

## Effects of polyethyleneimine molecular weight and proportion on the membrane hydrophilization by codepositing with dopamine

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**ABSTRACT:** Mussel-inspired chemistry has attracted widespread interest in the surface modification of polymer membranes. We have previously demonstrated a dopamine (DA) assisted codeposition process of polyethyleneimine onto polypropylene microfiltration membranes (PPMMs) for surface hydrophilization. In this work, we further investigate the effects of PEI molecular weight and DA/PEI mass ratio on the codeposition process and membrane performance. The results indicate that only low-molecular-weight PEI bring a distinct promotion in both surface wettability and water permeation flux for PPMMs. On the other hand, either excess DA or PEI is detrimental to the surface hydrophilicity of the studied membranes. The optimized PEI molecular weight is 600 Da and the corresponding mass ratio is 1:1 for the surface hydrophilization of PPMMs. These results are beneficial to understand those codeposition processes of dopamine with other polymers. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43792.

**KEYWORDS:** coatings; membranes; surfaces and interfaces

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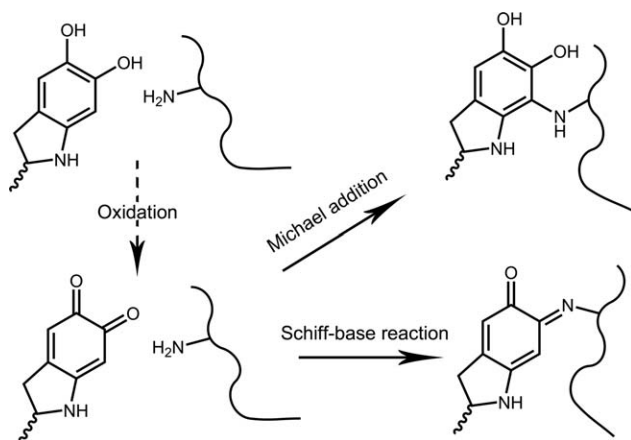
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### INTRODUCTION

Recently, mussel-inspired chemistry has attracted much attention in surface science due to its simplicity, universality, and versatility. Since Messersmith *et al.* reported the self-polymerization of dopamine and corresponding polydopamine (PDA) coating in 2007,<sup>1</sup> numerous of studies concerning PDA-modified materials have emerged for potential applications including biomedicine, energy storage and water treatment.<sup>2</sup> As a famous “bio-glue,” PDA can attach to nearly all kind of substrate surfaces including low-surface-energy materials such as polypropylene and polytetrafluoroethylene,<sup>3,4</sup> which shows great potentials in the membrane modification because most of commercial membranes are composed of these nonpolar polymers.<sup>5</sup> It provides a facile and universal approach to improve the surface wettability of polymer membranes. The method has also been employed to enhance anti-fouling properties for various membranes covering microfiltration, ultrafiltration, nanofiltration and reverse osmosis, *etc.*<sup>6–10</sup> However, the aromatic rings in PDA limits its hydrophilization effect for surface modification. Freeman *et al.* anchored amino-terminated PEG (PEG-NH<sub>2</sub>) onto the PDA-modified membranes to further promote the fouling resistance.<sup>11</sup> Likewise, polyzwitterion was also immobilized onto the PDA layer to enhance the antifouling property of RO membranes.<sup>12,13</sup> Grafting polymerization was realized

through the surface-induced atomic transfer radical polymerization initiated by the initiators anchored onto the PDA layer.<sup>14,15</sup> Besides, inorganic components including TiO<sub>2</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub> were introduced onto the PDA-modified membranes via non-covalent or covalent interactions for promoted surface wettability.<sup>16–18</sup> It can be noted that all of these methods are suffering from the multistep manipulation.

One-step codeposition is an emerging and facile approach to fabricate mussel-inspired hybrid coatings.<sup>19,20</sup> Lee *et al.* developed several kinds of functional surfaces via DA-assisted codeposition with tertiary amine, ATRP initiator, quaternary ammonium, polysaccharide, and growth factor in their previous work.<sup>21</sup> Some researchers also reported the codeposition of PDA and polymers. For example, PDA/dextran coating was fabricated for antifouling applications.<sup>22</sup> The deposition behaviors was also investigated for DA and nonionic polymers by Städler *et al.*<sup>23</sup> They found the hydrogen bonds between PDA and other polymers play a crucial role during the codeposition process. We also fabricated poly(sulfobetaine methacrylate)/PDA coating on polypropylene microfiltration membranes (PPMMs) with promoted antifouling performance.<sup>13</sup> However, chemical stability and solvent resistance of aforementioned coatings are worried because there are no covalent connections between PDA and those polymers. Recently, we have developed a codeposition



**Scheme 1.** Proposed mechanism for the reactions between PDA and PEI.

protocol of DA with low-molecular-weight polyethyleneimine (PEI), an amino-rich polymer.<sup>24,25</sup> In this case, Michael addition and Schiff-base reactions take place to accelerate the deposition process, improve the intrinsic hydrophilicity and enhance the coating stability in alkaline environment. The modified membranes show excellent wettability and high water permeation flux, which have been employed in oil-in-water emulsion separation under atmospheric pressure. Moreover, the PDA/PEI coating acts as an intermediate layer for further modification such as surface mineralization.<sup>18,26</sup> Because of its great potential in surface science, more details in this process should be elucidated such as the effects of PEI molecular weight and dopamine/PEI ratio on deposition.

