Oxidoreduction-Sensitive Control of Water Permeation through a Polymer Brushes-Grafted Porous Membrane

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ABSTRACT: An oxidoreduction-sensitive polymer, poly[3-carbamoyl-1-(*p*-vinylbenzyl)pyridinum chloride] (PCVPC), was grafted on a porous membrane, and the water permeation through the membrane was investigated. PCVPC homopolymer was found to be water soluble in the oxidized state but insoluble in the reduced state. It could be reversibly dissolved and precipitated in aqueous solutions of high ionic strengths. The polymer was grafted onto a glow-discharged fluoropolymer membrane. In the oxidized state the grafted chains were ionized and extended to cover the pores and decrease water permeation. The rate of permeation depended significantly upon the ionic strength of the aqueous solution. In the reduced state, however, the polymer brushes were deionized and increased water permeation. These changes in permeability were reversible by oxidoreduction, when the formation of an insoluble polymer complex in the reduction process was avoided under high ionic strength. The response of polymer chains grafted on the membrane corresponded to that of polymers in solution.

Introduction

The design and synthesis of materials able to rapidly respond to external physical and chemical signals have increasingly become of interest.[1] Polymeric hygrogel is a typical example, which undergoes abrupt changes in volume in response to external stimuli such as changes in solvent compositions, pH, electric field, temperature, or chemical concentration.[2−5] However, the potential applications of these materials are limited owing to the material's physical fragility and their inability to swell and contract quickly. The response time of the swelling and contracting is limited by the rate of diffusion of the stimulants through the polymer network in water. Therefore, for example, a sharp control of drug release based on gel swelling is difficult in principle, although several strategies have been explored.[6]

On the other hand, by using the principle of hydrodynamic measurement performed by Webber et al.[7,8] to evaluate thermal expansion and contraction of diblock copolymers adsorbed on pores of a track-etched mica membrane, we have designed some stimuli-responsive materials by grafting stimuli-responsive "polymer brushes" on the surface of a porous membrane. pH-responsive,[9,10] glucose-responsive,[11] or photo-responsive[12,13] release or permeation systems have been devised. The mechanical strength of the grafted material is the same as that of the original ungrafted membrane. Furthermore, we expected polymer brushes to respond quickly to external stimuli because they are in direct contact with their external environment. A computational study was also carried out to design a polymer channel that would open and close in response to changes in solvent pH.[14] Recently the gating of poly(acrylic acid) or poly(methacrylic acid) grafted on a porous membrane in response to pH change was visualized by atomic force microscopy.[15,16]

In this study, an oxidoreduction-sensitive polymer, poly[3-carbamoyl-1-(*p*-vinylbenzyl)pyridinum chloride], was grafted on a porous membrane and the water permeation through the membrane in response to oxidoreduction was investigated. The polymer brushes are short polymer filaments whose conformations with respect to the membrane surface differ in the oxidized and reduced states.

Materials and Methods

Synthesis of 3-Carbamoyl-1-(*p*-vinylbenzyl)pyridinium Chloride (CVPC). CVPC was synthesized using a previously reported method.[17] A solution containing 11.9 g of chloromethylstyrene in 200 mL of *N*,*N*-dimethylformamide (DMF) was mixed with a solution containing 15 g of nicotinamide (15 g) in 50 mL of DMF, and the mixture was allowed to stand for 24 h at 40 °C and yielded a white precipitate. The precipitate was collected by filtration and crystallized from ethanol, giving 19.5 g of CVPC (91% yield). The melting point was found to be 233−235 °C (lit. 234−236 °C).[18]

Copolymerization of CVPC and Acrylamide. Aqueous solutions (10 wt %) containing CVPC and acrylamide (molar percentage: 0/100, 20/80, 40/60, 60/40, 80/20, or 100/0) were prepared. Potassium persulfate (1/1000 moles per monomer) was dissolved in the solution. The resulting solution was degassed, sealed, and allowed to stand at 60 °C for 5 min. The solution was poured into acetone in order to precipitate reaction products. The precipitate was collected by centrifugation. The dissolving and precipitation process was performed twice, and the product was lyophilized. The yield of copolymer was less than 5%. Its composition was determined by elemental analysis, and the monomer reactivity ratio was obtained using the Fineman−Ross method.

