

# pH-Induced Hysteretic Gating of Track-Etched Polycarbonate Membranes: Swelling/Deswelling Behavior of Polyelectrolyte Multilayers in Confined Geometry

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**Abstract:** pH-induced hysteretic gating of track-etched polycarbonate membranes (TEPC) has been achieved by depositing layer-by-layer assembled polyelectrolyte multilayers comprising poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) at a high pH condition (pH > 9.0). Scanning electron microscopy and transmission electron microscopy showed that the average bilayer thickness of multilayers was greater within the cylindrical pores of track-etched polycarbonate membranes compared to the multilayers on planar substrates (e.g., Si wafers and the face of TEPC membranes). Swelling/deswelling properties of multilayers and gating properties of the multilayer-modified TEPC membranes were studied by measuring the flux of pH-adjusted deionized water. Large discontinuous changes in the transmembrane flux were observed, indicating that the multilayers within the cylindrical pores of TEPC membranes exhibit the discontinuous swelling/deswelling behavior observed previously for planar systems. The degree of swelling as estimated by simple models, however, showed that (PAH/PSS) multilayers in the confined geometry swelled to smaller extents compared to the same multilayers on planar substrates under the same conditions. Multilayer-modified membranes showed reversible gating properties as the pH condition of feed solution was alternated between pH 2.5 and 10.5. In situ atomic force microscopy (AFM) was used to visualize the closing of the pores as a function of time. The hysteretic gating property of the multilayer-modified TEPC membrane was utilized to achieve either a "closed" or "open" state at one pH condition depending on the pretreatment history, thereby enabling either the retention or passage of high-molecular weight polymers by varying the membrane pretreatment condition.

## Introduction

Porous membranes that change their permeation/separation properties in response to environmental stimuli have been the focus of research for the last few decades.<sup>1–22</sup> Permeation properties of these membranes can be controlled by changing

pH,<sup>1–6,8–10,13,22</sup> temperature,<sup>11,12,14,15</sup> electric field,<sup>16,20,21</sup> concentration of chemical species,<sup>17,18</sup> or ionic strength<sup>2,19</sup> of their environments. Potential applications for these stimuli-responsive membranes include controlled drug delivery, wastewater treatment, chemical sensors and the separation of macromolecules including biological molecules such as proteins.

One of the most widely utilized approaches to create stimuli-responsive membranes is to graft polymer chains such as weak polyelectrolytes onto the surfaces of porous membranes. Ito et al. have demonstrated that it is possible to create pH-responsive membranes by surface graft polymerization of a weak polyacid onto track-etched polycarbonate (TEPC) membranes.<sup>3,4,7</sup> Also polypeptides that exhibit conformation changes as a function

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of environmental pH have been grafted to the surface of TEPC membranes to create stimuli-responsive membranes.<sup>5,6</sup> Mayes et al. also have reported a one-step fabrication of pH-responsive membranes by immersion precipitation with no post-coagulation processing steps.<sup>13</sup> In these pH-responsive membranes, the degree of ionization of a weak polyelectrolyte changes as a function of environmental pH; the chain conformation, hence, changes as a function of pH and controls the permeation and separation properties of porous membranes providing a “mechanochemical valve”. Using the approach of surface graft polymerization, stimuli-responsive membranes that can respond to changes in environmental temperature, light, concentration of chemical species, and redox properties also have been created.<sup>1–7,9–12,15,17,19</sup> Other approaches to create stimuli responsive membranes include the methods introduced by Martin and co-workers where gold nanotube membranes are utilized to modulate the transport properties of ions and organic molecules.<sup>20–22</sup>

While surface graft polymerization of polymers provides a useful means to create stimuli-responsive membranes, it is often difficult to precisely and reproducibly control the grafting density and degree of polymerization of grafted chains in the confined geometries of porous membranes.<sup>2,13,23</sup> In addition, most, if not all, of the stimuli responsive membranes generated to date via surface graft polymerization or other approaches show a nonhysteretic response to stimuli. This means that, while it is possible to achieve changes in the permeation properties by changing environmental conditions such as pH condition, ionic strength, and temperature, it is not possible to achieve either an “open” or “closed” state at one specified condition. Having “open” or “closed” states at one specified condition will be preferred for various applications that involve filtration of materials that are stable only in a narrow range of pH conditions. For example, most proteins are only stable in narrow pH ranges (pH 6–8).<sup>24</sup> Also, many types of nanoparticles, which have stabilizing agents on their surfaces, can only retain their colloidal stability in certain pH conditions;<sup>25</sup> therefore, it would be advantageous to use membranes that can filter or allow the passage of these pH-sensitive proteins or nanoparticles within the narrow pH ranges where their stability is maintained.

Layer-by-layer (LbL) assembly of polymers based on electrostatic or hydrogen-bonding interactions provides a versatile means to engineer and modify the physical and chemical properties of various surfaces including planar supports, colloidal particles, and porous membranes.<sup>26–31</sup> By choosing appropriate processing conditions and materials, it is possible to create polymer thin films that are responsive to various environmental stimuli such as ionic strength, pH, and temperature.<sup>32</sup> In particular, polyelectrolyte multilayers comprising weak polyelec-

trolytes offer a great advantage in creating stimuli-responsive polymer thin films.<sup>32–36</sup> A number of studies have shown that the permeation properties of multilayer hollow microcapsules containing weak polyelectrolytes can be controlled by various stimuli including temperature, ionic strength, and pH conditions.<sup>37–41</sup> It also has been shown that, by creating thin films of weak polyelectrolyte multilayers atop nanoporous anodized aluminum oxide (AAO) membranes or on planar electrode surfaces, ion diffusion characteristics can be modulated.<sup>42–46</sup> Sukhishvili et al. recently showed that, by depositing thermo-responsive hydrogen-bonded multilayers onto AAO membranes, the permeation of dyes could be controlled by changes in the temperature.<sup>41</sup> Hollman and Bhattacharyya also have assembled multilayers comprising polypeptides in the pores of track-etched polycarbonate membranes for enhanced ion separation.<sup>47</sup>

