Application of DMAEMA-Grafted Expanded PTFE Films to Positively Charged ultrafiltration Membranes and Their Electrostatic Sieve Separation Properties

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ABSTRACT: A study was done of the ultrafiltration properties of expanded polytetrafluoroethylene (ePTFE) films with two average pore sizes, 0.5 and 3.0 μm, grafted with 2-(dimethylamino)ethyl methacrylate (DMAEMA)—grafted 0.5-ePTFE and grafted 3.0-ePTFE—using dextran (Dxt) and quaternized dextran (qDxt) in water and in buffer solutions with a pH in the range of 4–10. The water permeability was found to be proportional to the operating pressure below 2.0 kgf/cm^2. Grafted 0.5-ePTFE films apparently had a higher rejection than did the grafted 3.0-ePTFE films, and the cutoff value for grafted 0.5-ePTFE films decreased with an increase in the grafted amount. The apparent rejection of Dxt and qDxt increased with a decrease in the pH value, and the apparent rejection of qDxt was higher than that of Dxt when the pH was in the range of 4–8 because of an electrostatically repulsive interaction between positively charged grafted PDMAEMA chains and qDxt molecules. For grafted 0.5-ePTFE films, 40KDxt was selectively separated from the 40KDxt/250KDxt mixture systems in water and from the 40KDxt/40KqDxt mixture systems at pH 6 using the difference in their apparent rejection; the separation factors in both systems increased with the grafted amount. These results indicate that grafted ePTFE films are applicable to positively charged ultrafiltration membranes. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1595–1604, 2001

Key words: polytetrafluoroethylene; photografting; 2-(dimethylamino)ethyl methacrylate; positively charged ultrafiltration membrane; selective separation

INTRODUCTION

The permeation properties of a polymeric substrate can be improved by grafting polymerization. Because a graft copolymer consists of a long sequence of one monomer, referred to as the backbone, with branches of a long sequence of another monomer, compatibilization of a pair of polymers with different characteristics can be achieved. We studied surface modification by photografting of hydrophilic monomers onto hydrophobic polymer substrates such as polyethylene (PE) and polytetrafluoroethylene (PTFE). Surface properties such as the wettability and adhesivity of PE plates can be drastically modified at a low grafted amount by photografting with hydrophilic monomers because the photografting proceeds in the vicinity of their surface regions. When the photografting of hydrophilic monomers is carried out throughout the bulk of PE films used in place of PE plates, the grafted PE films possess high water absorptivity

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together with reasonable mechanical strength in their water-swollen state[1,2] and can be applied to various functional membranes.[3–7]

PTFE films are superior to PE films in chemical resistance and stability. Therefore, grafting polymerization of various monomers onto PTFE films can be expected to widen their application to functional membranes. We have reported that ionic monomers such as methacrylic acid (MAA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) can be more effectively grafted onto flat, porous, and expanded PTFE (fPTFE, pPTFE, and ePTFE) films at short grafting times by the combined use of plasma treatment and photografting, as compared to results using the thermal grafting technique.[8] The permeability to glucose of MAA-grafted pPTFE and ePTFE (pPTFE-*g*-PMAA and ePTFE-*g*-PMAA) and DMAEMA-grafted pPTFE and ePTFE (pPTFE-*g*-PDMAEMA and ePTFE-*g*-PDMAEMA) changed in response to the pH values of the buffer solutions used. The on/off regulations of glucose permeation for pPTFE-*g*-PDMAEMA and ePTFE-*g*-PDMAEMA films could be repeated by changing the temperatures below and above the cloud point, 27°C, of PDMAEMA in a NaOH–$NaHCO_3$ buffer solution of pH 10.[9] The ePTFE-*g*-PDMAEMA films had the highest glucose permeability along with adequate mechanical strength in the water-swollen state of the four kinds of grafted PTFE films mentioned above. In addition, ePTFE-*g*-PDMAEMA films had relatively high permeability to dextran (Dxt) of different molecular weights, and it was possible to selectively separate 40KDxt ($M_r = 4 \times 10^4$) from the mixture solutions consisting of 40KDxt and 250KDxt ($M_r = 2.5 \times 10^5$). Therefore, we tried to separate macromolecular solutes using ePTFE-*g*-PDMAEMA films by ultrafiltration and to apply them to positively charged ultrafiltration membranes.[9]

Several methods exist for characterizing the size of macromolecular solutes in solution, including size-exclusion chromatography and ultrafiltration. Among them, ultrafiltration is a relatively inexpensive, versatile, and nondestructive technique for fractionating macromolecular solutes in solution. Therefore, the use of ultrafiltration membranes for the separation of dissolved macromolecular solutes of different sizes and characteristics has become of interest in recent years. Many studies on the mechanism of ultrafiltration and membrane properties of porous polymer films have been reported.[10–20] However, most of these studies were concerned with non-charged ultrafiltration membranes,[12–18] and few reported on charged ultrafiltration membranes.[19,20] Therefore, the separation of macromolecular solutes by the electrostatic sieve properties of charged ultrafiltration membranes did not seem to be clearly established. In positively or negatively charged ultrafiltration membranes, the fixed charges electrically interact with ionic macromolecular solutes. If the sign of the fixed charges in the membranes is the same as that of the ionic solute, the charged ultrafiltration membrane will markedly restrict the passage of the ionic macromolecular solutes.

