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pH-Controlled Gating of a Porous Glass Filter by Surface Grafting of Polyelectrolyte Brushes

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Poly(acrylic acid) (PAA, a polyelectrolyte brush) was grafted onto a porous glass filter in order to construct a pH-dependent system for the control of liquid permeation. The porous glass filter was treated with octadecyldimethyl(*N*,*N*-diethylamino)silane and subjected to glow-discharge treatment to facilitate graft polymerization of the acrylic acid. The surface was analyzed using measurement of the water contact angle, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The surface wettability of the glass filter decreased following silane-coupling treatment and increased following PAA grafting. Water permeation of the PAA-grafted glass filter was pH dependent. The permeation rate was high under low pH conditions and low under high pH conditions. A possible explanation for this permeation profile is that under low pH conditions protonated PAA chains shrink, thereby opening the pores of the filter, and that under high pH conditions dissociated PAA chains are extended to cover the pores. The permeation rate of a water/acetone mixture through the grafted glass filter was also pH dependent. The PAA-grafted glass filter was more stable for the mixture in comparison with a polymer filter.

Introduction

Hydrogels are a unique class of material that change volume in response to external stimuli such as pH, temperature, light, ions, electric field, and chemicals.[1−7] However, the mechanical fragility and slow kinetics of the swelling and deswelling processes have limited the number of practical applications of this material. Swelling and deswelling are governed by diffusion-controlled transport of water molecules through the polymer network. Therefore, rapid control of drug release based on gel swelling is in principle difficult, although several attempts have been made to use hydrogels for drug release.[6] To overcome this difficulty, we previously grafted stimuli-responsive polymer brushes onto porous polymer membranes.[8−13] However, these polymeric membranes were not solvent tolerant and were not stable enough to transport organic liquids under pressure.

In the present investigation, poly(acrylic acid) (PAA) was grafted onto a porous glass filter. The flow of water or a water/acetone mixture through the PAA polyelectolyte brushes was investigated under various pH conditions. The combination of a stimulus (pH)-responsive polymer brush and porous inorganic film may produce a new solvent-tolerant and stable stimuli-responsive material.

Experimental Section

Materials. A glass filter (diameter, 30 mm; thickness, 3 mm; average pore diameter, 5 μm) was purchased from Sansyo Co. (Tokyo, Japan). The pore size distribution was measured by Hg porosimetry.[14] The result is shown in Figure 1. Acrylic acid was purchased from Nacalai Tesque Inc. (Kyoto, Japan) and purified by distillation under reduced pressure. Acetone and distilled water, used for measuring the permeation rates, were purified by ultrafiltration before use. Commerical hydrochloric acid, potassium hydroxide, and potassium chloride were used without further purification.

Graft Polymerization onto a Porous Glass Filter. The preparative scheme for the PAA-grafted glass filter is shown in Figure 2. A porous glass filter was treated in 0.1 M HNO_3 at 70 °C for 3 h, washed with distilled water several times, and dried in vacuo at 140 °C for 6 h. The treated glass filter was then immersed in a toluene solution containing 10 wt % of octadecyldimethyl(*N*,*N*-diethylamino)silane (ODS−DEA) which was synthesized as previously reported.[15,16]

The silane-coupled filter was glow-discharged in air using a high-frequency wave generator (200 W, HSF-005 Nihon

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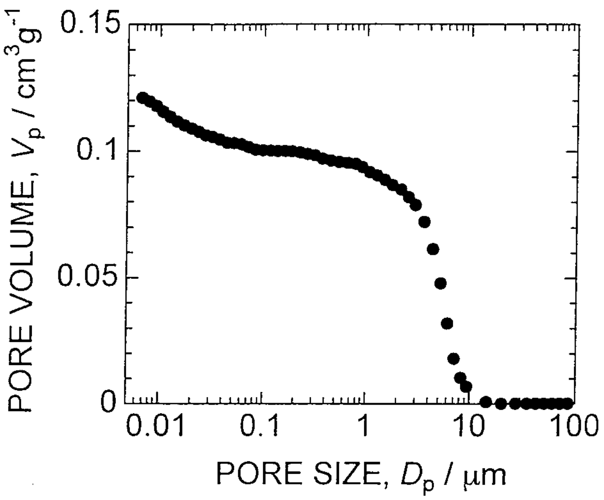

Figure 1. Pore size distribution curve of glass filter.