In this study, we report pH-responsive membranes that show discontinuous changes in the permeation properties. The responsive membranes are produced by depositing polyelectrolyte multilayers on the inner pore walls as well as on the surfaces of track-etched polycarbonate membranes. Our group has recently demonstrated that polyelectrolyte multilayers comprising a strong polyanion, poly(sodium 4-polystyrene sulfonate) (PSS) and a weak polycation, poly(allylamine hydrochloride) (PAH), assembled at a high pH condition (pH > 9.0) show discontinuous swelling/deswelling transitions as a function of pH conditions.<sup>34,35</sup> These reversible discontinuous transitions are induced by discontinuous changes in the degree of ionization of free amine groups of PAH and a dramatic shift in the  $pK_a$  value of PAH due to its local environment (hydrophobic association of free amine groups) within the multilayers.<sup>35,48</sup> Such a mechanism leads to a history-dependent swelling behavior of these multilayers. We investigate the swelling/deswelling behavior of these multilayers in a confined geometry based on simple models that enable the calculation of the pore diameters from the experimental flux values. We also demonstrate that it is possible to filter or allow the passage of high molecular weight polymers at the same pH condition utilizing the hysteretic gating properties of these membranes, demonstrating our proof-of-concept of achieving a “open” or “closed” state at a single pH condition depending on pretreatment conditions. The hysteretic gating of membranes overcomes one of the problems of conventional (nonhysteretic) stimuli-responsive membranes in that one membrane can be used to allow either

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retention or passage of pH-sensitive materials. To our knowledge, this is the first demonstration of hysteretic gating of porous membranes as well as the first study of swelling behavior of polyelectrolyte multilayers in a confined cylindrical geometry.

## Experimental Section

**Materials.** Poly(allylamine hydrochloride) (PAH) ( $M_w = 70\,000$ ), poly(sodium 4-styrenesulfonate) (PSS) ( $M_w = 70\,000$ ), and poly(ethylene oxide) (PEO) ( $M_v = 2\,000\,000$ ) were purchased from Sigma-Aldrich and used as received. Viscosity-average molecular weight ( $M_v$ ) of PEO was determined by measuring the intrinsic viscosity ( $[\eta]$ ) of PEO in water at 20 °C and using the relation  $[\eta] = 2.0 + 0.016 M_v^{0.76}$ .<sup>49</sup> The nominal molecular weight of PEO provided by the manufacturer was 5 000 000. Track-etched polycarbonate membranes (25 mm in diameter) whose pore diameters are 400 and 800 nm were purchased from Sterlitech.

**Modification of Track-Etched Polycarbonate Membranes with Polyelectrolyte Multilayers.** Polyelectrolyte solutions of 10 mM (based on the repeat unit molecular weight) were prepared from deionized (DI) water (18 M $\Omega$ ·cm Millipore), and the pH of both polyelectrolyte solutions and the rinse water were adjusted to pH 9.3 with 1 M NaOH. Unless otherwise noted, all the (PAH/PSS) multilayers were assembled at pH 9.3 in this study. The pH of both the assembly solutions and swelling solutions was monitored to ensure that a significant drift in pH did not occur during experiments. The drift in pH was typically less than 0.2 units. If the drift exceeded this amount, the solution was replaced with fresh solution. Polyelectrolyte multilayers were assembled onto track-etched polycarbonate (TEPC) membranes at room temperature (19–20 °C, relative humidity ~30%) by using an automated HMS programmable slide stainer (Zeiss, Inc.). Polyelectrolyte multilayers were deposited by dipping into the polycation (PAH) solution and the polyanion (PSS) solution alternately (for 20 min each) with dips in pH-adjusted water rinsing between (for 2, 2, and 1 min before the next dip into a polyelectrolyte solution). The role of the rinse steps is to remove loosely bound and unbound polyelectrolytes from the pores of the TEPC membranes. Dipping and rinsing steps were repeated until the predetermined number of bilayers was deposited (corresponding to 18.5 and 6.5 bilayers on 800 and 400 nm pore TEPC membranes, respectively).<sup>50</sup>

**Flux Measurement.** Flux measurements were performed on 25 mm diameter TEPC membranes using an Amicon 8010 dead-end filtration cell (Millipore) having an effective filtration area of 4.1 cm<sup>2</sup>. pH-adjusted deionized water was delivered from a stainless steel dispensing vessel (Millipore) pressurized with nitrogen gas (Figure S1 in the Supporting Information).

Polyelectrolyte multilayer modified TEPC membranes were pretreated by soaking the membranes in either pH 2.5 or pH 10.5 adjusted water for 3 min. After the pretreatment, the membranes were dried in the air for 2–3 min and then loaded into the filtration cell. The cell and the pressure vessel were filled with pH adjusted water and pressurized to 20 and 10 psi for 800 and 400 nm pore membranes, respectively. Each measurement consisted of a 3-min equilibration period, followed by a gravimetric flux measurement over a 3 min period. All of the filtration steps and flux measurements were performed at room temperature with a stirring speed of ~500 rpm. For reversibility tests, the transmembrane flux was measured during 5 cycles consisting of a pH 10.5 measurement followed by a pH 2.5 measurement. Each measurement consisted of a 3-min equilibration followed by a 3-min gravimetric flux measurement. Flux ( $J$ ) was calculated from the following relation:

$$J = \frac{V}{A_m \cdot t} \left[ \frac{\text{mL}}{\text{cm}^2 \cdot \text{min}} \right] \quad (1)$$

where,  $V$  is the volume of pH-adjusted water collected during 3 min,  $A_m$  is the superficial area of the TEPC membrane (4.1 cm<sup>2</sup>), and  $t$  is

the time of collection which was 3 min. For filtration experiments, a dilute solution (0.01 g/dL) of PEO dissolved in deionized water (pH 5.5–6.0) was filtered with pH 2.5 or 10.5 pretreated membranes. During each filtration experiment, the pressure was adjusted so that the flux was maintained at ~0.01 mL/(cm<sup>2</sup>·min). The concentration of filtrate solution was determined by measuring the relative viscosity by using a Cannon-Fenske viscometer (size 100). A calibration curve was obtained beforehand with polymer solutions of known concentrations.