In this study the dependence of the molecular cutoff properties of ePTFE-*g*-PDMAEMA films on the grafted amount and pH value by ultrafiltration was followed up by using Dxt of different molecular weights and quaternized Dxt (qDxt) of different degrees of quaternization. Selective separation was also discussed in the binary mixtures consisting of Dxt of different molecular weights or Dxt and qDxt.

Table I Properties of ePTFE Films

Substrate	Thickness (μm)	Pore Size (μm)	Vacancy (%)
0.5-ePTFE	75	0.5	78
3.0-ePTFE	83	3.0	83

EXPERIMENTAL

Materials

Two kinds of ePTFE films, both obtained from Toyo Roshi Co. Ltd., (Japan), were used as a polymeric substrate for the photografting of DMAEMA, as shown in Table I. DMAEMA monomer was purified by distillation under reduced pressure. Four kinds of Dxt, each with a different molecular weight—1.0×10^4 (10K), 40K, 250K, and 2.0×10^6 (2000K)—were used as the macromolecular solute in the ultrafiltration experiments.

Plasma Treatment and Photografting

The plasma treatment and photografting were carried out in the manner described in our previous articles.[8,9] Both sides of the ePTFE films were treated with oxygen plasmas for 120 s at an output of 200 W and a frequency of 15 kHz under a vacuum of 6.67 Pa (0.05 Torr) using a Shimadzu

LCVD 20–type plasma treatment apparatus. Then DMAEMA was photografted onto the plasma-treated ePTFE films for a prescribed time at 60°C by applying UV rays emitted from a 400-W high-pressure mercury lamp to an aqueous DMAEMA monomer solution of 1.0 mol/dm^3 adjusted to a pH of 8 with concentrated HCl.[21] The membrane properties of grafted ePTFE films, such as water absorptivity and mechanical strength in the water-swollen state, were also described in detail in our previous article.[8,9]

Preparation of Quaternized Dxt

Quaternized Dxt (qDxt) samples were prepared from 40KDxt with 3-chloro-2-hydroxypropyltrimethylammonium chloride.[22] In a 500-cm^3 round flask with equipped with a reflux condenser, 10 g of 40KDxt was dissolved in 30 cm^3 of water. To this solution, 8 g of NaOH and 66 cm^3 of 50 wt % 3-chloro-2-hydroxypropyltrimethylammonium chloride solution were added, and the mixture solution was stirred for 1–3 h at 50°C. The resulting reaction mixture was neutralized with concentrated HCl. Quaternized 40KDxt (40KqDxt) was isolated by precipitation into a large amount of ethanol, purified by reprecipitation from water into ethanol, and dried *in vacuo*. The degree of quaternization of 40KqDxt was determined from colloid titration measurements.[4,23,24] A 0.2-g portion of 40KqDxt was dissolved in twice-distilled water to make a total volume of 1 dm^3. Using an ART-3 type HIRAMA automatic recording titrator, the aqueous qDxt solutions were titrated with an aqueous potassium poly(vinyl alcohol) sulfate (KPVS) solution containing 0.00251 mol/dm^3 of sulfate groups adjusted to the pH values of the qDxt solutions. The endpoint of the titration was determined by measuring turbidity at 420 nm. The degree of quaternization was calculated using eq. (1):

$$\text{Degree of quaternization} = \frac{C_{\text{KPVS}} \cdot V_t}{C_{\text{KPVS}} \cdot V_t + \dfrac{C_{\text{qDxt}} \cdot V_{\text{qDxt}} - C_{\text{KPVS}} \cdot V_t \cdot 313.78}{162.14}} \times 100 \quad (1)$$

where C_{KPVS} is the concentration of sulfate groups of an aqueous KPVS solution (mol/dm^3), V_t is the volume of a titrated aqueous KPVS solution (dm^3), C_{qDxt} is the weight concentration of aqueous qDxt solution (g/dm^3), and V_{qDxt} is the volume of aqueous qDxt solution (0.050 dm^3). The quantities of 162.14 and 313.78 are the molecular weights of the repeat units, respectively, of Dxt and qDxt.

Ultrafiltration of Dxt and qDxt

PE-*g*-PDMAEMA films with different grafted amounts were allowed to swell in water or the buffer solutions of pH values 4–10 (I = 0.01 mol/dm^3) at 25°C before use.[9] Ultrafiltration experiments were carried out with a stirred cell-type ultrafilter (Amicon Co. Ltd., Type 8050 cell). The cell had placed in it 50 cm^3 of Dxt or qDxt dissolved in water or the buffer solutions at 0.010 g/cm^3, and this was stirred at 350 rpm under pressurization by argon gas from a cylinder (effective membrane area = 13.4 cm^2). After each aliquot taken from the permeates was diluted 10-fold with distilled water, the concentration of Dxt or qDxt was spectrophotometrically determined according to its color-developing reaction with sulfuric acid and phenol at 490 nm.[19,25,26] The apparent rejection was calculated using Eq. (2):

$$\text{Apparent rejection} = \frac{C_f - C_p}{C_f} \quad (2)$$

where C_f and C_p are, respectively, the solute concentrations in the feed and permeate.

