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Antifouling Ultrafiltration Membranes with Retained Pore Size by Controlled Deposition of Zwitterionic Polymers and Poly(ethylene glycol)

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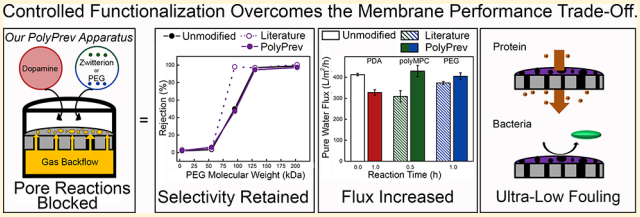
Supporting Information

ABSTRACT: We demonstrate antifouling ultrafiltration membranes with retained selectivity and pure water flux through the controlled deposition of zwitterionic polymers and poly(ethylene glycol) (PEG). Molecules for polymerization were immobilized on the membrane's surface yet prevented from attaching to the membrane's pores due to a backflow of nitrogen (N_2) gas achieved using an in-house constructed apparatus that we named the polymer prevention apparatus, or "PolyPrev". First, the operating parameters of the PolyPrev were optimized by investigating the polymerization of dopamine, which was selected due to its versatility in enabling further chemical reactions, published metrics for comparison, and its oxidative self-polymerization. Membrane characterization revealed that the polydopamine-modified membranes exhibited enhanced hydrophilicity; moreover, their size selectivity and pure water flux were statistically the same as those of the unmodified membranes. Because it is well documented that polydopamine coatings do not provide a long-lasting antifouling activity, poly(2-methacryloyloxyethyl phosphorylcholine) (polyMPC, M_n = 30 kDa) and succinimidyl-carboxymethyl-ester-terminated PEG (M_n = 40 kDa) were codeposited while dopamine was polymerizing to generate antifouling membranes. Statistically, the molecular-weight cutoff of the polyMPC- and PEG-functionalized membranes synthesized in the PolyPrev was equivalent to that of the unmodified membranes, and the pure water flux of the PEG membranes was equivalent to that of the unmodified membranes. Notably, membranes prepared in the PolyPrev with polyMPC and PEG decreased bovine serum albumin fouling and *Escherichia coli* attachment. This study demonstrates that by restricting antifouling chemistries from attaching within the pores of membranes, we can generate high-performance, antifouling membranes appropriate for a wide range of water treatment applications without compromising intrinsic transport properties.



INTRODUCTION

The World Health Organization and World Economic Forum have recognized the ever-growing water crisis as a leading risk because more than 10% of the world's population lacks access to cleaned drinking water.[1] Furthermore, the improved drinking water that ∼1.7 billion people have access to still suffers from poor microbial quality and sanitary risks, leading to the death of a child every 19 s.[2] Membrane-based water purification is an accessible technology that provides a solution to this global issue.[3] Specifically, pressure-driven separation processes using ultrafiltration membranes can remove the biological species (bacteria and viruses) that cause waterborne illnesses with low energy requirements. Unfortunately, when ultrafiltration membranes become fouled they need to be cleaned or replaced, which increases their operation cost and ultimately limits the production of clean drinking water.[4]

To delay membrane fouling and prolong membrane lifetime, researchers have modified the surface of ultrafiltration membranes with antifouling polymers.[5] A variety of chemistries, including catechol, amine, imine, click chemistry, and atom transfer radical polymerization (ATRP), have been used to attach antifouling polymers (i.e., poly(ethylene glycol) (PEG) or polymer zwitterions) to membranes. Unfortunately, all functionalized membranes exhibit decreased function, such as reduced flux and increased size selectivity.[6−11] Furthermore, complex processes, such as chemical vapor deposition and atmospheric plasma-induced surface copolymerization, were developed to improve the controllability, coating quality, and pH stability of polymer zwitterion-modified membranes.[12−14] However, these surface modifications decreased the molecular-weight cutoff (MWCO) of the membranes, turning them into nanofiltration membranes.[8,15,16] Using ATRP, Davenport et al. grafted zwitterionic polymer brushes onto an ultrafiltration membrane, which successfully retained membrane flux but

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unfortunately, still decreased the membrane's pore size and increased size selectivity.[17]

A facile approach to modifying the surface of a membrane involves the formation of an ultrathin, self-adhering polydopamine (PDA) layer, which occurs under aerobic and alkaline conditions.[18−23] Using the setup shown in Figure 1A,

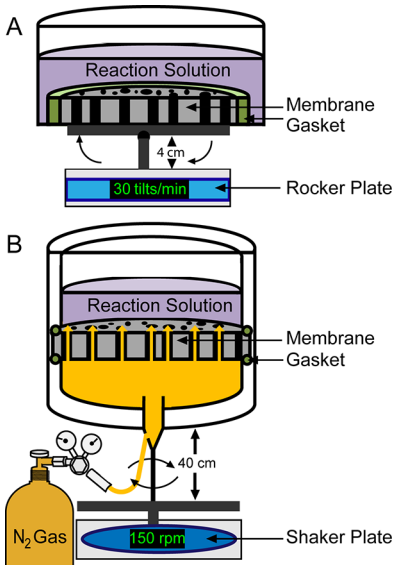

Figure 1. Schematic of methods used to modify the surface of membranes. (A) In the literature method,[26,30] the membrane was submerged in a reaction solution. (B) In the polymer prevention (PolyPrev) apparatus, nitrogen (N_2) gas was backflowed into the support side of the membrane to prevent chemical reactions from occurring in the pores of the membrane.

