

# Mussel-Inspired Dopamine- and Plant-Based Cardanol-Containing Polymer Coatings for Multifunctional Filtration Membranes

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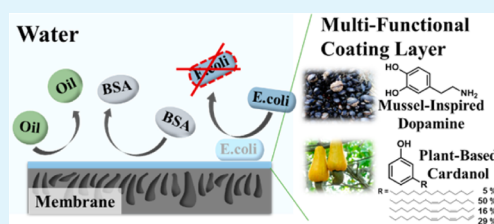
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## S Supporting Information

**ABSTRACT:** A series of copolymers [PCD#s, where # is the weight percentage of dopamine methacrylamide (DMA) in polymers] containing mussel-inspired hydrophilic dopamine and plant-based hydrophobic cardanol moieties was prepared via radical polymerization using DMA and 2-hydroxy-3-cardanylpropyl methacrylate (HCPM) as the monomers. PCD#s were used as coating materials to prevent flux decline of the membranes caused by the adhesion of biofoulants and oil-foulants. Polysulfone (PSf) ultrafiltration membranes coated with PCD#s showed higher biofouling resistance than the bare PSf membrane, and the bactericidal properties of the membranes increased upon increasing the content of HCPM units in the PCD#s. Serendipitously, the PSf membranes coated with the more or less amphiphilic PCD54 and PCD74, having the optimum amount of both hydrophilic DMA and hydrophobic HCPM moieties, showed noticeably higher oil-fouling resistance than the more hydrophilic PCD91-coated membrane, the more hydrophobic PCD0-coated membrane, and the bare PSf membrane. Therefore, multifunctional coating materials having biofouling- and oil-fouling-resistant and bactericidal properties could be prepared from the monomers containing mussel-inspired dopamine and plant-based cardanol groups.

**KEYWORDS:** cardanol, dopamine, antifouling, bactericidal, membrane, amphiphilicity



## INTRODUCTION

Foulants, such as proteins, bacteria, and oils, can be deposited on polymeric membrane surfaces and/or in their pores by the interactive forces between the foulants and the polar surfaces, and then water flux through the membrane decreases markedly, either temporarily or permanently, in various water filtration processes.<sup>1,2</sup> Therefore, the modification of material surfaces with antifouling and/or antibacterial moieties to prevent fouling has been widely used to maintain the membrane filtration performance in various applications.<sup>3–7</sup> Poly(ethylene oxide) (PEO) is one of the intensively studied coating materials due to its good fouling-resistant properties.<sup>8–10</sup> It is generally accepted that water–PEO interactions and the mobility of PEO segments in an aqueous environment provide repulsive interactions between PEO and foulants, resulting in the fouling resistance of PEO coatings.<sup>11–15</sup> Recently, a new surface modification using mussel-inspired polydopamine (PDA) has attracted significant attention for improving fouling resistance.<sup>16–19</sup> The catechol groups of PDA can form strong hydrogen bonds with water molecules, so the interactions between the PDA-coated membranes and foulants can be minimized.<sup>17</sup> Additionally, because the PDA coated on the material surfaces is not washed out by water, including acidic and basic aqueous solutions, it has been applied to stable hydrophilic coating materials on devices operated even under harsh conditions.<sup>20,21</sup>

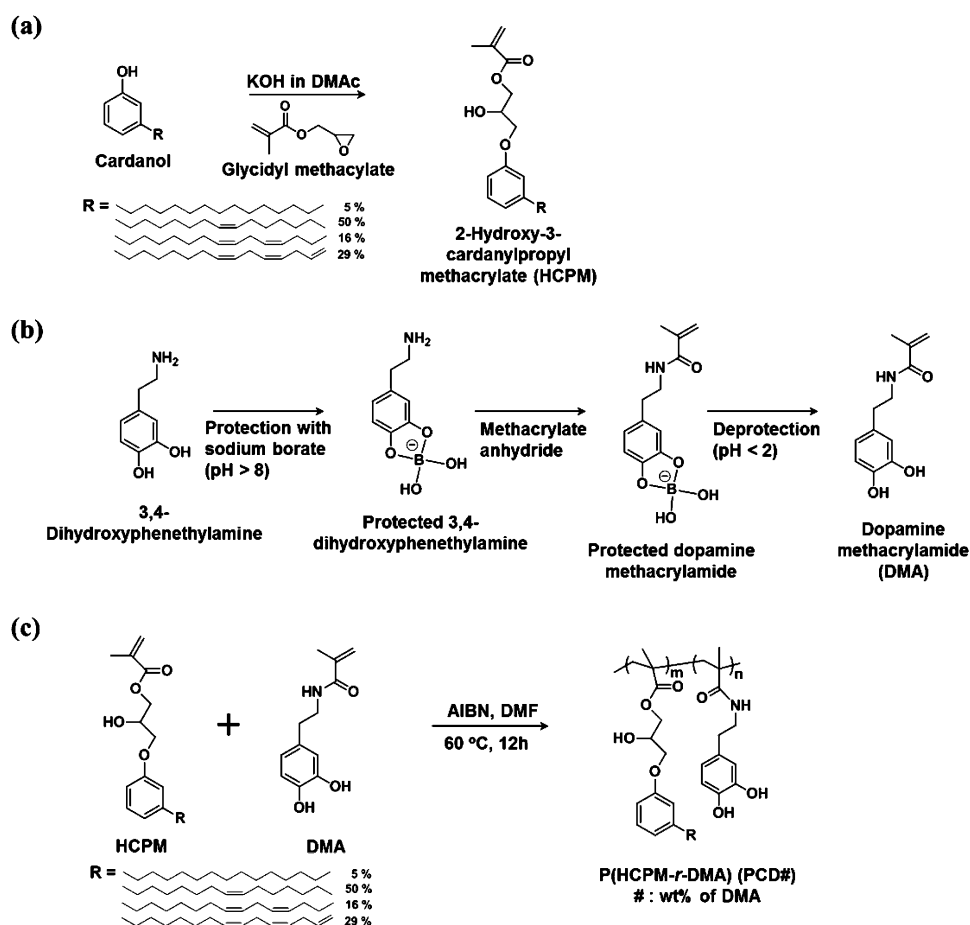
Although hydrophilic polymers such as PEO and PDA have excellent antifouling properties against the biorelated foulants, such as bacteria and proteins, their anti-oil-fouling properties have not been fully studied, because the formation of the oil-fouling layers could not be perfectly prevented by the hydrophilic layers. It is known that the oil-fouling layers are formed by the continuous coalescence, spreading, and migration process.<sup>22–25</sup> Therefore, the enhanced anti-oil-fouling properties of ultrafiltration membranes could be achieved by coating the membranes using amphiphilic polymers. For example, block and random copolymers consisting of hydrophilic poly(ethylene glycol) methyl ether methacrylate (PEGMA) and hydrophobic methyl methacrylate moieties were found to increase anti-oil-fouling properties because the hydrophilic units can increase the oil-fouling resistance and the hydrophobic units can increase the oil-releasing property.

