Membrane Properties of Porous and Expanded Poly(tetrafluoroethylene) Films Grafted with Hydrophilic Monomers and Their Permeation Behavior

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SYNOPSIS

Porous and expanded poly(tetrafluoroethylene) (pPTFE and ePTFE) films grafted with methacrylic acid (MAA) and 2-(dimethylamino)ethyl methacrylate (DMA) were prepared by the combined use of the plasma treatment and photografting. Their membrane properties and permeation behavior to saccharides and dextrans were investigated. Water absorptivity and electrical conductivity considerably increased around the grafted amounts at which the individual grafted polymer chains reached the center of each PTFE film. The glucose permeability of all four types of grafted pPTFE and ePTFE films showed the maximum values at pH 8, and grafted ePTFE films had higher permeabilities than grafted pPTFE films. It was made clear from the viscometric measurements of the aqueous solutions of polyMAA (PMAA) and polyDMA (PDMA) that the glucose permeability of MAA-grafted pPTFE (MAA-*g*-pPTFE) and MAA-grafted ePTFE (MAA-*g*-ePTFE) films increased more as grafted PMAA chains expanded. Those of DMA-grafted pPTFE (DMA-*g*-pPTFE) and DMA-grafted ePTFE (DMA-*g*-ePTFE) films increased more as grafted PDMA chains contracted. These results explain that the glucose permeability of the grafted pPTFE and ePTFE films depend not only on the grafted amount but also on the distribution of the corresponding grafted polymer chains in the direction of depth inside both PTFE films. The on–off regulation of permeation for DMA-*g*-pPTFE and DMA-*g*-ePTFE films could be repeated in response to the alternate temperature change and their on–off regulation patterns were completely opposite to those of many other hydrogel samples consisting of thermosensitive polymers with lower critical solution temperatures. In addition, it was found from permeation experiments, using three types of saccharides and dextrans with different molecular weights as a permeant, that permeation flux of DMA-*g*-ePTFE films decreased with an increase in molecular weight of the permeant. Separation factors showed the maximum value at the grafted amount of 0.8 mmol/g. The tensile strength measurements showed the grafted pPTFE and ePTFE films possessed adequate strength in the water-swollen state to be of use for a functional membrane. DMA-*g*-ePTFE films are most suitable for a separation membrane of polymeric species of four grafted PTFE films.

INTRODUCTION

Many studies have been carried out on graftings of hydrophilic or functional monomers onto hydrophobic polymer substrates using UV rays,[1–5] ^{60}Co γ rays,[6–14] or plasma[15–18] as an energy source. It is difficult to directly graft hydrophilic monomers onto chemically stable poly(tetrafluoroethylene) (PTFE) by only the photografting technique.[6,13,14] In many studies the radiation grafting technique using ^{60}Co γ rays was mainly utilized to graft hydrophilic monomers onto PTFE film. However, no PTFE

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films with a high grafted amount were prepared without any considerable damage to their physicochemical properties caused by the long-time irradiation. In our previous articles we reported that hydrophilic monomers such as methacrylic acid (MAA) and 2-(dimethylamino)ethyl methacrylate (DMA) could be grafted satisfactorily onto flat, porous, and expanded PTFE (fPTFE, pPTFE, and ePTFE) films by the combined use of the plasma treatment and photografting.[15,19]

Several polymeric membranes such as water-insoluble cast films,[20] hydrogels,[21,22] and grafted polymer films[23-26] were used in an attempt to control permeation behavior to some molecules or ions by use of conformational changes in the polymer chains. However, the mechanical strength of these polymeric membranes is not necessarily adequate to be of use for a functional membrane in the swollen state.

In this study, membrane properties of grafted pPTFE and ePTFE films, such as water absorptivity, electrical conductivity, and the tensile strength in the water-swollen state, were explored on the basis of the extent of progression of grafted polymer chains into the interior of the pPTFE and ePTFE films. In addition, the control of the permeation behavior to glucose was examined by making use of a conformational change of grafted polymer chains in response to the pH or temperature change. The possibility of molecular separation of dextrans with different molecular weights was also discussed.

EXPERIMENTAL

Materials

The polymer substrates used for grafting were a pPTFE film (thickness, 125 μm; average pore size, 5 μm; degree of vacancy, 68%) obtained from Nihon Millipore Co. Ltd. (Japan) and an ePTFE film (thickness, 75 μm; average pore size, 3 μm; degree of vacancy, 83%) from Toyo Roshi Co. Ltd. (Japan). The pPTFE and ePTFE films were cut into strips of 3.3-cm length and 3.3-cm width and were washed for 6 h with reagent-grade methanol and acetone by use of a Soxhlet's extractor, respectively, and then dried under reduced pressure. MAA and DMA were purified by distillation under reduced pressure.

Plasma Treatment and Photografting

The plasma treatment and photografting were carried out in the manner described in our previous articles.[15,18] The pPTFE and ePTFE films were first treated with oxygen plasmas for 120 s at output of 200 W and frequency of 15 kHz using a Shimadzu LCVD 20-type plasma polymerization apparatus. Then MAA and DMA monomers were photografted onto the plasma-treated pPTFE and ePTFE films for 2 h at 60°C by applying UV rays emitted from a 400-W high pressure mercury lamp in the individual aqueous monomer solutions at monomer concentrations of 1.0 or 1.5 mmol/mL. The photografting of DMA was carried out in an aqueous monomer solution adjusted to pH 8 with concentrated HCl to prepare DMA-grafted PTFE films with a high grafted amount.[27] For the photografting of MAA, the aqueous monomer solution was used without adjusting any pH levels.

Membrane Properties of Grafted pPTFE and ePTFE Films

The membrane properties of the grafted pPTFE and ePTFE films were pursued in the manner described in our previous studies.[1,3] The photoelectron spectra on C1*s*, O1*s*, N1*s*, and F1*s* for the grafted pPTFE and ePTFE films were recorded on a Shimadzu ESCA 750-type spectroscope with MgKα (1253.6 eV) operating at 8 kV and 30 mA. Binding energy was adjusted to $Au4f_{7/2}$ = 84.0 eV.[28,29] The above-mentioned measurements were made according to the procedure reported earlier.[1] The surface coverage of pPTFE and ePTFE films with grafted polymer chains was evaluated from the intensity ratios, O1*s*/C1*s* and F1*s*/C1*s*, for MAA-grafted pPTFE (MAA-*g*-pPTFE) and MAA-grafted ePTFE (MAA-*g*-ePTFE) films and from N1*s*/C1*s* as well as the above two intensity ratios for DMA-grafted pPTFE (DMA-*g*-pPTFE) and DMA-grafted ePTFE (DMA-*g*-ePTFE) films.[15,30,31]

Viscometric Measurement

The reduced viscosity of aqueous solutions of polyMAA (PMAA) and polyDMA (PDMA) (2 g/dm^3) was measured with a change in the pH level in the presence of 0.01 mol NaCl at 25 $\pm$ 0.1°C using an Ubbelohde viscometer. The pH levels of the polymer solutions were adjusted with HCl or NaOH solutions of 0.1–2 mol/dm^3.

