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Membrane Surface Modification Using Thiol-Containing Zwitterionic Polymers via Bioadhesive Polydopamine

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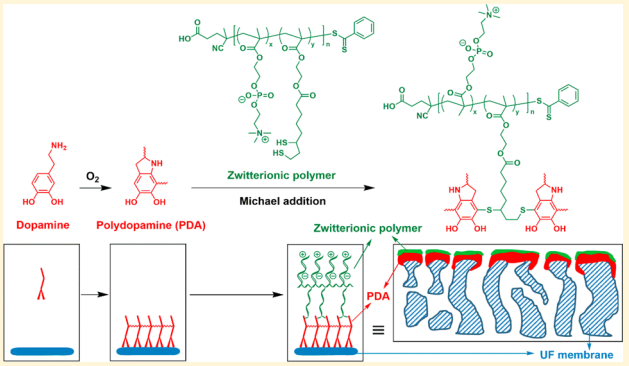
Supporting Information

ABSTRACT: Zwitterionic materials have been widely used to modify membrane surfaces to increase surface hydrophilicity and mitigate fouling, which would otherwise decrease water permeance. However, zwitterionic materials are water-soluble, and it is challenging to graft or coat zwitterions for long-term underwater operation. In this work, we demonstrate a facile two-step coating of membrane surface using a novel zwitterionic copolymer that contains thiol groups, which is achieved using bioadhesive polydopamine (PDA) as the intermediate layer. The copolymers were synthesized by reverse addition−fragmentation chain transfer (RAFT) copolymerization of phosphobetaine methacrylate (MPC) and 2-(methacryloyloxy) ethyl lipoate (MAEL), followed by reducing the MAEL units of the resulting copolymers to dithiol-containing units (i.e., DTMAEL). While strongly bound to the membrane surface, PDA reacted with the thiol groups through Michael addition reaction to covalently graft the zwitterionic polymer (p(MPC_{160}-*co*-$DTMAEL_{42}$) or PMD) onto the membrane surface. The modified membrane surface was characterized using X-ray photoelectron spectroscopy (XPS) and water contact angle measurement. The effect of surface modification on pure water permeance was investigated. The modified membranes were challenged with water containing bovine serum albumin (BSA) using a crossflow filtration system. The modified membrane exhibited less flux decline (38% reduction) than the PDA-coated one (45% reduction) or the unmodified one (53% reduction), but lower water flux than the unmodified one.



1. INTRODUCTION

Polymeric membranes are a key technology for water purification and wastewater treatment, because of their high energy efficiency.[1−5] One of the great challenges in membrane technology is fouling, where contaminants in wastewater accumulate on the membrane surface or block internal pores, decreasing water flux.[2,4,6−12] An effective strategy to mitigate fouling is to enhance hydrophilicity of membrane surface, which forms a hydration layer and reduces favorable interactions between the membrane surface and contaminants.[6,7] For example, membrane surfaces can be grafted or coated with hydrophilic polymers, such as hydroxyethyl methacrylate (HEMA)-based polymers,[13] poly(ethylene glycol) (PEG)-based polymers,[14,15] and polydopamine (PDA).[16−21] Such modification has been demonstrated to increase the steady-state water permeance, depending on the foulant's nature. For example, the PDA coating on the ultrafiltration (UF)/microfiltration (MF) membranes increases the water permeance during the oil/water filtration,[18,22] but not for the solution containing biofoulants such as bovine serum albumin (BSA).[23,24]

Betaine-based zwitterionic materials have emerged as a new platform with superior antifouling properties against proteins,[25−30] such as phosphobetaine (with PO_4^-), carboxybetaine (with COO^-), and sulfobetaine (with SO_3^-).[8,31−34] Despite neutral charges, the zwitterions generate a strong hydration layer on the surface through electrostatic force and hydrogen bonding, yielding superior antifouling properties. In particular, poly(methacryloyloxyethyl phosphorylcholine) (pMPC) has a structure similar to phospholipid cell membranes,[35] and it has been widely studied.[29,36−39] The low fouling nature of the zwitterionic surface has been adopted to develop antifouling membranes with stable permeance using a variety of techniques.[8,34] For example, copolymers containing zwitterionic components can be used to prepare membranes with the zwitterionic surface;[36,40,41] zwitterionic materials can also be grafted[42−44] or coated on the membrane surface.[37,45,46]

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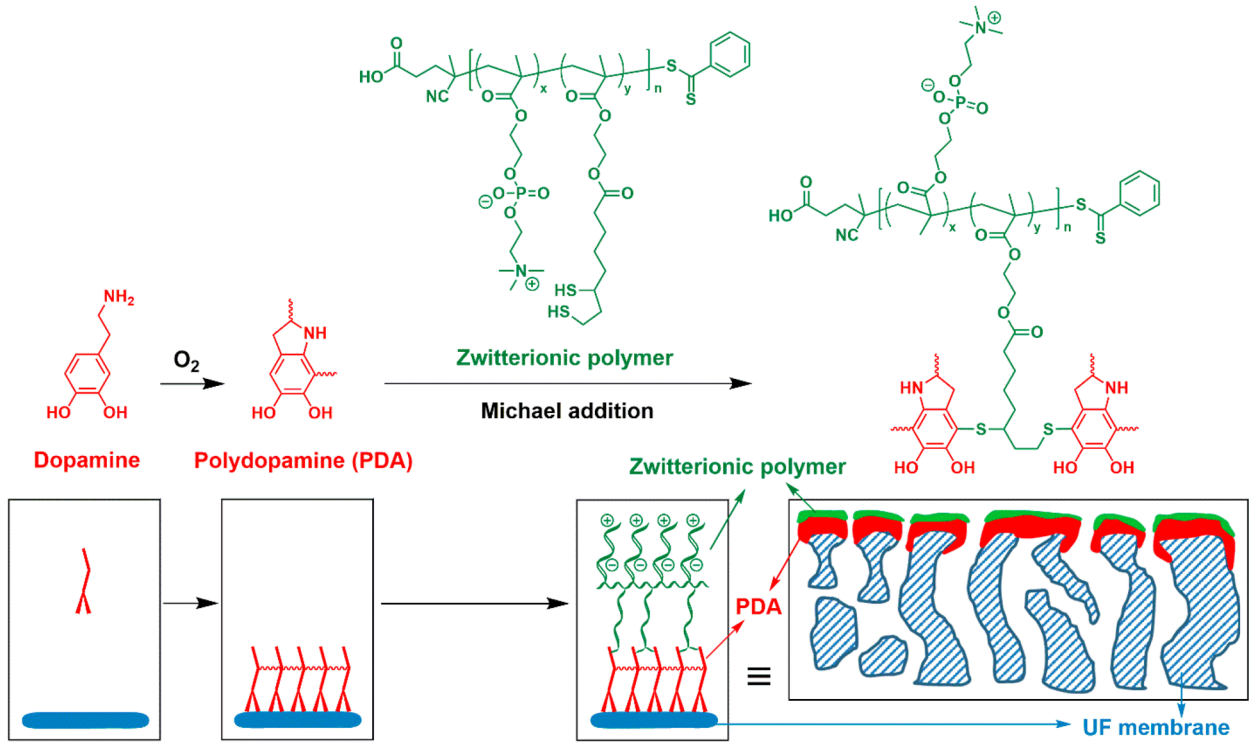