**Multilayer Film Characterization.** The degree of swelling on planar Si (100) wafers was obtained using in situ ellipsometry as previously reported.<sup>35</sup> A spectroscopic ellipsometer (M-2000D, J. A. Woollam Co., Inc.) was used, and the data were fitted to a Cauchy model.<sup>51</sup> A refractive index of 1.333 was used for water during in situ ellipsometry. A self-built fluid cell based on a design described in the literature was used.<sup>52</sup> Measurements were made after a 3 min pretreatment either in pH 2.5 or 10.5 adjusted water followed by drying with blown air and then 3 min equilibration in pH-adjusted water.

To measure the multilayer growth in pores of track-etched polycarbonate membranes, scanning electron microscopy (SEM) was performed on a JEOL 6320 FEG-SEM operating at 2.0 kV. Cross-section transmission electron microscopy (TEM) images were generated on a JEOL 200CX operated at 200 kV. Multilayer-coated membranes were first stained with 1 mM sodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>) solution and then embedded in epoxy (Electron Microscopy Sciences). Ultrathin sections (50–70 nm) for TEM observation were microtomed at room temperature with a diamond knife using an RMC MT-X ultramicrotome and collected on copper grids.

In situ atomic force microscopy was performed under pH-adjusted water by a Molecular Imaging Pico Plus SPM. Contact mode with a Si<sub>3</sub>N<sub>4</sub> cantilever was used to scan a 10  $\mu$ m square area of the film in pH-adjusted deionized water.

## Results and Discussion

**Growth of (PAH/PSS) Multilayers in Cylindrical Pores of TEPC Membranes.** Growth of multilayers comprising PAH and PSS was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). (PAH/PSS) multilayers were deposited onto 800 nm pore TEPC membranes at pH 9.3. Figure 1 shows SEM images of the pores at various stages of multilayer deposition. The diameter of pores decreased as the number of deposited layers increased (Figure 2a), and no clogging of the pores was observed up to 24.5 bilayers. As can be seen in Figure 2b, the thickness of multilayers grown within the pores of TEPC membranes (estimated from SEM images in Figure 1) is larger than those grown on planar Si wafers for a given number of bilayers deposited (determined via ellipsometry). Also the difference in the thickness increases with the number of bilayers deposited onto each substrate. Previous studies by others also have observed thicker multilayer growth in cylindrical pores of anodized aluminum oxide (AAO) membranes and polycarbonate membranes.<sup>53</sup> In our case, since the SEM images only show the face of the multilayer coated membranes, the multilayer growth could be greater around the entrance regions of the cylindrical pores compared to the inner regions of the pores. Also, the nature of the substrate (Si wafer vs TEPC membrane

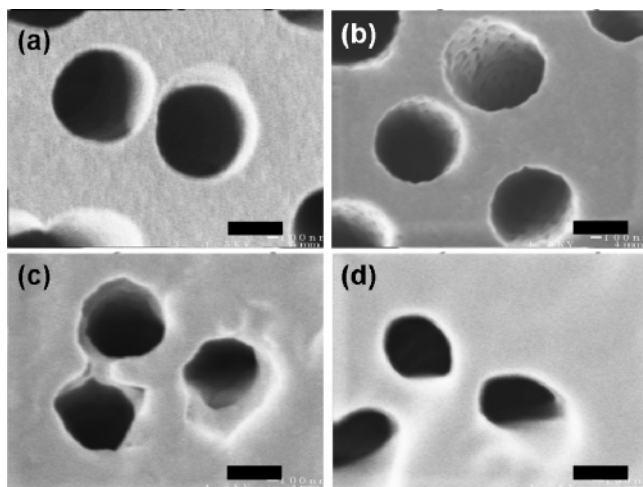
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**Figure 1.** SEM images of (PAH/PSS) multilayer coated TEPC membranes. (a) 0, (b) 8.5, (c) 14.5, and (d) 20.5 bilayers of (PAH/PSS) multilayers deposited at pH 9.3 onto 800 nm pore TEPC membranes. (Scale bar = 500 nm).

surface) could have an effect on the growth behavior of multilayers, a result that has been observed previously by others.<sup>54</sup> To address both of these issues, we carried out cross-sectional TEM studies of our multilayer-coated membranes.

Cross-sectional TEM images in Figure 3 clearly show that the thickness of a multilayer film assembled on the interior of the pores is larger than that on the face of the TEPC membranes; the same multilayer comprised of 24.5 (PAH/PSS) bilayers on a planar Si wafer has a thickness of 155 nm, in comparison to the approximate thickness of 250 nm seen in the membrane pores. This result shows that neither the nature of the surface nor an entrance effect is contributing to the enhanced growth behavior of multilayers in TEPC membrane pores. The small difference in the thickness of multilayers on planar Si wafers (155 nm) and on the face of the TEPC membrane (~175 nm) could be attributed to the difference in the thickness measurement techniques (i.e., cross-sectional TEM vs ellipsometry).<sup>55</sup> Others have suggested that the conformational changes induced by a curved surface may lead to enhanced growth of multilayers.<sup>53</sup> The conformation of polymer chains, however, was most likely not affected by the curvature of the pores since the size of pores in our study is much larger than the radius of gyration (~10 nm)<sup>56,57</sup> of the polyelectrolytes used in this study.