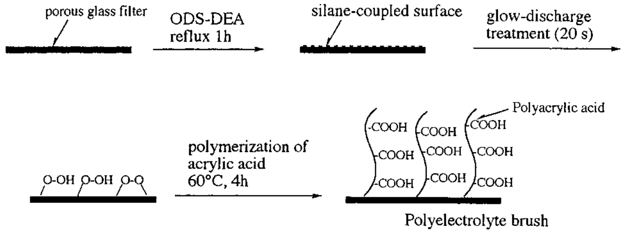

Figure 2. Preparative scheme of surface-grafted glass filter.

Koshuha, Yokohama, Japan) for 20 s under a pressure of 6.7 Pa, according to the method used for polymeric membranes as previously described.[10,11] The glow-discharged filter was immersed in a 20% solution of acrylic acid in water (300 mL) and left to stand at 60 °C in a nitrogen atmosphere. After 4 h, the glass filter was taken out and washed repeatedly with distilled water until the pH of the washing liquid became neutral. The washed glass filter was dried in vacuo.

The contact angle for the water side of air bubbles on the treated glass filter surface was measured in aqueous solutions. The filter was immersed in the solutions for 3 h before measurement.

The sample filter was crushed, and then 2 mg was mixed with 20 mg KBr to form disks which were then analyzed using a FT-IR spectrometer (Perkin-Elmer System 2000 FT-IR).

The sample filters were also freeze-dried and analyzed using X-ray photoelectron spectroscopy (Perkin-Elmer 5500-Series Multi-Technique).

Permeation Measurement. The permeation measurements were performed as previously described.[9–12] The permeation rate of an aqueous solution at a certain pH value was determined by the volume of water that flowed through the glass filter per minute. When the pH was changed, the old solution was discarded and a new solution was applied to the glass filter. When the membrane was incubated in water or water/acetone mixture, the permeation rate was measured during 1 min after incubation over the prescribed time.

Results

Graft Polymerization. The surface wettability of the porous glass filter was reduced by a silane-coupling treatment (26 ± 5° to 69 ± 7°) and raised by PAA-graft polymerization (69 ± 7° to 29 ± 4°) in pure water. These changes indicate that silane coupling rendered the glass filter surface hydrophobic whereas PAA grafting rendered it hydrophilic. No difference in the surface wettability of the PAA-grafted glass filter was observed between pH 1 (the contact angle, 29 ± 5°) and pH 6 (the contact angle, 29 ± 4°).

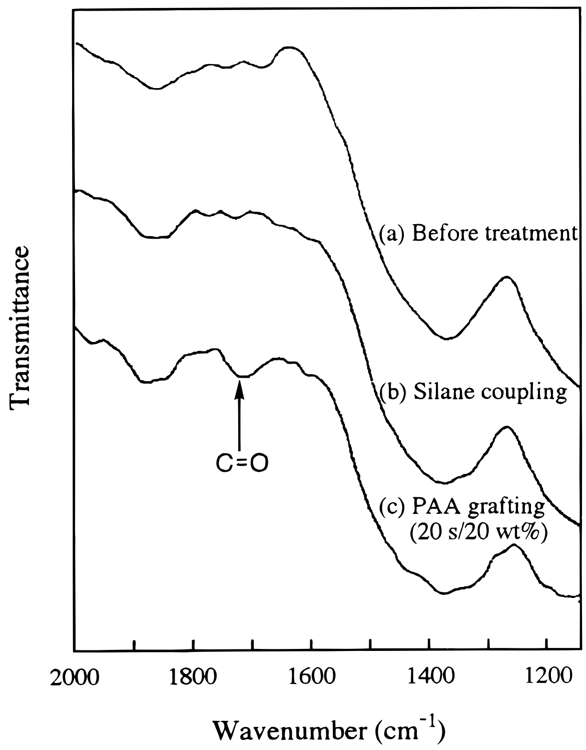

Figure 3. FT-IR spectra of the surface of glass filter: (a) untreated, (b) silane-coupled, and (c) PAA-grafted glass filters.

The FT-IR spectra of the glass filter did not differ markedly before and after silane coupling, whereas PAA grafting exhibited a new absorption peak at 1720 cm^{-1} (Figure 3).