Figure 1. Schematic illustration of the two-step coating of a UF membrane with PDA as the "bioadhesive" layer, followed by a thiol-containing zwitterionic polymer.[16,57]

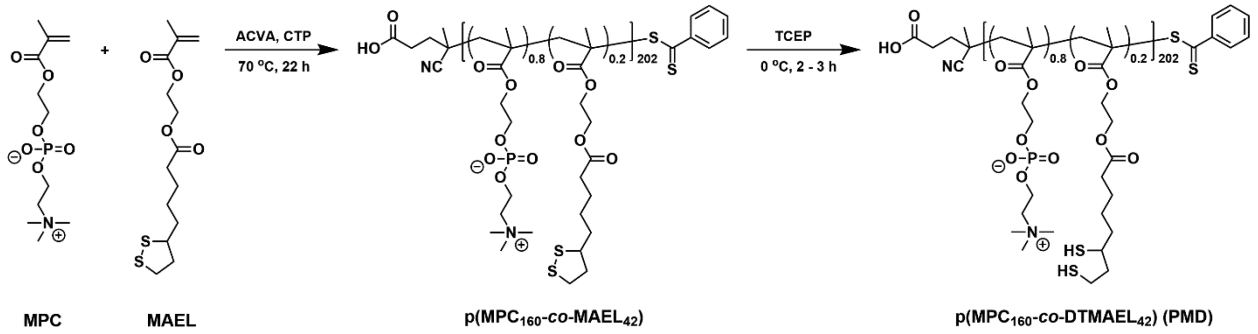

Figure 2. Schematic representation of the RAFT copolymerization of MPC and MAEL, and the reduction of the disulfide-containing zwitterionic copolymer, p(MPC_{160}-*co*-$MAEL_{42}$), to the thiol-containing PMD.

Bioinspired adhesion using PDA as a hydrophilic underwater "bioglue" has attracted significant interest.[38,39,47−49] As a key component in proteins for mussels to adhere to surfaces underwater, dopamine can be converted to PDA through $\pi-\pi$ stacking and hydrogen bonding under alkaline conditions in the presence of oxygen.[16,50,51] PDA serves as a versatile bioglue to covalently anchor a second layer, which can be self-assembled monolayers or polymer coatings.[8,16] Specifically, the hydroxyl groups of PDA adhere to the surface, and the amine groups react with the second layer, which can contain thiol, amine, and (meth)acrylate groups through Michael addition and Schiff base reactions.[8,16−18,22,24,39,52−55] For example, membranes were first coated with PDA and then with PEG-NH_2 as the second layer in an aqueous solution.[17,18,22] The modified membrane modules were used to treat fracking wastewater from shale gas wells in the field and showed improved resistance to fouling derived from the oil emulsion, in comparison with the untreated ones.[22] The PDA coating was also stable with the regular cleaning conditions such as heated caustic and citric acid.[22]

The direct codeposition of PDA and zwitterionic polymers has been demonstrated to form thin films through noncovalent linkages.[37,38,47] However, the lack of covalent bonds between PDA and the water-soluble zwitterionic polymers presents a concern for the long-term underwater operation of membranes. Herein, we synthesize copolymers consisting of hydrophilic zwitterionic pMPC and thiol side groups. The latter is designed to react with catechol and thus covalently graft the zwitterionic polymers onto the membrane surface through PDA, via Michael addition reaction.[16,53,56] As another example, in a study performed by our group, a modified module using PDA and sulfobetaine methacrylate (SBMA) demonstrated stable flux during four cycles of fouling tests, presumably, because of covalent linkages between PDA and SBMA.[24]

The two-step surface modification for a poly(ether sulfone) (PES) UF membrane is shown in Figure 1, and it is briefly described below:

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(1) A thin PDA layer is first deposited onto the membrane surface, which is hydrophilic and can adhere to hydrophilic and hydrophobic surfaces.
(2) Zwitterionic copolymers containing thiol groups with promising antifouling properties are covalently anchored to the PDA layer through Michael addition reaction.

Figure 2 shows the synthesis of a representative thiol-containing zwitterionic copolymer (p(MPC_{160}-*co*-$DTMAEL_{42}$) or PMD). First, disulfide-containing zwitterionic polymers, p(MPC_{160}-*co*-$MAEL_{42}$), was synthesized from phosphobetaine methacrylate (MPC) and 2-(methacryloyloxy) ethyl lipoate (MAEL) using reverse addition−fragmentation chain transfer (RAFT) copolymerization. The employed polymerization technique yields polymers under a metal-free condition.[58−61] Second, the resulting well-defined p(MPC_{160}-*co*-$MAEL_{42}$) was converted to PMD using a reducing agent (i.e., tris(2-carboxyethyl)phosphine hydrochloride or TCEP) to reduce the MAEL units.