Cardanol is a renewable and plant-based resource, having a C15 unsaturated hydrocarbon chain with one to three double bonds at the meta-position of the phenol group, and can be obtained from cashew nut shell liquid (CNSL) by a double distillation method. Himejima and Kubo reported the bactericidal properties of phenolic compounds from CNSL,

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**Figure 1.** Synthesis of (a) 2-hydroxy-3-cardanylpropyl methacrylate (HCPM), (b) dopamine methacrylamide (DMA), and (c) poly(HCPM-*r*-DMA) (PCD#).

such as anacardic acid, cardol, 2-methylcardol, and cardanol, although the detailed antibacterial mechanism remains unclear.<sup>26</sup> Recently, we newly found that methacrylate polymers having cardanol moieties have excellent bactericidal properties when the cardanol moieties were connected with a variety of chemical structures.<sup>27</sup> Thus, we believe that multifunctional coating materials for membranes could be developed by making polymers containing both fouling-resistant dopamine and bactericidal cardanol moieties. In addition, since the cardanol group contains a hydrophobic C15 hydrocarbon chain, the incorporation of such a hydrophobic moiety can also increase the oil-releasing property.

In this study, we designed and synthesized multifunctional polymers, called PCD#s (where # is the weight percentage of dopamine methacrylamide in the polymers), having biofouling/oil-fouling resistance and antibacterial properties using mussel-inspired dopamine methacrylamide and plant-based 2-hydroxy-3-cardanylpropyl methacrylate. These polymers were coated on polysulfone (PSf) ultrafiltration membranes, and the surface properties, flux behavior, fouling resistance, and bactericidal properties of PCD#-coated PSf membranes were studied and compared with those of the bare PSf membrane.

## EXPERIMENTAL SECTION

**Materials.** Cardanol was provided by Mercury Co., Ltd. Glycidyl methacrylate and triethylamine were purchased from TCI Co., Ltd. 3,4-Dihydroxyphenethylamine hydrochloride, azobis(isobutyronitrile) (AIBN), acryloyl chloride, and acetyl chloride were purchased from

Sigma-Aldrich Co., Ltd. Potassium hydroxide (KOH), sodium hydroxide (NaOH), *N,N*-dimethylacetamide (DMAc) were obtained from Daejung Chemicals & Metals Co., Ltd. Tetrahydrofuran (THF) was dried by refluxing over sodium and benzophenone, followed by distillation. *N,N*-Dimethylformamide (DMF) was passed through a column filled with alumina to remove the inhibitor before use. *Escherichia coli* (ATCC 8739) and *Staphylococcus aureus* (ATCC 6538) were obtained from American Type Culture Collection (ATCC). Bacto agar, Difco nutrient broth, and Difco tryptic soy broth were obtained from Becton, Dickinson and Co. (BD). All other reagents were used as received from standard vendors. 2-Hydroxy-3-cardanylpropyl methacrylate (HCPM) and dopamine methacrylamide (DMA) were synthesized according to the procedure described elsewhere as shown in Figure 1 and outlined in the Supporting Information.<sup>27,28</sup>

**Synthesis of Poly(2-Hydroxy-3-Cardanylpropyl Methacrylate-*r*-Dopamine Methacrylamide) (P(HCPM-*r*-DMA), PCD#s).** The following procedure was used for the preparation of PCD54 containing 54 wt % of DMA monomeric units. DMA (4.02 g, 18.2 mmol), HCPM (2.00 g, 4.54 mmol), AIBN (0.241 g, 1.47 mmol), and DMF (21 mL) were added to a round-bottomed flask fitted with a condenser and a magnetic stirring bar. The flask was purged with N<sub>2</sub> and sonicated for 10 min to degas the mixture and remove dissolved oxygen. After polymerization was carried out for 12 h at 60 °C, the solution was exposed to air. The crude product was poured into an excess of hexane with moderated stirring to precipitate the synthesized copolymer. After the dissolution–precipitation procedure was repeated two times, the product was dissolved in THF and precipitated over deionized water three times for further purification. The purified polymer was dried overnight in a vacuum oven. The final product was a light-brown powder. The absolute molecular weight

Table 1. Results of the Synthesis of the PCD#s from Different Comonomer Feeding Ratios

polymer	composition (HCPM:DMA)			$M_n/M_w^b$ ( $\times 10^{-3}$ )	PDI <sup>b</sup>	solubility <sup>c</sup> in H <sub>2</sub> O/MeOH
	feed (mol %)	in polymer <sup>a</sup> (mol %)	in polymer (wt %)			
PCD0	100:0	100:0	100:0	5.5/13.8	2.51	I/I
PCD9	60:40	83:17	91:9	28.5/51.4	1.80	I/I
PCD25	40:60	60:40	75:25	16.9/32.1	1.90	I/I
PCD54	20:80	30:70	46:54	51.7/75.0	1.45	I/S
PCD74	10:90	15:85	26:74	27.9/48.5	1.62	I/S
PCD91	5:95	4:96	9:91	16.8/24.2	1.44	I/S

<sup>a</sup>Determined by <sup>1</sup>H NMR. <sup>b</sup>Determined by GPC using a MALLS detector (THF). <sup>c</sup>S = soluble, I = insoluble.

( $M_n$ ) and polydispersity index (PDI) of PCD54 were 51 700 g mol<sup>-1</sup> and 1.45, respectively, by gel permeation chromatography (GPC) coupled with a multiangle laser light scattering (MALLS) detector using THF as an eluent. Other PCD#s with different compositions were prepared using the same procedure except the monomer feed ratio (Table 1), and the yields were always larger than 50%. Since the catechol group in the DMA acts as inhibitor in free radical polymerization, we could not prepare PCD100 having only the DMA unit in the polymer.<sup>29</sup> <sup>1</sup>H NMR [300 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, TMS ref]:  $\delta$  = 0.8–1.1 (3 H, -CH<sub>3</sub>), 1.20–1.90 (m, CH<sub>3</sub>(CH<sub>2</sub>)<sub>12</sub>CH<sub>2</sub>- and backbone), 1.47 (m, 2 H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>12</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.94 (m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>2</sub>- and C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>(NH)-C(=O)-), 2.73 (m, -CH<sub>2</sub>CH=CHCH<sub>2</sub>CH=CH- and C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>(NH)-C(=O)-), 4.20–3.70 (m, 5 H, -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OC(O)-), 5.90–4.80 (m, -CH<sub>2</sub>CH=CHCH<sub>2</sub>-), 6.36 (m, 1 H, aromatic in DMA), 6.87–6.50 (m, 2 H, aromatic in HCPM and DMA), 7.09 (m, 1 H, aromatic in HCPM), 7.44 (1 H, -C(=O)-NH-), 8.90–8.50 (2 H, (OH)<sub>2</sub>-Ar-).

**Coating of Polysulfone Ultrafiltration Membranes Using PCD#.** PSf ultrafiltration membranes were activated in methanol (MeOH) for 10 min. After drying in a vacuum oven at 25 °C for 24 h, the membranes were immersed in running distilled water for 1 h and dried in a vacuum oven at 50 °C for 48 h. The pretreated membranes were used as a supporting layer for the antifouling and antibacterial polymer coatings. PCD54, -74, and -91 were dissolved in MeOH, and PCD0 was dissolved in 1-decanol to prepare the coating solutions (1 wt %). PSf membranes were coated using the solutions by a spin-coating method (2000 rpm, 60 s), and the coated membranes were then transferred into an uncovered glass Petri dish and in a vacuum oven at 50 °C for 48 h.