McCloskey et al. demonstrated that PDA-modified microfiltration membranes improved oil emulsion filtration flux and the resistance to protein adhesion by 20 and 99%, respectively. However, the PDA layer also coated the inside of the membrane's pores, thus detrimentally impacting performance. When ultrafiltration membranes were PDA-modified using a 1.0 h reaction time, they exhibited a 30% decrease in pure water flux.[24] Despite additional process improvements, including controlling dopamine polymerization[25,26] and implementing industrially relevant membrane modules,[27] all demonstrated PDA coatings reduced membrane flux and altered size selectivity.[28−30] Moreover, long-term testing of PDA-modified membranes demonstrated their propensity to foul,[21,31] making the inclusion of antifouling agents a necessity to improve the membrane's lifetime.

Conveniently, PDA offers many functional groups, such as catechol, amine, and imine, which can be used to immobilize antibacterial agents or antifouling polymers.[8−11,18,33−35] For example, Tang et al. formed antimicrobial silver nanoparticles in situ on PDA-modified microfiltration membranes that reduced *E. coli* cell growth by 99% but unfortunately also increased their hydraulic resistance by two to three times.[36] Reverse addition−fragmentation chain transfer (RAFT) copolymerization, ATRP, and click chemistry were used to attach polymer zwitterions to PDA-modified membranes that decreased the attachment of proteins and bacteria but also decreased water flux.[37,38] Li et al. grafted PEG to PDA-modified ultrafiltration membranes, which successfully increased their resistance to proteins but led to a 65% reduction in pure water flux and extreme pore narrowing.[39] Researchers have also further modified membranes with PDA by grafting PEG monoamine[40] and methyl-terminated PEG amine,[32] which successfully decreased protein fouling but also reduced pure water flux by 60%.

Several research groups have codeposited dopamine with other molecules—dextran, heparin, hyaluronic acid, PEG, and zwitterions—to create antifouling membranes using a one-step process.[32,41−46,51,56] For example, Kirschner et al. simultaneously deposited a poly(2-methacryloyloxyethyl phosphorylcholine) (polyMPC)−PEG copolymer with dopamine onto ultrafiltration membranes, which resulted in membranes with great fouling resistance but increased hydraulic resistance and a lowered nominal pore size.[48] We suggest that a new method toward facile and effective membrane surface modification that does not change size selectivity is needed.

Here we report a new method to modify the surface of ultrafiltration membranes that yields strong antifouling properties and a retained MWCO. Counter to all previously demonstrated systems, we prevent the attachment of polymers inside the membrane pores using an in-house constructed polymer prevention (PolyPrev) apparatus. As shown in Figure 1B and Figure S1, the PolyPrev apparatus features nitrogen (N_2) gas that backfills the pores (through the support side of the membrane) to create an inert physical barrier so that the oxidative polymerization of dopamine occurs only on the active side of the membrane. First, the effect of agitation method/rate, reaction time, and backflow pressure were tuned to maximize PDA-functionalized ultrafiltration membrane performance and to benchmark them against membranes prepared using the literature method. Next, high-molecular-weight antifouling polymers, including polyMPC and succinimidyl-carboxymethyl-ester-terminated PEG, were immobilized on the membrane using the PolyPrev apparatus to demonstrate the versatility and performance of the functionalized membranes.

EXPERIMENTAL SECTION

Materials and Chemicals. All materials were used as received unless otherwise stated. Dopamine hydrochloride (dopamine), succinimidyl-carboxymethyl-ester-terminated poly(ethylene glycol) (PEG, >95%, M_n = 40 kDa, PDI <1.10), bovine serum albumin (BSA, 66 kDa, heat shock fraction, >98%), Bradford reagent (1−1400 μg/mL), phosphate-buffered saline (PBS, 1× sterile biograde), Luria−Bertani broth (LB), sodium chloride (NaCl), M9 minimal salts (M9 media), D-(+)-glucose, and calcium chloride (anhydrous) were purchased from Sigma-Aldrich (St. Louis, MO). Tris(hydroxymethyl)aminomethane (tris), acetone (histological grade), sodium hydroxide (NaOH), ethanol (absolute anhydrous), and isopropyl alcohol (IPA, Certified ACS Plus) were purchased from Fisher Scientific (Pittsburgh, PA). Poly(2-methacryloyloxyethyl phosphorylcholine) (polyMPC, M_n = 30 kDa) was prepared according to a previously published method.[47] Hydroxy-terminated PEG (M_n = 4, 55, 95, 130, and 203 kDa) was purchased from Polymer Source (Quebec, Canada). Deionized (DI) water was obtained from a Barnstead Nanopure Infinity water purification system (Thermo Fisher Scientific, Waltham, MA).

Modification of Membranes Using the PolyPrev Apparatus. Flushed Biomax poly(ether sulfone) ultrafiltration membranes with a reported nominal molecular-weight limit of 100 kDa were acquired from EMD Millipore (Billerica, MA) and served as the control membrane in this work; they are referred to as unmodified membranes in the Results and Discussion. In the flushing procedure, membranes (10.2 cm diameter circles) were immersed in IPA for 0.5 h, rinsed three times with DI water, immersed in DI water for 0.5 h,

