

## Visualization of Critical pH-Controlled Gating of a Porous Membrane Grafted with Polyelectrolyte Brushes

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Polymer chains extend and contract in response to changes in environmental conditions. The molecular behavior can be magnified by fabricating a three-dimensional network in a hydrogel. The polymeric hydrogels undergo abrupt volume changes in response to changes in environmental conditions, such as solvent composition,<sup>1</sup> electric field,<sup>3</sup> temperature,<sup>4</sup> and chemical concentration.<sup>5</sup> However, the observation of the extension and contraction of polymer chains in solution in a solvated state using microscopy is difficult due to the requirement for polymers to be dried. In the present study, the extension and contraction of the polymer chains in "polyelectrolyte brushes"<sup>6–13</sup> grafted on a nanoporous polymeric membrane were visualized using atomic force microscopy, which enables direct microscopic observation in water.

Poly(methacrylic acid) which acted as the polyelectrolyte brush was grafted on track-etch porous polycarbonate membrane (DuPont Nuclepore membrane; average pore diameter 200 nm) by glow-discharge treatment.<sup>14</sup> Under low pH conditions, the poly(methacrylic acid) chain is protonated and contracted; under high pH conditions, the chain is deprotonated and extended.

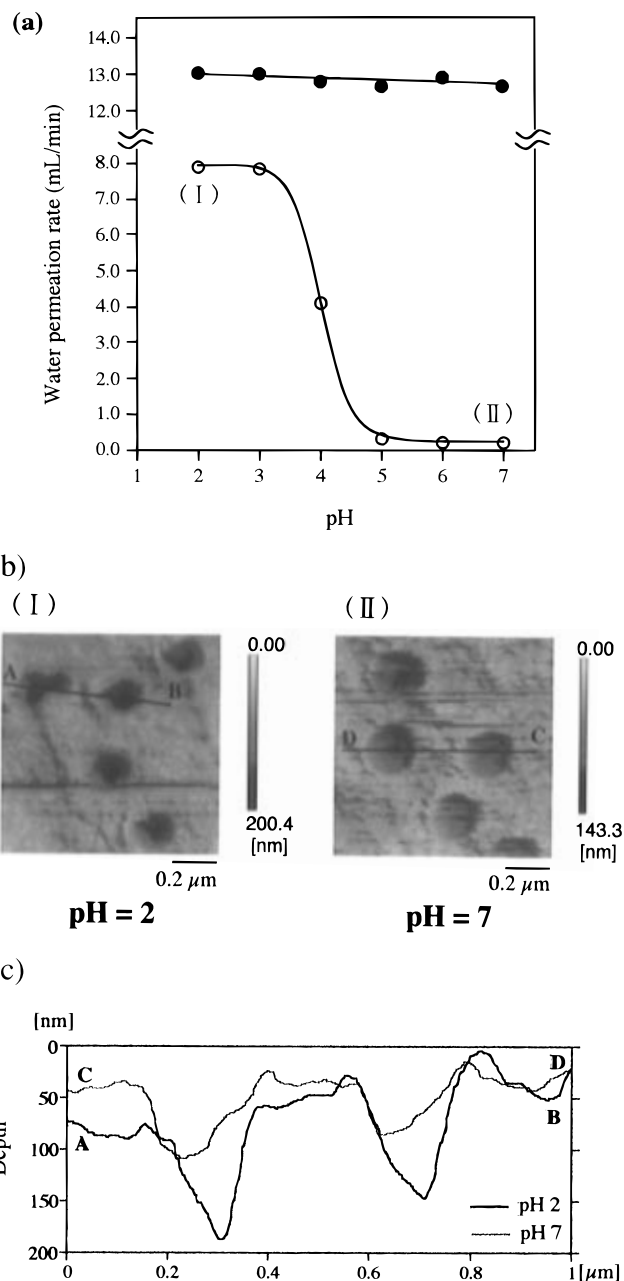
Pore size was estimated by measuring the rate of water permeation through the membrane (Figure 1a). The rate of water permeation through an ungrafted membrane was independent of pH. The rate of permeation through the grafted membrane was found to be less than that of the ungrafted membrane, but was dependent upon pH. The rate was high at low pH, but was nearly zero at neutral pH. These changes in permeation were repeatedly carried out by pH changes, because the polyelectrolyte brush was covalently grafted on the membrane.

An atomic force microscope (AFM) was used for *in situ* observation of pore shape in an aqueous solution<sup>15</sup> (Figure 1b).

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- (14) The polycarbonate membrane was glow-discharged in air for 30 s at room temperature. The treated membrane was immersed in an aqueous solution of methacrylic acid (20 wt %) for 3 h at 60 °C. The membrane was washed with deionized water until the pH of the washing liquid became constant. The amount of grafted poly(methacrylic acid) was calculated to be 25  $\mu\text{g}/\text{cm}^2$  based on carboxylic acid using the Rhodamine 6G method.
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**Figure 1.** (a) Dependence of water permeation on pH for the poly(methacrylic acid)-grafted (○) and nongrafted (●) membranes. Permeation experiments: The prepared membrane was then mounted on an ultrafiltration cell (Toyo Roshi UHP-25). Under constant nitrogen gas pressure, aqueous solutions which had been adjusted to different pH values using NaOH and HCl were allowed to flow through the membrane. The permeation rate was calculated by measuring the mass of water that was able to pass through the membrane each minute. (b) Atomic force micrograph (AFM) of a poly(methacrylic acid)-grafted membrane at pH 2 and 7. An atomic force microscope, SPM-9500 (Shimadzu, Kyoto, Japan), equipped with a fluid cell containing an aqueous solution of varying pH was utilized to record the images. For the repulsive mode, commercial  $\text{Si}_3\text{N}_4$  cantilevers with a nominal force constant of 0.06 N/m were used. (c) Cross sectional plots showing the depths of the holes along A–B at pH 2 and along C–D at pH 7 in (b).

Black areas represent a deep concave region on the surface of the membrane: in other words, the presence of a pore. At a high pH, ionized polymer brushes should be strongly solvated to cover the pores. Black circles are clearly visible at pH 2, but not at pH 7. Thus, the polyelectrolyte grafts behave like a gate to open and close the pores. The cross-sectional plots of

showing the depths of the holes is shown in Figure 1c. The average depths of holes at pH 2 and 7 were  $127.7 \pm 5.1$  and  $73.2 \pm 9.3$  nm ( $n = 15$ ), respectively.

The sharp dependence of permeation on pH was of interest in this study. Bergbreiter and Bandella reported that the titration curve of poly(acrylic acid) in solution is not as sharp as that of a poly(acrylic acid) graft.<sup>16</sup> They speculated that a cooperative conformational change of polyelectrolyte brushes was induced by a change in pH. A significant polarity difference between the low-dielectric polycarbonate film surface and the polar aqueous buffer solution might exaggerate the solubility difference of the partially deprotonated polyelectrolyte. As a result, even a small pH change could induce a significant conformational change.

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Klein et al.<sup>17</sup> demonstrated that a pair of opposing brushes, slid past one another in the presence of a good solvent, experiences a repulsive normal force. Therefore, the use of (nonpolyelectrolytic) polymer brushes as microvalves for controlling flow through pores was theoretically described by Sevick and Williams.<sup>18</sup> On the other hand, theoretical studies have predicted the control of permeability using polyelectrolyte-grafted porous membranes.<sup>19</sup> In the present study, we were able to successfully synthesize such a membrane and obtain an AFM image of the channel-gating process.

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