**Membrane Filtration Experiments.** Membrane filtration experiments were performed on 76 mm diameter membranes using a stirred dead-end filtration cell (Amicon 8400) having an effective filtration area of 41.8 cm<sup>2</sup>. The feed side of the system was pressed under 1 bar by N<sub>2</sub> gas, and all the experiments were carried out at an agitating speed of 200 rpm and room temperature. Pure water flux [L (m<sup>2</sup> h)<sup>-1</sup>] was obtained from the volume of the permeated water within 1 h. For the fouling resistance test, bovine serum albumin (BSA) dispersed in phosphate buffer solution (PBS) (1.0 g L<sup>-1</sup>, pH 7.0) or an oil/water emulsion [0.9 g L<sup>-1</sup> for oil and 0.1 g L<sup>-1</sup> for sodium dodecyl sulfate (SDS)] was forced to permeate through the membrane at the same pressure, and the water flux at each time was recorded. The flux decline ratio (DR) of the membranes was defined and calculated as follows:

$$DR = (1 - J_{w,180}/J_{w,0}) \times 100\% \quad (1)$$

where  $J_{w,0}$  is the initial flux and  $J_{w,180}$  is the flux recorded after 180 min of dead-end filtration. The smaller the DR value, the better the antifouling property. All the filtration experiments for each sample were conducted more than three times, and the average values were used as the data.

**Characterization.** The chemical structure of the monomers and polymers was characterized by <sup>1</sup>H NMR spectroscopy (ZEOL LNM-LA 300, 300 MHz) using CDCl<sub>3</sub> as a solvent. Molecular weight ( $M_n$ ,  $M_w$ ) and PDI were analyzed by GPC. Absolute molecular weight measurements were carried out using a Waters 515 HPLC pump

equipped with three columns, including a PLgel 5.0  $\mu$ m guard, MIXED-C, and MIXED-D from Polymer Laboratories in series with a Wyatt Technology MiniDAWN triple-angle light scattering detector ( $\lambda$  = 690.0 nm) and a Wyatt Technology Optilab DSP interferometric refractometer. The data were processed using Wyatt's ASTRA V software. HPLC grade THF (J. T. Baker) was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup> at 30 °C. Mass spectra were recorded in EI mode at 70 eV with a JEOL JMS-700 mass spectrometer. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer (Thermo Scientific) using attenuated total reflectance (ATR) equipment (FT-IR/ATR). For atomic force microscopy (AFM) analysis, polymer thin films were prepared on silicon wafer by spin-coating (2000 rpm, 60 s) of 1.0 wt % polymer solution (PCD#s in MeOH or 1-decanol and PSf in THF). Interaction forces between the polymer-coated surface and BSA- or dodecyl-tethered AFM tips were measured by contact mode AFM (Seiko Instrument, SPA-400). The BSA- and dodecyl-tethered silicon cantilevers were prepared according to the procedure described in our previous studies.<sup>30</sup> We used a spring constant of 0.2 N m<sup>-1</sup>, provided by the manufacturer. A speed of 0.1  $\mu$ m s<sup>-1</sup> was applied to obtain the force-extension curves during approach and retraction of the polymer-coated surface from the AFM tip. The experiments were carried out in PBS and deionized water for BSA- and dodecyl-tethered tips, respectively, at room temperature. More than 30 approach/retraction cycles were performed for each polymer surface, collected from at least 10 positions on the sample. Contact angles of air and decane captive bubbles on membrane surfaces in water were measured by a Kruss DSA100 contact angle analyzer interfaced to a computer running drop shape analysis software. The contact angles for each sample were measured more than five times on five independently prepared membranes, and the average values were used as the data.

**Antibacterial Activity of PCD#-Coated Membranes.** The antibacterial activity of the PCD#-coated membranes was investigated using a shake flask method. This method was specially designed for specimens treated with nonreleasing antibacterial agents under dynamic contact conditions. In antibacterial tests, *E. coli* (ATCC 8739) and *S. aureus* (ATCC 6538) were used as an example of Gram-negative and Gram-positive bacteria, respectively. To prepare the bacteria suspension, bacteria were grown in the corresponding broth solutions for 18 h at 37 °C. A representative colony was lifted off with a platinum loop, placed in 30 mL of nutrient broth, and incubated with shaking for 18 h at 37 °C. After washing twice with PBS, they were resuspended in PBS to yield (1.0–1.5)  $\times 10^5$  colony forming unit (cfu)/mL.<sup>31</sup> Bacterial cell concentration was estimated by measuring the absorbance of cell dispersions at 600 nm and referenced to a standard calibration curve.

For evaluating the antibacterial activity of PCD#-coated membranes, 1  $\times 1$  cm<sup>2</sup> of PCD#-coated membranes and bare PSf were dipped into a Falcon tube containing 5 mL of 1.0 mM PBS culture solution with a cell concentration of (1.0–1.5)  $\times 10^5$  cfu/mL. The Falcon tubes were then shaken at 200 rpm on a shaking incubator at 25 °C for 24 h. After vigorous shaking to detach adherent cells from the membrane surfaces, the solution mixture was serially diluted and then 0.1 mL of each diluent was spread onto the corresponding agar plates. Viable microbial colonies were counted after incubating for 18 h at 37 °C. Each test was repeated at least three times. The percentage bacterial reduction was calculated according to the following equation:

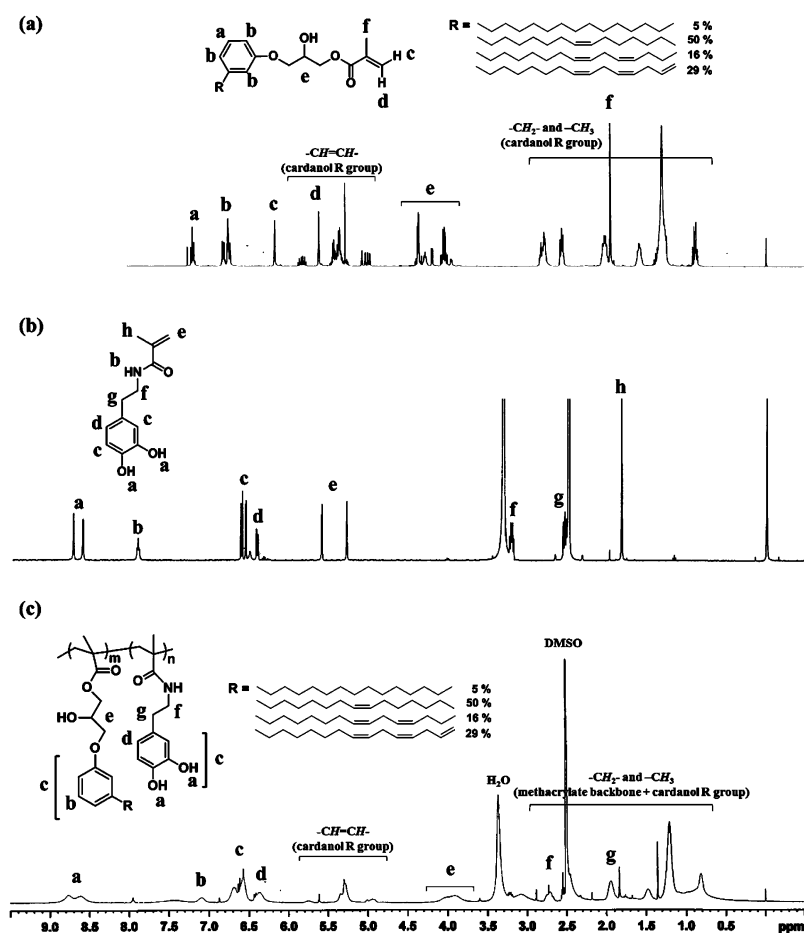


Figure 2.  $^1\text{H}$  NMR spectrum of (a) HCPM, (b) DMA, and (c) PCD54.

$$\text{bacterial inhibition (\%)} = (N_p - N_s) / N_p \times 100 \quad (2)$$

where  $N_p$  is the bacterial cfu of bare PSf and  $N_s$  is the bacterial cfu of tested sample.

## RESULTS AND DISCUSSION

**Synthesis of Copolymers with Mussel-Inspired Dopamine and Plant-Based Cardanol Moieties.** Parts a and b of Figure 1 show the synthetic procedures for DMA and HCPM, respectively, and their chemical structures were confirmed by  $^1\text{H}$  NMR, as shown in Figure 2a,b.<sup>27,32</sup> A series of methacrylate copolymers (PCD#s) was synthesized via free radical polymerization of HCPM and DMA as comonomers using AIBN as the initiator (Figure 1c).

Figure 2c shows the  $^1\text{H}$  NMR spectrum with assignments of the respective peaks of PCD54. The proton peak observed at  $\delta = 7.09$  was clearly assigned to the proton at the meta-position of the aromatic rings of the HCPM moieties. Additionally, the peaks from the unsaturated hydrocarbon chain (R group in Figure 1) of the cardanol moieties ( $\delta = 4.80\text{--}5.90$ ) were observed in the spectrum, demonstrating that the double bonds in the side chains of cardanol segments remained intact during the free radical polymerization. Also, the inclusion of DMA in the polymers was confirmed by the proton peaks of dopamine moieties [ $\delta = 6.36$  ppm, aromatic in DMA,  $8.50\text{--}8.90$ ,  $(\text{OH})_2\text{--Ar}$ ]. Table 1 shows the compositions of PCD#s prepared using different feed ratios of HCPM and DMA via free radical polymerization. The DMA content in PCD#s was calculated from the  $^1\text{H}$  NMR data as follows:

$$\text{DMA content in PCD\# (mol\%)} = I_d / (I_d + I_b) \times 100 \quad (3)$$

where  $I_d$  and  $I_b$  are the intensities of the d and b proton peaks in Figure 2c, respectively. The DMA content in the polymer is smaller than that in the feed, indicating that the DMA monomer is less reactive than the HCPM monomer. The absolute molecular weights of the polymers were analyzed by GPC coupled with a MALLS detector (Table 1). Since the molecular weights of the polymers are large enough ( $>10\,000$ ), it is expected that polymers can be stably coated on the membrane and other substrates.<sup>33</sup> PCD100 having 100 mol % of DMA monomeric units could not be prepared due to the large chain transfer constant of DMA. Because DMA has two hydroxyl groups on the benzene ring, its large chain transfer constant value can be anticipated.<sup>34</sup>

### Preparation of Multifunctional Filtration Membranes.

PSf ultrafiltration membranes were coated using PCD#s by a spin-coating method. Since PSf is soluble or partially soluble in commonly used aprotic polar solvents, such as NMP, DME, and DMAc, and many other organic solvents having lower polarities, such as THF and  $\text{CHCl}_3$ , the PSf membrane was found to be damaged by the PCD#s solutions prepared from these solvents; membrane surfaces were washed out and/or the pores were filled by the polymer solutions during the coating process. Therefore, it is important to choose solvents that do not damage the membrane surfaces or pore when they are coated with polymer solutions.<sup>30,35,36</sup> Because PSf is not soluble in polar alcoholic solvent such as methanol and 1-decanol, they

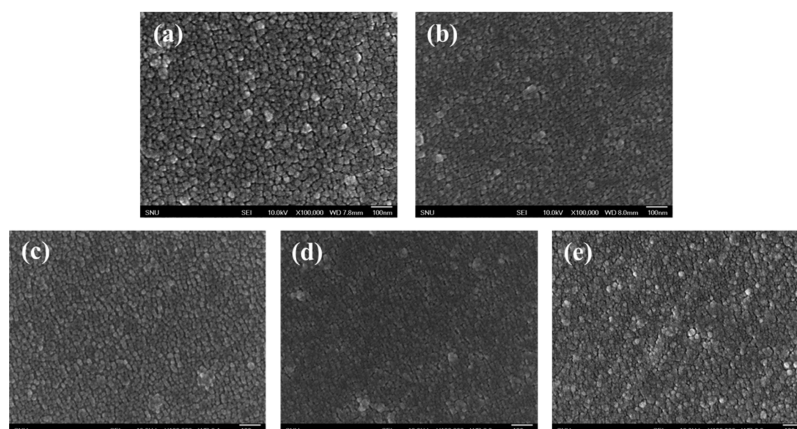


Figure 3. SEM micrographs of (a) PSf and (b) PCD0-, (c) PCD54-, (d) PCD74-, and (e) PCD91-coated membrane surfaces.

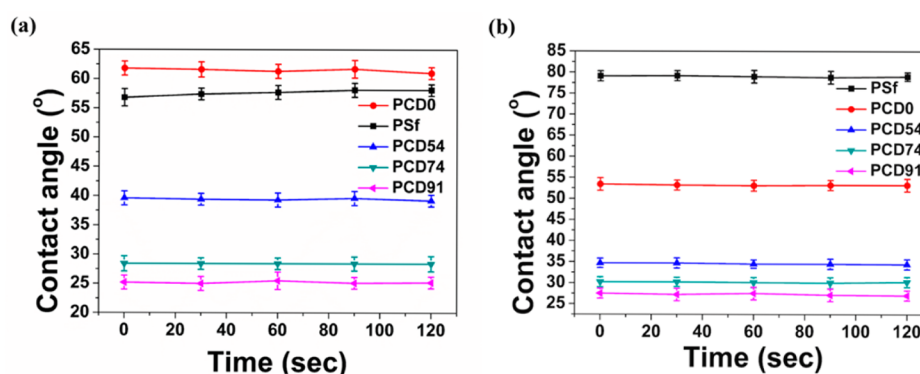


Figure 4. (a) Air and (b) decane captive bubble contact angles of the surfaces of PCD0-, PCD54-, PCD74-, and PCD91-coated membranes and bare PSf membranes.

can be used as the coating solvent; PCD54, PCD74, and PCD91 are soluble in methanol and PCD0 is soluble in 1-decanol, while other PCD#s having DMA units in the range of 5 to 50 wt % are poorly soluble or insoluble in any pure and/or mixed alcoholic solvents. For this reason, only PCD0, PCD54, PCD74, and PCD91 could be coated on the PSf membrane and used for detailed studies of membrane performance and bactericidal properties.