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and then rinsed three times with DI water.[49] An in-house polymer prevention chamber, "PolyPrev" (Figure 1B and Figure S1), was constructed to prevent polymers from attaching within the pores of the membranes. A membrane was loaded so that nitrogen (N_2) gas backflowed through the support side of the membrane. A polymer solution was added to the active side of the membrane and allowed to react for 0.5, 1.0, or 2.0 h under shaking agitation (0, 75, 100, and 150 rpm, MaxQ2000, Thermo Fisher Scientific), while a backflow of N_2 gas (0, 3, 5, and 10 psi) was provided. The polymer reaction solution was composed of either (I) polyMPC (M_n = 30 kDa, 2 g/L) or (II) succinimidyl-carboxymethyl-ester-terminated PEG (M_n = 40 kDa, 4 g/L) dissolved in 100 mL of 10 mM tris (pH 8.5) to which dopamine (2 g/L) was added. For PDA membranes (no polyMPC or PEG), 100 mL of tris and dissolved dopamine (2 g/L) was added to the active side of the membrane, while a backflow of N_2 gas (5 psi) was provided with an agitation rate of 150 rpm. In the Results and Discussion, b-polyMPC, b-PEG, and b-PDA membranes refer to the membranes that were surface functionalized with N_2 gas backflow. Membranes without N_2 backflow were fabricated in the PolyPrev apparatus; a nonporous polypropylene sheet (3.5 mil, HDX, Home Depot, Atlanta, GA) was placed under the membrane during the reaction process. Samples prepared in the PolyPrev (but without backflow) are named PDA, polyMPC, and PEG membranes throughout the Results and Discussion. A second control membrane was created in the PolyPrev with gas backflow for 1.0 h (without surface functionalization) and is referred to as b-unmodified membranes. All membranes were submerged in ethanol for 10 min, washed three times with DI water, submerged in DI water for 0.5 h washed three times with DI water and transferred to a new DI water bath for storage in the refrigerator until use.[50] Prior to evaluation, the membranes were acclimated to room temperature (23 ± 1°) by submerging them in DI water for 20 min.

Characterization of Functionalized Membranes. Digital photos were acquired using a Samsung Galaxy S7 Active camera. To determine the surface chemical composition, high-resolution X-ray photoelectron spectroscopy (XPS, Physical Electronics Quantum 2000 Microprobe, Physical Electronics, Chanhassen, MN) scans were obtained. A monochromatic Al X-ray instrument at 50 W was used with a spot area of 200, and the takeoff angle was set 45°.[51] Contact angle measurements were acquired using a home-built apparatus equipped with a Nikon D5100 digital camera with a 60 mm lens and 68 mm extension tube (Nikon, Melville, NY).[52] Data represent the average of four drops of water (4 μL) measured on eight different sample replicates. Micrographs were acquired using a Magellan 400 scanning electron microscope (SEM, FEI, Hillsboro, OR). A 208 HR sputter coater (Cressington Science Instruments, Watford, England) was used to coat samples with 3 nm of platinum. Average pore diameter distributions were determined by measuring 50 random pores from five micrographs using ImageJ1.47 software (National Institutes of Health, Bethesda, MD).

Performance of Functionalized Membranes. Pure water flux was evaluated in a 10 mL dead-end stirred cell (Sterlitech, Kent, WA) equipped with a circular acrylic spacer to create an active area of 3.8 cm^2 where DI water (1 L) was delivered from a pressure vessel at an applied pressure of 1 bar with a 600 rpm stir rate for 1 h. The permeate mass was recorded every 5 min using a balance (Symmetry, Cole Parmer, Vernon Hills, IL) connected to the Serial Port Monitor (Eltima, Frankfurt, Germany). Flux was calculated as the volume of water that permeated through the membrane as a function of membrane area and time. At least three membranes were evaluated, and membranes were considered compacted after 1.0 h because they displayed a flux change <5%.

Size selectivity was determined through MWCO experiments, as previously described.[32,49] PEG was used as a model molecule due to its high solubility in water, limited propensity to foul, and wide range of available molecular weights. Membranes (active area 0.72 cm^2) were compacted in the dead-end stirred cell with DI water (1 L) at an applied pressure of 1 bar with 600 rpm stir rate for 1.0 h. Individual PEG solutions were prepared with different molecular weights of PEG, including 4, 55, 95, 130, and 203 kDa. Each membrane was challenged with 5 g of an individual PEG solutions prepared at 2 g/L at 2 bar and a 600 rpm stir rate, and the permeate was collected. PEG concentrations were determined via a standard curve generated by high-performance liquid chromatography (HPLC, Agilent 1260, Lexington, MA) equipped with an Optilab T-rEX differential refractive index detector with Astra 6.1 software (Wyatt, Santa Barbara, CA). PEG rejection (%) was taken as one minus the concentration of PEG in the permeate solution divided by the concentration of PEG in the initial feed solution. By definition, the MWCO of a membrane is the lowest molecular weight of PEG at which the membrane exhibits a rejection of ∼90%.

Dynamic Protein Fouling of Functionalized Membranes. Dynamic fouling experiments were performed on the membranes used for pure water flux (active area of 3.8 cm^2) with the model protein BSA.[49,53] BSA (1 g/L) in PBS (11 mL, pH 7.4 to 7.6) was passed through a membrane in the dead-end stirred cell at an applied pressure of 2 bar with a 600 rpm stir rate while the permeate was collected and the flux rate was recorded. Directly after BSA filtration, membranes were rinsed with 5 mL of DI water, and the final pure water flux was measured. The flux recovery ratio (FRR) was calculated as the final pure water flux divided by the initial pure water flux of the membranes.

Bacterial Fouling of Functionalized Membranes. Bacteria antifouling tests were conducted as previously reported.[51] In brief, the model Gram-negative strain *Escherichia coli* K12 MG1655 (*E. coli*) was purchased from DSMZ (Leibniz-Institut, Germany) and contained a green fluorescent protein (GFP) plasmid. Membrane samples (0.95 cm diameter circles) were placed at the base of six-well plates (Fisher Scientific) to which 5 mL of M9 media with 100 μg/mL ampicillin was added. Internal controls (glass coverslips) were run in parallel (data not shown). *E. coli* was grown overnight in LB, washed, and resuspended in M9 media; each of the six wells was inoculated with 25 μL of resuspended *E. coli* (1.00×10^8 cells/mL) and placed in an incubator at 37 °C for 24 h. Membranes were removed from the six-well plates and lightly rinsed with PBS to remove loosely adherent bacteria. *E. coli* attachment was evaluated within a 366 964 μm^2 area using an Axio Imager A2M microscope (20× magnification, Zeiss, Thornwood, NY). The particle analysis function in ImageJ was used to calculate the bacteria colony area coverage (%) by analyzing five randomly acquired images over two parallel replicates on two different days.