In this research, we investigate the effects of DA/PEI ratio in deposition solution and PEI molecular weight on the structure and performance of PDA/PEI-modified PPMs. The results show that only low-molecular-weight PEI ( $M_w = 600$  Da) shows good hydrophilization effect and it is difficult to form a stable coating on the membrane surface with the increase of PEI molecular weight. The optimized mass ratio of DA/PEI in solution is in the range from 1:0.5 to 1:1. Though the surface wettability and the water permeation flux are improved in all experimental conditions compared to the nascent membranes, both DA-rich and PEI-rich solutions are detrimental to the modification process and the membrane performance.

## EXPERIMENTAL

### Materials

PPMs (mean pore size  $0.2 \mu\text{m}$ , porosity 75%) were purchased from Membrana GmbH (Germany). The membranes were cut into rounds (the diameter is 25 mm) and washed by acetone under oscillation overnight. Then the as-treated membranes were dried in a vacuum oven at  $40^\circ\text{C}$ . Dopamine hydrochloride and PEI with different molecular weights ( $M_w = 600$  Da, 1800 Da, 10,000 Da, and 70,000 Da) were procured from Sigma-Aldrich and Aladdin, respectively. Other reagents such as tris(hydroxymethyl) aminomethane, ethanol, and acetone were obtained from Sinopharm Chemical Reagent. All the reagents were used without further purification.

### Deposition of PDA/PEI onto PPMs

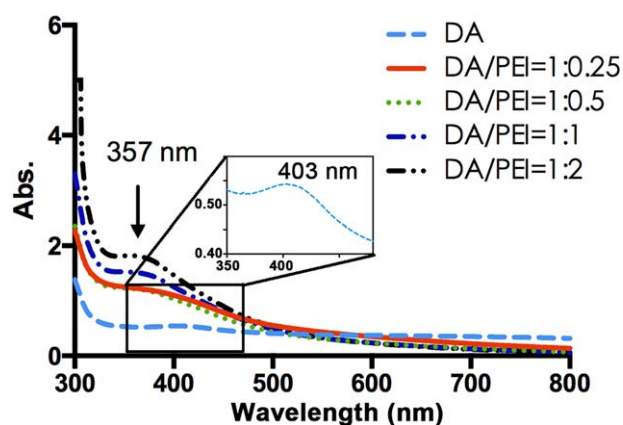
The deposition process was conducted as described in previous work.<sup>24</sup> First, the membranes were immersed into the DA/PEI mixed solution (Tris-buffer solution,  $\text{pH} = 8.5$ , 50 mM) for 4 h. DA concentration was  $2 \text{ mg mL}^{-1}$  in the solution. To study the effects of mass ratio, DA/PEI (w/w) were controlled as 1:2, 1:1, 1:0.5, and 1:0.25 for PEI-600. To investigate the differences between PEI with distinct molecular weight, we fixed the DA/PEI ratio to 1:1, and change the PEI molecular weight from 600 Da to 70,000 Da. The as-prepared membranes were rinsed by deionized water. Then they were dried in a vacuum oven overnight for further characterization.

### Characterization

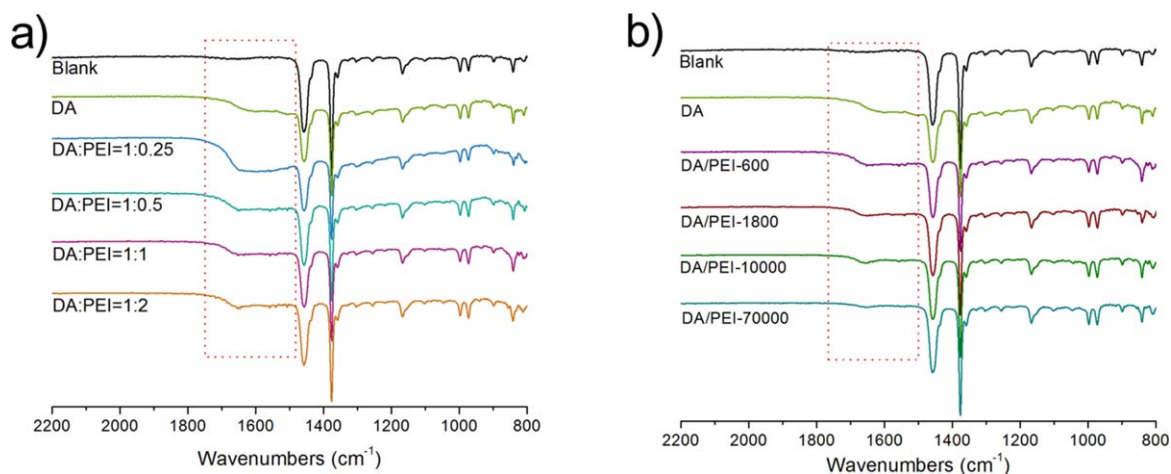
Surface morphology of the membrane samples was characterized by field emission scanning electron microscopy (FESEM, Hitachi, S4800, Japan). Surface chemistry was revealed by attenuated total reflectance Fourier transform infrared spectrophotometer (FT-IR/ATR, Thermo, Nicolet 6700, USA) and X-ray photoelectron spectroscopy (PerkinElmer, USA). Surface wettability was characterized by measuring static water contact angles from a contact angle system (MAIST Vision Inspection & Measurement, DropMeter A-200, China). UV-vis spectra were collected for PDA/PEI solutions with different initial dopamine/PEI ratios and PEI molecular weight by ultraviolet spectrophotometer (Shimadzu, UV 2450) from 800 to 200 nm. Each solution was diluted to one-sixth of its origin concentration.