Permeation Experiment

Temperature Dependence of Permeation of Glucose

Grafted pPTFE and ePTFE films, which had been equilibrated in a $NaHCO_3$/NaOH buffer solution of

Table I Saccharides Used in Study

Saccharide	Molecular Weight (g/mol)	Abbreviation	Intrinsic Viscosity[a] (100 g/mL)
Glucose	180.16	—	—
Maltose · H_2O	360.32	—	—
Raffinose · $5H_2O$	594.52	—	—
Dextran	10,000[b]	10K dextran	0.084
	40,000[b]	40K dextran	0.145
	250,000[b]	250K dextran	0.369

[a] Intrinsic viscosity was determined in water at 25°C.
[b] Molecular weights were declared on the product label.

pH 10 (ionic strength, 0.01 mol/dm^3) at 10°C in advance, were clamped between two chambers of a permeation cell (effective membrane area, 3.14 cm^2). A 100-mL quantity of buffer solution, pH 10, containing 1 g of glucose as a neutral permeant was put into one chamber and 100 mL of buffer solution, pH 10, was put into the other chamber. Then the solutions in both chambers were stirred slowly. Permeation experiments were made by alternatively changing the temperature of the medium between 10 and 50°C in a stepwise manner. A 0.05-mL aliquot was taken out of the permeation solution at fixed time intervals. The amount of glucose permeated through grafted pPTFE and ePTFE films was determined by measuring the absorbance (at 505 nm) of the solutions colored by adding a glucose CII-test solution (purchased from Wako Chemicals Co. Ltd., Japan) on the basis of the color-developing reactions by the β-D-glucose oxidase–peroxidase system.[32]

pH Dependence of Permeation of Glucose

Glucose permeation experiments were carried out in the buffer solutions of pH 4–10 at 25°C in order to discuss the pH dependence of the glucose permeability of grafted pPTFE and ePTFE films. Grafted pPTFE and ePTFE films equilibrated in the pH 4–10 buffer solutions at 25°C were clamped between the same two chambers as the mentioned above. The glucose permeability of grafted pPTFE and ePTFE films was investigated in the buffer solutions of the same pH level as the buffer solutions in which the grafted pPTFE and ePTFE films were immersed. The glucose permeability of grafted pPTFE and ePTFE films was estimated by calculating the permeation flux (mg/h cm^2) from the permeation rate at a steady state (mg/h) and the effective membrane area (3.14 cm^2).[33]

Permeation of Saccharides

Permeability of DMA-*g*-ePTFE films to glucose, maltose, raffinose, and dextrans with molecular weights of 1.0×10^4, 4.0×10^4, and 2.5×10^5 shown in Table I[34] was investigated in water at 50°C using the same cell as mentioned above. The DMA-*g*-ePTFE film was equilibrated in water before use. The concentration of each saccharide solution as a feed was set at 10 g/dm^3. The amounts of permeated saccharides other than glucose were estimated by the color-developing reaction with sulfuric acid and phenol as follows.[35–37] After 5 mL of concentration HCl and 2 mL of 2% (w/v) of an aqueous phenol solution were added to a 0.1-mL aliquot taken from the permeate at fixed time intervals, the solutions were stirred well for 5 min. The amounts of permeated saccharides were determined by measuring the absorbance of the colored solutions at 490 nm.[35–37]

In addition, permeation experiments were made using a mixture of 40,000 and 250,000 molecular weight (40K and 250K) dextrans in the ratio of 1 : 1 (w/w) at 50°C to discuss molecular separation behavior of DMA-*g*-ePTFE films to two types of dextrans with different molecular weights. After permeation flux to dextran mixture of 40K and 250K dextrans (mg/h · cm^2) was determined according to the color-developing reaction, the solution in the permeate was concentrated to about one-third of its original volume at 50–60°C. The concentration of dextran was determined from the refractive index of the concentrated solutions. The weight fraction was estimated from the reduced viscosity measurements of the concentrated solutions using an Ubbelohde viscometer at 25°C. Separation factor α_{sp} was calculated using eq. (1),

$$\alpha_{sp} = \frac{Y_{40K}(\text{wt }\%)/Y_{250K}(\text{wt }\%)}{X_{40K}(\text{wt }\%)/X_{250K}(\text{wt }\%)} \quad (1)$$

where X and Y denote the weight fractions of dextrans in the feed and in the permeate, and the subscripts 40K and 250K are the abbreviations of the dextrans.

RESULTS AND DISCUSSION

Membrane Properties of Grafted pPTFE and ePTFE Films

Progression of grafted polymer chains into the interior of the pPTFE and ePTFE films was estimated from microscopic observation of the cross sections of the samples and surface analysis by ESCA of grafted pPTFE and ePTFE films. Because the only grafted layers consisting of grafted polymer chains and PTFE chains were stained in the aqueous dye solutions,[11] the grafted layers could be distinguished from the ungrafted layers by photographing the cross sections through an optical microscope. Figure 1 shows the changes in the thickness of the grafted and ungrafted layers with the grafted amount for grafted pPTFE and ePTFE films. The thickness of the grafted layer increased with an increase in the grafted amount. The disappearance of the ungrafted layers indicates that grafted polymer chains reach the centers of the pPTFE and ePTFE films. Here, the G_2 values refer to the grafted amounts at which grafted polymer chains reach the centers of the pPTFE and ePTFE films. The results obtained from microscopic observation together with surface analysis by ESCA are summarized in Table II. The constant intensity ratios for grafted pPTFE and ePTFE films indicate the finally attainable coverage of the pPTFE and ePTFE films with individual grafted polymer chains. The G_1 values refer to the grafted amounts at which the intensity ratios became constant. Grafted PDMA chains covered the pPTFE and ePTFE surfaces swiftly and reached the centers of their films at lower grafted amounts than grafted PMAA chains did. Because a similar tendency was observed in photograftings of MAA and DMA onto polyethylene (PE) films,[23,24] it is considered that DMA monomers have a better affinity for the PTFE substrate than MAA monomers. In a previous article the expansion of fPTFE films by photograftings was not observed at all,[15] because the location of photografting was restricted to the surface regions of fPTFE films. Therefore, it was first supposed that the photograftings of MAA and DMA on pPTFE and ePTFE films hardly proceeded into the interior of their bulk phase and were restricted only to the surfaces of the pores inside the pPTFE and ePTFE films. However, the area ratio increased with the grafted amount irrespective of the monomer concentration for grafted pPTFE films as shown in Figure 2. In particular the area ratio for DMA-*g*-pPTFE

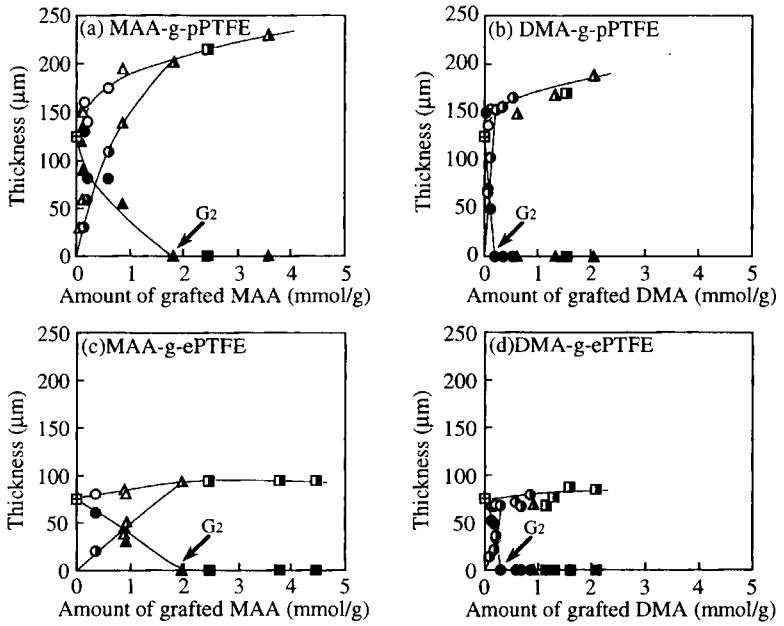

Figure 1 Changes in the thickness of (○, △, □) grafted film, (○, △, □) grafted layer, and (●, ▲, ■) ungrafted layer with the grafted amount for (a) MAA-*g*-pPTFE, (b) DMA-*g*-pPTFE, (c) MAA-*g*-ePTFE, and (d) DMA-*g*-ePTFE films prepared at monomer concentration of (○, ○, ●) 0.5, (△, △, ▲) 1.0, and (□, □, ■) 1.5 mol/dm^3.

