Macromolecules **1992,** *25,* 7313-7316

Control of Water Permeation by pH and Ionic Strength through a Porous Membrane Having Poly(carboxylic acid) Surface-Grafted

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Received April 9, 1992; Revised Manuscript Received September 3, 1992

ABSTRACT: A straight-pored membrane, which controls the rate of water permeation according to pH and ionic strength, was synthesized by surface-graft polymerization of vinyl monomers carrying a carboxylic acid substituent. The rate of water permeation through the prepared membrane changed reversibly in response to pH variation of the aqueous solution. The pH response of water permeation was controlled by changing the density and length of graft chains. The most sensitive pH response was attained with a membrane having poly(carboxylic acid) of a high degree of polymerization grafted in low densities. The drastic change of the water-permeation rate occurred at pH 3.0, 4.0, and 6.8 with membranes having poly(acrylic acid), poly(methacrylic acid), and poly(ethacrylic acid) surface-grafted, respectively. The pH response of water permeation was affected by the ionic strength of the aqueous solution.

Introduction

The design and synthesis of molecular devices, which respond sensibly and appropriately to external chemical signals, have become a focus of interest. A number of investigations in this regard have been reported: the control of pore size of porous membranes by the pH-dependent extension/contraction of polyelectrolyte graft chains,[1,2] the control of mass permeation by the variation of electric charge through porous membranes coated with ion-exchange polymers,[3] the control of permeability in response to the temperature variation by using thermosensitive hydrogels,[4] the control of permeation through a membrane with photosensitive polypeptide grafted by photoirradiation,[5] the pH-responsive permeation through an LB (Langmuir-Blodgett) membrane complexed with poly(methacrylic acid)-containing polyions,[6] and the insulin-releasing enzyme device in response to glucose concentration.[7]

Polyelectrolytes are particularly useful for sensoring and modulating external chemical signals, because they change the chain extension according to electrostatic interactions between charged groups which are sensitive to pH and ionic strength of the aqueous solution. In the present investigation, to synthesize an intelligent membrane device, poly(acrylic acid), poly(methacrylic acid), and poly(ethacrylic acid) were chosen for polyelectrolytes to be grafted on the surface of a straight-pored polycarbonate membrane, and the pH-dependent water permeation through the poly(carboxylic acid)-grafted membrane was investigated.

Materials and Methods

Materials. A straight-pored polycarbonate (PC) membrane (Nucleopore, Pleasanion, CA) with a 25-mm diameter, a 10-μm thickness, and a 3×10^8 cm^{-2} pore density was used. Acrylic acid (AA) and methacrylic acid (MAA) were purchased from Nacalai Tesque (Kyoto, Japan). The monomers were purified by distillation under reduced pressure and used for graft polymerization. Diethyl ethylmalonate, which is the source material in the synthesis of ethacrylic acid (EAA), was purchased from Sigma (St. Louis, MO). 1,1-Diphenylpicrylhydrazyl (DPPH) which was used for the determination of peroxides produced by the glow-discharge treatment and Rhodamin 6G (R6G) which was used for the determination of poly(carboxylic acid) graft were purchased from Wako Pure Chemicals Industry (Osaka, Japan) and used without further purification. Commercial toluene and *N,N*-dimethylformamide (DMF) were used after purification by distillation under normal and reduced pressure, respectively. Commercial hydrochloric acid, sulfuric acid, potassium hydroxide, diethylamine, ethanol, diethyl ether, and formalin (37%) were used without further purification.

Synthesis of Ethacrylic Acid. Ethacrylic acid was synthesized according to the method reported by Tirrell et al.[8] and identified by elemental analysis using a CHN-Corder (Yanaco, Tokyo, Japan). Anal. Calcd for $C_5H_8O_2$: C, 60.0; H, 8.1. Found: C, 60.1; H, 8.2.

Determination of Peroxides Produced by Glow-Discharge Treatment. The straight-pored PC membrane received a glow-discharge treatment with a 6-mA discharge current for variable discharge times under 0.02 mmHg of pressure by using an ion coater IB-3 type (Eiko Engineering, Ibaraki, Japan). The peroxides produced on the membrane surface were determined with DPPH.[9] DPPH (4 mg) was dissolved in toluene (100 mL) which was degassed and substituted with nitrogen. The solution was stored in the dark at low temperature, and used for the determination after a further degassing and substitution with nitrogen immediately before use. 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.