### Water Flux and Antifouling Property Measurements

To assess the water permeation properties of the membranes, a dead-end apparatus was employed to obtain the pure water flux under 0.1 MPa after pre-compacted under 0.3 MPa for 20 min. On the other hand, bovine serum albumin (BSA) and lysozyme (Lys) were selected as the model proteins for anti-fouling test. The concentration of the protein solution is  $1 \text{ g L}^{-1}$  (phosphate-buffered saline solution,  $\text{pH} = 7.4$ ). We selected the membrane modified by DA/PEI-600 with a mass ratio of 1:1 as the optimum modified membrane. The pristine membrane was pre-wetted by ethanol and deionized water to overcome the high liquid penetration pressure. Before the test, the membranes were



**Figure 1.** UV-vis absorption spectra of DA/PEI solutions with different DA/PEI mass ratios after 4 h reaction. The molecular weight of PEI is 600 Da. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 2.** ATR/FTIR spectra of PDA/PEI-modified membranes with different DA/PEI mass ratios in the deposition solution (a) and PEI molecular weights (b). The PEI molecular weight in (a) is 600 Da, and the DA/PEI mass ratio in (b) is 1:1. The legend is assigned to the components in deposition solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

precompact for 20 min under 0.3 MPa. The permeate flux was collected each 2 min under 0.1 MPa. The relative flux reduction (RFR) and flux recovery ratio (FRR) were calculated by the following equations:

$$\text{RFR}(\%) = [1 - J_p/J_w] \times 100\%$$

$$\text{FRR}(\%) = [J_r/J_w] \times 100\%$$

where the  $J_w$  is the initial buffer solution flux,  $J_p$  is the protein solution flux and  $J_r$  is the recovery flux after rinsing by the buffer solution.

#### The Coating Stability Test

To evaluate the coating stability, we immersed the PDA/PEI modified membranes into the 0.1 M HCl, NaOH, and NaCl solution respectively overnight, and rinsed them by the deionized water. The pure water flux was measured according to the above-mentioned steps before and after the treatments.

## RESULTS AND DISCUSSION

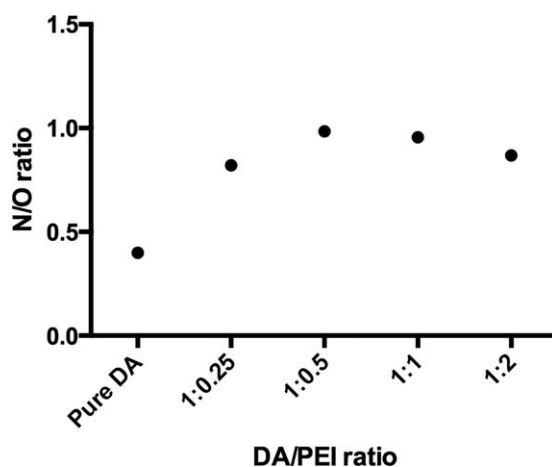
### Properties of the DA/PEI Deposition Solutions

PDA/PEI-coated membranes were simply fabricated by immersing the nascent samples into DA/PEI solutions under mild oscillation. The deposition solutions turn to brown or black with reaction time. This is due to the oxidation of DA and the reactions of catechol and amino groups as reported previously<sup>24,27</sup> (Scheme 1). Compared to the pure DA solution, the DA/PEI ones turn brown instead of black for the same time. We can speculate possible chemical reactions from UV-vis spectra of the solutions. Figure 1 indicates that a small peak at 403 nm arises after 4 h reaction in the pure DA solution, assigning to the C=C—C=O structure of in quinone. It shifts to 357 nm with the addition of PEI, and we ascribe the blue shift to the formation of C=C—C=N structure in Schiff base. The peak strength increases with the amount of PEI in the deposition solution, while the absorption in visible region shows an opposite change, implying the turbidity decline. That is because PEI incorporates into PDA aggregates and destroys those noncovalent interactions including hydrogen bond and  $\pi$ - $\pi$  stacking. For

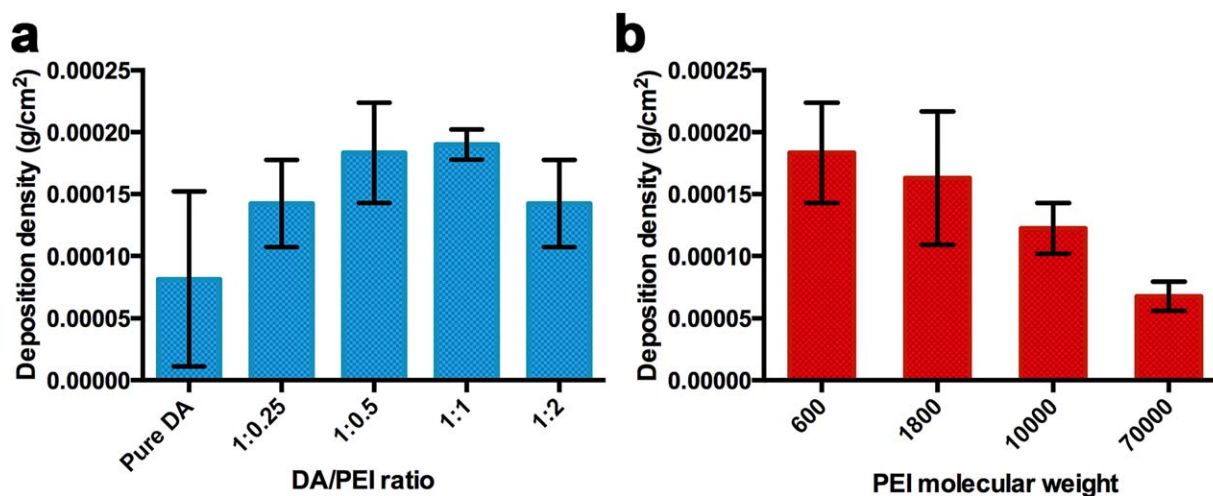
the deposition solution with different PEI molecular weights, the spectra show similar shape with different absorption strengths.