Table II Covering of pPTFE and ePTFE Films with Grafted Polymer Chains and Progression into pPTFE and ePTFE Films

Substrate	Monomer	G_1 (ESCA) (mmol/g)	G_2 (Cross Section) (mmol/g)
pPTFE	MAA	0.3	1.8
	DMA[a]	0.2	0.2
ePTFE	MAA	0.5	2.0
	DMA[a]	0.2	0.3

G_1, the grafted amounts at which grafted polymer chains cover the pPTFE and ePTFE surfaces entirely. G_2, the grafted amounts at which grafted polymer chains reach the center of the pPTFE and ePTFE films.

[a] The photografting of DMA onto pPTFE and ePTFE films was carried out at pH 8.

films considerably increased in the range of a low grafted amount. This result showed that the higher order structure of PTFE chains in the pPTFE films was destroyed by grafted polymer chains. On the other hand, the area ratio for the grafted ePTFE films gradually decreased at a low grafted amount region. The slight area contraction for the grafted ePTFE films at a low grafted amount region can be considered to be caused by hydrogen bonding between polar groups affixed to the grafted polymer chains. This is consistent with the relation between the tensile strength in the swollen state and the grafted amount described below.

The amount of absorbed water for grafted pPTFE and ePTFE films was measured in order to estimate their hydrophilicity. Figure 3 shows that the amount of absorbed water for the grafted pPTFE and ePTFE films increased with the grafted amount. It is apparent that DMA-*g*-pPTFE and ePTFE films have higher water absorptivity than MAA-*g*-pPTFE and ePTFE films. In addition, the n_{water} value, the number of water molecules assigned to a monomer segment, was calculated from both the amount of absorbed water and the grafted amount.[1-3] Figure 4 together with the expanded views in the range below 2 mmol/g shows that the n_{water} values went through the maximum values, followed by decreasing with an increase in the grafted amount. Grafted polymer chains located in the vicinity of the substrate surface are considered to be capable of occluding a large amount of water molecules compared to those restrained in the porosity structure of the PTFE films. Therefore, it is inferred that the location of the photografting is restricted to the vicinities of the pPTFE and ePTFE surfaces in the beginning of the photografting and that grafted polymer chains in the range of higher grafted amounts are forced to progress into the inner pore structure of the PTFE films, leading to a slower increment of the amount of absorbed water. In a previous study, it was found from the comparison between the SEM pictures of MAA-*g*-ePTFE and DMA-*g*-ePTFE films with almost the same grafted amount that the pores were filled with grafted PMAA chains in the MAA-*g*-ePTFE films,

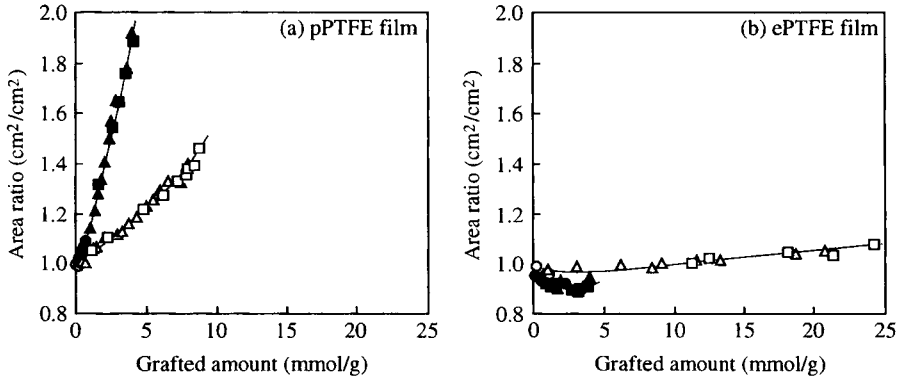

Figure 2 Variations in area ratio with the grafted amount for (a) (○, △, □) MAA-*g*-pPTFE and (●, ▲, ■) DMA-*g*-pPTFE films and (b) (○, △, □) MAA-*g*-ePTFE and (●, ▲, ■) DMA-*g*-ePTFE films. Monomer concentration (mol/dm³): circle, 0.5; triangle, 1.0; and square, 1.5.

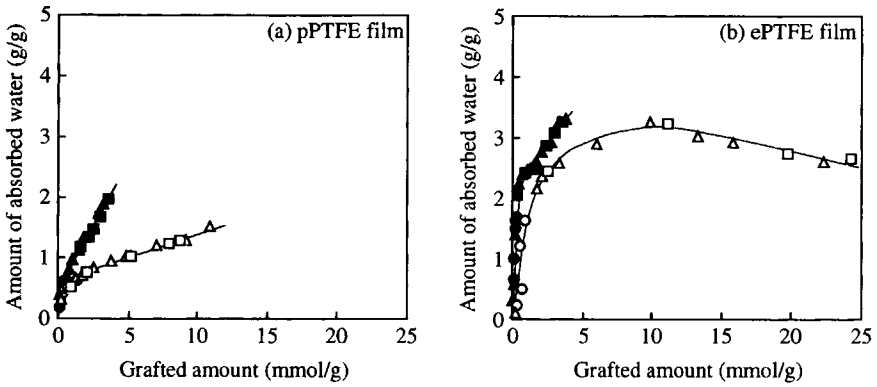

Figure 3 Variations in the amount of absorbed water with the grafted amount for (a) (○, △, □) MAA-*g*-pPTFE and (●, ▲, ■) DMA-*g*-pPTFE films and (b) (○, △, □) MAA-*g*-ePTFE and (●, ▲, ■) DMA-*g*-ePTFE films. The symbols representing the monomer concentration have the same meaning as Figure 2.

while the size of pores of DMA-*g*-ePTFE films only became smaller.[15] This result indicates that the DMA-*g*-ePTFE films have a space for occluding a large amount of water. Therefore, the grafted ePTFE films could absorb more water than the grafted pPTFE films. The amount of absorbed water of the DMA-*g*-ePTFE film of 5 mmol/g, which possessed the highest absorptivity in the range measured here, was 3.3 g/dry g. This value was about three times the amount of absorbed water of the DMA-*g*-PE film with the grafted amount of 7 mmol/g. In addition, the grafted pPTFE and ePTFE films can be regarded as hydrogels from the much higher n_{water} values. Figure 5 shows that electrical conductivity for the grafted pPTFE and ePTFE films sharply increased and then became constant. The grafted amounts at which electrical conductivity sharply increased also almost agreed with those at which grafted polymer chains reached the centers of the used substrates as shown in Table III.[1,38] It seems that grafted PMAA and PDMA chains formed in the vicinity of the pPTFE and ePTFE surfaces participate in the increase in both water absorptivity and electrical conductivity.