This study explores the effect of surface modification by grafting PMD with PDA on the water permeance and antifouling properties. The copolymers were synthesized and characterized by ^{1}H NMR spectroscopy. The modified membrane surface was characterized using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and a contact angle goniometer to verify the successful coating. The effect of coating conditions on pure water permeance was investigated, and the coating conditions were optimized to increase the surface hydrophilicity without significantly decreasing the water flux. A crossflow filtration system was used to evaluate the antifouling properties of the modified membranes with 1 g/L bovine serum albumin (BSA) solution.

2. EXPERIMENTAL SECTION

2.1. Materials. For the polymer synthesis, D,L-α-lipoic acid (LA, 98+%), and 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 98+%) were purchased from Acros Organics (Geel, Belgium). 4-(dimethylamino)pyridine (DMAP, 99+%), 2-hydroxyethyl methacrylate (HEMA, 99+%), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTP, 97+%), and 4,4′-azobis(4-cyanovaleric acid) (ACVA, 98+%) were purchased from Sigma−Aldrich (St. Louis, MO). MPC (96+%) was purchased from TCI America (Portland, OR). Sodium bicarbonate, sodium chloride, magnesium sulfate, dichloromethane (DCM, ACS grade), chloroform (HPLC grade), anhydrous acetone (HPLC grade), diethyl ether (ACS grade), hydrochloric acid, *N*,*N*-dimethylformamide (DMF, 99.8+%), methanol (ACS grade), and ethanol were purchased from Fisher Scientific (Pittsburgh, PA). DCM was dried by distillation over CaH_2 before it was used, and other chemicals were used as received.

PES UF membrane (PES-2) with a molecular weight cutoff (MWCO) of 4 kDa was provided by Sepro Membranes, Inc. (Oceanside, CA). Chemicals for membrane surface modification and characterization such as dopamine hydrochloride, Trizma base (Tris), BSA, and phosphate buffered saline (PBS) were purchased from Sigma−Aldrich. Nitrogen cylinders with ultrahigh purity were obtained from Airgas, Inc. (Buffalo, NY, USA).

2.2. Synthesis of MAEL, pMAEL, and pMPC. MAEL was prepared by mixing LA (2.20 g, 10.7 mmol) and HEMA(1.40 g, 10.8 mmol) with 33.4 mL of anhydrous DCM in an ice bath.[62] EDC·HCl (3.07 g, 16.0 mmol) and DMAP (0.630 g, 5.20 mmol) were then added, and the solution was stirred at 21 °C overnight. The reaction mixture was then diluted using 100 mL of DCM and then extracted with 1 N HCl, saturated $NaHCO_3$, and then saturated brine. The organic layer was dried over $MgSO_4$ and filtered, which was further dried using rotary evaporation and vacuum to obtain the MAEL (3.12 g, 87% yield). The chemical structure of MAEL was verified using a Varian INOVA 500 NMR Spectrometer (Varian Medical Systems, Palo Alto, CA).

The pMAEL was prepared by dissolving MAEL (0.479 g, 1.50 mmol), CTP (0.0084 g, 0.030 mmol), and ACVA (0.00280 g, 0.010 mmol) in 3.1 mL of $CHCl_3$ and a trace amount of DMF. After degassing with nitrogen for 30 min, the solution was stirred at 70 °C for 22 h before exposure to the air to terminate the polymerization. The product was first precipitated in diethyl ether and then in methanol before centrifugation at 4000 rpm for 10 min. The dissolution, precipitation, and centrifugation were repeated four times to remove the remaining monomer and impurities. The pMPC was synthesized following the same procedure as outlined above for pMAEL using MPC (0.444 g, 1.50 mmol) and methanol (2.90 mL), instead of MAEL and $CHCl_3$.

2.3. Synthesis of Copolymers of p(MPC-*co*-MAEL)s. Copolymers of p(MPC_x-*co*-$MAEL_y$) were synthesized using RAFT copolymerization.[63] For example, to prepare p(MPC_{160}-*co*-$MAEL_{42}$), MAEL (0.2394 g, 0.75 mmol) was slowly added in 1.00 mL of methanol, followed by the addition of a methanol solution (1.55 mL) containing MPC (0.888 g, 3.0 mmol), CTP (0.0042 g, 0.015 mmol), and ACVA (0.0014 g, 0.005 mmol). After degassing for 30 min, the solution was kept at 70 °C for 22 h, before the polymerization was terminated using liquid nitrogen and exposure to the air. The reaction mixture was precipitated into cold diethyl ether and then purified by dialysis using Spectra/Por Dialysis Membrane with a MWCO of 1 kDa (Spectrum Laboratories, Inc., Rancho Dominguez, CA) with methanol for two days and then water for one day. The p(MPC_{160}-*co*-$MAEL_{42}$) (0.92 g, 89% yield) was finally obtained by freeze-drying. To prepare copolymers with different compositions, the MPC and MAEL contents were varied, while the $[MAEL]_0$:$[CTP]_0$:$[ACVA]_0$ molar ratio was maintained at 150:3:1.

2.4. Synthesis of PMD. To prepare PMD, a known amount of p(MPC_{160}-*co*-$MAEL_{42}$) was dissolved in a water/methanol solution in an ice bath under N_2 protection. A reducing agent of TCEP ($[TCEP]_0$:$[MAEL]_0$ = 4) was then added to the solution, which was stirred continuously until its color became light yellow. After 2−3 h of reaction, 1 N HCl was added to the mixture to decrease the pH to ∼3 to quench the reaction. The product was obtained in 87% yield by dialysis in an ice bath in darkness for 2 days, followed by freeze-drying.