### Surface Chemistry and Morphology of PDA/PEI-modified PPMs

The surface chemistry was characterized by ATR-FTIR and XPS spectra for the PDA/PEI-modified PPMs. In Figure 2, a wide band appears in the range of 1700–1500  $\text{cm}^{-1}$  after the membrane surface is deposited with PDA or PDA/PEI. The peak at 1610  $\text{cm}^{-1}$  is generally ascribed to the C—C vibrations of the aromatic ring and the N—H bending vibrations. This peak is broadened after adding PEI for codeposition. It should be noted that the absorption reaches the maximum value when the DA:PEI mass ratio is 1:0.25 in the solution and then decreases. It seems the results are in contradiction to the weight gain with PEI addition. That is because more PDA is deposited on the membrane surface with low PEI amount, which is easy to be detected by ATR, while more PDA/PEI is deposited in the pores



**Figure 3.** N/O ratio of the membrane surfaces fabricated from the deposition solutions with different DA/PEI mass ratios.

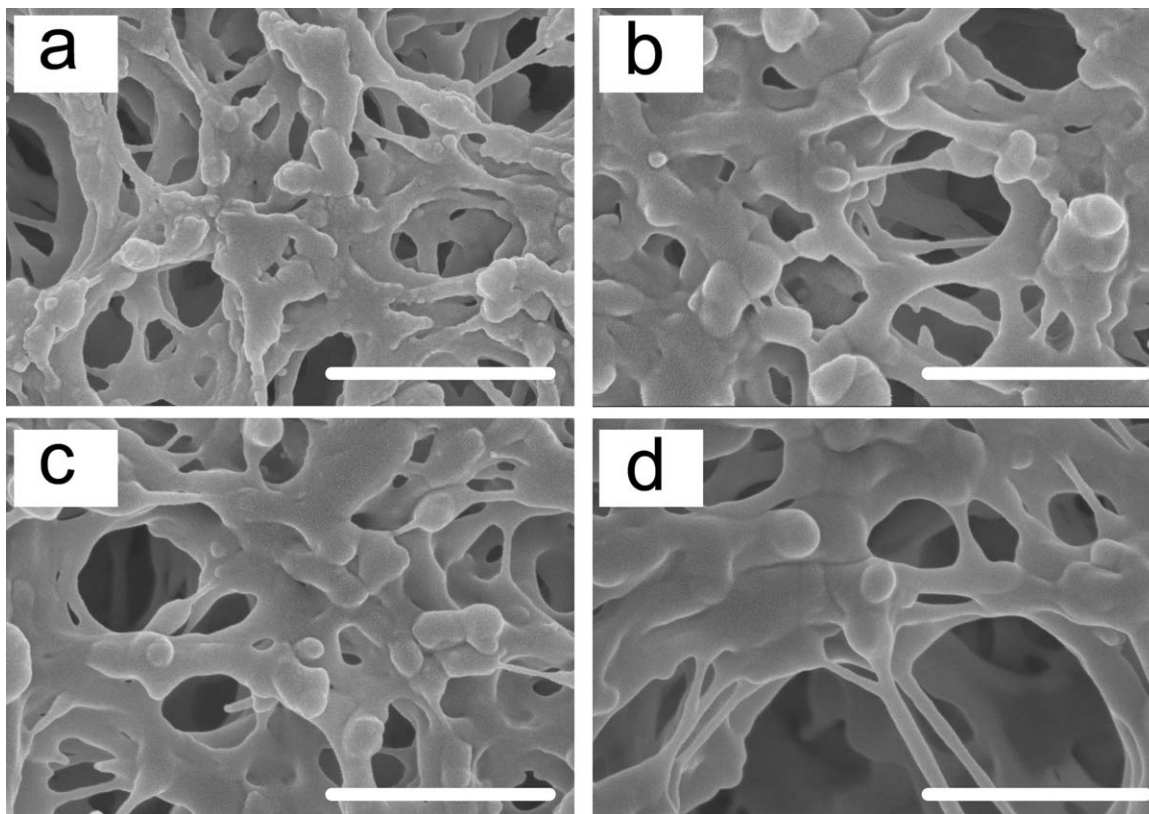


**Figure 4.** The deposition density of PDA/PEI-modified membranes with (a) different DA/PEI ratios and (b) PEI molecular weights. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