Control of Permeation in Response to Temperature Change

PDMA is a thermosensitive polymer with a cloud point at 27°C in a buffer solution of pH 10.[23,24] The control of permeation of glucose in response to the temperature change was investigated by making use of the expansion/contraction behavior of grafted PDMA chains derived from their thermosensitivity. Figures 6 and 7 show the change in the glucose permeability of DMA-*g*-pPTFE and DMA-*g*-ePTFE

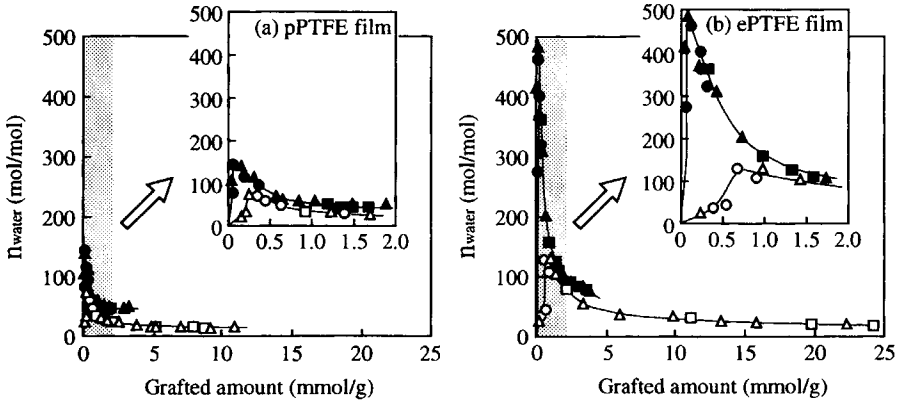

Figure 4 Variations in n_{water} with the grafted amount for (a) (○, △, □) MAA-*g*-pPTFE and (●, ▲, ■) DMA-*g*-pPTFE films and (b) (○, △, □) MAA-*g*-ePTFE and (●, ▲, ■) DMA-*g*-ePTFE films. The symbols representing the monomer concentration have the same meaning as Figure 2.

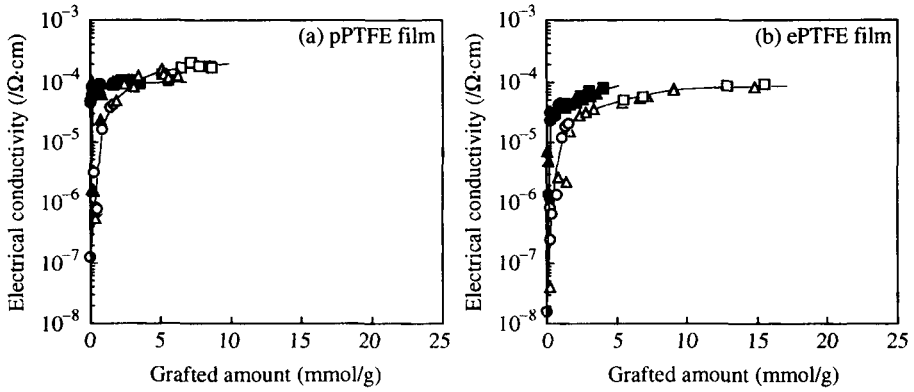

Figure 5 Variations in the electrical conductivity for (a) (○, △, □) MAA-*g*-pPTFE and (●, ▲, ■) DMA-*g*-pPTFE films and (b) (○, △, □) MAA-*g*-ePTFE and (●, ▲, ■) DMA-*g*-ePTFE films. The symbols representing the monomer concentration have the same meaning as Figure 2.

films with different grafted amounts in a buffer solution of pH 10 by changing the temperature of the medium between 10 and 50°C, respectively. DMA-*g*-pPTFE and DMA-*g*-ePTFE films were permeable to glucose molecules at 50°C. However, when the temperature was decreased to 10°C, permeation of glucose was considerably depressed. This on–off regulation of permeation could be repeated by the alternate temperature change. Although the glucose permeability for DMA-*g*-ePTFE films was higher than that for DMA-*g*-pPTFE films at the on state, it was difficult for DMA-*g*-ePTFE films to depress the glucose permeability at the off state of 10°C because of the higher vacancy of ePTFE films. Therefore, it is considered that the DMA-*g*-ePTFE films used here do not have enough grafted amount to decline the permeability to glucose due to a dense layer formed by the contraction of grafted PDMA chains at an increased temperature, and the increase in the glucose permeability at 50°C is due to an increase in the pore size caused by the contraction of grafted PDMA chains.[23,24] In addition, the on–off regulation of permeation for DMA-*g*-pPTFE and ePTFE films could be controlled at lower grafted amounts than that for DMA-*g*-PE films because both pPTFE and ePTFE films have the porosity structure. The on–off regulation patterns in response to the temperature change for DMA-*g*-pPTFE and ePTFE films were completely opposite to those for many other polymer gel samples consisting of thermosensitive polymers with lower critical solution temperatures.[39–41]

Control of Permeation in Response to pH Change

The glucose permeability of the grafted pPTFE and ePTFE films was examined in buffer solutions of different pH levels. Figures 8 and 9 show the variations in the permeation flux of glucose with the grafted amount in the buffer solutions of pH 4–10

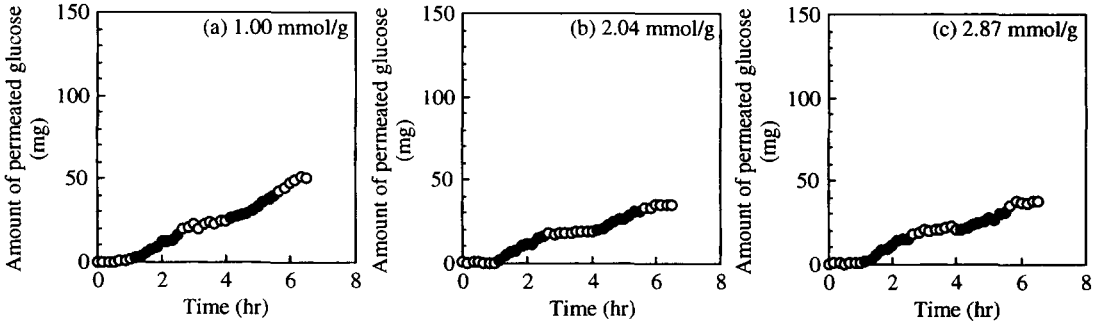

Figure 6 Reversible permeation of glucose through DMA-*g*-pPTFE films with the grafted amounts of (a) 1.00, (b) 2.04, and (c) 2.87 mmol/g in a $NaOH/NaHCO_3$ buffer solution of pH 10 by alternatively changing the temperature of the medium between (○) 10°C and (●) 50°C.