Selective Separation by Ultrafiltration

Here ultrafiltration experiments were carried out using a mixture solution consisting of 40KDxt and 250KDxt in a weight ratio of 1:1 and with a total weight concentration of 0.010 g/cm^3 in order to assess the molecular cutoff properties of both grafted ePTFE films. The concentrations of 40KDxt and 250KDxt were determined by the combined use of the refractive index and reduced viscosity measurements.[9] The permeates taken at the state in which the permeation flux was kept constant were concentrated to about one-third of their original volume at 50–60°C. A Ubbelohde viscometer at 25°C was used to determine the total weight concentration of 40KDxt and 250KDxt from the reduced viscosity measurements. The separation factor in the binary 40KDxt/250KDxt mixture systems was calculated using eq. (3):

$$\text{Separation factor} = \frac{C^p_{40\text{K}}/C^p_{250\text{K}}}{C^f_{40\text{K}}/C^f_{250\text{K}}} \quad (3)$$

where the subscripts 40K and 250K are the abbreviations for the type of Dxt used.

In addition, the electrostatic sieve properties of grafted ePTFE films were estimated from the selective separation between 40KDxt and quaternized 40KDxt prepared from 40KDxt (40KqDxt). Here, the total weight concentration of Dxt and qDxt in the permeates was determined from the refractive index measurements. The weight concentration of qDxt was determined from the colloid titration with KPVS.[4,23,24] After an aliquot was diluted between 5- and 10-fold with distilled water, the solution was titrated with an aqueous KPVS solution. The separation factor for the 40KDxt and 40KqDxt mixture system was calculated using eqs. (4) and (5).

$$\text{Separation factor} = \frac{C^p_{\text{Dxt}}/C^p_{\text{qDxt}}}{(C_T - C^f_{\text{qDxt}})/C^f_{\text{qDxt}}} = \frac{C^p_{\text{Dxt}}/C^p_{\text{qDxt}}}{C^f_{\text{Dxt}}/C^f_{\text{qDxt}}} = \frac{C^p_{\text{Dxt}}/C^p_{\text{qDxt}}}{0.5/0.5} \quad (4)$$

$$C_T = C^f_{\text{Dxt}} + C^f_{\text{qDxt}} \quad (5)$$

RESULTS AND DISCUSSION

Determination of Operating Pressure

PDMAEMA-grafted ePTFE films with varied amounts grafted were prepared by changing the UV-irradiation times for the photografting onto ePTFE films with average pore sizes of 0.5 and 3.0 μm (grafted 0.5-ePTFE and 3.0-ePTFE films). The change in their membrane pore structure under the applied pressure was examined by looking at the dependence of the water permeability on the operating pressure. The water permeation flux was calculated from the linear relation between the amount of permeated water and the permeation time. Figure 1 shows the changes in the water permeation flux with the operating pressure for both grafted 0.5-ePTFE and 3.0-ePTFE films. The water permeation flux was proportional to the operating pressure up to 2.0 kgf/cm^2. However, the water permeation flux deviated from the straight lines at operating pressures higher than 2.0 kgf/cm^2. This indicates that both grafted 0.5-ePTFE and 3.0-ePTFE films undergo little structural change below an operating pressure of 2.0 kgf/cm^2. The deviation of water permeation flux above 2.0 kgf/cm^2 is probably a result of membrane compression influencing the membrane pore structure.[27,28] Therefore, the ultrafiltration experiments were carried out at an operating pressure of 2.0kgf/cm^2 in this study.

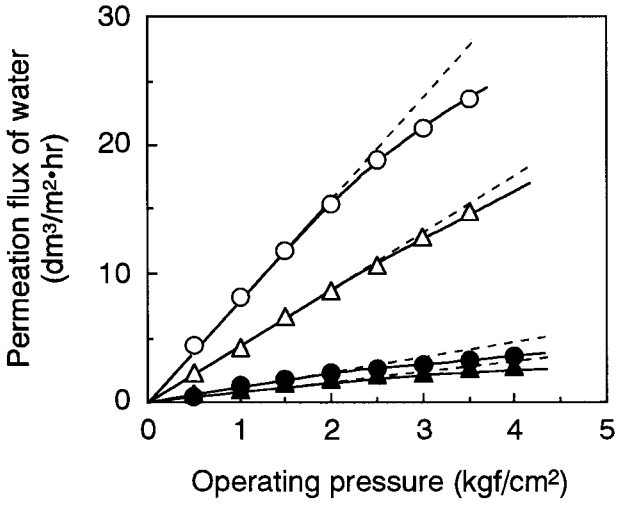

Figure 1 Changes in water permeation flux with operation pressure for grafted 0.5-ePTFE (closed) and grafted 3.0-ePTFE (open) films at 25°C. Grafted amount (mmol/g): (○) 3:25, (△) 5.73, (●) 4.41, and (▲) 5.01.