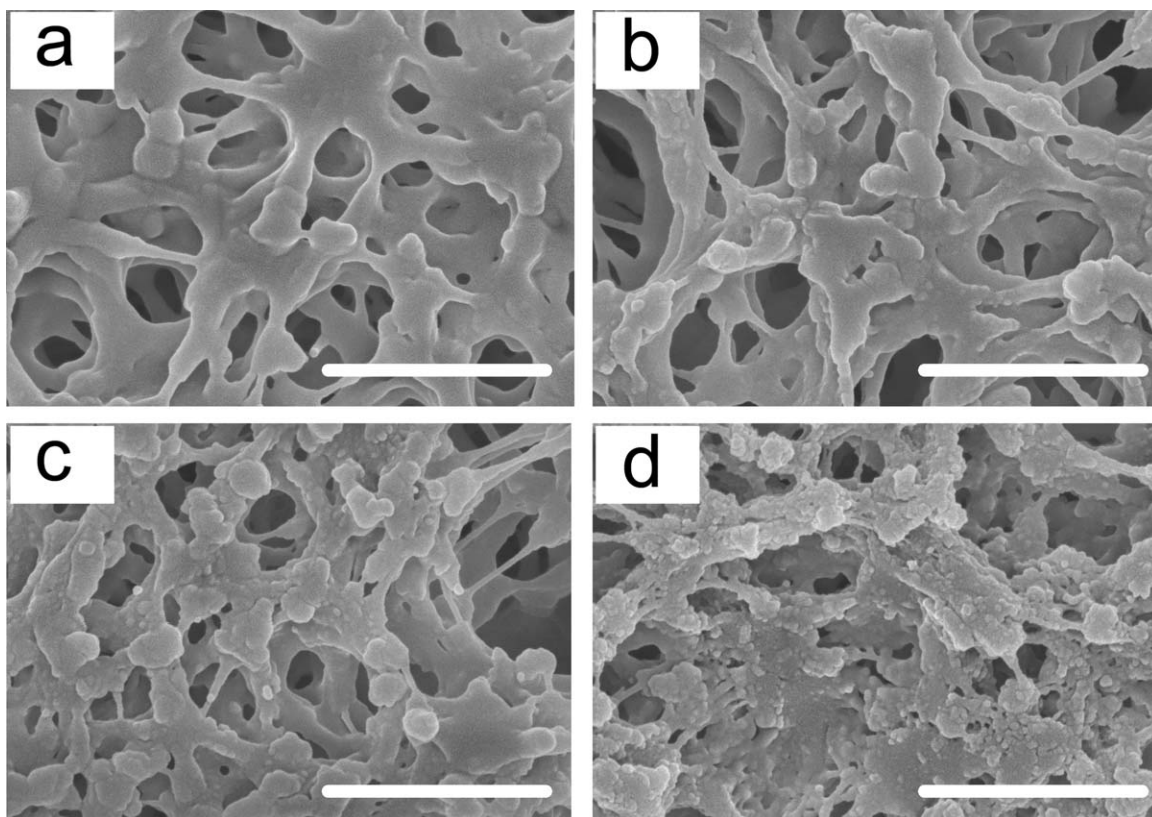
with increasing PEI amount. It can be also identified by the water permeation measurement.

More details are revealed by the XPS spectra of the PDA/PEI-modified membranes from solutions with different DA/PEI ratios. Figure 3 shows that the surface *N/O* ratio increases first and then decreases with DA/PEI ratio in the codeposition solution. According to the molecule structures, the *N* element is originated from both PEI and PDA, while the *O* element is from

PDA only as we know. Therefore, the *N/O* ratio can reflect PEI content in the coatings. It is reasonable that the *N* content increases with the addition of PEI at the beginning. It reaches the maximum value at DA/PEI = 1:0.5. After that, the *N/O* decreases if we continue to add the PEI in the codeposition solution. It can be rationalized by the chemical differences along the coating thickness. It is well known that PDA plays a crucial role during the codeposition process. PDA or PDA-terminated PEI absorb to the membrane surface via the hydrophobic



**Figure 5.** SEM images of the PDA/PEI-modified membranes with different PEI molecular weights: (a) 600 Da, (b) 1800 Da, (c) 10,000 Da, and (d) 70,000 Da. The scale bar is 1 μm.



**Figure 6.** SEM images of the PDA/PEI-modified membranes with different DA/PEI mass ratios in the solution: (a) DA/PEI = 1:0.25, (b) DA/PEI = 1:0.5, (c) DA/PEI = 1:1 and (d) DA/PEI = 1:2. The scale bar is 1  $\mu\text{m}$ .