2.5. Pretreatment and Surface Modification of Membranes. The PES-2 membrane was pretreated by removing the pore preservers such as glycerin.[24,64] Membrane samples were first soaked in excessive ethanol for 24 h and then rinsed with the deionized (DI) water. The samples were then immersed in the DI water for 24 h before use.

The modification of membrane surface by grafting zwitterionic polymers follows two steps. The first step involves depositing the PDA layer on the membrane as a "bioglue," which has been widely documented[17,18,24] and is briefly described here. A pretreated PES-2 membrane sheet was placed on a plastic plate, using a gasket and a plastic frame. A 2 g/L dopamine solution was prepared with a pH value of 8.5

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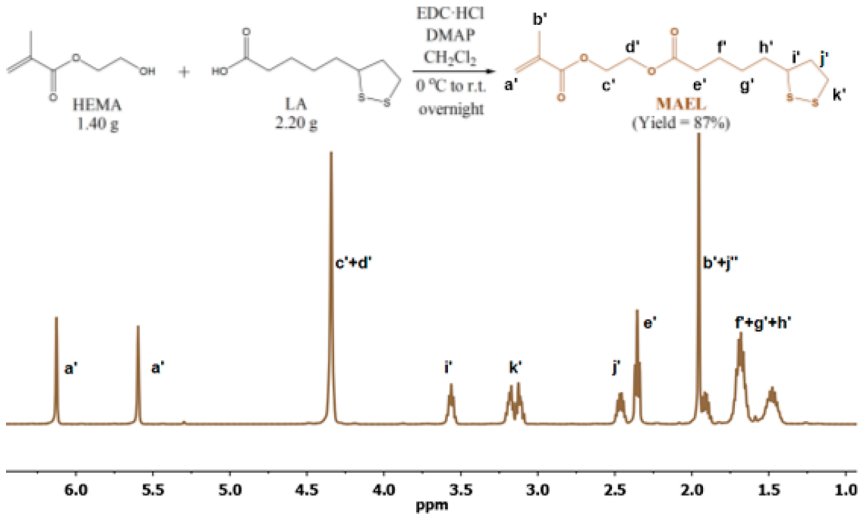

Figure 3. ^{1}H NMR spectrum of MAEL.

using Tris, which was then poured onto the active side of the membrane. A rocking platform shaker (VWR International, Radnor, PA) was used to expose the dopamine to oxygen for 1 h to produce a uniform PDA coating on the membrane surface. The membrane sample was then rinsed with the DI water before soaking in the DI water overnight to remove any unbounded dopamine. The coating condition is denoted as 2-PDA-1h.

The second step is to graft PMD onto the membrane surface. The polymer (at 1, 2, or 3.5 g/L) was dissolved in water at a pH of 8.5 (prepared using Tris) and poured onto the PDA-coated membrane sheet for 2 h. The modified sample was then rinsed using the DI water and stored in the DI water before tests. The two-step coating condition is denoted as 2-PDA-1h/*x*-PMD-2h, where *x* indicates the PMD concentration in the coating solutions.

2.6. Characterization of Coating Layer on Membranes. The thickness and chemistry of the coating layer on UF membranes may not be characterized directly, because of the porous nature of the membranes. Therefore, a model dense thin films of polysulfone (PSf) spin-coated is often used, with an assumption that the thickness and chemistry of the coating layer are independent of the porous or nonporous nature of the substrates.[17,24]

The thickness of the coating layer was determined using a Filmetrics F20 thin film measurement instrument (Filmetrics, Inc., San Diego, CA). First, dense PSf films (with a thickness of 144 ± 4 nm) were spin-coated on a silicon wafer. Second, the PSf films were coated with PDA and PMD using the same method as that described in the previous section. The PSf thin films were used to enable the direct measurement of the coating layer thickness using the F20 equipment.[24] The thickness values were taken as an average of at least five points. In fitting the F20 curves, a refractive index value of 1.6 was used for both PSf[65] and PDA.[66] The PMD is assumed to have the same refractive index as the PDA.[38]

XPS system (PHI 5600ci, Physical Electronics, Inc., Chanhassen, MN) was used to confirm the coating of PDA and zwitterionic polymers on the PSf surface. The molar percentage of elemental composition was calculated from the relative area of component peaks. The analysis was repeated in two different regions for each sample to confirm the uniform coating.

The surface morphology of the modified PES-2 membranes was characterized using focused ion beam-scanning electron microscopy (FIB-SEM, Zeiss Auriga, Germany). Before the SEM analysis, the samples were coated with a thin layer of gold nanoparticles using a sputtering coating machine to eliminate the charging effect.

A contact angle goniometer (Model 190, Ramé-hart Instrument, Succasunna, NJ) was used to determine the effect of surface modification on the hydrophilicity using a sessile drop method.[24,67] The membrane samples were dried and then water drops with a volume of 10 μL were injected onto the sample surface using a syringe.

2.7. Measurement of Water Permeance in Membranes. Pure water permeance was determined using dead-end permeation cells (Sterlitech Corp., Kent, WA). A circular membrane coupon with an active area of 11.3 cm^2 was installed in the cell, and compressed N_2 was used to provide hydraulic pressure. The water permeance (A_W, given in units of L/m^2 h bar (or LMH/bar)) can be calculated using eq 1:

$$A_W = \frac{1}{\Delta p \cdot A_m}\frac{dV}{dt} \quad (1)$$

where A_m is the effective membrane area (m^2), Δp is the pressure difference between the feed and permeate (bar), and dV/dt is the water flow rate through the membrane (L/h). For each membrane, six samples were tested, and an average value of water permeance is reported.