Ultrafiltration in Water

Rejection of Dxt

The ultrafiltration properties of grafted 0.5-ePTFE and 3.0-eETFE films were investigated in water using four kinds of Dxts, each with a different molecular weight. With the grafted amount, there were changes in the permeation flux and apparent rejection, as shown in Figure 2(a) and Figure 2(b) for grafted 0.5-ePTFE and 3.0-ePTFE films, respectively. For both grafted ePTFE films the permeation flux decreased and the apparent rejection increased with an increase in the grafted amount. It was reported in our previous article[8] from SEM observation that the pore size of grafted 3.0-ePTFE films becomes smaller with an increase in the grafted amount. This means photografting of DMAEMA occurs on the pore surfaces in the inside of the ePTFE films as well as in the region of their outer surfaces. In addition, the grafted layers that have formed on the pore surfaces of ePTFE films can swell in water. Therefore, the pores would diminish in size with an increase of the grafted amount in the

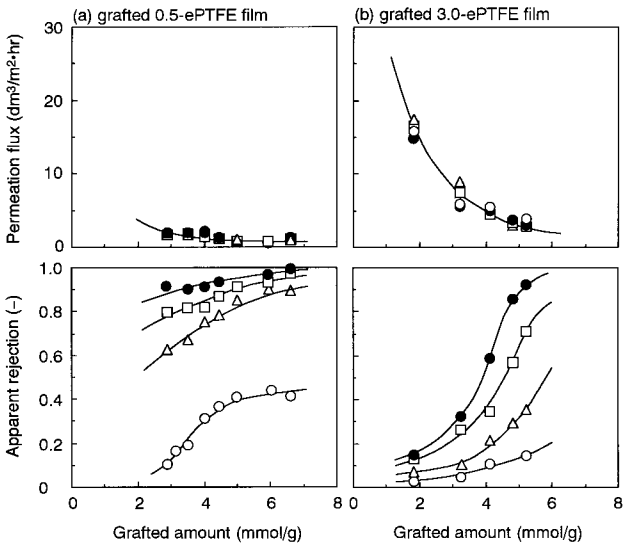

Figure 2 Changes in permeation flux and apparent rejection with the grafted amount for (a) grafted 0.5-ePTFE and (b) grafted 3.0-ePTFE films in water at 25°C. Molecular weight of dextran (mol/g): (○) 1×10^4 (10KDxt), (△) 4×10^4 (40KDxt), (□) 25×10^4 (250KDxt), and (●) 200×10^4 (2000KDxt).

water-swollen state. The apparent rejection of grafted 0.5-ePTFE films was higher than that of grafted 3.0-ePTFE films at the same grafted amount. This can be ascribed to a difference in the pore sizes of the original ePTFE films used here. Although the apparent rejection increased with an increase in the molecular weight of the Dxt used, the permeation flux was almost independent of the molecular weight of used Dxt. It is probably because the tough structure of the ePTFE film makes bearable the applied operating pressure and high hydrophilicity of the grafted layers. This feature peculiar to the grafted ePTFE films prepared in this study is favorable to an ultrafiltration membrane because for most ultrafiltration membranes, permeation flux usually decreases with an increase in the molecular weight of the macromolecular solute.[20,29]

The cutoff value was determined from the molecular weight cutoff curve of each grafted ePTFE film. Here the cutoff value is defined as the molecular weight of the macromolecular solute of 90% rejection according to the standardization committee of the European Society of Membrane Science and Technology (ESMST).[30,31] Figure 3 shows the changes in the cutoff value with the grafted amount for grafted 0.5-ePTFE and 3.0-ePTFE films. The apparent rejection of grafted 3.0-ePTFE films reached 90% at the grafted amount of 5.2 mmol/g (cutoff value = 1×10^6), and below this grafted amount, no cutoff value was obtained in the molecular-weight range of 1.0×10^4–2.0×10^6. On the other hand, a grafted 0.5-ePTFE film with a grafted amount of 2.3 mmol/g had a cutoff value of 8×10^5, and above this grafted amount the cutoff value decreased with an increase in the grafted amount. It was found from the above results that the cutoff value for 0.5-grafted ePTFE films can be controlled by the grafted amount in water.