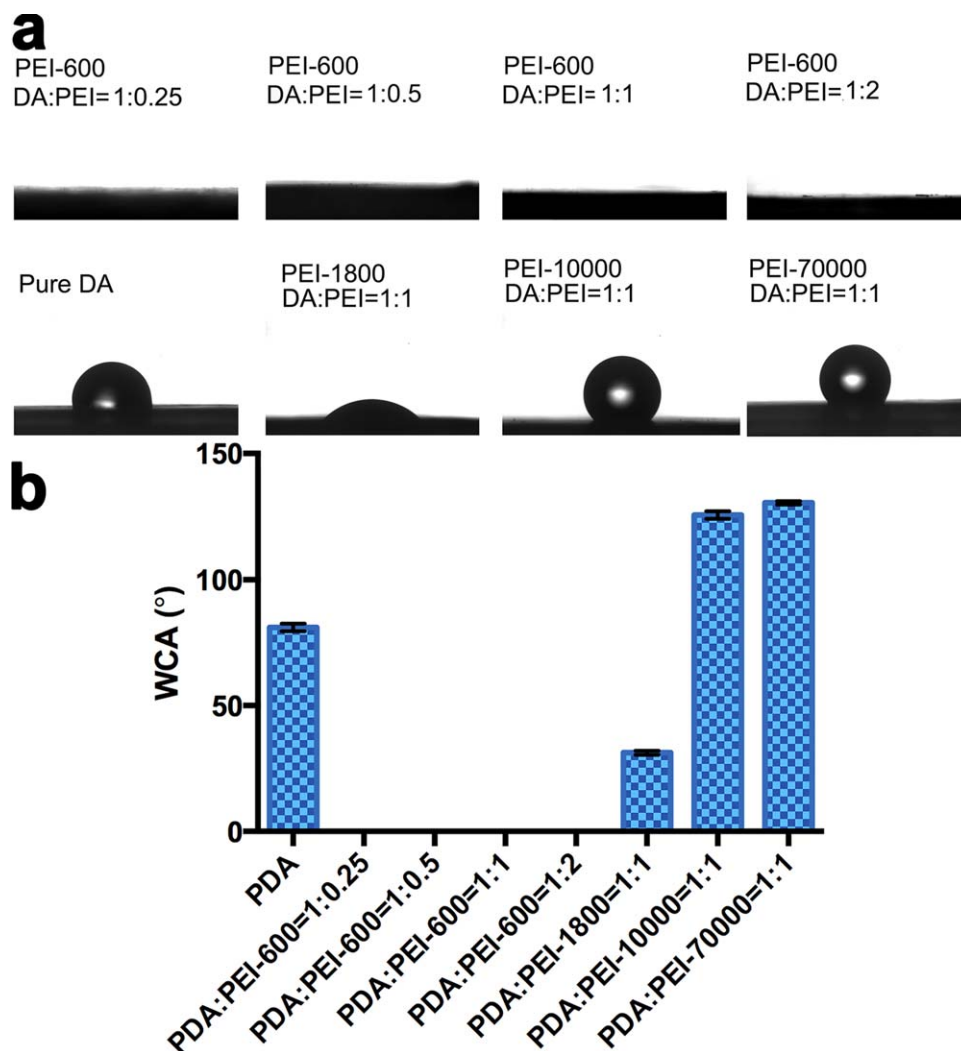
interactions to form the first layer at the initial stage. Then, more PEI is grafted onto the layer and PDA in the solution acts as the crosslinking point during the crosslink stage. More branching molecules form in the solution instead of crosslinked coating with the increase of PEI content, leading to a thinner coating layer and increased *O* content. It can be also indicated by the weight gain decline in Figure 4.

It is well known that the self-polymerization of DA results in PDA aggregates or precipitates in the solution, which is a problem for the surface modification of porous membranes. Figure 5 and 6 indicate that the membrane surfaces become rough due to the deposition of PDA/PEI particles. However, the particles become smaller and even disappear with the increase of PEI content in the deposition solution. The PEI molecules interrupt the formation of aggregates by conjugation with PDA, which makes it difficult to form hydrogen bonds and  $\pi$ - $\pi$  stacking structures as reported in our previous work.<sup>24</sup> For microfiltration membranes, the PDA particles affect little to their separation performance such as permeation flux and rejection because the particles are too small to block membrane pores. However, it would be a problem if the deposition protocol was employed for the surface modification of ultrafiltration or nanofiltration membranes. For ultrafiltration membranes, it was found that pore blocking by PDA particles decreased the water permeation flux compared to the nascent membranes even though the hydrophilicity of membrane surfaces was promoted.<sup>6</sup> For nanofiltration membranes, PDA particles formed thick coating and

large gaps among particles, which in turn resulted in poor separation performance in both permeability and selectivity due to the thick particle layer and large gap between particles.<sup>28</sup> In our cases, the codeposition process can be used to form thin, uniform and stable coatings, or even selective separation layer with acceptable hydrophilicity for microfiltration, ultrafiltration, and nanofiltration membranes.<sup>24,29</sup>

#### Surface Wettability and Membrane Performance

The surface wettability is a crucial membrane property for water treatment. In general, the hydrophilic surface is preferred because it can not only promote the water permeation under relatively low trans-membrane pressure but also improve the fouling resistance of the membrane. Therefore, we evaluated the membrane surface wettability by measuring water contact angle (WCA). Figure 7 shows that all of PPMs modified by PDA/PEI have excellent hydrophilicity with an apparent WCA below  $5^\circ$ . The water drops permeate through the membranes fast as soon as they contact the membrane surfaces. This is due to the large amount of amino group from PEI in the PDA/PEI coatings. We also investigated the effects of PEI molecular weight on the surface hydrophilicity. The mass ratio of DA/PEI was fixed at 1:1 to ensure the same number of  $-\text{CH}_2\text{CH}_2\text{NH}-$  unit. For a porous substrate, both spread and permeation can be observed during the WCA measurement. The spread phenomenon is arose from the hydrophilic top surface while the permeation is caused by the hydrophilic inner pores. Our results demonstrate that only low-molecular-weight PEI could