Graft Polymerization of Carboxylic Acid Monomers. The PC membrane, on which peroxides were produced by glow-discharge treatment under reduced pressure, was quickly transferred to an aqueous solution containing AA (20 wt %), MAA (5, 10, or 20 wt %), or EAA (5 wt %). The mixture was degassed, substituted with nitrogen, and sealed. The graft polymerization using the peroxides produced on the membrane surface as initiators was continued for 2 h at 60 °C. After the graft polymerization, the PC membrane was washed repeatedly with distilled water until the washing liquid became neutral.

Confirmation of Grafting Poly(carboxylic acid). The PC membrane with glow-discharge treatment and the PC membrane after graft polymerization were investigated by attenuated total reflection (ATR) Fourier transform (FT) infrared (IR) spectroscopy using a Digilab FTS-15E/D spectrometer (Cambridge, MA). Furthermore, the grafted PC membrane was immersed in a diluted NaOH solution and subjected to ATR-FT-IR spectroscopy to confirm the presence of carboxylate groups.

Determination of the Poly(carboxylic acid) Graft. The grafted PC membrane was washed well with distilled water, dried, and dissolved in DMF. The DMF solution was subjected to the determination of carboxyl groups by the Rhodamin method.[10] R6G (10 mg) was dissolved in a phosphate-buffered saline (PBS; pH 11, 10 mL) and extracted with toluene. The R6G/toluene

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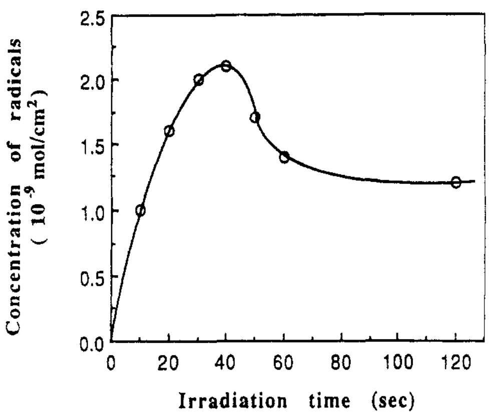

Figure 1. Amount of peroxide formed by glow discharge for varying times under 0.2 mmHg of pressure and a 6-mA current.

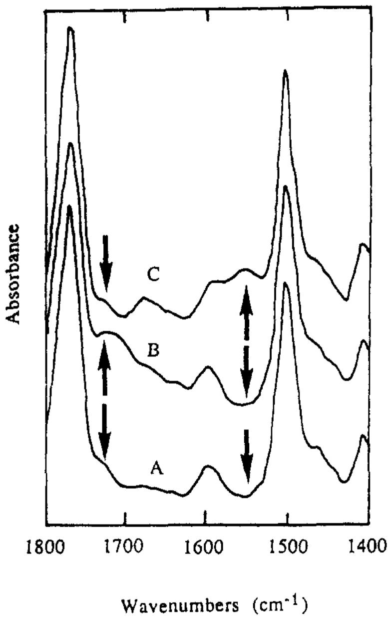

Figure 2. ATR-FT-IR spectra of the glow-discharged PC membrane (A), PMAA-grafted PC membrane (B), and PMAA-grafted PC membrane after dipping in aqueous NaOH (C).

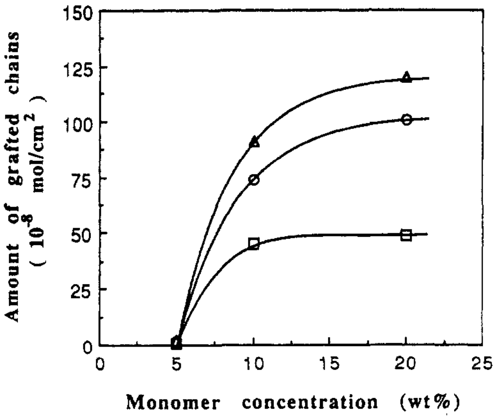

Figure 3. Relation between the amount of PMAA grafted and the feed concentration of MAA. Glow discharge time: □, 10 s; ○, 20 s; △, 40 s.

extract (2 mL) was mixed with a DMF solution (2 mL) of the grafted PC membrane. The mixture was incubated in the dark for 30 min, and the absorbance at 534 nm was measured. A calibration curve was obtained with DMF solutions containing AA of known concentrations.

Measurement of the pH-Responsive Rate of Water Permeation through the Poly(carboxylic acid)-Grafted PC Membrane. The poly(carboxylic acid)-grafted membrane was immersed in an aqueous solution of a certain pH value and mounted on the ultrafiltration cell (Toyo Roshi UHP-25, Tokyo, Japan). An aqueous solution of a prescribed pH value and a certain ionic strength (I = 0.05 mol/L) was added to the cell. The rate of water permeation was calculated from the weight of water permeated per unit time under a nitrogen atmosphere at 0.2 kg/cm^2. The pH of the permeating solution was adjusted by adding diluted hydrochloric acid or aqueous NaOH solution, and the ionic strength by the addition of NaCl.