We believe the incomplete drainage of solutions during the layer-by-layer deposition process leads to the larger growth behavior within the cylindrical pores. On planar substrates (e.g., Si or glass substrates) that are held vertically during the LbL process, it is often observed that, due to the incomplete drainage of solutions on the bottom portion of the substrates during the deposition steps, the multilayers are thicker in this part of the substrate than in the uniform regions. Capillary forces that act on solutions within the cylindrical pores of TEPC membranes during the LbL process can lead to a similar effect, causing multilayers to grow thicker within the pores. Incomplete

drainage, however, does not necessarily indicate that residual polyelectrolytes are left in the pores during the rinse cycles of the LbL process. The characteristic diffusion time for polyelectrolyte chains to travel through the cylindrical pores estimated from a simple scaling argument ( $\tau_{\text{diff}} \approx L^2/D$ , where  $D \sim 10^{-7}$  cm<sup>2</sup>/s for polymer chains whose radius of gyration is ~10 nm<sup>56</sup>) is on the order of 10 s. Therefore, during the rinse cycles, which lasted 2, 2, and 1 min, any residual polyelectrolyte chains should be removed. The mechanism underlying the observed enhanced growth due to incomplete drainage of solution during the LbL process is, however, still unclear.

**Hysteretic Gating and Swelling/Deswelling Behavior of the Multilayers in Confined Geometry.** Hysteretic gating and discontinuous swelling/deswelling behavior of (PAH/PSS) multilayers in the pores of TEPC membranes were studied by measuring the flux of pH-adjusted water through these membranes. 18.5 bilayers of (PAH/PSS) multilayers were deposited onto the 800 nm pore TEPC membranes. A membrane was pretreated by soaking it in either pH 2.5 or 10.5 adjusted water for 3 min. After the pretreatment, a 3-min equilibration in pH-adjusted water was followed by a 3-min gravimetric flux measurement. Figure 4 shows the changes in flux as a function of pH treatment. A large discontinuous hysteresis loop in the flux is observed. After the pH 10.5 pretreatment, the multilayers within the pores of the TEPC membranes are only slightly hydrated down to a pH of about 5.0; therefore, the pores of the TEPC membranes remain “open”. However, as the pH condition of water that is permeated through the membranes is further lowered, the multilayers undergo a swelling transition which, in turn, effectively “closes” the pores. For the case of the multilayer-modified membranes that are pretreated at pH 2.5, the multilayers within the pores of the TEPC membranes retain their swollen structure up to pH 9.0; hence, the pores are “closed” and the flux is extremely low. It should be noted that the values of flux measured for the “closed” states are not equal to zero and are quantitatively in the range of about 0.2 mL/(cm<sup>2</sup> · min), smaller than the flux in the “open” state by a factor of about 500. At a pH environment higher than 9.0, the multilayers begin to deswell and open up the pores. These results confirm that the discontinuous swelling/deswelling transitions that were observed on planar substrates<sup>34,35</sup> can also be realized in the submicron pores of TEPC membranes. Taking advantage of the LbL process, the difference in the trans-membrane flux between the open and closed states (the vertical gap of the hysteresis loop) can be easily varied by changing the number of bilayers deposited and the original diameter of the pores in the TEPC membranes (see Figure S2 in the Supporting Information for examples). It should be noted that in all cases multilayers were characterized within 24 h after their preparation. Our previous studies have shown that these multilayers slowly, over a period of days and weeks, undergo molecular rearrangements, especially in a moist environment, that prevent multilayers from achieving its high level of swellability.<sup>34,35</sup> Their ability to gate the pores of TEPC membranes has been correspondingly observed to diminish as a result of this molecular reorganization. The stability of the multilayers can be maintained, however, by storing the multilayer-modified membranes in dry conditions (e.g., vacuum) as mentioned by Itano et al.<sup>35</sup>

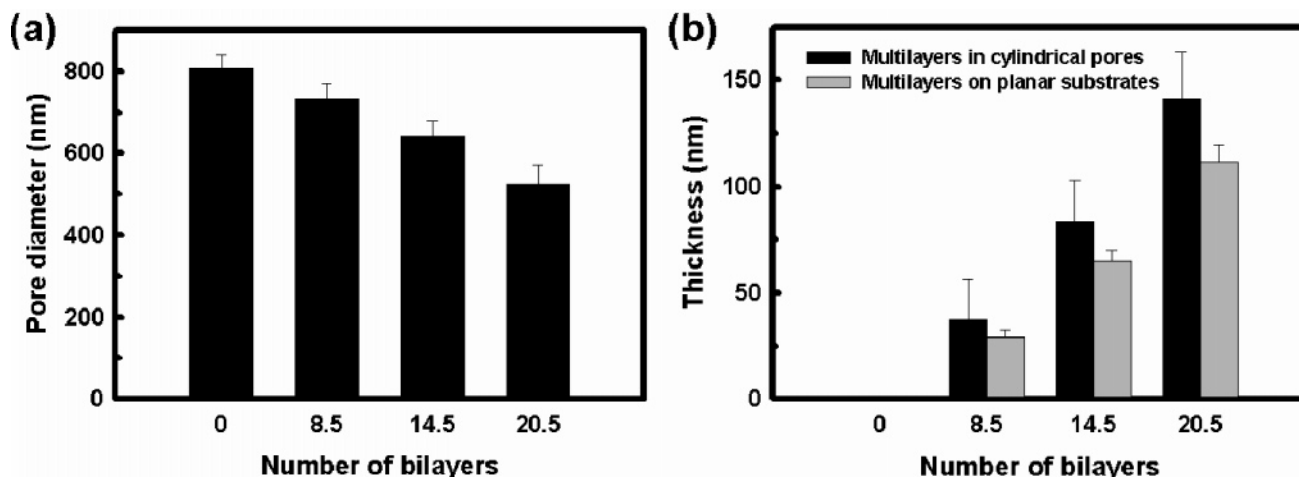
A more quantitative analysis of the phenomena described above would provide valuable information about the swelling/