Statistics. Significant differences between samples were determined with a two-sided unpaired Student's *t* test. The significance is denoted in the graphs using asterisks and defined in the figure captions.

RESULTS AND DISCUSSION

Optimized Agitation Rate and N_2 Backflow in the PolyPrev Apparatus. In previous reports, when researchers modified membrane surfaces, they also decreased their flux and likely their nominal pore diameter. To prevent reactions from occurring within the pores, we designed a polymer prevention "PolyPrev" apparatus (Figure 1B and Figure S1). The PolyPrev allows chemical reactions to occur on the active side of the membrane, and because of a backflow of nitrogen (N_2) gas, an inert physical barrier was created that blocked reactions from occurring inside the pores. To optimize the operating parameters of the PolyPrev, dopamine was selected due to its oxidative self-polymerization, published metrics for comparison, and versatility in enabling further chemical reactions.[26,29,32,45,50,54] Our first set of experiments reacted dopamine on the surface of the ultrafiltration membranes for 1.0 h and evaluated if agitation using a shaker plate (0, 75, 100, and 150 rpm) improved coating uniformity in comparison to common methods described in the literature (Figures S2 and S3 and Supplemental Methods). The fastest agitation, 150 rpm, created membranes with the most intense XPS peaks

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Table 1. Summary of the Elemental Analysis of the High-Resolution XPS That Provides Compositional Analysis of the Surface of the b-PDA and Unmodified Membranes as a Function of Reaction Time

membrane	reaction time (h)	C (%)	N (%)	O (%)	P (%)	S (%)
unmodified	0	73 ± 0.1	1.5 ± 0.3	20 ± 0	0.4 ± 0.4	5.5 ± 0.2
b-PDA	0.5	70 ± 0.5	3.5 ± 0.2	22 ± 0.1	0.2 ± 0.2	4.4 ± 0.4
b-PDA	1.0	68 ± 1.8	3.5 ± 0.1	24 ± 1.6	0 ± 0	4.4 ± 0.1
b-PDA	2.0	67 ± 1.0	5.7 ± 0.3	25 ± 0.9	0.1 ± 0.0	2.3 ± 0.6

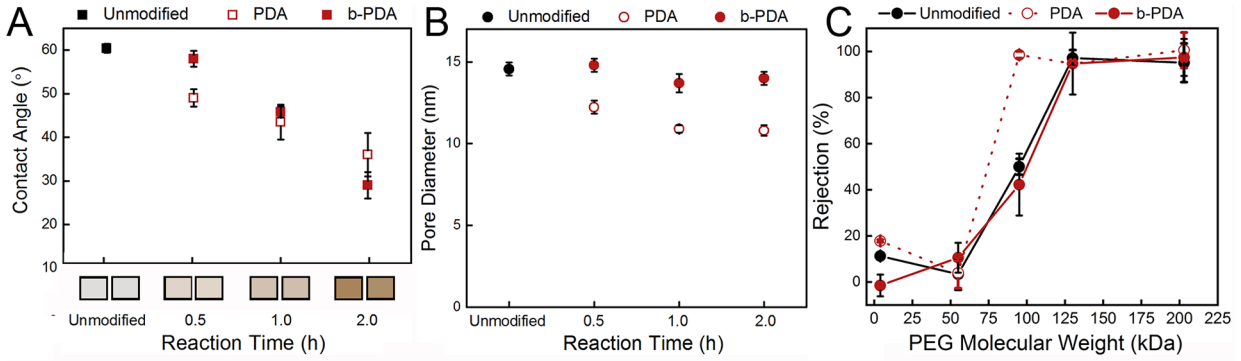

Figure 2. (A) Contact angle and digital images and (B) pore diameter of membranes as a function of dopamine reaction time. (C) Rejection as a function of PEG molecular weight. The solid and dashed lines are provided to guide the eye. (A–C) Membrane surface functionalization was conducted in the PolyPrev for the b-PDA membranes (with backflow at 5 psi) and PDA membranes (without backflow). Data on unmodified (control) membranes are also provided. Error bars denote standard error.

representative of PDA, and the membranes had a more uniform color than samples prepared with slower agitation or by following the literature methods. The static water contact angle decreased from 59 ± 1 to 41 ± 2° when the agitation was increased from 75 to 150 rpm, suggesting that more PDA was on the surface of the membrane, consistent with the literature.[29,55]

Next, we tested the pure water flux performance of membranes that were PDA functionalized using the PolyPrev as a function of backflow pressure; these samples are called b-PDA membranes. Back pressures in the PolyPrev were evaluated from 0 to 10 psi (Figure S3). The pure water flux increased with increasing pressure until a maximum value was obtained at 5 psi. These b-PDA membranes (prepared at 5 psi) had a pure water flux of 425 ± 15 L/m^2/h, which was statistically greater than that of the PDA membranes (those prepared in the PolyPrev without backflow, 328 ± 13 L/m^2/h) and statistically identical to that of the unmodified membrane (413 ± 6 L/m^2/h). Our b-PDA membranes also had the same flux as the control "literature" membranes that we reproduced in-house and a higher flux than the control "inverted literature" samples (Figure S4, Supplemental Methods).

Control membranes that were placed in the PolyPrev and exposed to N_2 gas backflow (at 5 psi) without polymerization solution are called b-unmodified membranes. The b-unmodified membranes had the same pore diameter and pure water flux as the unmodified membranes, 383 ± 18 and 413 ± 6 L/m^2/h, respectively. Thus N_2 backflow did not alter the membranes. For the rest of the Results and Discussion, membranes functionalized in the PolyPrev apparatus were agitated at a rate of 150 rpm for proper solution mixing and had a N_2 backflow pressure of 5 psi to prevent pore reactions from occurring.