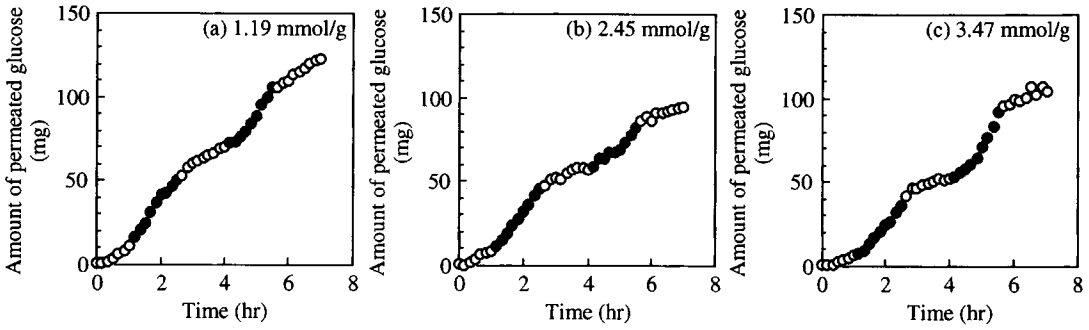

Figure 7 Reversible permeation of glucose through DMA-*g*-ePTFE films with the grafted amounts of (a) 1.19, (b) 2.45, and (c) 3.47 mmol/g in a buffer solution of pH 10 by alternatively changing the temperature of the medium between (○) 10°C and (●) 50°C.

for DMA-*g*-pPTFE and DMA-*g*-ePTFE films, respectively. The glucose permeability went through the maximum values, followed by decreasing with the grafted amount irrespective of pH level. It seems that the films became more and more hydrophilic with an increase in the grafted amount at lower grafted amounts, and the pores diminished in size due to the swelling of the grafted layers above the grafted amounts at which the permeation flux of glucose reached the maximum values. Although the grafted amount dependence of the glucose permeability of MAA-*g*-PTFE films also showed a similar tendency to that of DMA-*g*-PTFE films, the grafted amount at which the glucose permeability had a maximum value for DMA-*g*-ePTFE films was lower than that for MAA-*g*-ePTFE films. In addition, the pH dependence of the permeation flux was examined using grafted pPTFE and ePTFE films that had the maximum permeation fluxes. Figure 10 shows the changes in the permeation flux with pH level. The permeation flux of all four types of grafted PTFE films had maximum values at pH 8. Therefore, it can be considered that because glucose is a neutral compound, the glucose permeability of the grafted pPTFE and ePTFE films are governed by a conformational change in grafted polymer chains in response to the pH level of the outer solution. So, to discuss the pH dependence of the conformation of grafted polymer chains, the reduced viscosities of aqueous solutions of PMAA and PDMA prepared

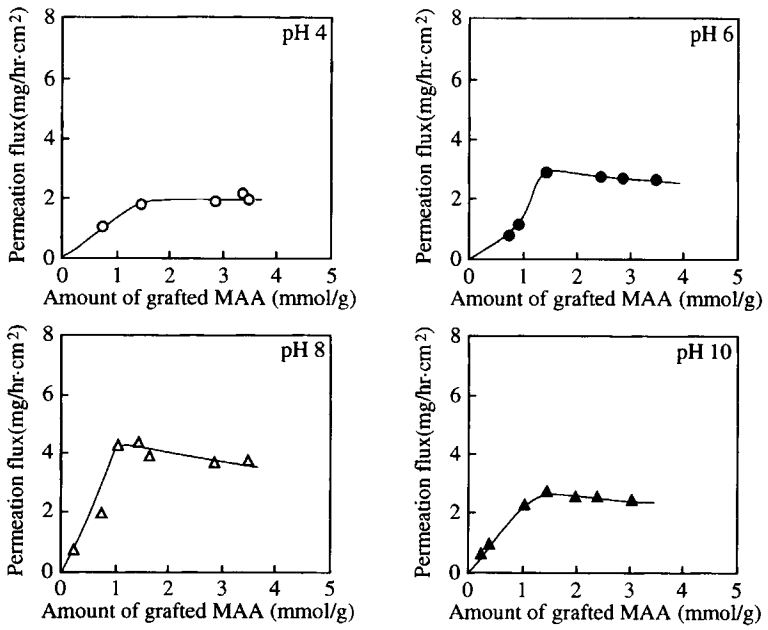

Figure 8 The glucose permeability of MAA-*g*-ePTFE film of 1.00 mmol/g in the buffer solutions of pH (○) 4, (●) 6, (△) 8, and (▲) 10 at 25°C.

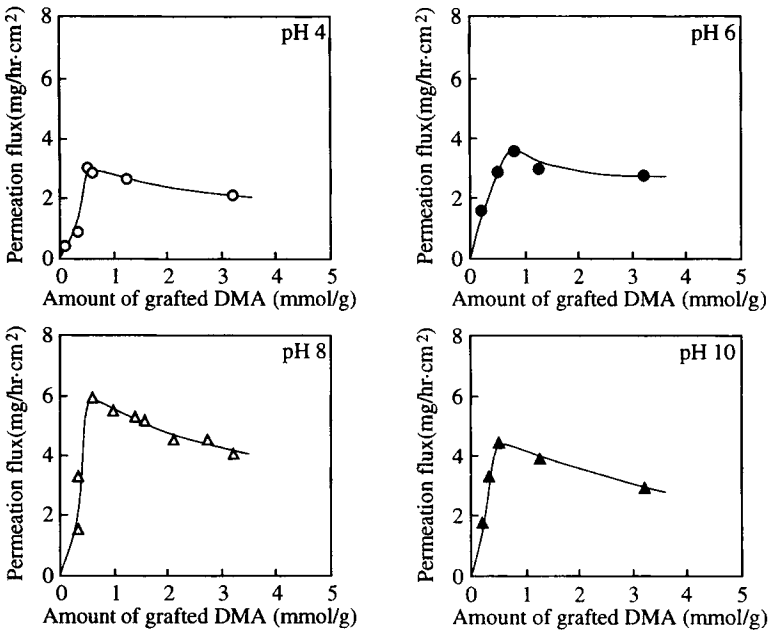

Figure 9 The glucose permeability of DMA-*g*-ePTFE film of 0.84 mmol/g in the buffer solutions of pH (○) 4, (●) 6, (△) 8, and (▲) 10 at 25°C.

by the photopolymerization were measured by varying the pH levels of the medium whose ionic strength was adjusted to 0.01 mol/dm^3 by addition of NaCl.

Figure 11 shows the changes in the reduced viscosities of aqueous PMAA and PDMA solutions with the pH level. The reduced viscosity of an aqueous PMAA solution increased with an increase in the pH level due to the progress of the dissociation of carboxyl groups affixed to the PMAA chains, while that of an aqueous PDMA solution increased with a decrease in the pH level due to the progress of the protonation of dimethylamino groups affixed to the PDMA chains. The reduced viscosities of aqueous solutions of PMAA and PDMA had the maximum values at pH 8 and 6, respectively, where both polymer chains were considered to have the most expanding conformation. Therefore, we can suggest that both grafted PMAA and PDMA chains also show such a conformational change as the corresponding polymer chains with the changing pH of the medium. It is found in Figures 10 and 11 that both glucose permeabilities of MAA-*g*-pPTFE and MAA-*g*-ePTFE films and reduced viscosity of aqueous PMAA solution went through the maximum value at about pH 8. This indicates that glucose molecules could permeate the most through MAA-*g*-pPTFE and MAA-*g*-ePTFE films at a state where grafted PMAA chains were expanded, and the glu-

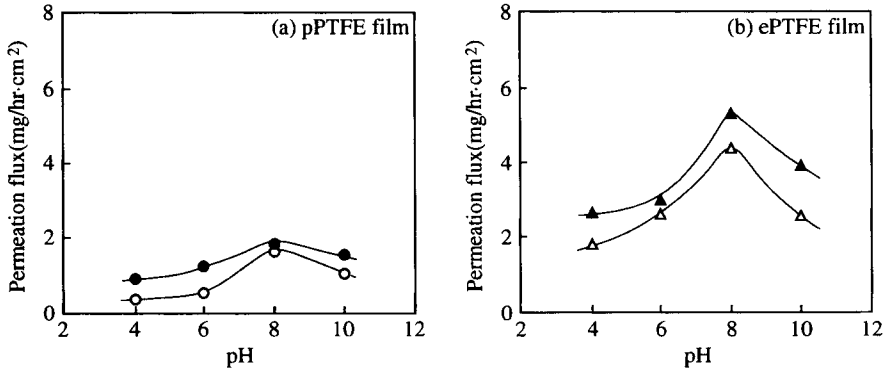

Figure 10 The glucose permeability of (a) (○) MAA-*g*-pPTFE and (●) DMA-*g*-pPTFE and (b) (△) MAA-*g*-ePTFE and (▲) DMA-*g*-ePTFE films in the buffer solution of pH 8 at 25°C.