Viscosity Measurement. The aqueous solution was first filtered through a cellulose membrane (pore diameter, 0.2 μm) and degassed with bubbling nitrogen gas. The viscosity was measured at 25 °C in the presence of 0.1, 0.01, or 0.001 mol/L added sodium chloride with a Ubbelode-type viscometer.

Surface Grafting of CVPC. CVPC was graft-polymerized on a porous polymer membrane (Omnipore membrane, a product of Millipore Co., which is composed of polyethylene and polytetrafluoroethylene: diameter, 47 mm; thickness, 80 μm; pore size, 0.2 μm). The membrane was glow-discharged with a high-frequency modulator (maximum, 400 W) under a pressure of 6.7 Pa. After the glow-discharge treatment, the membrane was incubated in an aqueous solution containing acrylamide and/or CVPC (20 wt %). The mixture was allowed to react for 2 h at 60 °C. After the graft polymerization the graft membrane was washed with distilled water until the 280-nm absorption due to unreacted monomer and nongrafted polymer became undetectable in the washing liquid.

The surface densities of peroxides produced on the membrane were determined with 1,1-diphenylpicrylhydrazyl (DP-

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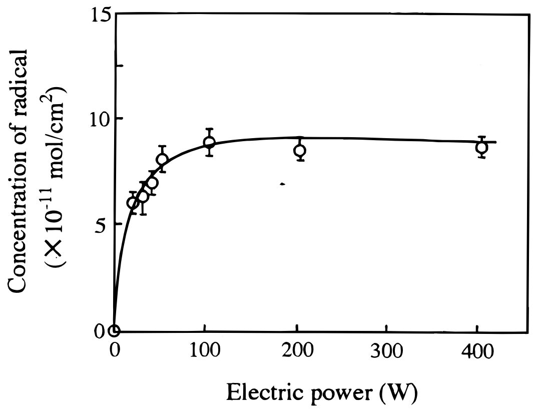

Figure 1. Free radicals formed by glow-discharge treatment at various electric fields. The concentration of the radicals was determined using 1,1-diphenylpicrylhydrazyl.

PH).[9,10] DPPH (4 mg) was dissolved in toluene (100 mL), which was degassed and substituted with nitrogen. The toluene solution of DPPH (10 mL) was added to the glow-discharged membrane, and the mixture was incubated in a sealed tube at 60 °C for 2 h. The determination of radicals produced from the peroxides was carried out by measuring the decreasing absorbance at 520 nm. A calibration curve was obtained by using toluene solutions containing DPPH of known concentrations.

Measurement of Water Permeation. Water permeation through the polymer membrane was investigated by using an apparatus previously reported.[9,10] The prepared membrane was mounted on a ultrafiltration cell (Toyo Roshi UHP-25) and placed 30 cm below a water reservoir. The reservoir was filled with an aqueous solution of oxidant (H_2O_2, 50 mM) or reductant ($Na_2S_2O_4$, 20 mM) containing a fixed concentration of sodium chloride. Upon equilibration, the aqueous solution was allowed to flow under a nitrogen atmosphere of 0.2 kg/cm^2 at 25 °C. The permeation rate was calculated by measuring the mass of water that was able to pass through the membrane each minute. The experimental errors were within 3%.

Spectroscopic Measurements. UV spectroscopy was performed on a JASCO Ubest-50 UV/vis spectrophotometer. FT-IR spectra were obtained on a Digilab FTS-15E/D infrared spectrometer. FT-ATR-IR was measured using a KRS-5 prism with an incident angle of 60°.