When 1.0 wt % PCD# solutions in the alcohols were used for the spin-coating of the PSf membrane, reasonably large pure water flux values, such as 420, 425, 410, and 410 L (m<sup>2</sup> h)<sup>-1</sup> for the PCD0-, PCD54-, PCD74-, and PCD91-coated membranes, were observed. These water flux values were slightly smaller, by 11.5–14.5%, than that of the bare PSf membrane [480 L (m<sup>2</sup> h)<sup>-1</sup>]. This small decrease in water flux could be attributable to the clogged pores on the membrane surfaces after the coating process, as confirmed by SEM images of the top surface of the membranes (Figure 3). Filtration polymer solutions of 1.0 wt % have been used commonly for the coating of the ultrafiltration membranes, as reported by others using other polymers to increase fouling resistance.<sup>30,35,36</sup> In addition, the stability of the polymer films coated on PSf membrane could be confirmed by XPS analysis of PCD74-coated membrane before and after 180 min of pure water filtration test as representative sample (Table S1 in the Supporting Information). The content of nitrogen elements from the DMA units was found to even increase after 180 min of pure water filtration test, indicating that PCD74 is stably attached on the PSf membranes and even surface reconstruction (hydrophilic DMA moieties are move to the top

of the surface in the aqueous environment) occurs.<sup>37,38</sup> The stability of the PCD74 as the coating materials on the PSf membrane was further confirmed by XPS analysis of PCD74-coated membrane washed with methanol, the very good solvent for PCD74, for 24 h. As shown in the Table S2 in the Supporting Information, DMA moieties on the membrane remain after the methanol washing process. Therefore, PCD74 on the PSf membrane is not perfectly removed, even by the good solvent of the polymer. The filtration test results shown later in the paper also indicate the better membrane performance of the PCD#-coated membranes than the PSf membrane. These results clearly indicate that PCD#s are stably attached on the PSf surfaces by the  $\pi$ - $\pi$  electron interaction and hydrogen bonds between the catecholic group in dopamine and the S=O and/or ether groups in PSf, as reported by others.<sup>39</sup>

#### Hydrophilicity and Oleophilicity of the Membranes.

The hydrophilicity and/or the oleophilicity of membrane surfaces are known to be the most important characteristics to impart the antifouling behavior on membrane surfaces,<sup>35,40,41</sup> and they have been estimated by the captive bubble contact angles on the membrane surfaces equilibrated in water.<sup>30,35,36,42</sup> For example, the smaller the air captive bubble contact angle, the more hydrophilic the surface, and the smaller the oil captive bubble contact angle, the less oleophilic the surface.<sup>35,43</sup> Figure 4a shows the air captive bubble contact angles measured by equilibrating up to 120 s. The contact angle value of the PSf membrane (58.1° ± 1.0°) was slightly smaller than or close to that of the PCD0-coated membrane (61.0° ± 1.0°), indicating

that both membranes were quite hydrophobic, while PSf membrane is slightly more hydrophilic. The air contact angle values of the PCD54-, 74-, and 91-coated membranes were  $39.2^\circ \pm 1.0^\circ$ ,  $28.4^\circ \pm 1.3^\circ$ , and  $25.2^\circ \pm 1.0^\circ$ , respectively, indicating that the increase in DMA content in the polymer increased the hydrophilicity of the PCD#-coated membrane. The relative oleophilicity of the membranes was estimated by the decane captive bubble contact angles (Figure 4b). The decane captive bubble contact angles also decreased with increased DMA content; they were  $53.2^\circ \pm 1.5^\circ$ ,  $34.4^\circ \pm 1.2^\circ$ ,  $30.2^\circ \pm 1.2^\circ$ , and  $27^\circ \pm 1.2^\circ$  for PCD0-, PCD54-, PCD74-, and PCD91-coated membranes, respectively. Thus, an increase in the DMA content decreases the oleophilicity. The decane captive bubble contact angle of the bare PSf membrane was found to be considerably larger than that of PCD0-coated membrane, even though the air captive bubble contact angle was similar, or even slightly smaller, indicating that PSf is slightly more hydrophilic than PCD0, while PSf is much more oleophilic than PCD0. It is possible that the interaction force of the oily decane with PSf is much larger than that with a PCD0-coated membrane, although the reason is unclear. A similar mismatch between the hydrophilicity and the oleophilicity of a polymer system was also reported previously.<sup>44,45</sup> However, it is clear that the PCD54-, PCD74-, and PCD91-coated membranes have more hydrophilic and less oleophilic properties than the PCD0-coated or bare PSf membranes.

The surface energies of the membranes were calculated from captive bubble contact angle values using Andrade's equation to study the effect of the coated polymers on the polarity of the membrane surfaces (Table 2).<sup>46</sup> The surface energy values

**Table 2. Captive Bubble Contact Angles and Surface Energies of the PCD#-Coated and Bare Membranes**

polymer	captive bubble contact angle, $\theta$ (deg) <sup>a</sup>		$\gamma_{sv}$ <sup>b</sup> (mN/m)
	air in water	decane in water	
bare PSf	$58.1 \pm 1.0$	$79.0 \pm 1.0$	48.43
PCD0	$61.0 \pm 1.0$	$53.2 \pm 1.5$	39.79
PCD54	$39.2 \pm 1.0$	$34.4 \pm 1.2$	56.75
PCD74	$28.4 \pm 1.3$	$30.2 \pm 1.2$	63.98
PCD91	$25.2 \pm 1.0$	$27 \pm 1.2$	65.69

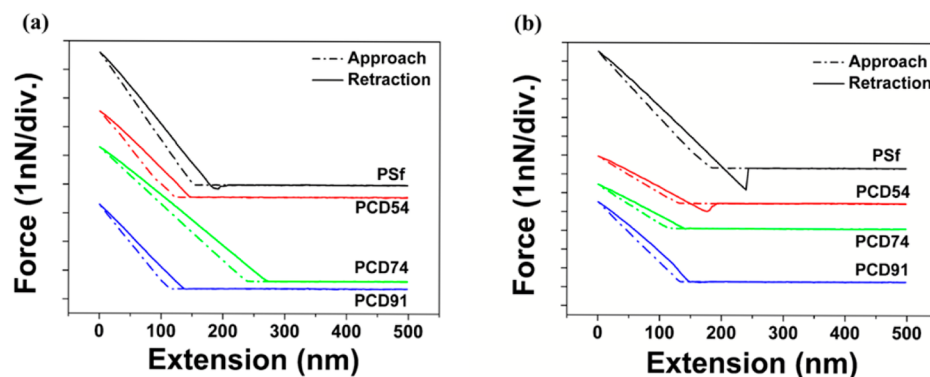
<sup>a</sup>Measured by equilibrating up to 120 s. <sup>b</sup> $\gamma_{sv}$  = total surface energy of the solid in equilibrium with vapor calculated by Andrade's equations.