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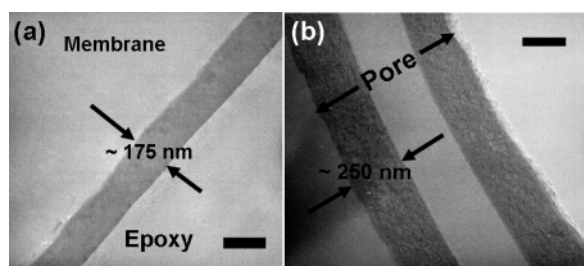
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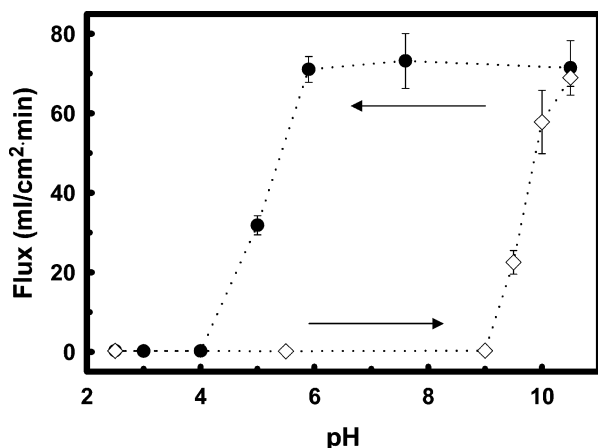
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**Figure 2.** Changes in the (a) average pore diameters and (b) the thickness of multilayers in the pores of TEPC estimated from SEM images. Black bars represent the thickness of multilayers in the cylindrical pores of TEPC membranes, and gray bars represent the thickness of multilayers on planar Si substrates. Diameters of at least 50 pores were measured for averaging.



**Figure 3.** Cross-section TEM images of 24.5 (PAH/PSS) bilayers (a) on the planar surface of the TEPC membrane and (b) in the pore of the TEPC membrane. (Scale bar = 200 nm).



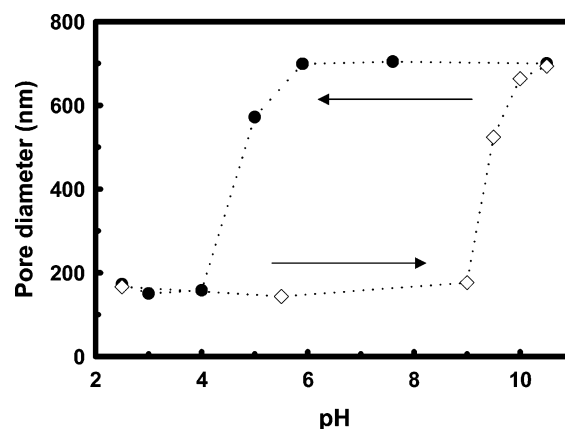
**Figure 4.** Changes in flux as a function of pH. The filled circles and open diamonds represent data generated after a pH 10.5 pretreatment and after a pH 2.5 pretreatment, respectively. Error bars represent standard deviations.

deswelling behavior of (PAH/PSS) multilayers in a confined geometry. To estimate the size of pores in the open and closed states, we first use the well-established Hagen–Poiseuille (HP) equation:<sup>58</sup>

$$\frac{Q}{A_m} = J = \frac{n\pi(D/2)^4 \Delta P}{8\eta L} \quad (2)$$

where  $Q$  is the volumetric flow rate,  $A_m$  is the external

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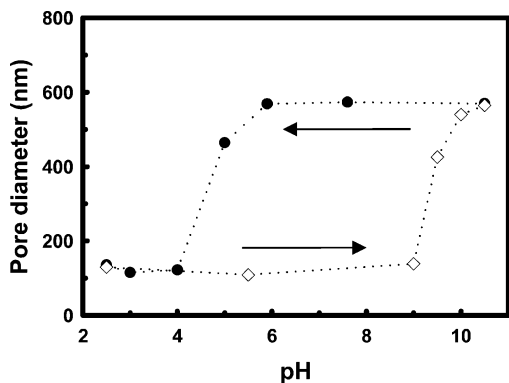
**Figure 5.** Changes in the pore diameter as a function of pH estimated from Hagen–Poiseuille equation. The filled circles and open diamonds represent data generated after a pH 10.5 pretreatment and after a pH 2.5 pretreatment, respectively.

membrane area,  $J$  is the flux,  $n$  is the number of pores per unit area of membrane,  $D$  is the average pore diameter,  $\eta$  is the fluid viscosity,  $\Delta P$  is the pressure difference across the membranes, and  $L$  is the average length of the pores. Therefore, at constant  $\Delta P$ , the transmembrane flux should depend on the pore diameter according to the following relation:

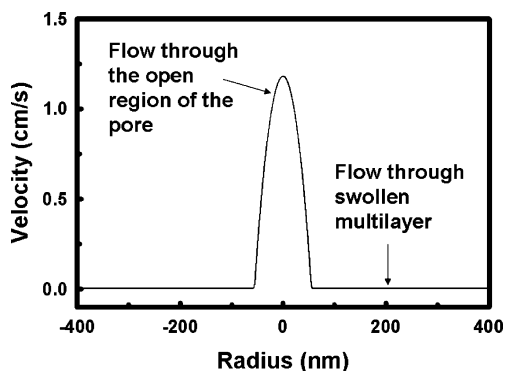
$$\frac{D}{D_{\text{ref}}} = \left( \frac{J_{\text{exp}}}{J_{\text{ref}}} \right)^{1/4} \quad (2)$$

By measuring the transmembrane flux of bare 800 nm pore TEPC membranes (reference state), the pore diameters ( $D$ ) of multilayer-modified membranes under different pH conditions can be estimated from the experimentally measured flux ( $J_{\text{exp}}$ ).

Figure 5 shows the discontinuous transitions in the pore diameter of multilayer-modified TEPC membranes as a function of pH conditions as estimated from the HP equation. As expected, the pore diameters decrease significantly in the “closed” states reducing the flux of water through the membranes. However, the estimated pore diameter in the open state is about 700 nm, whereas the pore diameter measured from SEM is approximately  $600 \pm 26$  nm. Previous studies that utilized the HP equation to estimate the size of cylindrical capillaries of TEPC membranes have shown that this equation overesti-



**Figure 6.** Changes in the pore diameter as a function of pH estimated from two-region flow (TRF) model. The filled circles and open diamonds represent data generated after a pH 10.5 pretreatment and after a pH 2.5 pretreatment, respectively.