Results and Discussion

Preparation of Grafted Membrane. The porous fluoropolymer membrane was glow-discharged to form peroxides on its surface.[9,10] The surface density of free radicals produced by decomposition of peroxides increased with increasing electric power and reached the maximum density at 100 W, as shown in Figure 1. In the present investigation, the polymer membrane was glow-discharged at 200 W.

CVPC and/or acrylamide was graft-polymerized on the plasma-treated porous membrane. FT-ATR-IR spectra of the grafted membranes show a 1700-cm^{-1} absorption which corresponds to the carbonyl group of CVPC and a 1650-cm^{-1} absorption which arises from amide I of acrylamide. The composition of graft copolymers was determined by the relative intensities of the peaks. The composition of the graft polymer was found to be nearly the same as the feed composition. These data are shown in Table 1.

The monomer reactivity ratios of the CVPC (M_1)/acrylamide (M_2) copolymerization were calculated to be $r_1 = 3.79$ and $r_2 = 0.089$. CVPC was found to be more reactive in a radical polymerization, which may be a result of stabilization of the propagation radical. If the solution copolymerization and graft copolymerization are assumed to be the same, a CVPC-rich domain should be formed in the graft polymer chain.

Table 1. Composition of CVPC/Acrylamide Copolymers Grafted on the Membrane Surface

symbol of copolymer	feed composition (% of CVPC)	copolymer composition (% of CVPC)
CA1	100	100
CA0.5	50	48
CA0.2	20	22
CA0	0	0

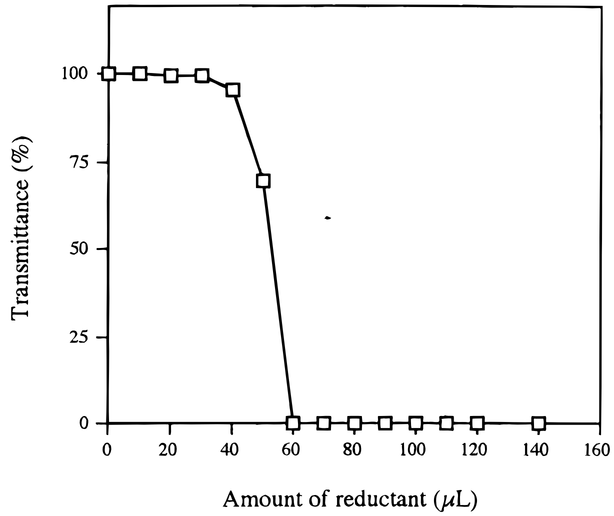

Figure 2. Transmittance of an aqueous solution containing CVPC homopolymer at 750 nm. Reductant ($Na_2S_2O_4$, 0.25 M) was added into 2 mL of polymer solution (10 mg/mL).

PCVPC Homopolymer Solution. Figure 2 shows the solubility change of an aqueous solution of PCVPC homopolymer with the addition of reductant. The homopolymer was soluble in water in its oxidized state but was precipitated by the addition of reductant. The amount of reductant required for precipitation was almost equal to that of deoxidized PCVPC unit in the polymer.

The precipitated homopolymer was not dissolved upon addition of an aqueous oxidant in solution (Figure 3). However, the homopolymer could be reversibly dissolved and precipitated when the aqueous solution contained NaCl. In the absence of NaCl, the PCVPC polymer formed an insoluble complex between the anioic adduct and the unreacted cationic polymer at the midway point of the reduction reaction.[19,20] Avoidance of this complex formation at high ionic strengths can make the polymer easily oxidizable, so that polyelectrolyte chains are regenerated.

To evaluate the degree of chain extension of the homopolymer of CVPC in the oxidized state in water, the viscosity of the solution was measured (Figure 4). In solutions not containing sodium chloride, the viscosity number (η_{sp}/c) increased with decreasing polymer concentration. This behavior is characteristic of polyelectrolyte solutions. The viscosity number decreased with increasing salt concentration, because of a decrease in electric repulsion between the polyelectrolyte chains.