obtained by Andrade's equation have been found to be close to those obtained by other commonly used methods, such as

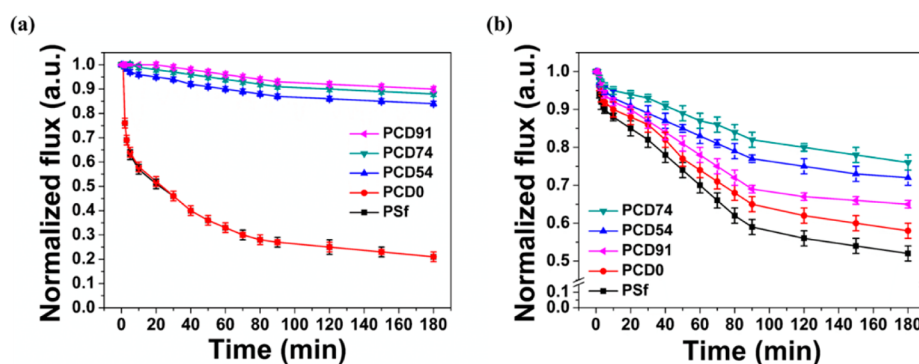
geometric and harmonic means and the acid–base approach, although Andrade's equation is based on the contact angles from the captive bubble method and the others are based on contact angle values on flat polymer surfaces.<sup>46–48</sup> The surface energy of the bare PSf membrane, 48.43 mN/m, is close to the literature value, about 46.6 mN/m,<sup>49</sup> and those of PCD#-coated membranes increase with increased DMA content, as expected. Furthermore, the surface energies of PCD54-, PCD74-, and PCD91-coated membranes in the range from 56.7 to 65.6 mN/m are close to those of very hydrophilic hydrogels based on poly(hydroxyethyl methacrylate) (P-(HEMA)) or poly(methacrylic acid), in the range of 54.4–68.6 mN/m.<sup>49</sup> Consequently, these membranes having very hydrophilic surfaces showed much better biofouling and oil-fouling resistance than the PSf membrane, as shown below.

**Interaction Forces.** The interaction force between the foulant and material surface is also an important parameter to directly estimate the foulant adsorption behavior on the surface.<sup>50–52</sup> In previous results by us and others, it was shown that the magnitude of the interaction force obtained by measuring the pull-off force of the AFM tips on the polymer films with the foulants correlated well with the fouling propensity of membranes and polymer-coated surfaces in the presence of the foulants.<sup>30,35,36,50–52</sup> Flat polymer surfaces prepared by spin-coating on silicon wafers are commonly used to obtain force–extension curves, because uneven membrane surfaces containing pores can affect the interaction forces between the tips and the polymer films. Since bovine serum albumin (BSA) and saturated hydrocarbon compounds are commonly used as the biofoulant and the oil-foulant, respectively, to estimate the biofouling and oil-fouling resistance of the membranes, respectively, they were tethered on the AFM tips to estimate the interactions of the membrane with the biofoulants and oil-foulants, respectively.<sup>30,35,36,53</sup>

Figure 5 shows typical force–extension curves when BSA- and dodecyl-tethered AFM tips interact with the PCD# and PSf films. However, we could not measure reliable interaction forces between the AFM tips with PCD0 film; equilibrated interaction force values were not obtained, possibly because the polymer surface of PCD0 is too sticky. In a separate experiment, we measured the glass transition temperature ( $T_g$ ) of PCD#s and found that the  $T_g$  of PCD0 was below room temperature,  $-5^\circ\text{C}$ , and those of other PCD#s such as PCD54, PCD74, and PCD91 were higher than room temperature, 74.9, 79.2, and 82.5  $^\circ\text{C}$ , respectively. It is well-known that the  $T_g$  of PSf is much higher than room temperature,  $\sim 185^\circ\text{C}$ .<sup>54,55</sup>



**Figure 5.** Force–extension curves recorded with (a) BSA-tethered and (b) dodecyl-tethered AFM tips against PCD54, PCD74, PCD91, and PSf surfaces coated on silicon wafer.



**Figure 6.** Time dependence of water permeation flux variations of the membranes during (a) BSA solution and (b) oil/water emulsion filtration experiments.

Therefore, reproducible AFM tip extension and force curves could be obtained from the nonmobile rigid surfaces of PSf, PCD54-, PCD74-, and PCD91 as shown in Figure 5, while fluctuating force behavior was observed from the sticky and mobile PCD0 surfaces.

A measurable pull-off force, such as  $0.153 \pm 0.038$  nN, was observed between the BSA-tethered AFM tip and PSf film, while no measurable interaction force was detected from the PCD# films, indicating that PCD54-, PCD74-, and PCD91-coated surfaces do not have any interaction forces with the polar compound with the AFM equipment resolution we have (Figure 5a).<sup>30,35,36</sup> Measurable pull-off forces, of about  $1.033 \pm 0.354$  nN, were observed from the PSf film using the dodecyl-tethered AFM tip, whereas relatively smaller forces such as  $0.459 \pm 0.249$ ,  $0.052 \pm 0.040$ , and  $0.030 \pm 0.033$  nN were observed for PCD54, PCD74, and PCD91 films, respectively, as shown in Figure 5b. The interaction forces between dodecyl-tethered AFM tip and PCD-coated films are consistent with the oleophilicity behavior of the PCD-coated membranes analyzed by the decane captive bubble contact angles (Figure 4b). An increase in the DMA content in the polymer decreased both the oleophilicity and the interaction force with the oily dodecane. Therefore, the force–extension results using the BSA-tethered AFM tips indicate that all the PCD#s having DMA units, such as PCD54, PCD74, and PCD91 films, can give excellent biofouling resistance, because none have any interactive force with polar compounds. Because the interactions of the PCD#s with oily compounds decrease with increasing DMA content, it is possible that PCD# having the highest DMA content, such as PCD91, may have the best oil-fouling resistance, too. However, this prediction, deduced from the interaction force results, does not match perfectly with the membrane performance results using the BSA and oil solutions shown in the next section, although the basic principle suggested by our work, that membranes coated with polymers having hydrophilic and oleophobic DMA units can increase the biofouling and oil-fouling resistance, is generally correct.