Separation of Dxts of Different Molecular Weights

In many studies ultrafiltration experiments were carried out using two kinds of macromolecular solutes, each with a different chemical structure.[32–34] In our investigation for the macromolecular solute we chose two kinds of Dxts, both identical in chemical structure but of different molecular weights, and tried to separate them from each other by the difference in their apparent rejection. Selective separation properties of grafted 0.5-ePTFE films by ultrafiltration were followed up in the binary 40KDxt/250KDxt mixture systems. The concentration and composition of the two kinds of Dxts in the permeates were determined by the combined use of the refractive index and reduced viscosity measurements. The detailed procedures of refractive index and reduced viscosity measurements and their results were described in our previous article.[9] Since the

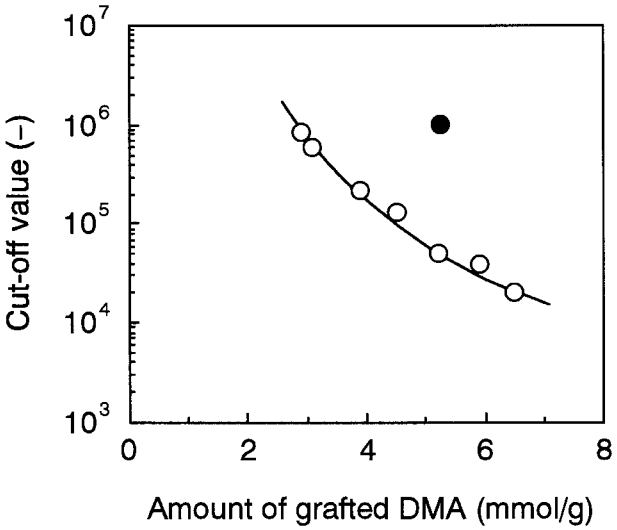

Figure 3 Change in the cutoff value to Dxt with the grafted amount for (○) grafted 0.5-ePFTE and (●) grafted 3.0-ePFTE films in water.

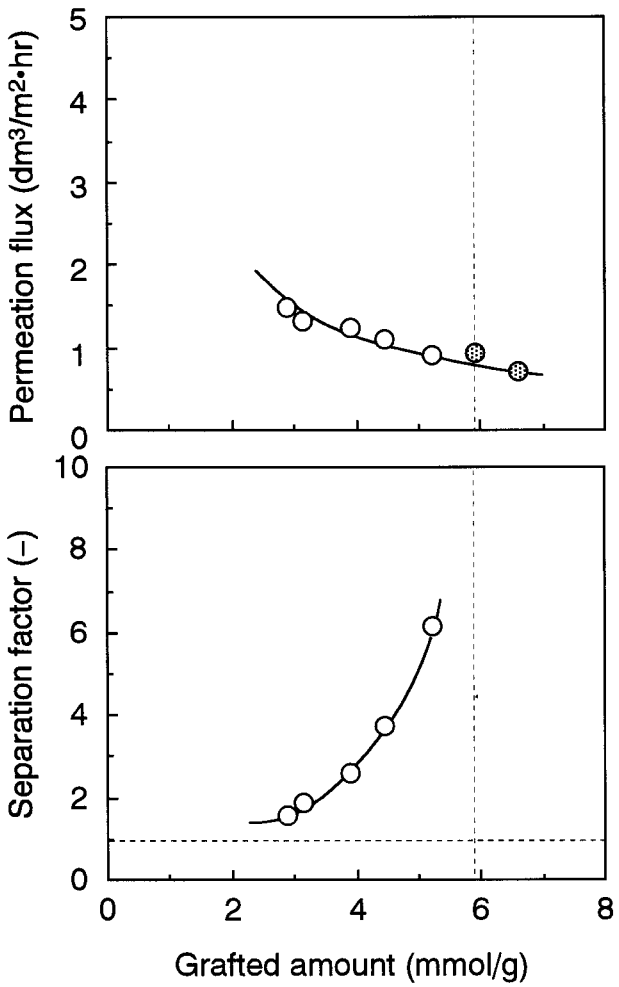

Figure 4 Change in permeation flux and apparent rejection with the grafted amount for grafted 0.5-ePFTE films in binary 40KDxt/250KDxt mixture systems in water.

refractive index of an aqueous Dxt solution increases with an increase in the total weight concentration of Dxt irrespective of the molecular weight and weight fraction of 250KDxt, the total weight concentration of the Dxt mixture solutions can be determined by the refractive index measurements. The reduced viscosity of the 40KDxt/250KDxt mixture solutions linearly increases with the weight fraction of 250KDxt. Therefore, the chemical composition of the 40KDxt/250KDxt mixture solutions can be determined by the reduced viscosity measurements. The separation factor was calculated from the concentration of 40KDxt and 250KDxt in the feed and the permeate using eq. (3).[9]

