resulted in a two-fold increase in membrane permeance. This is likely because the hydrophobic and zwitterionic domains of the amphiphilic copolymer experienced spatial rearrangement after membrane annealing. The rejections of negatively charged dyes were similar before and after membrane annealing in deionized water. The rejection of the neutrally charged dye Vitamin B12 decreased from 80 % to 60 % after membrane annealing in deionized water, although this decrease in solute rejection could only correspond to a small change to the “S-shaped” membrane selectivity curve. Neutrally charged molecules like Vitamin B12 have smaller hydration shells in aqueous solutions than negatively charged molecules due to solute-water interactions. Our method of calculating solute sizes does not account for the hydration shell. So the effective sizes of anionic dyes are likely more significantly under-estimated than those of neutral dyes like Vitamin B12. This may place Vitamin B12 at the high-slope region of a rejection vs. size curve, with high sensitivity to small variations in pore size. Therefore, the rejection change may arise from only a small shift in effective domain size, or even just be due to sample-to-sample variation. To better understand if annealing in deionized water leads to true changes in zwitterionic domain size, we need to perform further tests such as transmission electron microscopy imaging of an annealed zwitterionic amphiphilic copolymer sample.

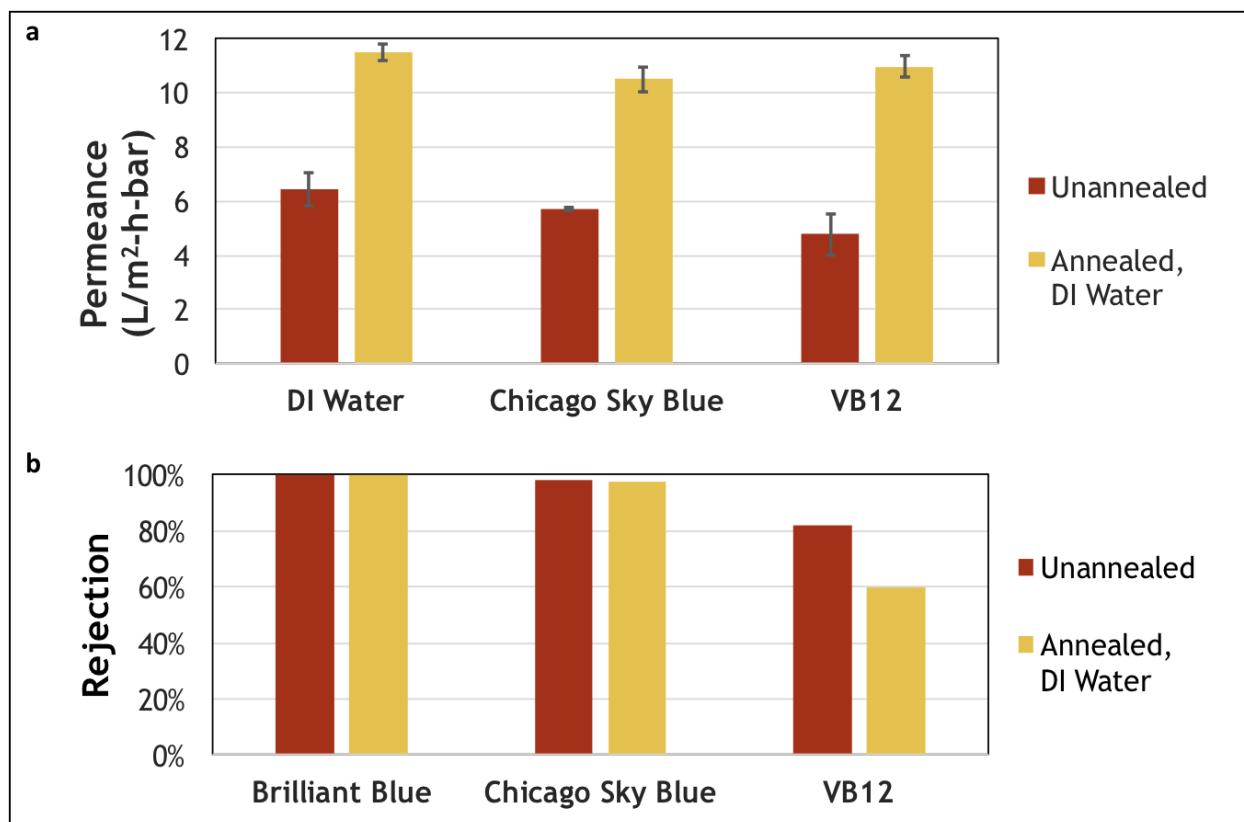


Figure 14: Water permeance (a) and solute rejection (b) of a PTFEMA-*r*-SBMA membrane before and after annealing in deionized water.