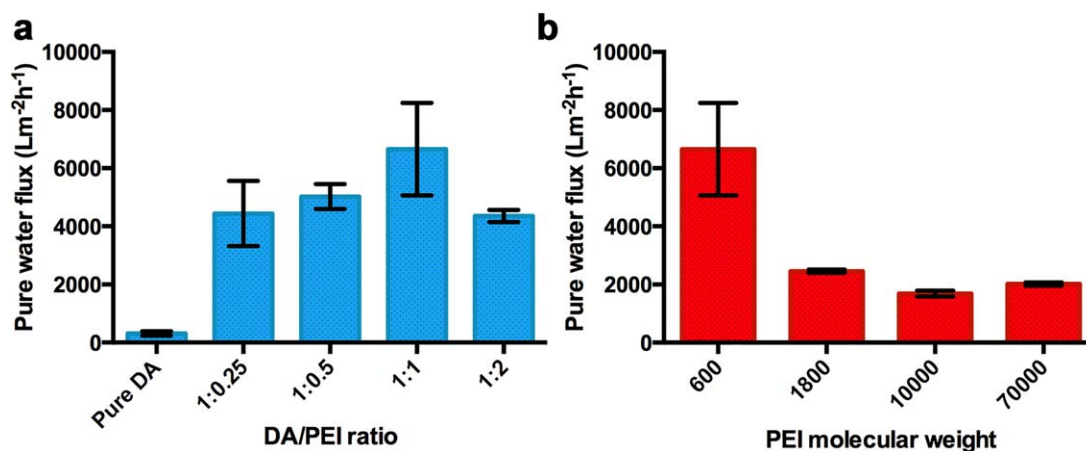
**Figure 7.** (a) Digital photographs of water drops on the PDA or PDA/PEI-modified membranes; (b) water contact angles of the PDA or PDA/PEI-modified membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

obviously improve the permeation property and the surface wettability of PPMs. WCA increases to  $35^\circ$  when the PEI molecular weight rises from 600 Da and 1800 Da. It seems that the membrane surfaces remain hydrophobic after immersing in a DA/PEI solution with PEI molecular weight above 10,000 Da, and WCA is even higher than that coated by pure PDA. This has been also indicated by the results of weight gain and water permeation flux in Figure 4. The deposition amount decreases with the increase of PEI molecular weight. These results may be interpreted by the decline of catechol “anchors” density in the PEI/PDA coatings, caused by the longer distance between terminal amino groups that can react with the catechol group. We previously found that free-standing films can be formed from PDA and PEI with molecular weight is 600 Da.<sup>25</sup> Increasing the molecular weight of PEI results in deep color solutions instead of free-standing films at the air–water interface. This is also the evidence to the unfavorable crosslinking between dopamine and PEI with high molecular weight.

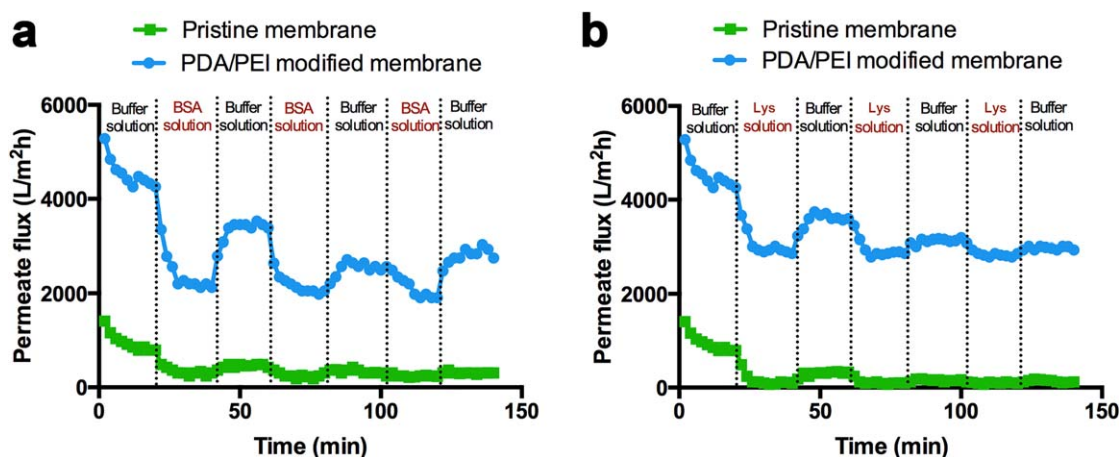
As we expected, the water permeation flux shows similar tendency with WCAs. As we can see from Figure 8, all the

PDA/PEI-modified membranes show higher flux than the PDA-modified ones. It reaches the maximum value about  $6651 \pm 1592 \text{ L m}^{-2} \text{ h}^{-1}$  for PPM codeposited by DA and PEI with molecular weight of 600 Da, whose mass ratio is 1:1. It can be seen that the permeate fluxes are all above  $4000 \text{ L m}^{-2} \text{ h}^{-1}$  for those membranes codeposited with PEI molecular weight of 600 Da. However, it declines to  $\sim 2000 \text{ L m}^{-2} \text{ h}^{-1}$  when the PEI molecular weight increases. Surprisingly, PPMs deposited by DA and high molecular weight PEI shows higher water permeation flux than those deposited only by PDA, whereas their surface wettability seems poorer than that of the PDA-modified membranes from WCA values. That is because PDA/PEI can diffuse and absorb in the membrane pores although it cannot form a dramatically hydrophilic coating on the membrane surfaces. On the other hand, the pure PDA aggregates can only deposited on the membrane surfaces and may block the membrane pores, both of which may cause a flux decline.