Figure 4 shows the changes in the permeation flux and the separation factor with the grafted amount in the 40KDxt/250KDxt mixture systems. The permeation flux decreased and the separation factor increased with an increase in the grafted amount. The concentration of 250KDxt in the permeates was too low to calculate the separation factor for grafted amounts in the range of higher than 5.9 mmol/g. It can be seen from Figure 3 that the cutoff value for grafted 0.5-ePTFE films reaches 4.0×10^4 at the grafted amount of 5.9 mmol/g. The increase in the grafted amount leads to an increase in the thickness of the grafted layers formed on the pore surfaces of the ePTFE films. Therefore, the permeation of 250KDxt through grafted 0.5-ePTFE films is more suppressed than that of 40KDxt, and this suppression leaves 250KDxt unable to permeate through grafted 0.5-ePTFE films above the grafted amount of 5.9 mmol/g. Consequently, the increase in the grafted amount gave rise to the increase in the selective permeation in the 40KDxt/250KDxt mixture systems for grafted 0.5-ePTFE films. On the other hand, the permeation flux slightly decreased over the grafted amount. The selective separation of 40KDxt from the 40KDxt/250KDxt mixture solution is considered to be mainly a result of the difference in their molecular sizes. Macromolecular solutes of identical chemical structure but different molecular weights were found to be selectively separated by ultrafiltration using grafted 0.5-ePTFE films in water. It should be also noted that, as can be seen from Figure 4, 40KDxt can be selectively separated from the 40K/250KDxt mixture solutions without a considerable decrease in the permeation flux by using grafted 0.5-ePTFE films with higher grafted amounts. This is a very favorable performance of applying grafted 0.5-ePTFE films to an ultrafiltration membrane.

Ultrafiltration in Buffer Solutions

Dependence of Apparent Rejection on pH Value

The dependence on the pH value of the rejection of grafted ePTFE films to Dxt was examined in buffer solutions with pH values ranging from 4 to 10. Figures 5(a) and 5(b) show the changes in the permeation flux and apparent rejection with the grafted amount in pH values in the range of 4 to 10 for grafted 0.5-ePTFE films using 40KDxt and for grafted 3.0-ePTFE films using 250KDxt, respectively. The permeation flux decreased and the apparent rejection increased with an increase in the grafted amount irrespective of the pH value of the buffer solution. In addition, as the pH value of

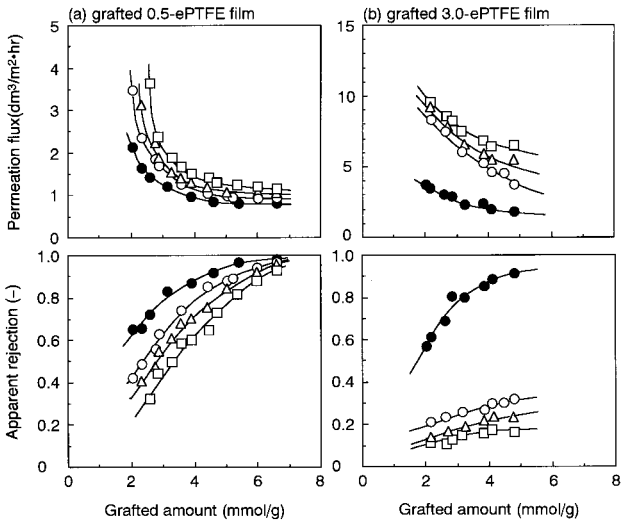

Figure 5 Changes in permeation flux and apparent rejection to 40KDxt with the grafted amount for (a) grafted 0.5-ePFTE and (b) grafted 3.0-ePFTE films in the buffer solutions of (●) pH 4, (○) pH 6, (△) pH 8, and (□) pH 10 at 25°C.

the buffer solution increased, the permeation flux became higher and the apparent rejection lower. We have reported that the viscosity measurement and colloid titration showed that the reduced viscosity and the degree of protonation increase with a decrease in the pH value because of increased electrostatic repulsion between grafted PDMAEMA chains.[1,4] Therefore, it may be considered that the pH dependence of the apparent rejection is the result of the diminution of pore sizes of the grafted ePTFE films caused by the extension of grafted PDMAEMA chains. In addition, the rejection of Dxts of different molecular weights was investigated using the grafted 0.5-ePTFE and 3.0-ePTFE films with the same grafted amount. Figure 6 shows the molecular cutoff curves for the grafted 0.5-ePTFE and grafted 3.0-ePTFE films with the grafted amount of 3.1 mmol/g in a buffer solution of pH 4 and in water. Although the apparent rejection of grafted 3.0-ePTFE film of 3.1 mmol/g did not proceed to 90% in the water medium, an cutoff value of 2.5×10^5 was obtained at pH 4. On the other hand, the cutoff value for a grafted 0.5-ePTFE film of 3.1 mmol/g decreased from 5.5×10^5 to 2.5×10^5 with the use of a pH 4 buffer solution as solvent instead of water. These results indicate that at pH 4 grafted 0.5-ePTFE films can more effectively block the passage of Dxt molecules than can grafted 3.0-ePTFE films because grafted PDMAEMA chains are expanded as a result of an increased protonation of dimethylamino groups.