Table I
Degree of Polymerization of a PMAA Chain Grafted onto a Polycarbonate Membrane

grafted membrane	glow-discharge time (s)	radical density[a] (10^{-9} mol/cm^2)	monomer concn (wt %)	DP of graft chains[b]
A-1	10	1.0	5	7
A-2	10	1.0	10	450
A-3	10	1.0	20	490
B-1	20	1.6	5	9
B-2	20	1.6	10	464
B-3	20	1.6	20	520
C-1	40	2.1	5	9
C-2	40	2.1	10	480
C-3	40	2.1	20	530

[a] Determined by the DPPH method. [b] The ratio of the carboxyl group concentration to the radical concentration.

Results and Discussion

Determination of the Initiator Site Produced by the Glow-Discharge Treatment. Radicals generated from peroxides produced on the PC membrane, which was glow-discharged under a reduced pressure of oxygen, were determined by the DPPH method, and the results are shown in Figure 1.

The density of radicals increased with increasing time of the glow-discharge treatment, reached the maximum value at the glow-discharge time of 40 s, and then decreased with further increasing the glow-discharge time. This phenomenon can be explained by considering that produced peroxides are partly converted to inactive species, which cannot yield radicals, after prolonged glow-discharge treatment.

Confirmation of Grafting Poly(carboxylic acid). The presence of poly(carboxylic acid) grafts on the surface of the PC membrane was investigated on the basis of IR absorptions due to the carbonyl stretching vibration of carboxyl and carboxylate groups.

As shown in Figure 2, the absorption at 1720 cm^{-1} due to the carboxyl group is stronger in the poly(methacrylic acid) (PMAA)-grafted PC membrane (B) than in the glow-discharged PC membrane (A). This difference indicates the presence of PMAA grafts in the former membrane. The 1720-cm^{-1} absorption became weak by immersing the membrane in a diluted aqueous NaOH solution, and an absorption at 1550 cm^{-1} became stronger, as shown in spectrum C. This change should indicate the dissociation of PMAA carboxyl groups into carboxylate groups. These experimental observations confirm the graft polymerization of MAA on the surface of the PC membrane. Similar results were obtained with poly(acrylic acid) (PAA) and poly(ethacrylic acid) (PEAA), indicating the presence of PAA and PEAA grafts on the membrane surface.

Determination of Poly(carboxylic acid) Grafts. The amount of poly(carboxylic acid) grafts was determined by the determination of the number of carboxyl groups present on the membrane surface. The number-average degree of polymerization (DP) of graft chains was calculated on the assumption that radicals produced on the membrane surface were all used for initiation of graft

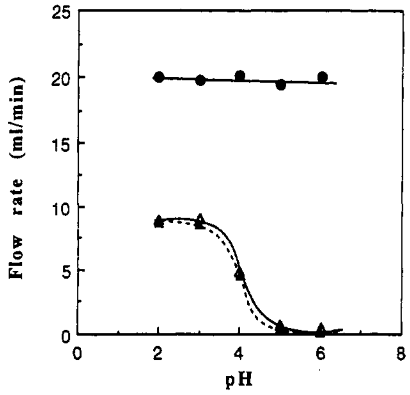

Figure 4. Reversibility of pH-dependent water permeability of the PMAA-grafted PC membrane B-2: △, pH 6 → pH 2; ▲, pH 2 → pH 6; ●, pH-dependent water permeability of the glow-discharged PC membrane without graft chains.

polymerization. First of all, the relationship between the amount of PMAA grafts on the membrane surface and the concentration of feed monomer is shown in Figure 3.

The amount of graft polymers increased with increasing glow-discharge time and concentration of feed monomer. Next, the number-average DP of PMAA chains grafted on the surface of the PC membrane under different conditions was calculated, and is shown in Table I.

It was found that the density of graft chains is controlled by the glow-discharge time and the DP of graft chains by the concentration of feed monomer. The pH-dependent water permeabilities can be compared among membranes with graft polymers of similar chain lengths (DP) but in different densities (A-1, B-1, C-1; A-2, B-2, C-2; A-3, B-3, C-3) and among membranes with graft polymers in similar densities but of different DPs (A-1, A-2, A-3; B-1, B-2, B-3; C-1, C-2, C-3).

pH-Dependent Water Permeability of the PMAA-Grafted PC Membrane. The effect of pH on the water permeation through the PMAA-grafted PC membrane B-2 was investigated, and the results are shown in Figure 4.