Membranes with promising water permeance were further tested with 1 g/L BSA using a crossflow filtration system at 30 psig.[24] BSA was used as a model biofoulant, and the solution was prepared at a pH value of 7.4 using the PBS. The system has three filtration cells in series with an active membrane area of 19.4 cm^2 for each. The Reynolds number was estimated to be 1000−1100. The water permeance in the presence of foulant was calculated using eq 1. The pure water permeance obtained in the crossflow system was much lower than that in the dead-end cells, probably because it was impossible to completely clean the cross-flow system. For simplicity, the pure water permeance from the dead-end cells is used for comparison if needed.[37,68]

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Table 1. Monomer Conversion, and Number-Average Degree of Polymerization Derived from the Monomer Conversion, and the End-Group Analysis for p(MPC$_x$-*co*-MAEL$_y$)s at Different Initial Molar Ratios of the Reactants[a]

			Theoretical		End-Group Analysis		
sample number	$[MPC]_0$: $[MAEL]_0$: $[CTP]_0$: $[ACVA]_0$	conversion (%)	DP_{MPC}[b]	DP_{MAEL}[c]	DP_{MPC}	DP_{MAEL}	M_n^{NMR} (kDa)
1	300:150:3:1	82	82	41	73	38	34
2	450:150:3:1	81	121	40	110	39	45
3	600:150:3:1	92	184	46	160	42	61

[a]The polymerization occurred at 70 °C for 22 h under N_2 atmosphere. [b]Equal to conversion (%) × ($[MPC]_0$:$[CTP]_0$). [c]Equal to conversion (%) × ($[MAEL]_0$:$[CTP]_0$).

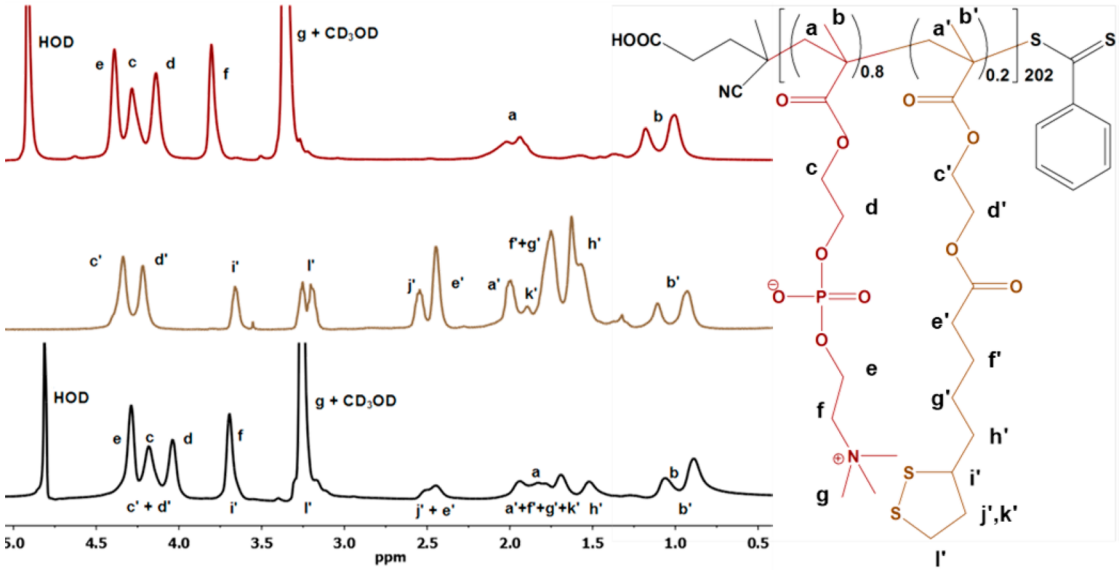

Figure 4. ^{1}H NMR spectra for pMPC (top), pMAEL (middle), and p(MPC$_{160}$-*co*-MAEL$_{42}$) (bottom) and the structure of p(MPC$_{160}$-*co*-MAEL$_{42}$) (right).

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Copolymers. Figure 3 shows ^{1}H NMR spectrum of MAEL, which was recorded at 500 MHz on solutions in $CD_3OD/D_2O/CDCl_3$ using tetramethylsilane (TMS) as an internal reference standard. The spectrum confirms the successful synthesis of MAEL (yield: 87%).

Table 1 records the amounts of reactants such as MPC, MAEL, CTP, and ACVA, which were used to prepare copolymers of p(MPC$_x$-*co*-MAEL$_y$)s. Figure 4 shows the spectra for homopolymers of pMPC and pMAEL, and an exampled copolymer, p(MPC$_{160}$-*co*-MAEL$_{42}$). The reaction conversion of the monomers were determined by comparing the resonance intensities of their vinyl protons (at 8.01−7.38 ppm; not shown in Figure 4, because the corresponding NMR peak is small, and there are no other NMR peaks at >5 ppm) with those of methyl protons of the polymers or copolymers (at 1.20−0.70 ppm). Based on the monomer conversion and the resonance intensities of protons *e*′ and *j*′ from MAEL in p(MPC$_x$-*co*-MAEL$_y$)s, the theoretical number-average degree of polymerization (DP_n) of MAEL in p(MPC$_x$-*co*-MAEL$_y$)s was calculated, and the results are presented in Table 1.

The DP values can also be directly estimated using the end-group analysis from the NMR results. The protons from the benzene ring end groups were used as a reference. The resonance intensities of f from MPC and i′ from MAEL were used to determine the experimental DP_n of MPC and MAEL in p(MPC$_x$-*co*-MAEL$_y$)s, respectively.

As shown in Table 1, the monomer conversions for p(MPC-*co*-MAEL)s were all above 80%, and it was as high as 92% for p(MPC$_{160}$-*co*-MAEL$_{42}$). Also, the copolymerization of MPC with MAEL was well-controlled, indicated by a good agreement between the theoretical and experimental DP_n values (see Table 1). Analysis of molecular weight dispersity of zwitterionic polymers by gel permeation chromatography (GPC) is often difficult.[69] In the current case, GPC analysis of p(MPC-*co*-MAEL)s could not be done because they are not soluble in DMF, the eluent for the GPC instrument. However, note that RAFT polymerization generally leads to narrowly dispersed polymers.[58−61]

With a disulfide moiety for "anchoring" and high hydrophilicity desired for the antifouling property, p(MPC$_{160}$-*co*-MAEL$_{42}$) was selected for reduction to the thiol-containing zwitterionic polymer, PMD. As shown in Figure 5, the successful synthesis of the PMD was verified through ^{1}H NMR analysis. Because of the post-polymerization reduction reaction, the peak of proton l′ is repositioned to ∼2.8 ppm (see Figures 4 and 5). The ^{1}H NMR integration values of protons i′, l′, and e′ are 1, 2 and 2, respectively, indicating the successful reaction of the ring opening.