Water Permeation through the Grafted Membrane. Figure 5 clearly shows that the rate of water permeation through a membrane grafted with CA1 (a homopolymer of CVPC) was regulated by the addition of NaCl solutions of varying ionic strengths. The change in permeability occurred immediately with changing ionic strength, and it was reversible. The reduced rate of water permeation at lower ionic strengths can be

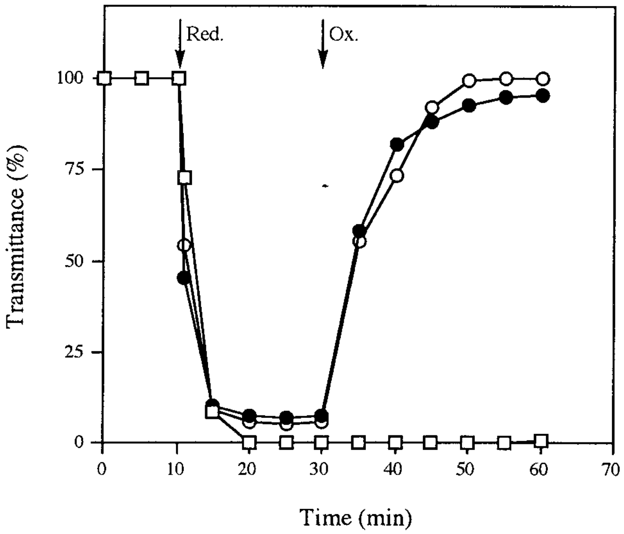

Figure 3. Transmittance of aqueous solutions containing CVPC homopolymer at 750 nm. Ionic strength (I) was adjusted with NaCl: (□) $I = 0$; (○) $I = 0.1$; (●) $I = 1.0$. Sixty microliters of reductant ($Na_2S_2O_4$, 0.25 M) or 80 μL of oxidant (H_2O_2, 30 vol %) was added to 2 mL of polymer solution (10 mg/mL).

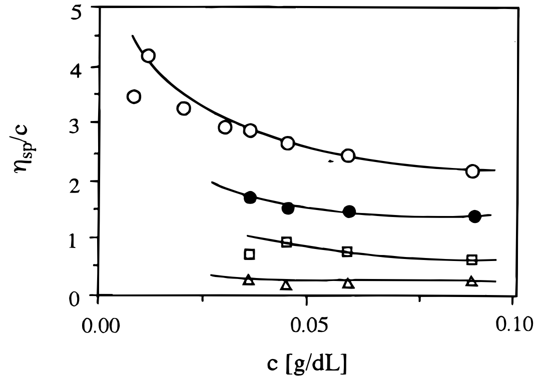

Figure 4. Viscosity of the CVPC homopolymer in aqueous solution at ionic strengths of (■) 10^{-1} mol/L, (□) 10^{-2} mol/L, (●) 10^{-3} mol/L, and (○) zero.

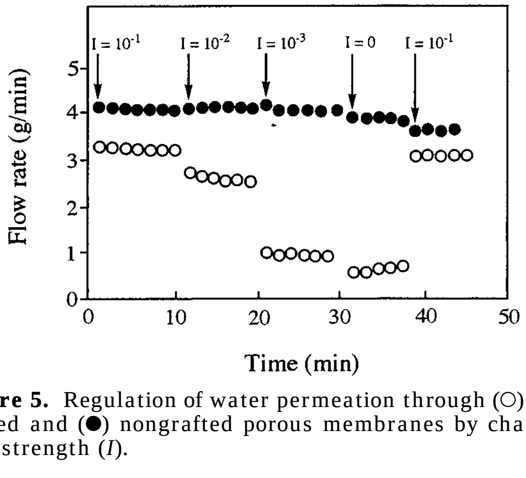

Figure 5. Regulation of water permeation through (○) CA1-grafted and (●) nongrafted porous membranes by changing ionic strength (I).

attributed to the contraction of the graft chains because of the primary salt effect. The rapid response is characteristic of this material because of direct contact of polymer brushes with the environment. Water permeation through a nongrafted membrane was negligibly affected by ionic strength.