**Figure 7.** Velocity profile of water flowing through a cylindrical pore in a closed state. The velocity profile was calculated based on the TRF model from experimental flux values taken from a pH 5.5 solution after a pH 2.5 pretreatment. The radius of the unmodified pore is 400 nm.

mates the size of pores.<sup>59–61</sup> Also the HP equation assumes that the multilayers are impenetrable to water; however, ample evidence in the literature supports the fact that polyelectrolyte multilayers are highly permeable to water.<sup>62</sup> Therefore, by making the assumption of impermeable multilayers, especially in the swollen state, the pore diameters would be overestimated.

To account for permeation of water through the hydrated multilayers, we employ a two-region flow (TRF) model (see Supporting Information for details), which has been used to model the flow of water through polymer brush grafted TEPC membranes.<sup>63,64</sup> Figure 6 shows the estimated pore diameter from the TRF model. The pore diameter ( $\sim 120$  nm) in the “closed” state obtained from the TRF model is smaller than that predicted by the HP equation ( $\sim 160$  nm). Figure 7 shows that, in the “closed” state (calculated for a solution of pH 5.5 after a pH 2.5 pretreatment), the velocity of water permeating through the hydrated multilayers is extremely small (ca.  $1.9 \times 10^{-3}$  cm/s) compared to that of water in the physically open region (i.e., multilayer-free region where the typical maximum value is ca. 1.2 cm/s). However, the fraction of the total flux

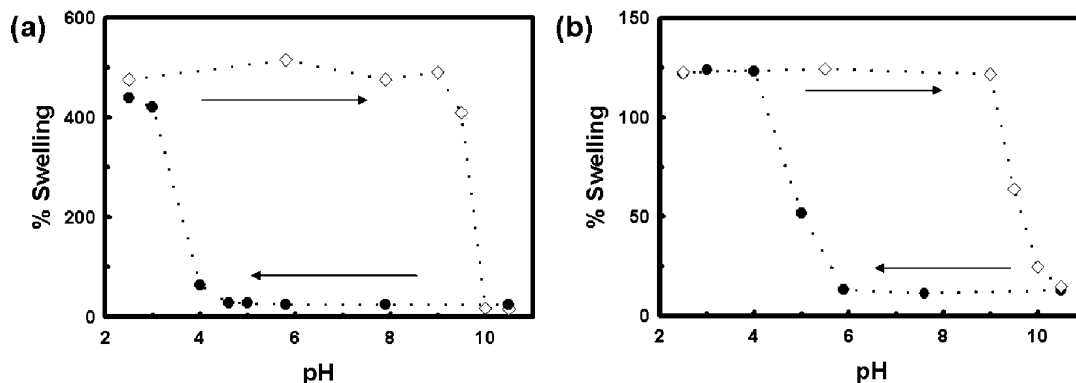
that passes through the hydrated region is nearly 0.13 since the hydrated multilayer region covers about 98% of the cross-sectional area of the pores. While we do not expect the values of the pore diameters estimated by the TRF model or HP equation to be exact, the values from the TRF model and HP equation provide us with plausible ranges for the dimensions of the constricted pores from the flux experiments.

The swelling behavior of the (PAH/PSS) multilayers on planar Si wafers and within the cylindrical pores of TEPC membranes was compared. Figure 8 shows the percent (%) swelling of the multilayers as a function of solution pH (18.5 bilayers) on a planar surface (determined by in situ ellipsometry; see Experimental Section) and within the pores of TEPC membranes. (For a definition of percent swelling in each geometry, see Supporting Information.) While the hysteresis is present in both cases, swelling in the confined geometry is clearly suppressed. We believe that this suppression of swelling in the confined geometry is caused by a decrease in the volume available to the multilayers during swelling. In the case of multilayers swelling on a planar substrate, the multilayer–liquid interface is essentially stress free as it undergoes swelling; however, in the case of multilayers in the confined geometry, as the multilayers swell, the volume available to the swelling multilayer decreases leading to stress at the multilayer–liquid interface. Also, another possibility is the contribution of electrostatic repulsive forces that may act across the physical opening hindering the close approach of multilayers as the pores become smaller. It is expected that the effect of confinement would be more pronounced as the ratio of multilayer thickness to radius of the pores becomes larger.

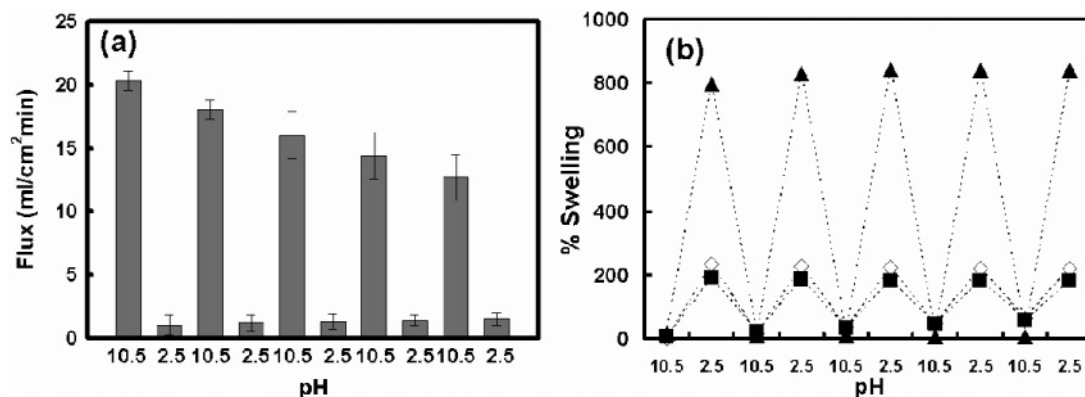
**Reversible Gating of Membrane Pores.** Reversibility of the multilayer gates was verified by changing solution pH between pH 2.5 and pH 10.5 five times (see Experimental Section for details). Figure 9 shows the reversible gating properties of the 400 nm pore TEPC membranes coated with 6.5 bilayers of (PAH/PSS) multilayers. Although a small decrease is seen in the flux of the “open” states as the number of acid/base treatment cycles increased, the multilayer-modified TEPC membranes retains reversibility as the conditions are cycled between the “open” and “closed” states with changes in solution pH. The small decrease in the flux may be attributed to slower deswelling kinetics as the number of cycles increased, possibly due to a reorganization of the polyelectrolyte chains in the multilayer structures. As can be seen in Figure 9b, the degree of swelling of a 6.5 bilayer-(PAH/PSS) multilayer in cylindrical pores (determined from flux experiments based on the TRF model and HP equation) was smaller compared to the same multilayers on planar Si wafers (determined by in situ ellipsometry). As described above, we believe that stress in the multilayer due to the decrease in available volume during multilayer expansion is responsible for the suppression of swelling in the confined geometry. Although it cannot be clearly seen in Figure 9b (due to the large scale in the ordinate), the % swelling of multilayers in the cylindrical pores indeed shows a small increase in the open, or deswollen, (pH 10.5) state with the number of acid/base cycles.