Analysis by X-ray photoelectron spectroscopy demonstrated that the silane-coupling treatment markedly increased the amount of carbon on the glass filter caused by the ODS–DEA treatment (Figure 4 and Table 1). The graft polymerization with PAA further increased the amounts of carbon and oxygen. A new peak centered at 286.5 eV may be ascribed to carbon atoms (C=O) involved in the side chains of the graft polymer. However, the area of these new peaks, which were due to PAA, was less than the peak area due to the ODS–DEA treatment. This result indicates that the thickness of the graft chain layer was small enough to allow X-ray photoelectron penetration.

pH Dependence of Water Permeation. The effect of pH on the rate of water permeation through the porous glass filters is shown in Figure 5. The silane-coupled glass filter did not permeate water. The glow-discharged glass filter was able to permeate water, and the permeation was independent of pH. On the other hand, the permeation through the PAA-grafted glass filter was pH dependent. The permeation profile of the PAA-grafted glass filter showed that the permeation rate was high under low pH conditions and low under high pH conditions.

The permeation rate versus pH profile obtained by decreasing the pH from 6 to 1 corresponded almost exactly with that obtained by increasing the pH from 1 to 6. The agreement shows that the conformational changes of PAA graft chains caused by changes in the pH of the solution are reversible and thus the pore size of the filter may be reversibly controlled.

The permeability change was very rapid as shown in Figure 6. The permeability changed within 2 min of

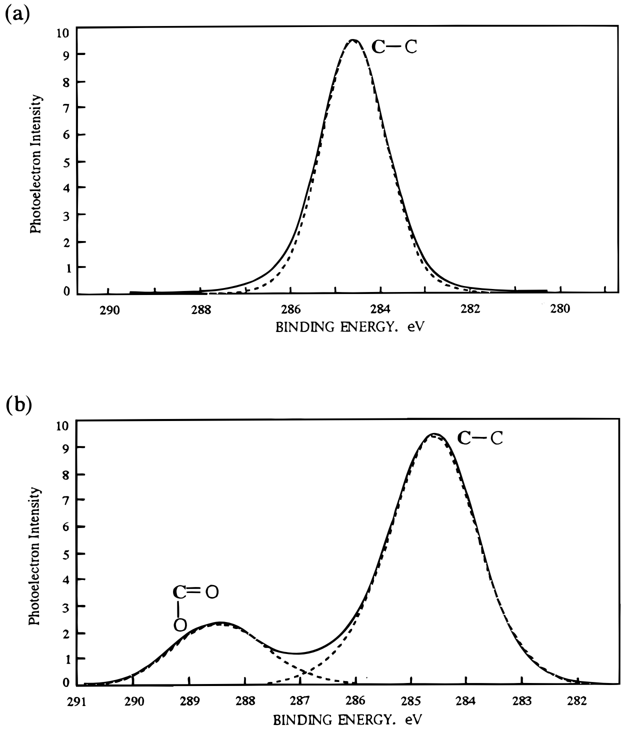

Figure 4. X-ray photoelectron spctra of (a) silane-coupled and (b) PAA-grafted glass filters. Solid line is an experimental curve and dotted line represents a deconvolution into individual components.

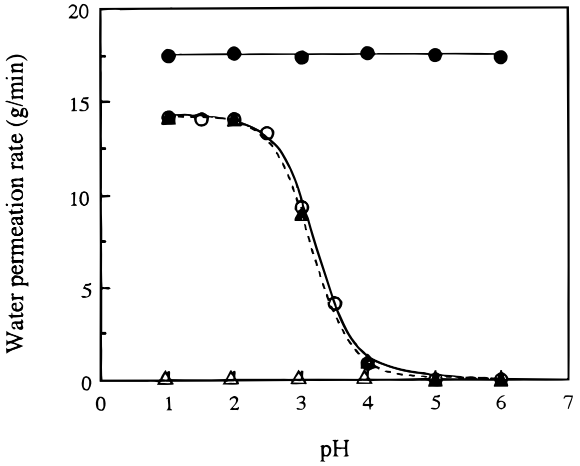

Figure 5. pH-dependent water permeation through PAA-grafted glass filter; pH 1 → pH 6 (○), and pH 6 → pH 1 (▲), silane-coupled glass filter (△) and glow-discharged glass filter (●).

Table 1. X-ray Photoelectron Analysis of the Surface of Glass Filter

	composition (%)		
treatment	Si 2p	C 1s	C 1s
before treatment	29.9	63.8	6.3
silane coupling	19.0	27.7	53.3
grafting	9.5	34.6	55.9

the pH change. Although the fastest reported response of a hydrogel network to pH changes is 20 min, in general, the response time is between a few hours and 1 day.[6] The rapid response of the polyelectrolyte brushes in the present study may be explained by the direct contact of each PAA brush chain with water.