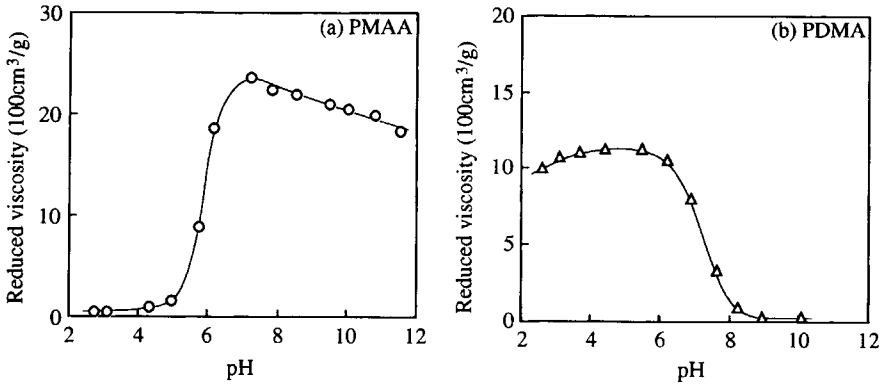

Figure 11 The pH dependence of reduced viscosities of aqueous solutions of (a) PMAA and (b) PDMA of 2 g/dm^3 in the presence of 0.01 mol NaOH.

cose permeability decreased as the pores were clogged due to the contraction of grafted PMAA chains caused by the decrease in the pH level. On the other hand, as the reduced viscosity of the aqueous PDMA solution decreased, the glucose permeability of the DMA-*g*-pPTFE and ePTFE films increased. Consequently, we can conclude that DMA-*g*-pPTFE and ePTFE films are permeable to glucose molecules due to the contraction of grafted PDMA chains, and glucose permeation is depressed due to the decrease in the pore size caused by the expansion of grafted PDMA chains. However, because hydrophobization of grafted PDMA chains due to deprotonation at pH 10 led to a decrease in an affinity to glucose molecules, the glucose permeability slightly decreased. On the basis of the results mentioned above and the SEM pictures of the surfaces of the grafted PTFE films with different grafted amounts, we can safely conclude as follows. The expansion of grafted PMAA chains located in the vicinity of the surfaces of the pPTFE and ePTFE films led to the increase in the glucose permeability. On the other hand, because a DMA monomer has a better affinity for PTFE film than an MAA monomer does, the photografting of DMA will easily occur on the surfaces of the pores inside the pPTFE and ePTFE films. Because many grafted PDMA chains were present on the surfaces of the pores inside the pPTFE and ePTFE films, the glucose permeability increased by the contraction of grafted PDMA chains. The above results reveal that the permeation of a small compound can be controlled by the conformational change in grafted polyelectrolyte chains in response to the pH change; and the glucose permeability of grafted pPTFE and ePTFE films is dependent not only on the pH level of the medium, but also on the distribution of grafted polymer chains in the direction of depth inside the films.

Permeation of Saccharides with Different Molecular Weights

Experiments were made to discuss the dependence of the molecular weight of the permeants on permeation through the DMA-*g*-ePTFE films that had the highest permeability of four types of grafted PTFE films. Taking into account that dextran was liable to be hydrolyzed in acidic solutions, permeation experiments were carried out in water. Figure 12 shows the change in the permeation flux of aqueous solutions of glucose, raffinose, maltose, and three kinds of dextrans with different molecular weights with the grafted amount for DMA-*g*-ePTFE films. The permeation flux had the maximum value at 0.8 mmol/g; and the higher the molecular weight of the permeant, the lower the permeation flux. Figure 13 shows the change in the permeation flux with molecular weight of the permeant for the same grafted PTFE films as used in Figure 12. The permeation flux decreased with an increase in the molecular weight of the permeant. It can be expected from this result that two types of different saccharides are separable by a difference in the permeation flux. Permeability of DMA-*g*-ePTFE film to the mixtures containing 40K and 250K dextrans was examined. The concentration of mixed dextran mixtures in feed was 1 wt % and its weight ratio of 40K and 250K dextrans was 1 : 1. The concentration and composition of the dextran solutions were determined from the refractive index and reduced viscosity measurements of the permeate, respectively. Figure 14 shows the changes in the refractive index with the concentration for aqueous mixed solutions of 40K and 250K dextrans and a mixed solution containing each dextran in the weight ratio of 1 : 1 at 25°C. Because the refractive index increased with an increase in the concentration, irrespective of the

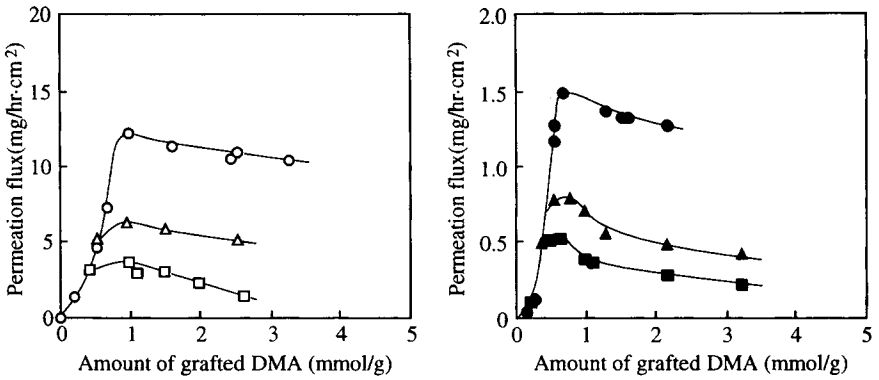

Figure 12 Variations in the permeability of DMA-*g*-ePTFE film (○) glucose, (△) maltose, (□) raffinose, (●) dextran 10K, (▲) 40K dextran, and (■) 250K dextran with the grafted amount in water at 50°C.

molecular weight and weight fraction, the weight concentration of the aqueous mixed solutions could be determined from the refractive index. Figure 15 shows the changes in the reduced viscosity of the aqueous mixed solutions with the concentration at 25°C. The reduced viscosity increased linearly with the weight fraction of 250K dextran. Therefore, the composition of the mixed dextran solutions could be determined from reduced viscosity measurements. Figure 16 shows the variation in the permeation flux of the mixed dextran solutions consisting of 40K and 250K dextrans with the grafted amount. The permeation flux passed through the maximum value around 0.8 mmol/g. Figure 17 shows the variation in the separation factor calculated using eq. (1). The separation factor more than unity indicates that DMA-*g*-ePTFE films are more permeable to 40K dextran than 250K dextran. By contrast to the permeation flux, the separation factor decreased with an increase in the grafted amount and then reached the minimum value around 0.8 mmol/g. The surfaces of the ePTFE films were allowed to be hydrophilic with grafted PDMA chains at lower grafted amounts, causing the increased permeation and decreased separation. However, increased grafted PDMA chains at higher grafted amounts were densely located inside pores of the ePTFE films, and therefore gave rise to lower permeation of the DMA-*g*-ePTFE films and more improved separation efficiency.