### 3.4.2 Effect of annealing in aqueous solution with high ionic strength

Based on results indicating membrane annealing in deionized water can improve polymer mobility, we annealed the same membrane swatch in aqueous solutions with higher ionic strength and characterized changes in membrane permeance and rejection. At increased temperatures, the polymer chain mobility increases, especially for the PTFEMA domains. The rearrangement and swelling of the zwitterionic domains of the copolymer may also potentially change the micro-phase separated structure of our amphiphilic copolymer, thereby influencing the effective pore size of our copolymer membranes. It may also alter the surface hydrophilicity, and the number of “nanochannels” open to water access on the membrane surface. These would lead to higher membrane permeance. Thus, annealing may enable us to better observe the anti-polyelectrolyte effect.

The water permeance of the PTFEMA-*r*-SBMA membrane is greatly improved when it is annealed in solutions with higher ionic strength (Figure 15). These results match our hypothesis that our amphiphilic copolymers experienced higher hydration and swelling in solutions of higher ionic strength during membrane annealing due to the anti-polyelectrolyte effect on zwitterions. We tested the reversibility of these changes by annealing the membrane swatch which was previously annealed in 0.1 M and 0.5 M NaCl(*aq*) in deionized water again. The permeance decreased, though not to the level observed after the initial annealing in deionized water. These results suggest that it is possible to partially reversibly tune membrane permeance by both membrane annealing and varying the ionic strength of the membrane annealing solution.

The increased response of amphiphilic copolymers to changes in ionic strength during membrane annealing also resulted in a possible small increase in the membrane’s effective pore size. Figure 16 shows changes in solute rejection of PTFEMA-*r*-SBMA membranes before and after annealing in aqueous solutions of varying ionic strength. All experiments were performed sequentially on the same membrane swatch, to minimize sample-to-sample variations. Based on the solute rejection results of both anionic and neutrally charged dyes over a range of calculated molecular diameters, the effective pore size of PTFEMA-*r*-SBMA membranes seemed to have slightly increased after membranes were annealed in solutions with higher ionic strength. Even though solute rejection did not significantly change for anionic dyes with calculated diameters greater than 8.79 Å, a 10–20 % decrease in solute rejections of smaller anionic dyes such as Ethyl Orange and Acid Blue 45 were observed. This corresponds to a small increase of the membrane’s effective pore size cut-off based on the “S-shaped” membrane selectivity curve. However, more experiments are needed to better understand if these changes are statistically significant, and to determine if any pore size change is significant enough to affect membrane performance in a true application. The only large change in rejection is that of Vitamin B12, from ~80 % before membrane annealing to ~30 % after membrane annealing in 0.5 M NaCl(*aq*). A similar, though slightly smaller, drop in VB12 rejection was also observed upon deionized water annealing. The exact cause of this significant decrease in VB12 rejection is still under investigation.

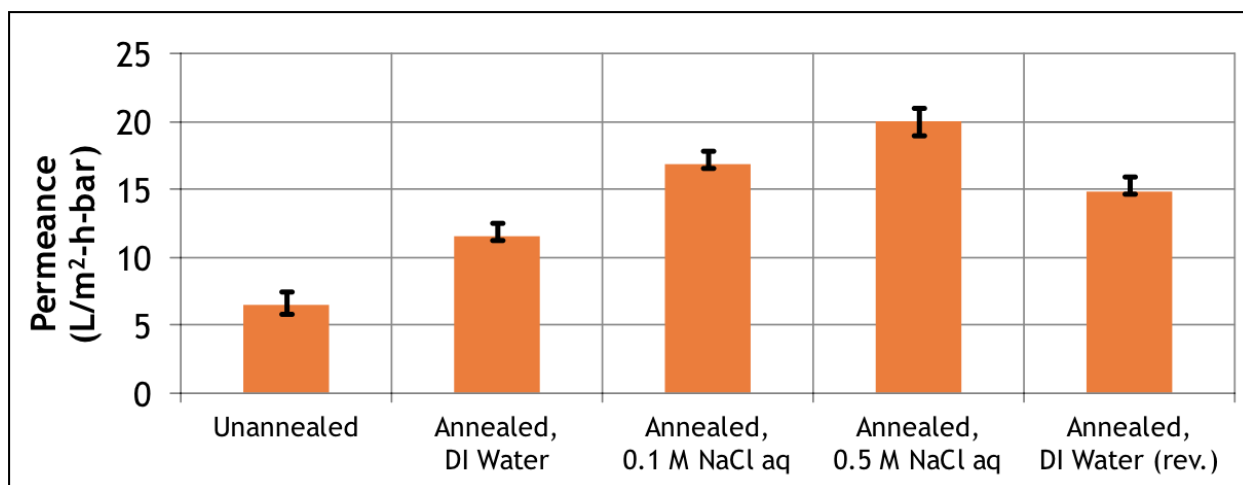


Figure 15: Water permeance values of a PTFEMA-*r*-SBMA TFC membrane before and after annealing in aqueous solutions of varying ionic strength when filtering deionized water through the membrane.