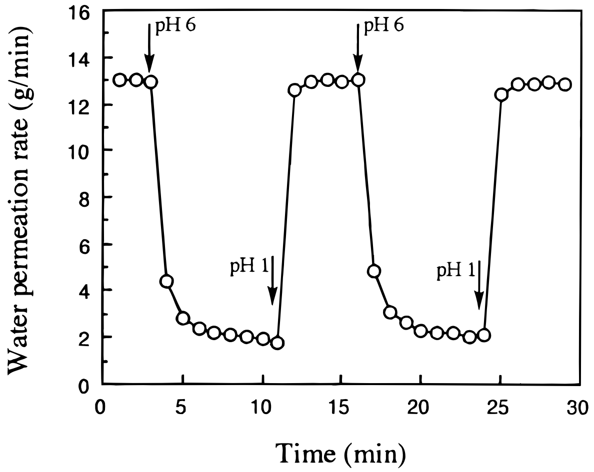

Figure 6. Time course of water permeation through PAA-grafted glass filter at different pHs.

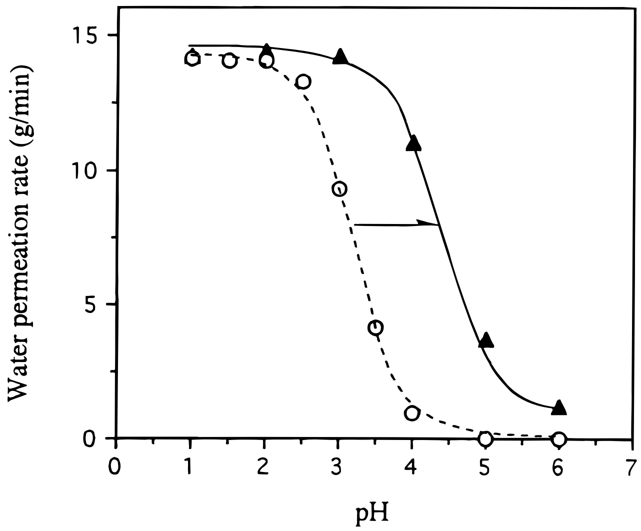

Figure 7. pH-dependent permeation of water/acetone (20/80 v/v) mixture (▲) and water (○) through PAA-grafted glass filter.

Permeation of a Water/Acetone Mixture. The permeation rate of a water/acetone (20/80 v/v) mixture through the PAA-grafted glass filter is shown in Figure 7. The permeation was also pH dependent. However, on going from water to the water/acetone mixture, the inflection point of permeation shifted to a higher pH. This change was most likely caused by the decrease of acid dissociation constant, resulting from the decrease of the dielectric constant of water by mixing with acetone.

Stability in a Water/Acetone Mixture. The results of a comparison between the stability of the grafted glass filter and a polymeric membrane (Omnipore membrane, Millipore) in water/acetone are shown in Figure 8. The polymeric membrane was suitably stable for water permeation, however the permeation of the mixture through the polymeric membrane became slower with time, which may have been due to swelling of the membrane. In contrast, the grafted glass filter tolerated extended immersion in the mixture.

Discussion

Although the silane-coupled glass filter did not permeate water, the glow-discharged glass filter did. This difference may be explained by the difference in the surface wettability. The hydrophobic pore surface

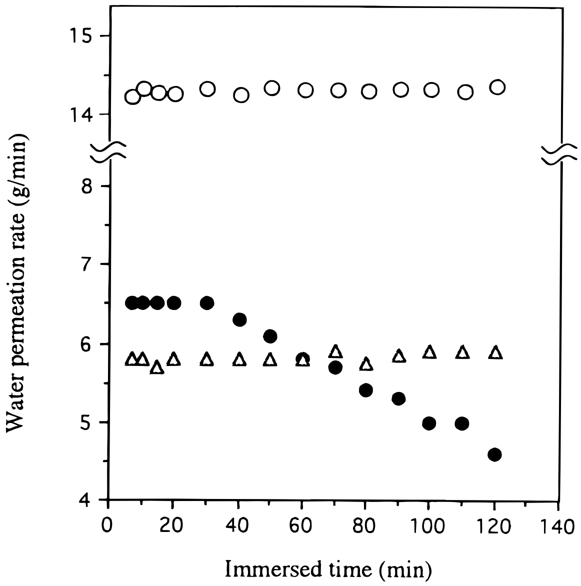

Figure 8. Permeation of water (pH 2)/acetone mixture (20/80 v/v) through PAA-grafted glass filter (○) and porous polymer membrane (●). Water (pH 2) permeation through porous polymer membrane (△).