Strength in Swollen State

The strength of grafted pPTFE and ePTFE films in the swollen state is one of the important factors required to make them useful for a functional membrane. Severe plasma treatment may lead to a decrease in the tensile strength of pPTFE and ePTFE films. Here, the mechanical strength was estimated

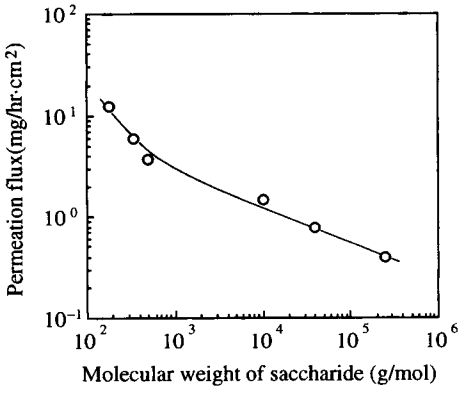

Figure 13 Permeability of DMA-*g*-ePTFE film of 0.8 mmol/g to saccharides and dextrans with different molecular weights in water at 50°C.

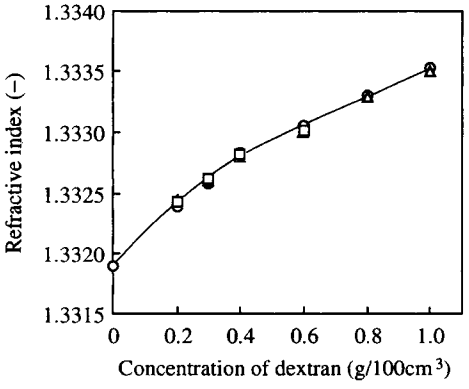

Figure 14 Changes in the refractive index of aqueous solutions of (○) 40K dextran, (△) 250K dextran, and (□) mixed 40K + 250K dextran solution at 25°C with the concentration.

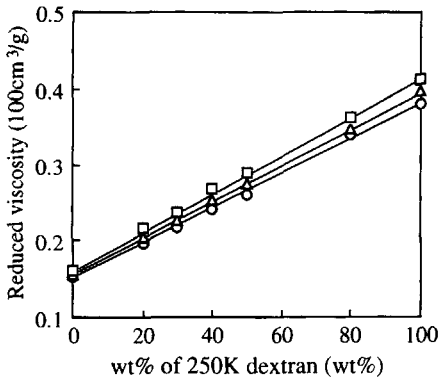

Figure 15 Changes in the reduced viscosity of the mixed dextran solutions at concentration of (○) 2, (△) 4, and (□) 6 g/dm³ in water at 25°C.

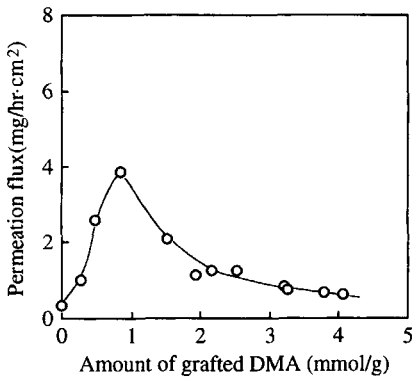

Figure 16 Variations in permeation flux of the mixed dextran solutions for DMA-*g*-ePTFE films with the grafted amount at 50°C.

from the tensile strength of grafted pPTFE and ePTFE films swollen in water at 25°C.[1,6,7,38,42] Figure 18 shows the variations in the tensile strength with the grafted amount. When MAA and DMA monomers were photografted onto the pPTFE and ePTFE films, the tensile strength slightly increased at a low grafted amount. Such a tendency was more remarkably observed for the grafted ePTFE films. It is considered that the increase in the tensile strength at a low grafted amount may be caused by hydrogen bonding between polar groups affixed to the grafted polymer chains. Hydrogen bonding between polar groups is considered to be easily formed for the grafted ePTFE film from the decrease in the surface area of the grafted ePTFE film at a low grafted amount (see Fig. 2). For DMA-*g*-pPTFE films the expansion with the increase in the grafted amount will also cause the decrease in the tensile strength because the higher order structure is broken. Because grafted PDMA chains reached the centers of the PTFE films at lower grafted amounts than grafted PMAA chains did, photografting of DMA led to more decrease in the tensile strength of pPTFE and ePTFE films at lower grafted amounts. Although the tensile strength of the grafted PTFE films decreased with an increase in the grafted amount to some degree, the grafted pPTFE and ePTFE films can be expected to be used for ultrafiltration membranes because they have molecular separation behavior to dextrans with different molecular weights and adequate mechanical strength in the swollen state.

CONCLUSION

We pursued membrane properties such as water absorptivity and electrical conductivity of pPTFE and ePTFE films grafted with MAA and DMA by the combined use of the plasma treatment and photografting. The glucose permeability of grafted pPTFE and ePTFE films in response to the temperature or pH change and their molecular separation behavior to two types of dextrans with different molecular weights were examined. In addition, the mechanical strength of the grafted pPTFE and ePTFE films was estimated from the tensile strength measurements in the swollen state. From the experimental results above, we can conclude the following:

1. The grafted pPTFE and ePTFE films possess good water absorptivity, and their electrical conductivity drastically increase around the grafted amounts at which grafted polymer chains reach the center of each PTFE film.
2. The glucose permeability of grafted pPTFE and ePTFE films can be controlled in response to the pH change, and the on–off regulation of the glucose permeation of DMA-*g*-pPTFE and ePTFE films is repeated in re-

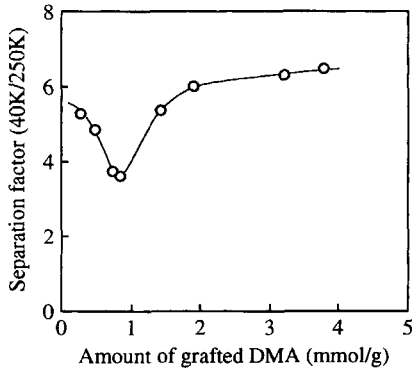

Figure 17 Variations in separation factor for DMA-*g*-ePTFE films with the grafted amount at 50°C.

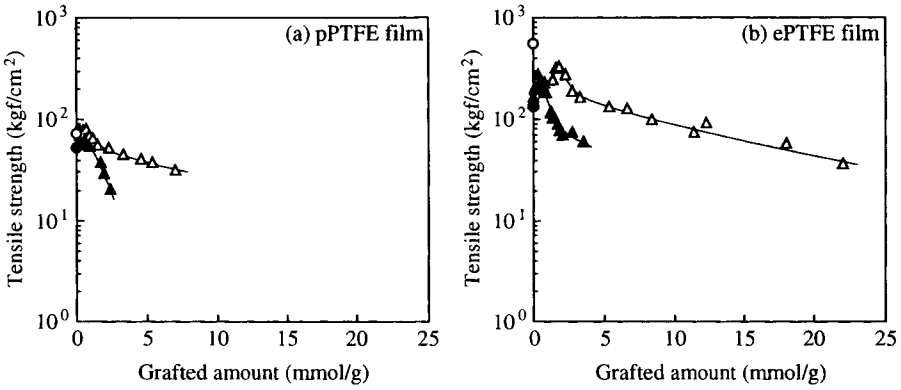

Figure 18 Variations in the tensile strength for (a) (△) MAA-*g*-pPTFE and (▲) DMA-*g*-pPTFE films and (b) (△) MAA-*g*-ePTFE and (▲) DMA-*g*-ePTFE films prepared at monomer concentration of (△, ▲) 1.0 mol/dm³ swollen in water at 30°C. (a) (○) untreated pPTFE film and (●) pPTFE film plasma treated for 120 s; (b) (○) untreated ePTFE film and (●) ePTFE film plasma treated for 120 s.

sponse to the alternate temperature change below and above the cloud point of PDMA at pH 10.