A glow-discharged PC membrane without a PMAA graft showed a higher water permeability than PMAA-grafted PC membranes. This result shows that the graft chains more or less close the pores of the membrane.

While the water permeability of a glow-discharged PC membrane without a PMAA graft was pH-independent, that of the PMAA-grafted membrane changed remarkably at pH ca. 4. This result shows that the dissociation of PMAA grafts changed remarkably at pH ca. 4 to change the extension of the graft chains. The permeation rate/pH of solution profile with decreasing pH from 6 to 2 agreed almost perfectly with that with increasing pH from 2 to 6. This result shows that the extension of graft chains varies inversely according to the pH of solution to control the pore diameter of the membrane inversely.

These results indicate the possibility of synthesizing a porous membrane, the permeability of which can be controlled inversely by the pH of the solution, by grafting PMAA chains on a straight-pored membrane.

Effect of the Density of Graft Chains on the pH-Dependent Water Permeation through the PMAA-Grafted PC Membrane. With reference to PC membranes (A-2, B-2, C-2) on which PMAA chains of intermediate DPs are grafted in different densities, the rate and pH response of water permeability decreased with increasing graft densities (Figure 5A). The reason could be that strong interactions of graft chains in high density (C-2) do not allow full contraction of graft chains even at low pH regions to keep pores closed.

Similar measurements were done with PC membranes (A-1, B-1, C-1) grafted with PMAA chains of low DPs in different densities, and the results are shown in Figure 5B. The water permeation rate became higher as a whole as compared with those in Figure 5A, but the pH response became very low. The density of graft chains did not affect these phenomena, indicating an impossibility for short graft chains to influence the pore size by different densities or degrees of chain extension.

With reference to PC membranes (A-3, B-3, C-3) on which PMAA chains of the highest DPs are grafted in different densities, either the water permeation rate or the pH response decreased with increasing densities of graft chains (Figure 5C). Similarly to the case of Figure 5A, interactions of long graft chains in high density do not allow full contraction of graft chains even at low pH regions to keep pores closed. Similar results in Figures 5A,C should be due to nearly the same DP of graft chains in both cases.

The above results indicate that the pH response of the water permeation rate can be controlled by changing the density of graft chains, except the case in which very short graft chains are involved.

Similar experimental results were obtained for the pH response of the water permeation rate through PC membranes grafted with PMAA chains of different DPs in nearly the same density.

These experimental results indicate the possibility to control the pH response of water permeation of changing the DP of PMAA grafts, except the case in which PC membranes grafted with PMAA chains of very high DPs are involved.

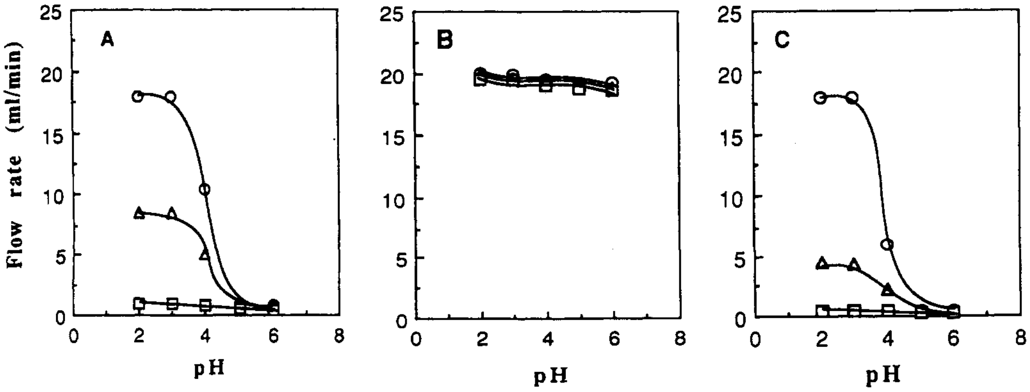

Figure 5. pH response of the water permeability of PC membranes grafted with PMAA chains in different densities: (A) ○, A-2, DP 450, 1.0 × 10^{-2} mol/cm^2; △, B-2, DP 464, 1.6 × 10^{-2} mol/cm^2; □, C-2, DP 480, 2.1 × 10^{-2} mol/cm^2; (B) ○, A-1, DP 7, 1.0 × 10^{-2} mol/cm^2; △, B-1, DP 9, 1.6 × 10^{-2} mol/cm^2; □, C-1, DP 9, 2.1 × 10^{-2} mol/cm^2; (C) ○, A-3, DP 490, 1.0 × 10^{-2} mol/cm^2; △, B-3 DP 480, 1.6 × 10^{-2} mol/cm^2; □, C-3, DP 530, 2.1 × 10^{-2} mol/cm^2.