Characteristics of b-PDA Membranes Prepared in the PolyPrev Apparatus. Representative survey scans and high-resolution XPS spectra confirmed the presence of PDA on the b-PDA membranes. Nitrogen signals indicative of PDA were statistically lower for the unmodified membrane, whereas the b-PDA membranes, at all synthesis times, exhibited a strong nitrogen signal at 399 eV[24] (Table 1). The phosphorus signal for the control and b-PDA membranes was within the noise of the instrument. Notably, by functionalizing membranes in the PolyPrev with backflow, the brown color associated with dopamine polymerization was eliminated on the support side of the membrane. Digital images show that the support side of the membrane remained white, whereas SEM micrographs displayed the lack of PDA aggregates on the b-PDA membrane (Figure S5).

The effect of PDA surface modification on membrane hydrophilicity was determined using static water contact angle measurements (Figure 2A). The unmodified membranes had a contact angle of 60 ± 1°, consistent with literature on poly(ether sulfone) ultrafiltration membranes.[56] The contact angle of the b-PDA membranes that were surface modified for the shortest time (0.5 h) exhibited a statistically higher contact angle (58 ± 2°) than the PDA membranes (49 ± 2°). The higher contact angle for the b-PDA membranes may have been due to decreased PDA deposition, possibly due to the introduction of N_2. However, differences in the contact angles between synthesis methods (with and without backflow) disappeared at longer reaction times (1.0 and 2.0 h).

SEM micrographs (Figure S6) were analyzed to determine the average pore diameter of the b-PDA and PDA membranes (Figure 2B). Excitingly, for all reaction time, the average pore diameter of the b-PDA membranes was statistically the same as the unmodified membrane. PDA membranes (prepared without backflow) at all reaction times had an average pore diameter that was statistically smaller than the unmodified membranes, consistent with previous reports.[32] This suggests that the N_2 gas is indeed preventing the deposition of PDA inside of the pores and that a 1.0 h reaction time deposits a

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sufficient concentration of PDA to alter surface hydrophilicity; thus a 1.0 h reaction time was used for further investigations.

Performance of b-PDA Membranes Prepared in the PolyPrev Apparatus. Figure 2C shows that the b-PDA membranes had the same molecular-weight cutoff (MWCO) value as the unmodified membrane: >95 kDa, which is the value reported by Millipore.[57] The PDA membranes (without backflow) differ from this finding because they exhibited a MWCO of 95 kDa, similar to previous work that reported that PDA functionalization decreased the nominal pore size and increased membrane size selectivity.[29,32,50] Our retained size selectivity corroborates with our pore diameter analysis by further confirming the benefit of conducting PDA functionalization in the PolyPrev with backflow.

The pure water flux of b-PDA membranes as a function of dopamine reaction time (0.5, 1.0, and 2.0 h) is provided in Figure 3. After a reaction time of 0.5 h, the b-PDA membranes exhibited a statistically equivalent pure water flux to the unmodified membranes, likely due to the lower PDA deposition. Furthermore, after a 1.0 h reaction time, the b-PDA membranes had a pure water flux (425 ± 15 L/m^2/h), which was statistically greater than that of the PDA membranes (without backflow, 328 ± 13 L/m^2/h) and statistically equivalent to that of the unmodified membrane (413 ± 6.3 L/m^2/h). Limitations of conducting the reaction in the PolyPrev apparatus with these operation parameters (150 rpm, 5 psi) emerged when the membranes were surface functionalized for 2.0 h. Here the flux of b-PDA membranes was statistically equivalent to the flux of PDA membranes and therefore, statistically lower than that of the unmodified membranes. It is not surprising that the performance of the hydrated b-PDA membranes differed from that of the unmodified membranes despite their statistically equivalent average pore diameter because their pore sizes were measured using SEM, which requires using a dry sample under vacuum. Potentially, while testing, the hydrated PDA layer may have altered the water flux. These results demonstrate that the b-PDA membranes reacted for 1.0 h in the PolyPrev (with backflow) have a 30% improvement over membranes functionalized using the literature method;[32,30] we have uniquely retained the size selectivity of surface-functionalized membranes.

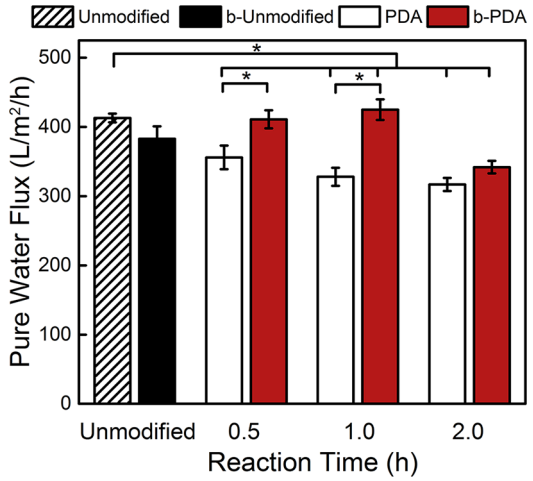

Figure 3. Pure water flux of membranes as a function of dopamine reaction time (0.5, 1.0, and 2.0 h). Error bars denote standard error, and one asterisk (*) denotes a $p \leq 0.05$ significance between samples.