Ultrafiltration of qDxt

A 40KqDxt sample with a 15% degree of quaternization of (15%40KqDxt) was prepared by the reaction of 40KqDxt with 3-chloro-2-hydroxypropyltrimethylammonium chloride. The properties of rejection of 40KDxt were investigated using grafted 0.5-ePTFE films, which had already demonstrated a higher rejection than grafted 3.0-ePTFE films, as shown in Figure 6. Figure 7 shows the change in the permeation flux and apparent rejection of 15%40KqDxt with the grafted amount. The rejection of 15%40KqDxt increased as the grafted amount increased and the pH value of the buffer solution decreased. It is clear from Figures 6 and 7 that the apparent rejection of 15%40KDxt is higher than that of 40KDxt for pH values the range of the 4–8. This would be caused by the electrostatically repulsive interaction between grafted PDMAEMA chains and qDxt molecules. The extension of grafted PDMAEMA chains leads to the diminution of pore sizes of the ePTFE films. These factors exercise a favorable influence on the increase in rejection of qDxt. To investigate the influence of quaternization of qDxt on the rejection, we followed up with an investigation of the rejection properties of grafted 0.5-ePTFE films of 2.92 and 3.57 mmol/g to 40KqDxts with different degrees of quaterniza-

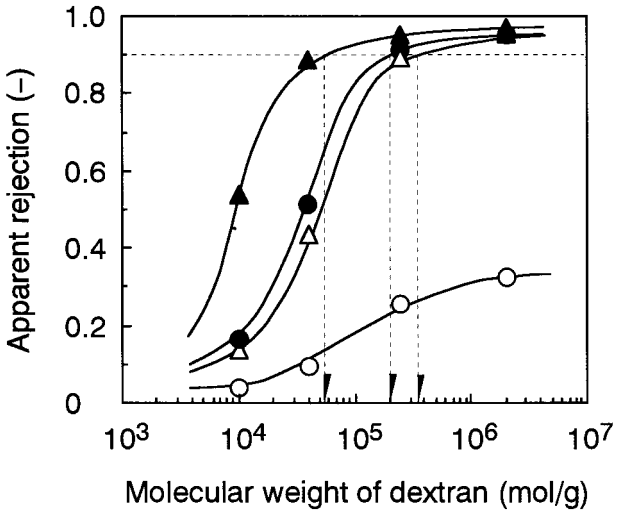

Figure 6 Determination of cutoff values to Dxt for grafted 0.5-ePFTE (shaded) and grafted 3.0-ePFTE (open) films of 3.1 mmol/g in water (○, ●) and buffer solution of pH 4(△, ▲) at 25°C.

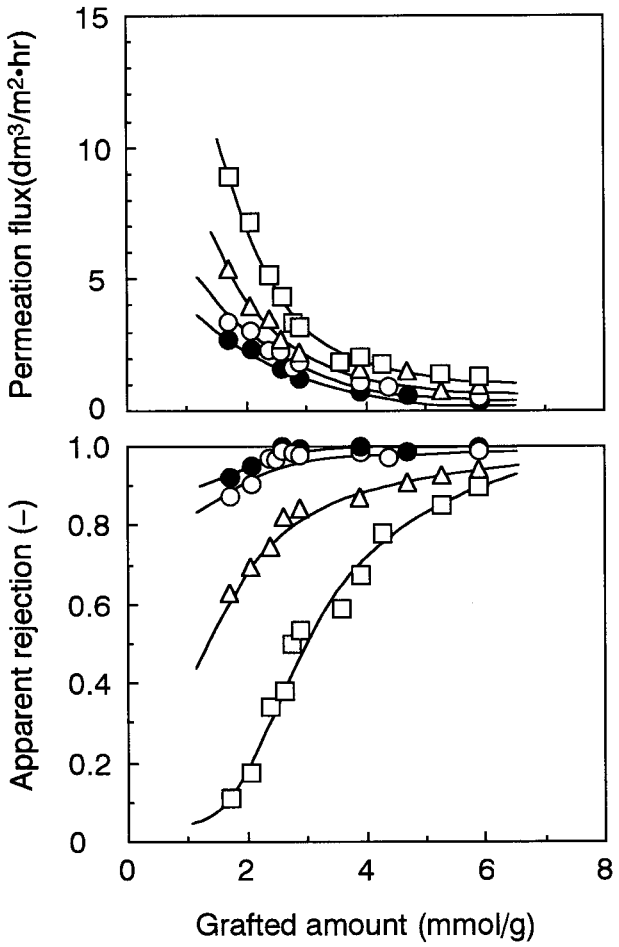

Figure 7 Changes in permeation flux and apparent rejection to 15% 40KqDxt with the grafted amount for grafted 0.5-ePFTE in buffer solutions of (●) pH 4, (○) pH 6, (△) pH 8, and (□) pH 10 at 25°C.

tion. Figure 8 shows that the apparent rejection sharply increases for degree of quaternization below about 7%, above which it gradually increases. This means that the introduction of strongly basic trimethylammonium groups to Dxt molecules leads to a considerable increase in rejection because of the electrostatically repulsive interaction between grafted PDMAEMA chains and qDxt molecules.