3.2. Characterization of Coating Layer on Membranes. To measure the thickness of the coating layers, dense thin films of PSf were used as a model substrate for UF membranes, since the porous membranes do not allow direct measurement of the thickness using the Filmetric F20 instrument.[24] First, a thin PSf film with a thickness of ∼140 nm was spin-coated on a silicon wafer. Second, a 2 g/L

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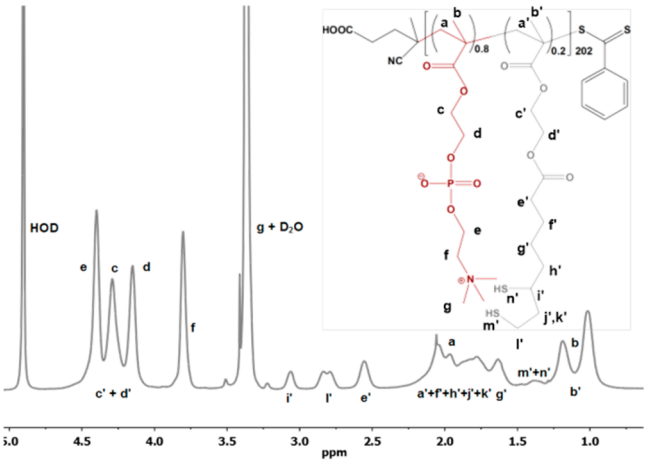

Figure 5. ^{1}H NMR spectrum for PMD, indicating the successful synthesis of the thiol-containing zwitterionic copolymer.

dopamine solution (100 mL) was coated on the PSf thin film for 1 h using the rocking platform shaker. After drying, the PDA layer was determined to have a thickness of 14 ± 2 nm, which is in good agreement with the literature.[17,24] Finally, a 3.5 g/L PMD solution (100 mL) was coated on the PDA-modified PSf film on the shaker for 2 h (i.e., 2-PDA-1h/3.5-PMD-2h). However, no noticeable increase in the thickness was observed, indicating that the coating layer of the zwitterionic polymer may be very thin.

The XPS analysis was used to verify the coating of both PDA and PMD layers. Because of the porous structure of the PES-2 membranes, XPS analysis was done using PSf coated wafers, instead of membrane samples. The pores existing in the structure of PES-2 may be detected via X-ray analysis, affecting the XPS results for the coated layers (i.e., PDA and/or PMD).

The coating of PDA on PSf has been thoroughly discussed in the literature,[24,55] and thus, the second step of coating of zwitterions is described in detail here. Figures 6a and 6b demonstrate the successful grafting of PMD on the PDA layer via the elements of P_{2p} (phosphorus) and S_{2p} (sulfur), respectively. Both PSf and PDA do not have the P_{2p} element,[37,38] while the two-step modification of PDA and PMD shows the P_{2p} element, confirming the grafting of the zwitterionic copolymer. The PSf layer contains the S_{2p} element,[70] while the PDA-coated PSf does not show the S_{2p} peak, indicating a full coverage of the PSf surface by the PDA. The probing depth for XPS is <10 nm, and it is less than the thickness of PDA layer (i.e., 14 ± 2 nm). In addition, when PMD is grafted on the PDA layer, two peaks at 169 and 164.5 eV are observed for S_{2p}, which can be attributed to the unbounded and bounded thiols, respectively,[56,71,72] suggesting the successful grafting of PMD on the surface.

The PMD content within the probing layer (<10 nm of PMD and PDA) can be estimated based on the determined content of elemental phosphorus and sulfur, and their theoretical content in PMD. The obtained value is 18 and 35 wt %, based on the content of the elemental phosphorus and sulfur, respectively. The difference could be due to the uncertainty in the XPS results. As the PMD content in the coating solution decreases to 2 g/L and 1 g/L, the PMD content decreases to 30 and 11 wt %, based on the elemental sulfur, respectively. These results indicate a significant content of the PMD is deposited on the membrane surface via Michael addition reaction (cf. Figure 1), which is also consistent with the literature.[16]

Figure 7 depicts the effect of coating on the surface morphology of the PES-2 membranes using SEM. As shown in Figure 7a, the uncoated membrane shows porous structure on the surface. For the membrane coated with 2-PDA-1h, the surface porosity decreases and there are large particles of PDA on the surface (cf. Figure 7b), which has been reported in the literature.[24,47] Figure 7c shows that the further grafting with the zwitterionic polymer covers more pores and there are fewer aggregates on the surface than the PDA-modified one. Both Figures 7b and 7c indicate that PDA and PMD/PDA modifications do not fully cover the membrane pores, as illustrated in Figure 1, which is also consistent with the literature.[19,24,37]