Characteristics of b-polyMPC Membranes Prepared in the PolyPrev Apparatus. It is well documented that PDA coatings do not provide a long-lasting antifouling activity;[21,31] therefore, polyMPC was incorporated into the membrane coating as a function of reaction time using the PolyPrev. With SEM imaging, the b-polyMPC membranes had a smooth surface, which was visually the same as the PDA membranes (Figure S7) and similar to previous work that demonstrated that codeposition yields smooth coatings.[58] All of the b-polyMPC membranes displayed a characteristic phosphorus P_{2p} signal at 132.4 eV due to the presence of polyMPC (Figure 4A). The P_{2p} signal of the b-polyMPC membranes was weakest when the shortest reaction time was tested (0.5 h), suggesting that less polyMPC was on the surface, consistent with static water contact-angle measurements (Figure 4B). After longer reaction times of 1.0 and 2.0 h, the phosphorus signal and contact angle of the b-polyMPC membranes were statistically the same, suggesting that a 1.0 h reaction time is critical for achieving a successful membrane coating.

Statistically, the b-polyMPC membranes reacted for 0.5 and 1.0 h had the same average pore diameter as the unmodified membranes (Figure 4C). However, after a 2.0 h reaction time, the b-polyMPC membrane pore size decreased to 12.3 ± 0.3 nm, which is statistically smaller than the unmodified membranes. Therefore, we have demonstrated, for the first

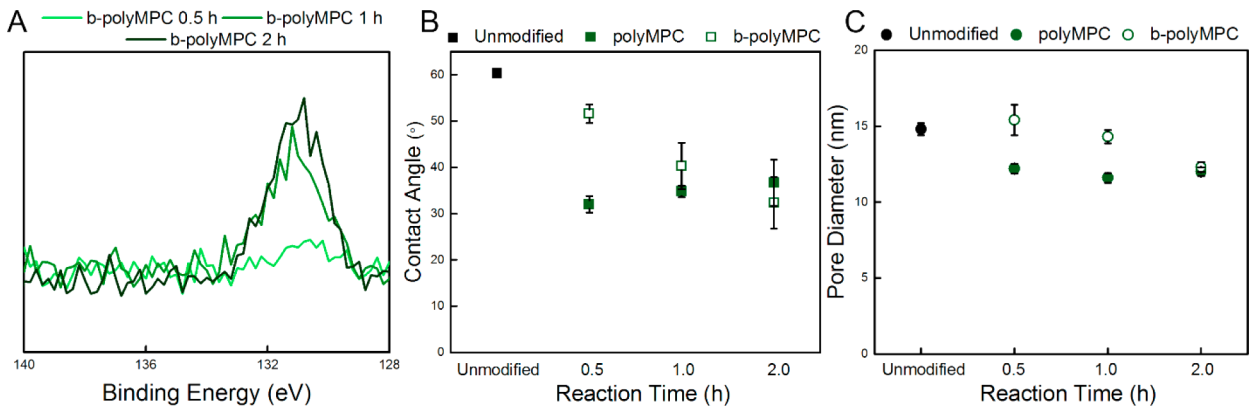

Figure 4. (A) High-resolution scans of P_{2p}, (B) contact angle, and (C) pore diameter as a function of reaction time for polyMPC-functionalized membranes. Error bars denote standard error.

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time, the ability to create membranes surface modified with polymers (~30 kDa) that do not alter pore diameter.

Performance of b-polyMPC Membranes Prepared in the PolyPrev Apparatus. The pure water flux of b-polyMPC membranes prepared with a 0.5 h reaction time was 430 ± 27 L/m^2/h, which was statistically the same as the unmodified membrane (Figure 5). Our retained flux is a great finding.

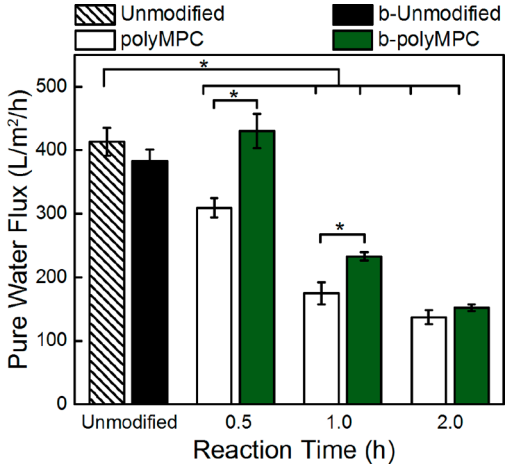

Figure 5. Pure water flux as a function of reaction time for membranes functionalized with polyMPC. Error bars denote standard error, and one asterisk (*) denotes a $p \leq 0.05$ significance between samples.

Previously, Kirschner et al. reported that to achieve a polyMPC-functionalized membrane with the same flux as a control membrane, they needed to account for pore narrowing by functionalizing a larger MWCO membrane.[48] Notably, the reaction time used in the Kirschner et al. study was also 0.5 h.

In general, we found that the pure water flux dramatically decreased for reaction times longer than 0.5 h. The b-polyMPC membranes reacted for 1.0 h had a statistically lower flux than the unmodified membranes, 232 ± 6.4 L/m^2/h, yet a statistically higher flux than the polyMPC membranes prepared without backflow. Increasing to a 2.0 h reaction time removed the benefit of backflow where the b-polyMPC and polyMPC membranes exhibited a statistically equivalent pure water flux, 152 ± 5 and 137 ± 11 L/m^2/h, respectively. This finding contrasts the b-PDA membranes whose pore diameter and flux were equivalent to the unmodified membrane at both 0.5 and 1.0 h reaction times; however, because of the larger size of the polyMPC polymer (30 kDa), our reported results are not surprising.