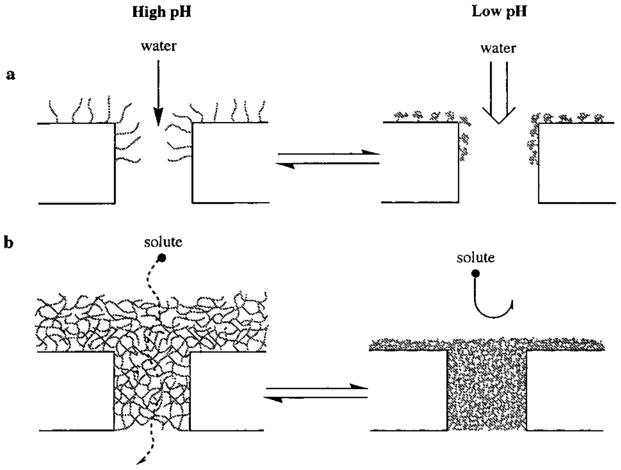

Figure 9. Schematic drawing of permeation mechanism through PAA-grafted porous glass filter (a) and PAA-based hydrogel (b). Under high pH conditions, deprotonation of PAA reduces pore size to decrease water permeation in (a) and leads swelling to enhance solute permeation in (b). Under low pH conditions, protonation of PAA increases pore size to increase water permeation in (a) and leads deswelling to reduce solute permeation in (b).

inhibited water permeation. However, the pH-dependent permeation through the PAA-grafted glass filter may not be explained by surface wettability, because the surface wettability was not dependent on pH conditions as clarified by the contact angle measurement.

Hydrogels composed of PAA networks also display pH-dependent permeability, although they do not permeate water and permeate solutes only slowly. The PAA-based hydrogels permeate solutes under high pH conditions but not under low pH conditions, due to swelling and deswelling, respectively, as schematically shown in Figure 9b.[17] However, the pH dependence of water permeation through the PAA-grafted porous glass filter was found to be opposite to that of solute permeation through the PAA-based hydrogels. The results of the present study most likely indicate that under low pH conditions, protonated PAA chains contract, thereby opening the pores of the filter, while under high pH conditions, deprotonated PAA chains extend to cover the pores as shown in Figure 9a. Recently Iwata et al. grafted 2.2×10^6 Da of PAA on porous membrane by the plasma-pretreated polymerization, which was the same method as the present investigation.[18] The thickness of the grafted PAA layer was estimated to be 3.9 μm.[18] In the present system, the similar length of PAA chains on the porous glass filter may regulate the gating of 5 μm pores.

The pore-size change in a poly(carboxylic acid)-grafted plain polymeric membrane was recently observed in water using atomic force microscopy.[18,20] However, when the membrane was freeze-dried from aqueous solution having different pHs, no significant difference was observed by a scanning electron microscope. The thickness of dried PAA was too thin to be detected. Therefore, the PAA layer was also enough to allow X-ray photoelectron penetration as described above.

Another characteristic phenomenon of the PAA-grafted glass filter was the rapid response. It usually takes half an hour to a day for the polymer networks of hydrogels to respond to environmental stimulation.[6] However, the PAA-grafted glass filter responded within several minutes. The rapid response may be explained by the rapid protonation−deprotonation process caused by direct contact between the graft chains and water molecules in contrast to the process occurring in the polymer networks of hydrogels, which limit the molecular diffusion.

A sharp inflection point at pH 3 is evident in the graph of permeation rate versus pH (Figure 2). A similar pH dependence of PAA graft chains was also observed by Bergbreiter and Bandella.[21] They reported that the titration curve for PAA grafted on a solid support is sharper than that for PAA in solution. They hypothesized a cooperative pH-induced conformational change of polyelectrolyte brushes. In other words, a significant difference in polarity between the nonpolar surface of polycarbonate film and the polar aqueous solution may exaggerate the solubility difference of partially deprotonated polyelectrolyte chains thereby enabling a significant change in the polyelectrolyte conformation to occur by a small pH change.

In the present study, a material capable of pH-controlled gating function was constructed. The combination of stimuli-responsive polymer brushes with porous inorganic materials may be used to produce new solvent-tolerant stimuli-responsive materials.

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