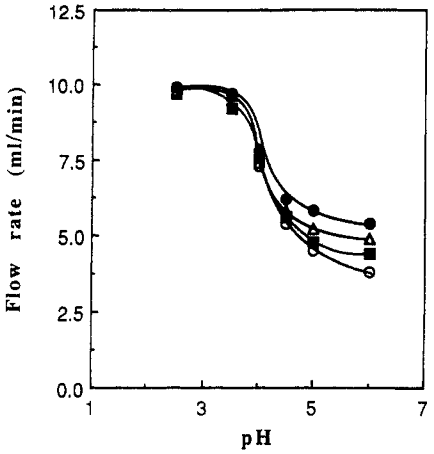

Figure 6. Influence of concentration of added salt on the water permeability of the PMAA-grafted PC membrane B-2 (DP 464; density 1.6×10^{-9} mol/cm^2). [NaCl]: ○, 0 mol/L; ■, 0.01 mol/L; △, 0.05 mol/L; ●, 0.1 mol/L.

Effect of Added Salt on the pH-Dependent Water Permeation through the PMAA-Grafted PC Membrane. The effect of the concentration of added salt on the water permeability of the PMAA-grafted PC membrane is shown in Figure 6.

The NaCl addition did not influence the water permeation rate in low pH regions but increased it a little in high pH regions, resulting in a moderately reduced pH response. The NaCl addition must have tolerated the electrostatic repulsion among carboxylate groups, which were produced in high pH regions, resulting in reduced extension of graft chains.

Effect of the Nature of Graft Chains on the pH-Dependent Water Permeation through the PMAA-Grafted PC Membrane. Graft polymerizations of AA and EAA were carried out using a PC membrane with an intermediate radical density (1.6×10^{-9} mol/cm^2) under an intermediate concentration of monomer (10 wt %). The properties of grafted membranes should correspond to the PMAA-grafted membrane B-2. The pH-dependent water permeation through the PAA- or PEAA-grafted membrane was measured, and the experimental results are shown in Figure 7.

The considerably higher water permeability of the PEAA-grafted PC membrane than others should be explained by the not-so-high DP of graft chains. Any kind of graft membranes showed higher permeabilities at lower pH regions than at higher pH regions. The most pH-sensitive change of water permeability occurred at pH ca. 3 with the PAA-grafted membrane, pH ca. 4 with the PMAA-grafted membrane, and pH ca. 7 with the PEAA-grafted membrane. The pH difference should reflect different pK_a values of graft chains: PAA, 4.8;[11] PMAA, 6.15;[12] PEAA, 7.2.[12] The lower pH values at the inflection points than the pK_a values of the corresponding graft polymers mean that the dissociation of poly(carboxylic acids) is promoted in an immobilized state on an insoluble matrix rather than in solution. The reason for this varied degree of dissociation is not clear.

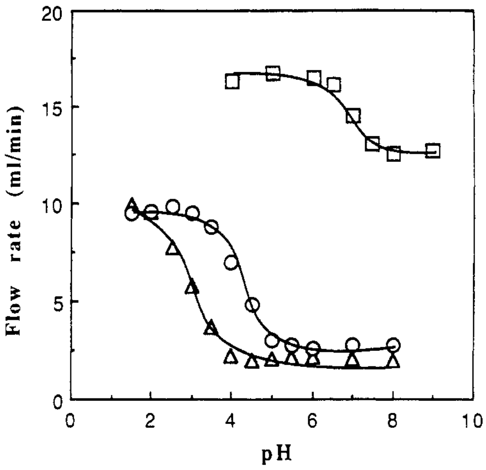

Figure 7. pH response of the water permeability of PAA-, PMAA-, and PEAA-grafted PC membranes (density 1.6×10^{-9} mol/cm^2): △, PAA-grafted membrane, DP 470; ○, PMAA-grafted membrane B-2, DP 464; □, PEAA-grafted membrane, DP 158.

The above results show the possibility of controlling the pH region, in which the water permeability changes most sensitively with pH, by choosing the nature of polymers to be grafted. This information is useful in the design of a polyelectrolyte-grafted, straight-pored membrane for a drug-delivery system under physiological conditions.

Acknowledgment. We are grateful to Prof. D. A. Tirrell of Polymer Science and Engineering, University of Massachusetts, for providing us with the information on the synthesis and polymerization of EAA and the properties of PEAA. This work was supported in part by a Grant for International Joint Research Project from the NEDO, Japan.

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Registry No. NaCl, 7647-14-5.