Optimizing b-PEG Membranes Prepared in the PolyPrev Apparatus. With the demonstrated success of immobilizing polyMPC, we explored the codeposition of PEG. As shown in Figure S8, when a 4 kDa hydroxyl-terminated PEG was codeposited with PDA without backflow for 1.0 h, the membrane's flux was statistically the same as that of the unmodified membranes. However, as the molecular weight of PEG increased, the flux decreased. As reported by McCloskey et al., highest MW PEGs immobilized on membranes better resist BSA adhesion.[32] Therefore, we aimed to incorporate a ~40 kDa PEG (similar size to the polyMPC) with minimal to no flux loss. We investigated a hydroxyl and a succinimidyl carboxymethyl ester PEG (Figures S7 and S8B). While both were immobilized on the membranes in the PolyPrev (without backflow), XPS suggested that a greater PEG immobilization was achieved using the succinimidyl carboxymethyl ester PEG (data not shown). Furthemore, the contact angles of the membranes prepared using succinimidyl carboxymethyl ester PEG in the PolyPrev with and without backflow were 35 ± 6 and 42 ± 14°, respectively, also suggesting that immobilization was successful once the polymer concentration was optimized (Figure S8C). Thus both PEG and polyMPC could be codeposited using dopamine to create antifouling membranes, as will be discussed in the next sections.

Performance of b-polyMPC and b-PEG Membranes Prepared in the PolyPrev Apparatus. Statistically, the b-polyMPC and b-PEG membranes exhibited the same rejection as the unmodified membrane, indicating an MWCO >95 kDa, Figure 6A. In contrast, the rejection of the polyMPC and PEG

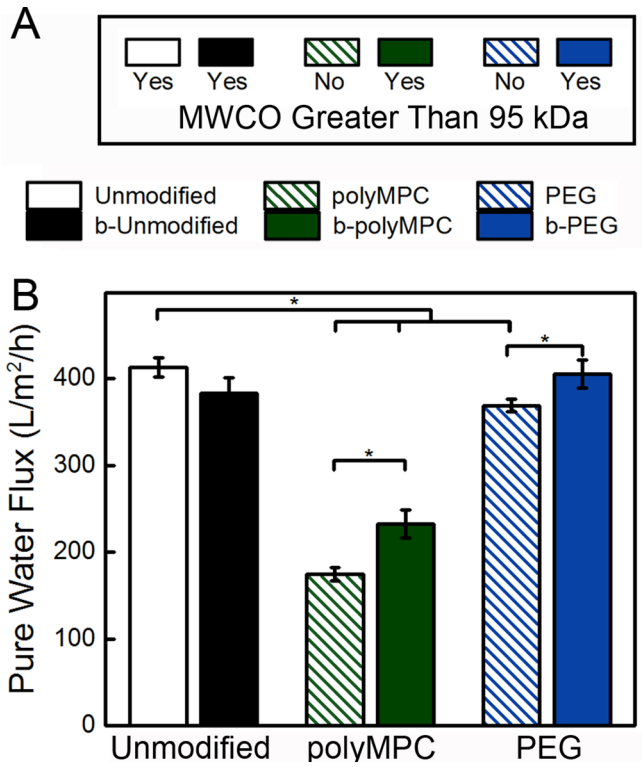

Figure 6. (A) MWCO and (B) pure water flux of polyMPC- and PEG-modified membranes fabricated using a reaction time 1.0 h. Error bars denote standard error and one asterisk (*) denotes $p \leq 0.05$ significance between samples. The legend applies to panels A and B.

membranes prepared without backflow exhibited a rejection greater than 90% of the 95 kDa PEG. This decreased MWCO corresponds well to previously reported codeposited results.[34,48] Therefore, we have demonstrated the ability to immobilize polymers (30 and 40 kDa) onto membranes with retained size selectivity.

After a 1.0 h reaction time, both the b-polyMPC and b-PEG membranes had a statistically greater pure water flux than the polyMPC and PEG membranes prepared without backflow (Figure 6B). While the flux of the b-polyMPC membranes was statistically less than that of the unmodified membranes, the b-PEG membrane flux (405 ± 16 L/m^2/h) was statistically equivalent to the unmodified membranes (413 ± 6.3 L/m^2/h). This is a noteworthy improvement from previous findings on membranes modified with PDA-grafted-PEG, which reported a 54% reduction in flux or required the transmembrane pressure

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to be increased from 20 to 40 psi to obtain similar flux values.[32,39] We successfully produced surface-modified membranes that have antifouling polymers with retained membrane size selectivity and high flux.

Protein Antifouling Activity of b-polyMPC and b-PEG Membranes Prepared in the PolyPrev Apparatus. In comparison with the unmodified and b-PDA membranes, the addition of the polyMPC or PEG (with or without backflow) led to a statistical increase in their FRR, which is a measure of the dynamic protein fouling resistance of a membrane (Figure 7). The FRR increased from 18 ± 1% for the PDA membranes

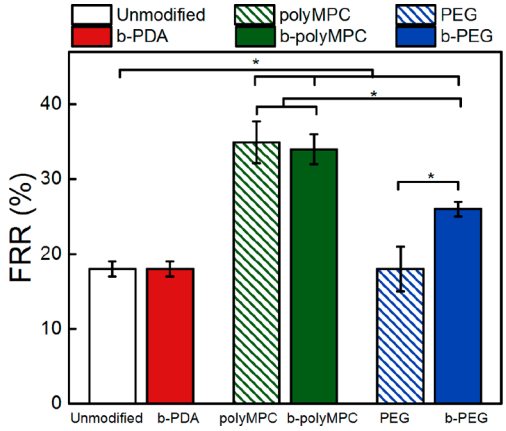

Figure 7. Flux recovery ratio (FRR) of b-PDA-, b-polyMPC-, and b-PEG-modified membranes. Error bars denote standard error, and one asterisk (*) denotes a $p \leq 0.05$ significance between samples.

to 34 ± 2 and 35 ± 3% for the b-polyMPC and the polyMPC membranes, respectively. Our improvement in FRR is greater than the previously reported FRR values acquired on zwitterion-functionalized membranes (prepared by codeposited with dopamine).[17] The FRR for the b-PEG membranes (26 ± 1%), was greater than the FRR of the PEG membranes (20 ± 3%), potentially due to the statistical increase in membrane flux (Figure 6B), which reduced protein-membrane contact time.[17] Therefore the FRR experiment, which exposed the membranes to foulants, the b-PEG membranes produced 40% more permeate (purified water) than the unmodified membrane. The polyMPC-functionalized membranes provided the best resistance to BSA fouling potentially due to the excellent hydration layer presented by the zwitterion.[59,60] However, protein resistance does not provide a full understanding of a membrane's antifouling properties; therefore, the membranes were challenged with bacteria.