**In situ Atomic Force Microscopy (AFM).** In situ AFM was performed to visualize the gating of the cylindrical pores by the swollen (PAH/PSS) multilayers at acidic conditions (pH 2.5). Figure 10 shows the time evolution of pores being closed by

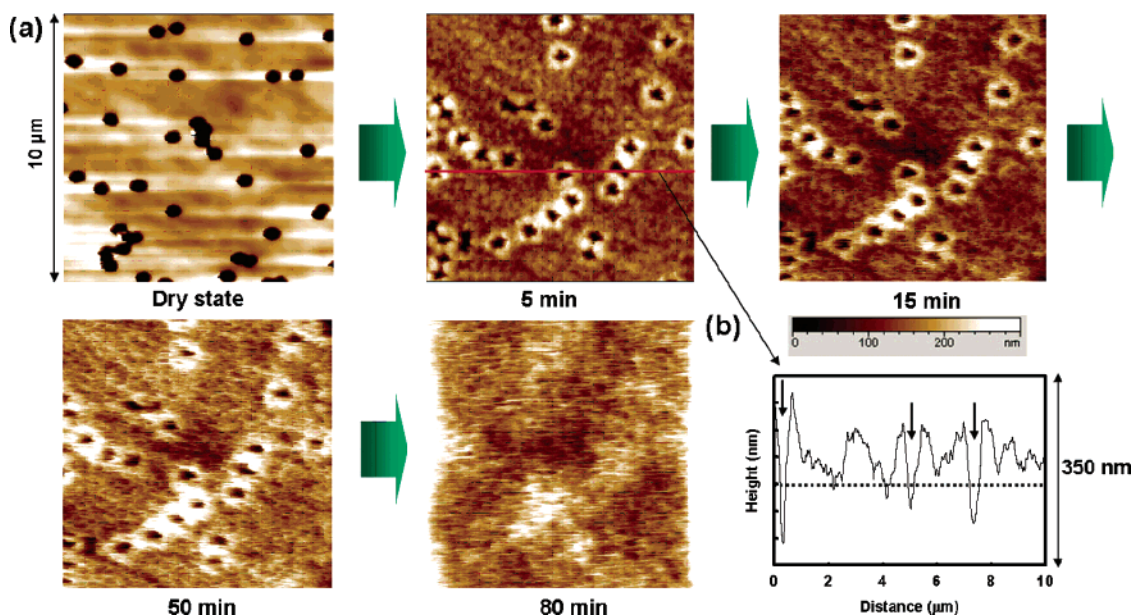
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**Figure 8.** Comparison of % swelling (a) on a planar Si substrate (determined by in-situ ellipsometry) and (b) in the cylindrical pores of the 800 nm pore TEPC membranes (from flux measurements and the TRF model). The filled circles and open diamonds represent data generated after a pH 10.5 pretreatment and after a pH 2.5 pretreatment, respectively.



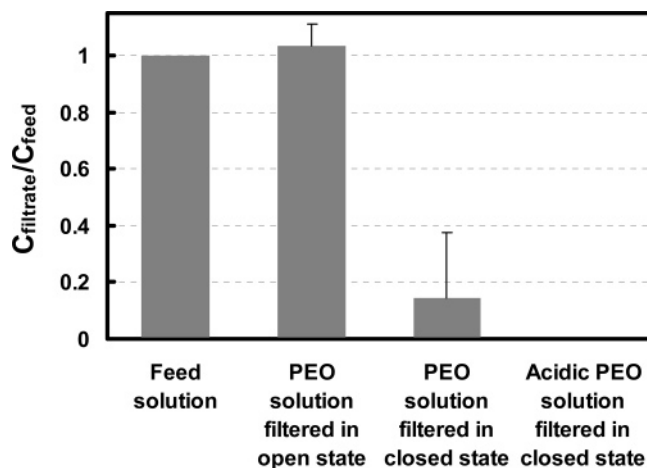
**Figure 9.** Reversible gating of 400 nm pore TEPC membranes with 6.5 bilayers of (PAH/PSS) multilayers. (a) Changes in the transmembrane flux as a function of pH and (b) % swelling of 6.5 bilayers of (PAH/PSS) multilayers on planar Si substrate ( $\blacktriangle$ ) (determined by in situ ellipsometry), and in the pores of 400 nm pore TEPC membranes based on the HP equation ( $\blacksquare$ ) and the TRF model ( $\diamond$ ).