As we mentioned above, the hydrophilic surface can improve the fouling resistance of the membrane during filtration. Therefore, we evaluated the anti-fouling property of the



**Figure 8.** Pure water flux of the PDA/PEI-modified membranes with (a) different DA/PEI mass ratios in the deposition solution and (b) PEI molecular weights. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** The protein fouling test of the pristine and PDA/PEI-modified membranes: (a) BSA solution and (b) Lys solution. The DA/PEI mass ratio is 1:1 and the molecular weight of PEI is 600 Da. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

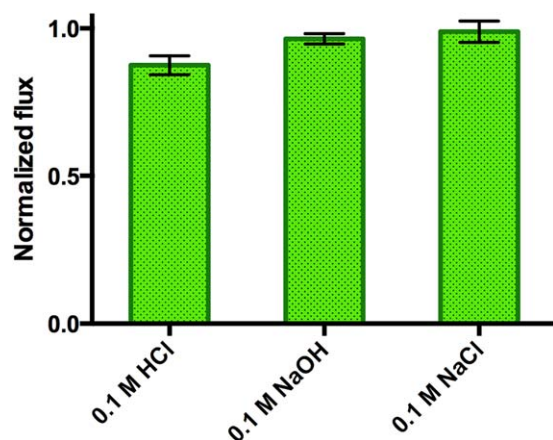
PDA/PEI-modified membrane by using proteins as the model foulants (Figure 9). Compared to the pristine membranes, the PDA/PEI-modified membrane shows higher permeate flux and better fouling resistance to both BSA and Lys solutions compared to the pristine one. In the case of the BSA solution, the RFR and FRR are 70.8% and 38.5%, respectively for the pristine membrane, while become 55.2 and 44.6% for the PDA/PEI-modified membrane correspondingly (Table I). It should be mentioned that the PDA/PEI-modified membrane shows better fouling resistance to the Lys solution, while the pristine membrane is fouled more seriously under the same condition. The results can be rationalized by the electrostatic interactions

between the membrane surface and proteins. The PDA/PEI-modified membrane is positively charged while the pristine one is negatively charged,<sup>26</sup> and the Lys is positively charged in our experiments (the isoelectric point is 11).

The stability of the PDA/PEI coating is also important for its practical applications. According to the previous work, the PDA/PEI coating shows improved acidic and alkaline stability in contrast to the pure PDA coatings due to the covalent bonds between PDA and PEI.<sup>24,30</sup> In this work, we further detected the flux evolution of the PDA/PEI-modified membranes after the acidic, alkaline and saline treatments. No significant decrease in pure water flux was observed for the membranes treated by the

**Table I.** The Relative Flux Reduction (RFR) and the Flux Recovery Ratio (FRR) of the Pristine and PDA/PEI-Modified Membranes

|                           | BSA     |         | Lys     |         |
|---------------------------|---------|---------|---------|---------|
|                           | RFR (%) | FRR (%) | RFR (%) | FRR (%) |
| Pristine membrane         | 70.8    | 38.5    | 88.5    | 15.4    |
| PDA/PEI modified membrane | 55.2    | 64.6    | 32.8    | 70.0    |



**Figure 10.** The normalized flux of the PDA/PEI-modified membranes before and after acidic, alkaline and saline treatment. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

alkaline and saline solutions (Figure 10). Only the membrane treated by the 0.1 M HCl solution shows a slight decrease in pure water flux, but still retains above 90% of the initial flux. It may be caused by the loss of some non-covalently bonded components on the surface. However, compared to the only PDA-modified membranes, the stability of the PDA/PEI-modified membrane is greatly improved, which makes the membranes applicable in some harsh environments.

#### In-depth Discussion of the DA/PEI codeposition

The DA/PEI codeposition technology provides us a novel insight into the mussel-inspired surface modification. In nature, the mussel foot protein is composed of not only the 3,4-dihydroxy-L-phenylalanine (DOPA) but also the lysine and other amino acids. In a recent research, the scientists revealed the synergy between catechol and lysine during the adhesion process.<sup>30</sup> They found only catechol groups could not provide strong adhesion underwater, and the positively charged amino group facilitated the contact between surface and adhesion molecules by replacing the hydrated cations on the surface. Another research also demonstrated the role of amino group during the wet adhesion.<sup>31</sup> Therefore, the amino group received more and more attentions in the research of mussel-inspired adhesives.<sup>32,33</sup> Although the dopamine molecule contains an amino group, it tends to form an indole structure during the oxypolymerization, which is quite different from the amino group from lysine. By contrast, the codeposition of DA/PEI can further imitate the adhesion of mussel foot protein. On the other hand, the covalent connections between DA and PEI can enhance the cross-linked network, which shows superior stability to the non-covalent interactions in PDA. Therefore, it can be referred as the “enhanced mussel-inspired modification” in contrast to the conventional mussel-inspired modification.

#### CONCLUSIONS

In conclusion, we investigate the effects of PEI molecular weight and DA/PEI mass ratio in the deposition solution on the hydrophilization of PPMMs via one-step co-deposition. The results show that only low-molecular-weight PEI can be easily co-deposited with PDA onto the membrane surface and greatly

improve the surface wettability, as well as the water permeation properties for PPMMs. With the increase of PEI molecular weight, the surface wettability dramatically decreases because the large PEI molecules impeded the deposition process. On the other hand, both excess PEI and DA are detrimental to the co-deposition process because the increased PEI suppresses the cross-linking in PDA/PEI coating. Therefore, the optimized DA/PEI mass ratio is in the range of 1:2 to 1:1. We think this study may provide guidance for the further research on DA/polymer co-deposition process.

#### ACKNOWLEDGMENTS

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