The rate of water permeation through membranes grafted with various copolymers could also be influenced by ionic strength, as shown in Figure 6. However, the water permeation rate through the CA0 poly(acrylamide)-grafted membrane was not significantly affected. Since the polymerization of acrylamide resulted in grafting of high molecular weight, the graft chains were considered to cover the pore to reduce the permeation.

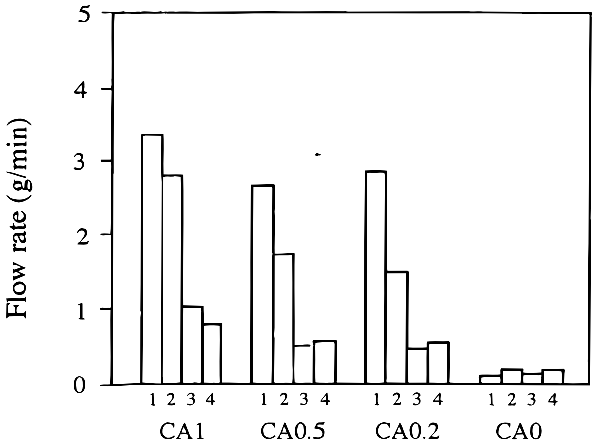

Figure 6. Ionic strength-dependent water permeation through different copolymer-grafted porous membranes. For notations, see Table 1. Ionic strength was 10^{-1} (1), 10^{-2} (2), 10^{-3} (3), and zero (4).

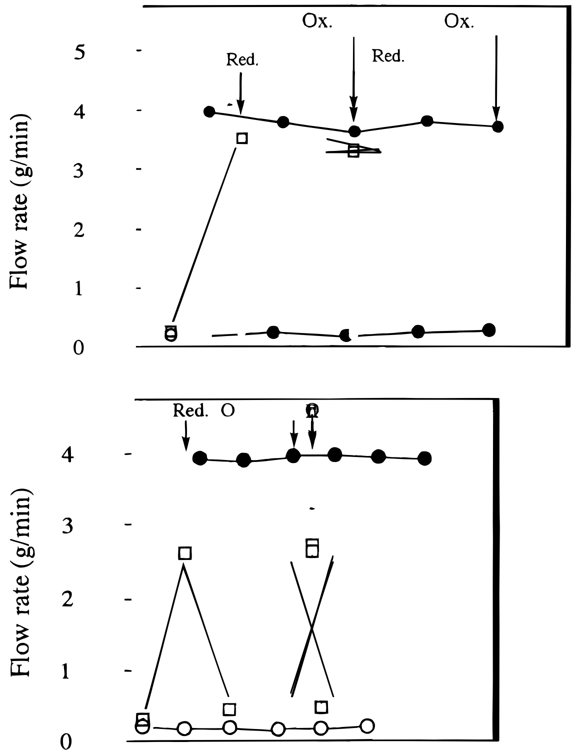

Figure 7. Water permeation (a, top) in the absence of added salt and (b, bottom) in the presence of 0.1 M NaCl through (○) CA0-grafted, (□) CA1-grafted, and (●) nongrafted porous membranes. Red and Ox represent addition of aqueous solutions containing 20 mM $Na_2S_2O_4$ and 50 mM H_2O_2, respectively.