**Figure 10.** (a) Time evolution of the pore structures observed by in situ AFM of (PAH/PSS) multilayer-modified 800 nm pore TEPC membrane under acidic conditions (pH 2.5). (b) Height profile from the "5 min" AFM image along the red line (arrows indicate the locations of pores).

the swelling multilayers. Multilayer-modified TEPC membranes show relatively smooth surfaces in a dry state. In the initial stages of the swelling (<15 min), the pores of the TEPC membranes become smaller and, at the same time, the raised ridges are formed around the pores (Figure 10b). These ridges around the pores indicate that the multilayers within the pores

are also swelling in the axial direction of the pores and the axial expansion could be accommodating some of the stress that is formed during the swelling in the radial direction. The pores are clearly visible up to 50 min, which indicates that swelling within the pores is suppressed. Swelling studies on planar substrates showed that the multilayers swell  $\sim$ 500% after only



**Figure 11.** Filtration of high molecular weight PEO (0.01 g/dL) using 18.5 bilayer (PAH/PSS) modified 800 nm TEPC membranes in different conditions. Flux during each filtration experiment was  $\sim 0.01$  mL/(cm<sup>2</sup> · min). Open and closed states were attained by the pretreatment of multilayer-modified membranes at pH 10.5 and pH 2.5, respectively. PEO was dissolved in DI water to make PEO solution (pH 5.5–6.0). Acidic PEO solution was made by adjusting the solution pH of PEO solution to pH 2.5. Error bars represent standard deviation.  $C_{\text{filtrate}}$  and  $C_{\text{feed}}$  denote the concentration of PEO in filtrate and feed solutions, respectively.

3 min (Figure 8a);<sup>35</sup> therefore, the pores should have been closed completely in less than 3 min if the multilayers exhibited the same swelling behavior within the confined geometry. In situ AFM again supports the idea that the swelling of (PAH/PSS) multilayers is suppressed by the confinement. A direct comparison between the swelling behavior of the multilayers in the pores observed from in situ AFM and the flux measurements is not made since the experimental conditions such as applied pressure under which each experiment was performed are different.

**Filtration of Macromolecules.** To demonstrate that it is possible to have either “open” or “closed” states at one pH condition depending on the pretreatment conditions, a high-molecular weight water soluble polymer, poly(ethylene oxide) (PEO), was filtered using multilayer-modified TEPC membranes. PEO was a suitable candidate for the filtration test since it is water soluble and, at the same time, does not carry any charges; therefore, it is possible to exclude any charge effect during the filtration process. The PEO solution was made with deionized water (pH range between 5.5 and 6.0). Figure 11 shows that when the multilayer-modified TEPC membranes were pretreated at pH 10.5, PEO chains could not be retained by the filter, and essentially all of the original concentration (0.01 g/dL) was recovered in the filtrate. After pH 2.5 treatment of the multilayer modified membranes, however, approximately 80% of the PEO was retained due to size exclusion. It is likely that only relatively short PEO chains passed through the constricted pores of the TEPC membrane resulting in the observed decrease in the total concentration of PEO in the filtrate.

Filtration was also performed by dissolving PEO in pH 2.5 adjusted-water. As shown in Figure 11, the PEO solution made with pH 2.5 adjusted-water shows a higher PEO retention. We believe that the lower filtration efficiency in DI water (pH 5.5–6.0) solutions may be due to the relaxation (or deswelling) of the swollen multilayers that occurs when the filtration is performed. A previous report showed that when the (PAH/PSS)

multilayer pretreated in acidic condition (pH 2) was immersed in DI water for a prolonged period (>60 min), the multilayer deswells to its original thickness.<sup>35</sup> Here we have observed that multilayers in the cylindrical pores of TEPC membranes deswell much more slowly than planar thin films. A negligible change in the flux was observed (for a membrane pretreated at pH 2.5) with DI water for at least 1 h. The observed slow deswelling kinetics are a consequence of the geometrical confinement of the multilayers. While the planar thin films are exposed to a semi-infinite reservoir of DI water, the swollen multilayer within the confined geometry comes in contact with only a small amount of DI water that permeates through the constricted pores. A more extensive study on the swelling/deswelling dynamics of multilayers in confined geometry is currently underway. In the case of the acidic PEO solution, the multilayers maintain a high level of swelling during filtration leading to higher filtration efficiency. These results clearly show the feasibility of retaining or passing high molecular weight polymer using the (PAH/PSS) multilayer-modified TEPC membranes at a specific pH condition by varying the pretreatment conditions. In other words, the pretreatment history of the multilayer-modified membranes determines whether high molecular weight polymers can be retained or passed through at a single pH condition.

## Conclusion

We have demonstrated that stimuli responsive membranes can be fabricated by modifying track-etched polycarbonate membranes with polyelectrolyte multilayers comprising poly(allylamine hydrochloride) and poly(sodium 4-styrenesulfonate). (PAH/PSS) multilayers were deposited on TEPC membranes at a high pH condition (pH > 9.0) which has been shown to produce multilayers that undergo discontinuous swelling/deswelling transitions. Multilayer-modified TEPC membranes showed discontinuous changes in the trans-membrane flux as a function of solution pH. Using two simple models, the diameters of the pores were predicted from experimental values of the flux. Compared to the swelling of these multilayers on planar Si substrates, the geometrically confined multilayers swelled to a smaller extent. We believe that stresses in the multilayers that arise from limitations on the available volume during multilayer swelling suppress the expansion of the multilayers within the confined geometry. Although a small decrease in the transmembrane flux was observed in the “open” state as the number of open/close cycles was increased, multilayer-modified TEPC membranes showed reversible gating properties during multiple alternate acid and base treatments. As demonstrated in a simple filtration experiment of water soluble PEO, these membranes can either retain or allow the passage of high molecular weight PEO chains at a specified pH condition, depending on the membrane pretreatment condition. Further studies on the swelling behavior as well as separation behavior of (PAH/PSS) multilayers in different types of media (e.g., buffer solutions) will be performed. By utilizing the overlap of an electrical double layer in the constricted pores, it may be also possible to use these membranes for pH-triggered separation of small molecular weight charged molecules such as charged dye molecules as well as small ionic species.<sup>65–67</sup> In addition,

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this new class of stimuli responsive mechanochemical valves can be used to gate the flow of water in microfluidic channels allowing either an open or closed state to exist at a single pH condition.<sup>68</sup>

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**Supporting Information Available:** Experimental setup for flux measurement, ratio of open state flux to closed state flux as a function of the number of deposited bilayers, two-region flow model, parameters used for modeling, and the definition of percent (%) swelling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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