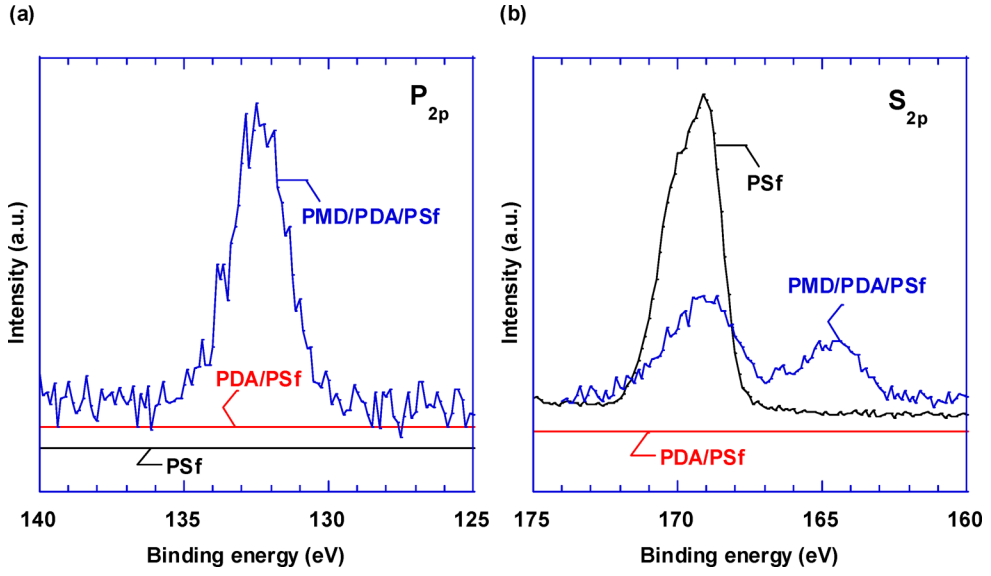

Figure 6. Comparison of XPS spectra of (a) P_{2p} and (b) S_{2p} for a PSf thin film, a PDA-coated PSf film (PDA/PSf) at 2-PDA-1h, and a PSf film (PMD/PDA/PSf) at 2-PDA-1h/3.5-PMD-2h.

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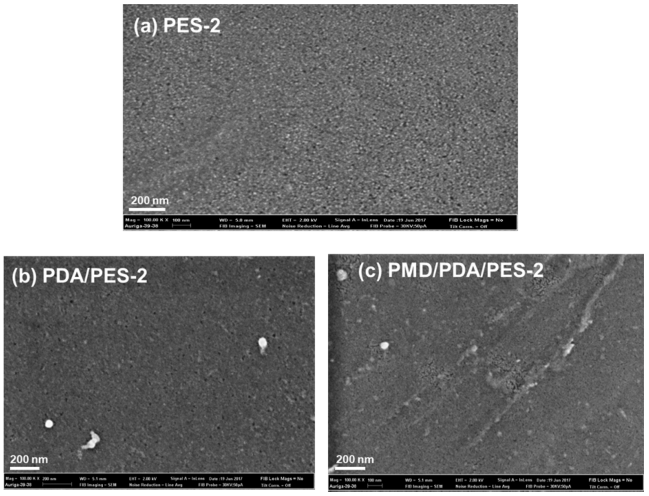

Figure 7. SEM microphotographs of the membrane surface for (a) a pristine PES-2 membrane, (b) a PDA-coated one (at 2-PDA-1h), and (c) a PMD/PDA-modified one (2-PDA-1h/3.5-PMD-2h).

Figure 8 exhibits the water contact angles on the PES-2 membrane samples modified using the solutions containing

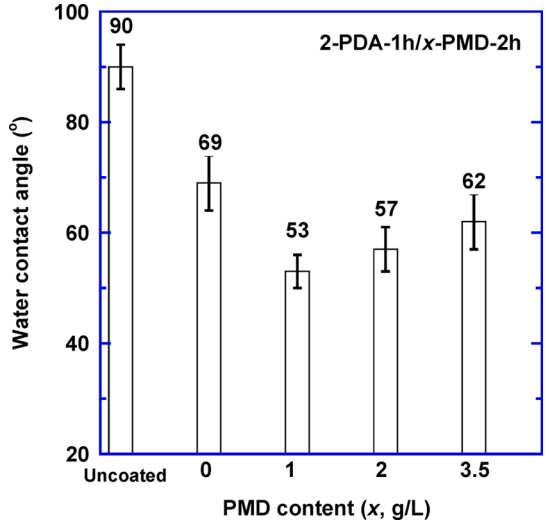

Figure 8. Effect of the PMD content in the coating solution on the water contact angle of the modified membranes.

different amounts of PMD. The PDA coating condition of 2-PDA-1h is selected based on earlier work to achieve a balanced increase in hydrophilicity and decrease in water permeance.[24,68,73] The PDA coating decreases the water contact angle from 90° ± 4° to 69° ± 5°. The introduction of PMD at 1 g/L further decreases the contact angle to 53° ± 3°, suggesting an enhancement in the surface hydrophilicity and indicating the presence of the thiol-containing PMD on the PDA layer. Further increase in the PMD content (from 1 g/L to 3.5 g/L) in the coating solution does not further enhance the surface hydrophilicity, considering the error bars. Such behavior has been observed for membranes coated with various contents of dopamine or sulfobetaine-based zwitterions.[24,68,73]

3.3. Effect of Surface Modification on Water Permeance and Antifouling Properties. Figure 9 exhibits the effect of the PMD concentration in the coating solution on the relative pure water permeance through the modified PES-2

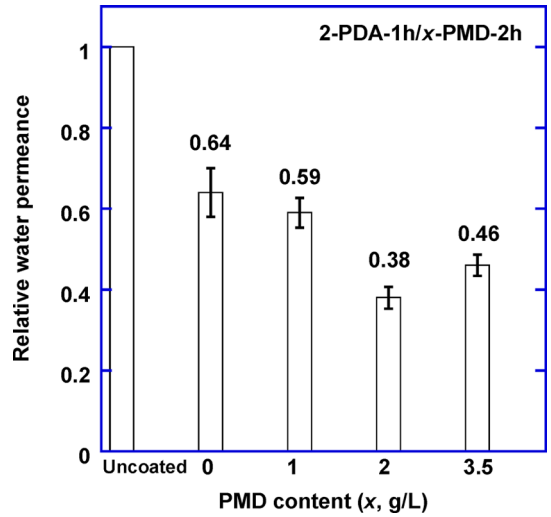

Figure 9. Effect of the PMD content in the coating solution on the relative water permeance of the modified membranes (2-PDA-1h/*x*-PMD-2h). The water permeance was measured at a feed pressure of 30 psig and 21 °C.

membranes, which is defined as the ratio of water permeance in the modified membranes to that in the uncoated one. (The raw data have been presented as Table S1 in the Supporting Information). The coating of PDA or PMD/PDA decreases the water permeance, because of the reduced pore size and porosity.[17,19,20,24,73] On the other hand, when the grafting solution contains 1 g/L PMD, there is essentially no decrease in the water permeance, compared to that coated with PDA. This may be caused by the increase in the membrane surface hydrophilicity, as indicated by the decrease in water contact angle (cf. Figure 8).[18] However, further increase in the PMD content in the coating solution decreases water permeance, presumably because of the dominant effect of the reduction of the surface porosity and negligible improvement of the surface hydrophilicity.