Figure 7 shows the rate of permeation as affected by additions of oxidant and reductant solution. In the absence of NaCl, the permeation rate through the CA1-grafted membrane increased as a result of the addition of reductant solution. However, it did not return to its original flow rate after the addition of oxidant solution. This is most likely a result of the formation of an insoluble polymer complex, as was explained previously and illustrated in Figure 3. This polymer complex was not dissolved upon addition of the oxidant solution and

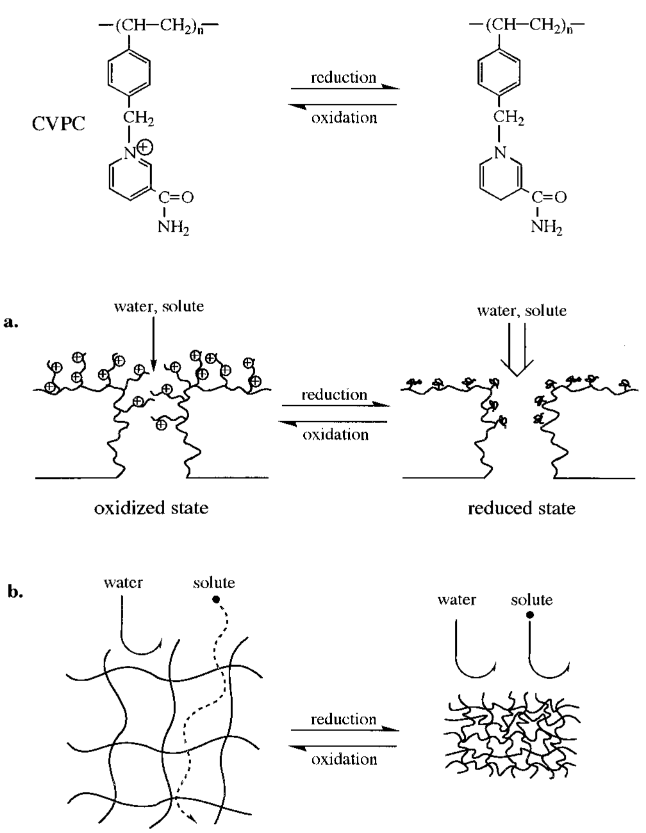

Figure 8. Mechanisms of controlling water and solute permeation through a polymer brushes-grafted porous membrane (a) and through a hydrogel membrane (b).

hindered the change of permeability. This can be seen in Figure 7a. In contrast, in the presence of NaCl (0.1 M), changes in flow rate due to the addition of reductant and oxidant solutions were completely reversible, as shown in Figure 7b.

The conformations of the redox-sensitive polymer brushes grafted to the porous membrane are responsible for the increased and decreased permeation rate. In the oxidized (ionic) state, in aqueous solutions, the polyelectrolyte brushes extend to cover the pores and reduce water permeation. In the reduced (nonionic) state, however, the polymer brushes do not extend, leaving the pores open and facilitating increased water permeation. This is schematically explained in Figure 8. Assuming Hagen-Poiseuille's law for the present system, as reported previously,[9,10] the thickness of the graft polymer was calculated to be 44 or 7 nm in the oxidized or reduced state, respectively.

Ishihara et al.[17] synthesized a cross-linked copolymer hydrogel of CVPC and 2-hydroxypropyl methacrylate. They found an increased rate of solute permeation through swollen hydrogels in the oxidized state and a lower rate through the nonionized (reduced) hydrogels, as shown in Figure 8b. In contrast, our investigation showed a greater rate of water permeation through CVPC-containing polymer brush-grafted membranes in the reduced state than in the oxidized state. The apparently differing results can best be explained by the differences in permeation mechanisms of hydrogels and porous membranes. In hydrogels, solute molecules permeate by diffusion through the polymer networks.[17,21,22] However, the flow of molecules through porous membranes is controlled by the polymer brushes on the surface. A similar difference was also observed in the pH-responsive polypeptide-grafted porous membrane and another polypeptide-based membrane.[23] Thus, the response of the same kind of polymers may differ depending upon the construction of the flow-regulating mechanism.

Various types of stimuli-responsive meterials have been designed and synthesized for controlled release of drugs,[1] chemical valves,[1] or micromachinery.[24] The present study demonstrated a new version of signal-responsive materials for drug delivery systems.

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