3. It is possible to separate 40K and 250K dextrans by DMA-*g*-ePTFE films, and the separation efficiency shows maximum values at the grafted amount of 0.8 mmol/g.
4. The grafted pPTFE and ePTFE films have adequate mechanical strength in the swollen state to be of use for a functional membrane.

REFERENCES

1. K. Yamada, S. Tatekawa, and M. Hirata, *J. Colloid Interface Sci.*, **162,** 144 (1994).
2. K. Yamada, T. Kimura, H. Tsutaya, and M. Hirata, *J. Appl. Polym. Sci.*, **44,** 993 (1992).
3. K. Yamada, H. Tsutaya, S. Tatekawa, and M. Hirata, *J. Appl. Polym. Sci.*, **46,** 1065 (1992).
4. H. Kubota and Y. Hata, *J. Appl. Polym. Sci.*, **42,** 2029 (1991).
5. H. Kubota, K. Kobayashi, J. F. Ding, and Y. Ogiwara, *Eur. Polym. J.*, **24,** 441 (1988).
6. E. A. Hegazy, N. H. Taher, and H. Kamel, *J. Appl. Polym. Sci.*, **38,** 1229 (1989).
7. N. H. Taher, A. M. Dessouki, and F. H. Khalil, *Radiat. Phys. Chem.*, **36,** 785 (1990).
8. B. D. Gupta and A. Chapiro, *Eur. Polym. J.*, **25,** 1137 (1989).
9. A. M. Dessouki, E. A. Hegazy, and M. M. Shaker, *Radiat. Phys. Chem.*, **28,** 11 (1987).
10. E. A. Hegazy, *Polymer,* **33,** 96 (1992).
11. A. K. Mukherjee and B. D. Gupta, *J. Appl. Polym. Sci.*, **30,** 2655 (1985).
12. I. Ishigaki, T. Sugo, K. Senoo, T. Okada, J. Okanoto, and S. Machi, *J. Appl. Polym. Sci.*, **27,** 1033 (1982).
13. E. A. Hegazy, N. H. Taher, and H. Kamal, *J. Appl. Polym. Sci.*, **38,** 1229 (1989).
14. M. T. Razzak, K. Otsuhata, and Y. Tabata, *J. Appl. Polym. Sci.*, **33,** 2345 (1987).
15. K. Yamada, K. Hayashi, K. Sakasegawa, H. Onodera, and M. Hirata, *Nippon Kagaku Kaishi* [*J. Chem. Soc. Jpn., Chem. Ind. Chem.*], 427 (1994) [in Japanese].
16. T. Hirotsu, *Ind. Eng. Chem. Res.*, **26,** 1287 (1987).
17. Y. Osada and Y. Iriyama, *Thin Solid Films,* **118,** 197 (1984).
18. M. Suzuki, A. Kishida, H. Iwata, and Y. Ikada, *Macromolecules,* **19,** 1804 (1986).
19. M. Hirata, J. Isoda, K. Yamada, and T. Ebihara, Polyelectrolytes Potsdam '95, First Int. Symp. Polyelectrolytes Int. Bunsen-Discussion-Mtg. Polyelectrolytes Solution Interface, Max-Planck-Institute for Colloid and Interface Research, 1995, p. 128.
20. K. Ishihara, M. Kobayashi, and I. Shinohara, *Polym. J.*, **16,** 647 (1984).
21. K. Sawahata, M. Hara, H. Yasunaga, and Y. Osada, *J. Controlled Release,* **14,** 253 (1990).
22. Y. H. Bae, T. Okano, and S. W. Kim, *J. Controlled Release,* **9,** 271 (1989).
23. K. Yamada, S. Tatekawa, and M. Hirata, Prepr. Joint Symp. Polym. Gels Networks—Gel Fundamentals Intell. Appl., Soc. Polym. Sci., Japan, 1993, p. 140.
24. K. Yamada, T. Sato, S. Tatekawa, and M. Hirata, *Polym. Gels Networks,* **2,** 323 (1994).
25. M. A. Islam, A. Dimov, and A. L. Malinova, *J. Membr. Sci.*, **66,** 69 (1992).
26. N. Nishioka, K. Watase, K. Arimura, K. Kosai, and M. Uno, *Polym. J.*, **16,** 867 (1984).
27. K. Hayashi, S. Tatekawa, F. Igi, K. Yamada, T. Ebihara, and M. Hirata, *Chem. Soc. Jpn., Annu. Mtg.*, Abstr. 1 C8 31, 1992, [in Japanese].

28. D. Briggs, D. M. Brewis, and M. B. Konieczo, *J. Mater. Sci.*, **11,** 1270 (1976).
29. D. Briggs, D. M. Brewis, and M. B. Konieczo, *J. Mater. Sci.*, **14,** 1344 (1979).
30. D. Briggs, V. J. I. Zichy, D. M. Brewis, J. Comyn, R. H. Dahm, M. A. Green, and M. B. Konieczko, *Surface Interface Anal.*, **2,** 107 (1980).
31. P. Cadman, G. Gossedge, and J. D. Scott, *J. Electron Spectrosc. Related Phenom.*, **13,** 1 (1978).
32. J. Okuda, K. Maeda, and G. Okuda, *Clin. Chim. Acta,* **37,** 538 (1972).
33. S. Nakatsuka and A. L. Andrady, *J. Appl. Polym. Sci.*, **44,** 17 (1992).
34. M. W. Kiciak, *Chem. Anal.*, **21,** 1105 (1976) [in Polish].
35. T. Kobayashi, K. Kumagai, Y. Nosaka, H. Miyama, N. Fujii, and H. Tanzawa, *J. Appl. Polym. Sci.*, **43,** 1037 (1991).
36. M. Bubois, K. A. Gilles, J. K. Hamilton, P. A. Rebers, and F. Smith, *Anal. Chem.*, **28,** 350 (1956).
37. M. Dubois, K. Gilles, J. K. Hamilton, P. A. Pebers, and F. Smith, *Nature,* **168,** 167 (1951).
38. A. M. Dessouki, E. A. Hegazy, N. B. El-Assy, and H. A. El-Boohy, *Radiat. Phys. Chem.*, **27,** 431 (1986).
39. Y. H. Bae, T. Okano, and S. W. Kim, *J. Controlled Release,* **9,** 271 (1989).
40. T. Okano, Y. H. Bae, H. Jacobs, and S. W. Kim, *J. Controlled Release,* **11,** 255 (1990).
41. K. Joseph, T. Okano, Y. H. Bae, and S. W. Kim, Eds., *Temperature Responsive Controlled Drug Delivery, Pulsed and Self-Regulated Drug Delivery,* CRC Press, Boca Raton, FL, 1990, p. 17.
42. J. P. Lawler and A. Chaelesby, *Radiat. Phys. Chem.*, **15,** 595 (1980).

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