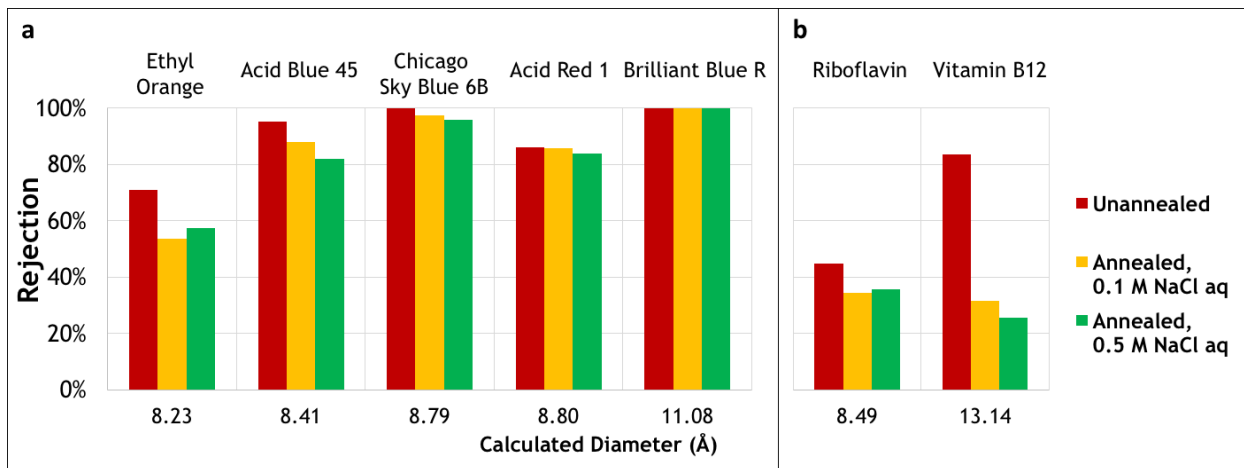


Figure 16: Solute rejection values of a PTFEMA-*r*-SBMA TFC membrane before and after annealing in aqueous solutions of varying ionic strength when filtering deionized water through the membrane. Both negatively charged solutes (a) and overall neutral solutes (b) are used for this experiment.

## 4 Conclusion and Future Work

We have found that this class of amphiphilic zwitterionic copolymer TFC membranes can maintain stable water permeances and solute rejection over a wide range of feed ionic strength, up to 1 M NaCl(*aq*). The rigid hydrophobic domains in the copolymer have low levels of mobility, restrict the movement of the hydrophilic zwitterionic domains, hence resulting in a lack of membrane response to feed ionic strength. This is advantageous for their use in various industrial separation processes with varying levels of feed salinity. In addition, annealing these amphiphilic zwitterionic copolymer membranes in different ionic strength solutions can further significantly boost membrane permeance, and only cause minor effects on membrane rejection except for uncharged solutes. Annealing at a higher temperature can enhance the movement of the hydrophobic domains and allow a more favorable rearrangement of the overall zwitterionic copolymer configuration. Annealing these membranes in moderate to high ionic strength solutions such as 0.1–0.5 M NaCl(*aq*) can lead up to a three-fold increase in membrane permeance with a very small increase in pore size cut-off. Therefore, annealing can be advantageous for high-throughput filtration applications, such as textile wastewater treatment, to dramatically improve the performance of these membranes.

Future work is needed to correlate and quantify how different ionic strength can change the membrane performance and pore-size cut-off during membrane annealing. Future work will include additional filtration experiments of annealed membranes using multiple membrane swatches and more dyes of different size and charge. Material characterization techniques such as TEM, Wide-Angle X-ray Scattering (WAXS) and Small-Angle X-ray Scattering (SAXS) can also be used to study changes to the copolymer domain size and resulting membrane “channel size” when these membranes are annealed in different ionic strength solutions. Contact angle measurements and Atomic-Force Microscopy (AFM) can be further used to study the effects of annealing on the surface hydrophility and morphologies of these membranes.

## 5 Acknowledgments

The author would like to sincerely thank Prof. Ayşe Asatekin and Prity Bengani for their tremendous support, mentoring and guidance throughout this work. The author also thanks members of Asatekin Lab for useful discussions and kind experimental advice. NMR spectroscopy was performed courtesy of Dr. David Wilbur and the Tufts University Department of Chemistry. The author thanks Dr. Anne Moore for organizing the Tufts Summer Scholars program, which supported preliminary studies of this work. The author acknowledges support from NSF Grant #CBET-1437772 and #CAREER-1553661, Tufts University Department of Chemical and Biological Engineering, the Tufts Summer Scholars program, and the Tufts Undergraduate Research Fund.

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