**Flux Behaviors and Antifouling Mechanism.** Figure 6 shows the fouling resistance behavior of the membranes evaluated from dead-end filtrations using BSA and vacuum pump oil as the model biofoulant and the model oil-foulant, respectively. The PCD0-coated membrane and PSf membrane both showed large flux decreases at the initial filtration stage, and about 79% flux decline was observed after 180 min during BSA solution filtration, as shown in Figure 6a. Thus, the hydrophobic PCD0 did not improve the biofouling resistance of the PSf membranes; both PCD0 and PSf are hydrophobic, as

expected from their contact angles and the surface energies in Table 2, and such hydrophobic surfaces do not have any antifouling properties against biofoulants as reported by us and others.<sup>30,35,36,46,56,57</sup> In contrast, much larger steady-state fluxes were observed from the membranes coated with other PCD#s; flux decline ratios of about 16, 12, and 10% were observed for the PCD54-, PCD74-, and PCD91-coated membranes, respectively. Thus, it is clear that PCD#-coated membranes with higher contents of DMA moieties have better antifouling properties against biofoulants. Hydrophilic poly(dopamine) (PDA) is known to be an effective coating material for preventing the adsorption of biofoulants such as proteins and bacteria because the hydrogen bonding between catechol groups in PDA and water molecules can provide an energetic and steric–entropic barrier against the adhesion of biofoulants to the membrane surfaces in an aqueous environment.<sup>17,18,58,59</sup> Although the interaction forces between the PCD54, PCD74, and PCD91 with a BSA-tethered AFM tip were not detected, possibly because they might be too small to be measured given the resolution of our equipment, it is clear that the increase in DMA content in the polymers increases the hydrophilicity of the membrane surfaces, as indicated by the contact angle studies, resulting in enhancement of biofouling resistance of the membranes.

Figure 6b shows the oil-fouling resistance behavior of the membranes characterized by the dead-end filtration test using an oil/water emulsion; smaller flux declines were observed from the membranes coated with less oleophilic PCD54, PCD74, and PCD91 (about 28, 24, and 35%, respectively) than more oleophilic PCD0-coated and PSf membrane (about 42 and 48%), although their difference was less than those obtained from the BSA solution filtration test. The membrane coated with PCD91, the most hydrophilic and least oleophilic sample among the PCD#s, exhibited larger flux decline values in oil-fouling test than the less hydrophilic and more oleophilic PCD54- and PCD74-coated membranes. Additionally, the PCD0-coated membrane showed smaller flux decline values than the PSf membrane in the oil/water filtration test, although they showed similar and much larger flux decline in BSA solution filtration.

These inconsistent behaviors may be attributable to the different fouling mechanisms by the oil-foulants and biofoulants. For example, the biofoulant on the hydrophilic surfaces can be removed effectively, because the interaction between the foulants and the hydrophilic surfaces can be minimized by the strong interactions of the polymers with water. It seems that the minor inconsistency of the biofouling

resistance and hydrophilicity behavior of PSf and PCD0 is not caused by the hydrophilicity difference but by other factors, such as the chemical structures and surface energies.<sup>57,60–63</sup> The oil-fouling resistance on the polymer surfaces is known to be affected by the formation of oil droplets on the membrane surfaces in the aqueous environment. When the oil/water emulsion is applied to membrane filtration, the poorly stabilized oil drops tend to adhere to the membrane surface and reorganize themselves, and they even coalesce with each other and spread to form a continuous oil-fouling film on the membrane surfaces.<sup>22–25</sup> The most hydrophilic PCD91-coating layer on PSf membrane could weaken the hydrophobic interactions between the oil droplets and the membrane surface in the stationary conditions (Figure 5b), whereas it could not effectively prevent the formation of the oil-fouling film, caused by coalescence and spreading of oil droplets on the membrane surfaces during the filtration (Figure 6b).<sup>23</sup> Thus, the most hydrophilic membrane cannot effectively prevent adhesion of oil-foulants, as stated above, and in previous results.<sup>23,35</sup> For this reason, the amphiphilic membrane surface is known to be most effective in imparting oil-fouling resistance. For example, the membrane surfaces containing both hydrophilic polymers, such as PEG, and hydrophobic moieties, such as perfluoroalkyl and polyhedral oligomeric silsesquioxane (POSS), exhibited excellent oil-fouling resistance because the hydrophobic moieties incorporated in the hydrophilic polymers could prevent the formation of a continuous oil-fouling film, originating from the coalescing and spreading of oil droplets, resulting in enhanced oil-fouling resistance of the membranes.<sup>23,35</sup> As a result, such amphiphilic membranes have been known to show both excellent biofouling and oil-fouling resistant behavior. Although the cardanol moiety is less hydrophobic than the perfluoroalkyl and POSS moieties, as estimated from surface energy values of polymers prepared from the HCPM, oxy[[2-(perfluorooctyl)ethyl]thiomethyl]ethylene], and methacrylate isobutyl POSS (3-(3,5,7,9,11,13,15-heptaisobutylpentacyclo[9.5.1.1.3,9]1.5,15]1,13]-octasiloxan-1-yl)propyl methacrylate), 39.79, 10.63, and 22.70 mN/m, respectively,<sup>64,65</sup> it is assumed that the hydrophobicity of the HCPM moiety is sufficient to interrupt the formation of a continuous oil-fouling film.

The fouling resistance behavior, hydrophilicity, oleophilicity, and interactions with biofoulants and oil-foulants are summarized in Table 3. The biofouling- and oil-fouling-resistant properties of these membranes from the filtration tests generally correlated well with their relative hydrophilicity/

**Table 3. Fouling Resistance, Hydrophilicity, Oleophilicity, Interactions with Biofoulants and Oil-Foulants**

biofouling resistance <sup>a</sup>	PCD91 > PCD74 > PCD54 > PSf $\cong$ PCD0
hydrophilicity <sup>b</sup>	PCD91 > PCD74 > PCD54 > PSf < PCD0
interaction forces with BSA <sup>c</sup>	PCD91 $\cong$ PCD74 $\cong$ PCD54 < PSf
oil-fouling resistance <sup>d</sup>	PCD74 > PCD54 > PCD91 > PCD0 > PSf
oleophilicity <sup>e</sup>	PCD91 < PCD74 < PCD54 < PCD0 < PSf
interaction forces with dodecane <sup>f</sup>	PCD91 < PCD74 < PCD54 < PSf

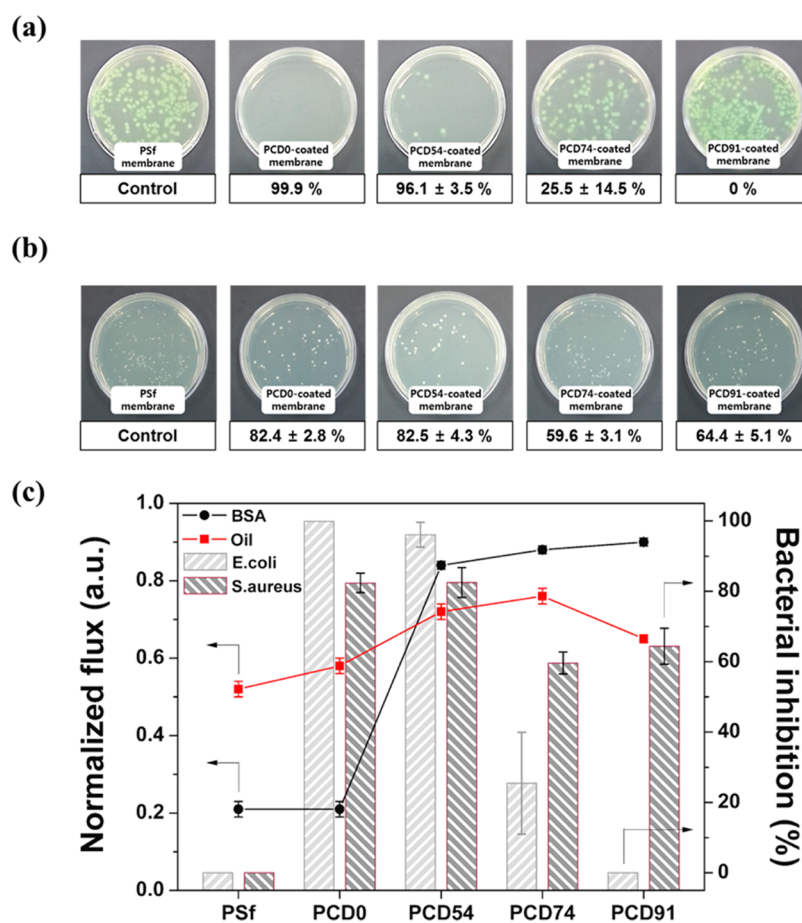
<sup>a</sup>Evaluated from the dead-end filtrations using BSA. <sup>b</sup>Estimated by air captive bubble contact angle. <sup>c</sup>Estimated by the interaction force with BSA-tethered AFM tip. <sup>d</sup>Evaluated from the dead-end filtration using an oil/water emulsion. <sup>e</sup>Estimated by decane captive bubble contact angle. <sup>f</sup>Estimated by the interaction force with dodecyl-tethered AFM tip.