To examine the impact of surface modification on antifouling behaviors, the PES-2 membranes were tested using a 1 g/L BSA solution in a crossflow filtration system. Three PES-2 membrane stamps were examined in series, including one virgin membrane, another coated at 2-PDA-1h, and the other coated at 2-PDA-1h/1-PMD-2h. The grafting solution containing 1 g/L PMD was chosen to achieve a balanced enhancement of surface hydrophilicity (cf. Figure 8) and reduction in water flux (cf. Figure 9). Figure 10a shows the relative water permeance (defined as the ratio of the water permeance at any time to the initial water permeance) as a function of operating time. The relative water permeance decreases with time, because of the BSA fouling on the surface. The PDA coating slightly increases the relative water permeance with a value of 0.55, compared with a value of 0.48 for the virgin membrane after 4-h operation, which can be ascribed to the improved surface hydrophilicity derived from PDA.[18,46,68,73] The PMD/PDA-modified membrane exhibits a higher value of the final relative water permeance than the one coated by PDA, presumably due to the improved surface hydrophilicity (derived from zwitterions). Figure 10b shows the relative water permeance as a function of the volume of the permeated water. To obtain the same amount of the purified water, the surface modification by PDA or PMD/PDA does not seem to show improved antifouling properties.

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Ind. Eng. Chem. Res. 2018, 57, 2336−2345

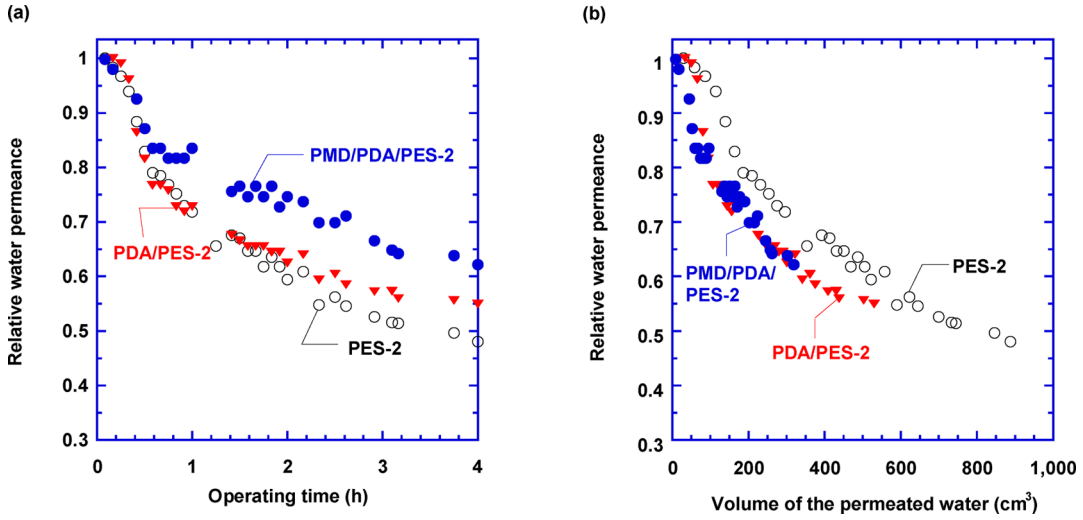

Figure 10. Relative water permeance as a function of (a) operating time and (b) the volume of permeated water for a virgin PES-2 UF membrane, one modified at 2-PDA-1h, and the other coated at 2-PDA-1h/1-PMD-2h, when challenged with 1 g/L BSA solution. The experiments were conducted at 21 °C, a feed pressure of 30 psig, and a flow rate of 0.9 L/min (Reynolds number = 1000−1100). The raw data have been presented in Figure S1 in the Supporting Information.

4. CONCLUSION

We demonstrated a new approach in grafting zwitterions on the membrane surface, i.e., a facile two-step coating of bioglue PDA and a zwitterionic polymer containing thiol groups. We synthesized zwitterionic copolymers of p(MPC-*co*-DTMAEL) (or PMD) containing hydrophilic zwitterions (derived from MPC) and thiol groups in DTMAEL through RAFT polymerization. This zwitterionic polymer was successfully deposited on PES UF membranes using bioadhesive PDA via Michael addition reaction, which is verified using XPS. The surface coating decreases pore size and porosity, resulting in a reduction of water permeance. On the other hand, the surface coating increases hydrophilicity, as indicated by the decrease in the water contact angles. For example, when PMD was coated on the PDA-modified membrane, the water contact angle decreased by 37° and 16°, relative to those of uncoated and PDA-coated samples, implying enhancement of surface hydrophilicity. When the surface-modified membranes were challenged with 1 g/L BSA solution, they exhibited less flux decline (38% reduction) than the PDA-coated one (45% reduction) and the unmodified membranes (53% reduction). However, when treating the same amount of water, the surface modification does not seem to enhance the relative water permeance values. Nevertheless, this work demonstrates a new facile approach in grafting zwitterions on the membrane surface using PDA and zwitterionic polymers containing thiol functional groups, which increases the surface hydrophilicity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b05025.

^{1}H NMR spectrum of p(MPC$_{160}$-*co*-MAEL$_{42}$); effect of surface modification on water permeance and antifouling properties (raw data) (PDF)

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Notes

The authors declare no competing financial interest.

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