Bacterial Antifouling Activity of b-polyMPC and b-PEG Membranes Prepared in the PolyPrev Apparatus. The decreased bacterial fouling due to the addition of PEG or polyMPC can be visually confirmed in the representative florescence micrographs (Figure 8). Statistically, less *E. coli* attached to the b-polyMPC and b-PEG than the unmodified membranes after a 24 h incubation period. The bacteria areal coverage on the membranes functionalized with PDA alone (b-PDA) was high, 83 ± 12% relative to the unmodified membrane, as expected based on previous reports.[21] The antifouling performance was markedly improved by the antifouling polymers; there was only 4 ± 2 and 6 ± 3% *E. coli* area coverage on the b-polyMPC and b-PEG membranes, respectively. The b-PEG membranes exhibited the same effective antifouling properties against *E. coli* as the b-polyMPC

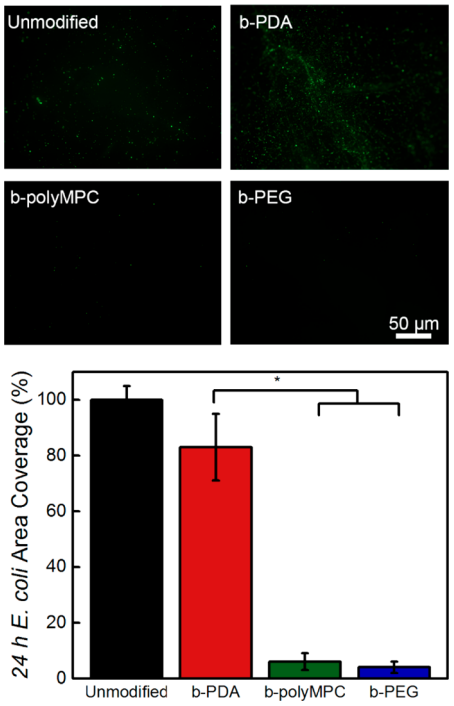

Figure 8. (Top) Representative fluorescence micrographs (366 964 μm^2) of *E. coli* attached after a 24 h incubation period on b-PDA-, b-polyMPC-, and b-PEG-modified membranes. (Bottom) Area coverage of *E. coli* after 24 h of incubation on polyMPC- and PEG-modified membranes. Error bars denote standard error, and one asterisk (*) denotes a $p \leq 0.01$ significance between samples.

membranes, similar to results published by Dang et al., who immobilized polyMPC/PEG on gold surfaces.[61]

The 20-fold improvement in bacterial antifouling capabilities was observed for the b-polyMPC and b-PEG membranes versus the unmodified membranes, which reiterates that a high quality coating was formed in the PolyPrev. Potentially, the reason that b-polyMPC and b-PEG membranes had a similar bacteria antifouling performance yet a different protein antifouling activity stems from the testing conditions. Whereas the protein fouling experiments are dynamic, the bacteria testing experiment is quiescent. Additionally, bacteria are much larger than the membrane's pores. Therefore, the bacteria should primarily interact with the membrane's surface, which we have successfully coated with antifouling polymers. Although, beyond the scope of this paper, we would expect that our zwitterion-functionalized membranes would continue to exhibit longer term resistance to bacterial adhesion, similar to the report by Miller et al.[21] Notably, further long-term studies should be conducted to quantify the long-term protein and bacterial resistance of antifouling membranes. In this study, we have demonstrated the preparation of polyMPC-functionalized membranes that have retained size selectivity, great membrane flux, and effective antifouling properties.

■ CONCLUSIONS

We have described the use of the "PolyPrev" apparatus as a facile method of providing gas backflow while fabricating antifouling membranes using polyMPC and PEG featuring PDA. Here PolyPrev operational parameters (backflow pressure, agitation, polymer concentration, reaction time, polymer chemistry, and polymer molecular weight) were explored to demonstrate the versatility of the apparatus to

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immobilize polymers to the surface of ultrafiltration membranes. XPS and contact-angle measurements confirmed that PDA, polyMPC, and PEG coatings were successfully deposited onto ultrafiltration membranes, whereas pore diameter analysis and MWCO experiments demonstrated that the PolyPrev enabled our modified membranes to retain the same selectivity as the unmodified membranes. Notably, the preservation of MWCO did not sacrifice the pure water flux, in which PDA-, polyMPC-, and PEG-functionalized membranes could all be fabricated to exhibit statistically identical flux as the unmodified membranes. Through BSA filtration experiments, we demonstrated a marked increase in protein antifouling properties of b-polyMPC membranes versus the polyMPC membranes (no backflow) and unmodified membranes. Additionally, the polyMPC and PEG membranes exhibited a high resistance to microbial attachment when challenged with *E. coli*. By improving upon commercially available ultrafiltration membranes, the PolyPrev apparatus offers a facile approach toward tailoring the surface functionality of membranes for water treatment and pharmaceutical purification.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b02184.

Figure S1. Digital images of the PolyPrev apparatus. Figure S2. Digital images of PDA-functionalized membranes. Figure S3. Effect of backflow pressure. Supplemental methods. Figure S4. Digital images, SEM micrographs, and flux values. Figure S5. Digital images and SEM. Figure S6. SEM micrographs. Figure S7. SEM micrographs. Figure S8. Pure water flux. (PDF)

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Notes

The authors declare no competing financial interest.

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