oleophilicity and interaction behavior, but not always. As mentioned above, the increase in DMA content in the polymers increased the hydrophilicity and decreased the interaction forces with BSA, which in turn improved biofouling (BSA-fouling) resistance. In the contrast, the increase of DMA content in the polymers decreased both the oleophilicity and interaction forces with dodecane (oil), while the membranes coated with PCD54 and -74, having proper DMA contents, showed a smaller flux decline ratio in oil/water emulsion than that coated with PCD91, having the largest DMA contents, due to their amphiphilicity. Still, PCD54, PCD74, and PCD91 containing the less oleophilic DMA moieties showed improved oil-fouling resistance than those with no DMA moieties, such as PSf and PCD0.

**Antibacterial Properties of the Membranes.** In our recent research, we reported the antibacterial property of PCD0 and systematically studied the effects of polymers backbone structures on the antibacterial property, although the antibacterial mechanism of cardanol-containing polymers still remains unclear.<sup>27</sup> Therefore, in addition to the “proper” hydrophobicity of the HCPM moiety, it also has bactericidal properties that the perfluoroalkyl and POSS moieties do not. In other words, the incorporation of the HCPM moiety into the polymers was found to give a balance of amphiphilic properties and bactericidal properties to the polymer coating materials. To maintain membrane filtration performance in practical applications, the bactericidal property is also important in addition to the biofouling and oil-fouling resistance. It is well-appreciated that bacteria attached to membranes can produce a biofilm causing membrane flux decline when the population of the bacteria on the membrane is larger than a certain concentration, known as the quorum sensing effect.<sup>66–68</sup>

The bactericidal properties of the membranes were evaluated against model Gram-negative (*E. coli*, ATCC 8739) and Gram-positive (*S. aureus*, ATCC 6538) bacteria by a shaking flask method to confirm the bactericidal effect of the HCPM content in the polymers. Parts a and b of Figure 7 show the results of antibacterial tests of PCD#-coated membranes and the calculated bacterial inhibition rates against *E. coli* and *S. aureus* obtained using eq 2. The PCD0- and PCD54-coated membranes showed excellent bactericidal activity, with bacterial inhibition rates higher than 90% (99.9 and 96.1% for PCD0 and PCD54, respectively), whereas the PCD74-coated membranes showed a relatively low bacterial inhibition rate of about 25.5%, and the PCD91-coated showed no bactericidal activity against *E. coli*. As expected, the increase in HCPM content in the polymers increased the bactericidal properties of PCD#-coated membranes, in accordance with our recent work on the bactericidal properties of cardanol-containing polymers.<sup>27</sup> Thus, at least 46 wt % of HCPM moiety (or 54 wt % of DMA moiety) in the polymers was found to be required to provides effective bactericidal properties against *E. coli*. Although the general trend of the membrane antibacterial property against *S. aureus* is similar to that against *E. coli*, the bacterial inhibition values were found to be quite different; bacterial inhibition rates of the PCD0- and PCD54-coated membranes (82.4 and 82.5%, respectively) are larger than those of PCD74- and PCD91-coated membranes (59.6 and 64.4%, respectively). It is assumed that the good antibacterial activity of all PCD#-coated membranes against *S. aureus* is due to the absence of outer membrane, although the maximum antibacterial activity of the PCD#-coated membranes against *S. aureus* was lower than that against *E. coli*.<sup>69</sup>





**Figure 7.** Photographs and calculated bacterial inhibition rates of PCD0-, PCD54-, PCD74-, PCD91-coated and bare PSf membranes via antibacterial test against (a) *E. coli* and (b) *S. aureus*. (c) Summary of results of water permeation flux variations of the membranes after 180 min of BSA solution and oil/water emulsion filtration experiments and antibacterial tests against *E. coli* and *S. aureus*.

The water permeation behavior of the PCD0-, PCD54-, PCD74-, PCD91-coated, and bare PSf membranes after 180 min of BSA solution and oil/water emulsion filtration experiments and antibacterial property against *E. coli* and *S. aureus* are summarized in Figure 7c. We believe that the PCD54-coated membrane showed the best performance in terms of having excellent bactericidal properties with reasonably good biofouling and oil-fouling resistances, because it had the amphiphilic properties, containing an appropriate amount of the hydrophilic DMA moiety, and the hydrophobic and bactericidal HCPM moiety.

## CONCLUSION

Membranes coated with the copolymer PCD54 containing the mussel-inspired dopamine (DMA, 54 wt %) and plant-based cardanol (HCPM, 46 wt %) moieties demonstrated noticeably enhanced biofouling and oil-fouling resistances and high bactericidal properties, compared with the bare PSf ultrafiltration membrane, because the hydrophilic dopamine moiety has fouling resistance against oil and biomolecules, such as proteins, and the hydrophobic cardanol moiety has bactericidal properties against both Gram-positive and -negative bacteria. The proper composition of dopamine and cardanol moieties imparting amphiphilicity to the copolymer plays a crucial role to give both biofouling and oil-fouling resistance and bactericidal properties to coating materials on the surface of polysulfone membranes. Therefore, a copolymer containing the

mussel-inspired dopamine and the plant-based cardanol moieties is a new material that may achieve breakthroughs, surpassing the limitations of existing technology as a consequence of synergistically combining biofouling resistance and bactericidal properties. As a result, this research provides a deep understanding of a new way to prepare coating materials with the biofouling and oil-fouling resistance and a bactericidal property, which can give great inspiration for the design and synthesis of multifunctional coating materials.

## ASSOCIATED CONTENT

### Supporting Information

Synthesis of 2-hydroxy-3-cardanolpropyl methacrylate and dopamine methacrylate and XPS elemental analysis of the membrane surfaces (Tables S1 and S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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