Selective Separation between Dxt and qDxt

A comparison of Figures 6 and 7 shows that the apparent rejection of qDxt was higher than that of Dxt for pH in the range of 4–8 for grafted 0.5-ePTFE films. We tried to selectively separate neutral and positively charged macromolecular solutes from each other using grafted 0.5-ePTFE

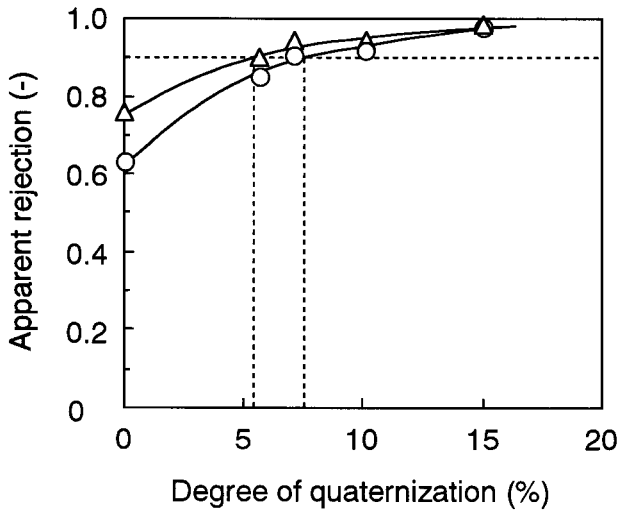

Figure 8 Changes in apparent rejection to 40KqDxt with degree of quarternization for grafted 0.5-ePFTE films of (○) 2.92 and (△) 3.57 mmol/g in a buffer solution of pH 6 at 25°C.

films. Using a typical example, changes with various pH values in the rejection of 40KDxt and 15%40KqDxt for a grafted 0.5-ePTFE film of 2.9 mmol/g are shown in Figure 9. The maximum difference in the rejection between 40KDxt and 15%40KqDxt was observed at pH 6. Therefore, it is possible to selectively separate 40KDxt from the 40KDxt/15%40KqDxt mixtures using the difference in the apparent rejection mentioned above. The concentrations of 40KDxt and 15%40KqDxt in

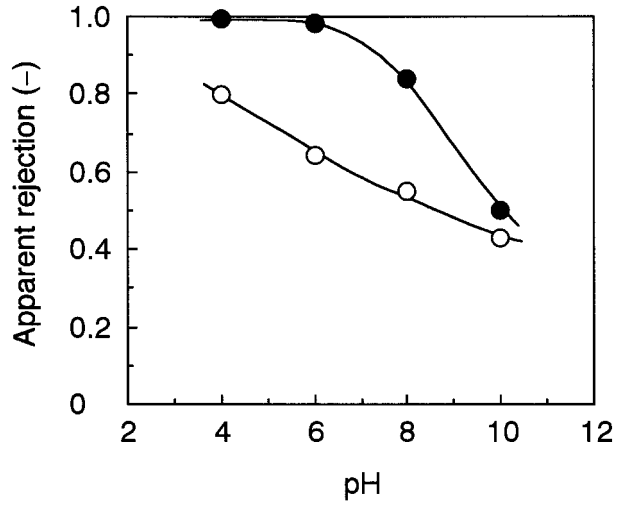

Figure 9 Differences in apparent rejections between (○) 40KDxt and (●) 15%40KqDxt for a grafted 0.5-ePFTE film of 2.87 mmol/g in buffer solutions of pH 4–pH 10 at 25°C.

the permeates were determined as follows: The total weight concentration of Dxt and qDxt and their chemical compositions were determined by the combined use of the refractive index measurement and colloid titration. Since the refractive indices of the 40KDxt/15%40KqDxt mixture solutions at the total concentration of 0.010 g/cm^3 were kept constant irrespective of the weight fraction of 15%40KDxt, the total weight concentration in the permeates was determined from the refractive index measurement. The mixture solutions with different weight fractions of 15%40KDxt were colloid-titrated with a 0.0025*M* KPVS solution at pH 6. The concentration of trimethylammonium groups was proportional to the weight fraction of 15%40KDxt in the mixture solutions. The experimental values calculated from the concentration of KPVS and its titrated volume were in fair agreement with the theoretical value obtained from the degree of quaternization of 15%40KqDxt and its weight concentration. These results indicate that the concentration of Dxt in the permeates and the separation factors can be calculated from eqs. (4) and (5).

Figure 10 shows the changes in the permeation flux and the separation factor with varied grafted amounts. The separation factor increased and the permeation flux decreased with an increase in the grafted amount. Very high separation properties were specifically observed above the grafted amount of 2.9 mmol/g. The increase in the grafted amount led to an increase in the rejection of both 40KDxt and 15%40KqDxt, as shown in Figures 6 and 7. However, because the passage of 15%40KqDxt molecules through grafted 0.5-ePTFE films is more suppressed than that of 40KDxt molecules, mainly through electrostatic repulsive interaction, the separation factor increases with the grafted amount. It was impossible to determine the concentration of 15%40KqDxt in the permeates by colloid titration above the grafted amount of 3.3 mmol/g. This means that above this grafted amount only 40KDxt permeates through grafted 0.5-ePTFE films, and the permeation of 15%40KqDxt is quite blocked.

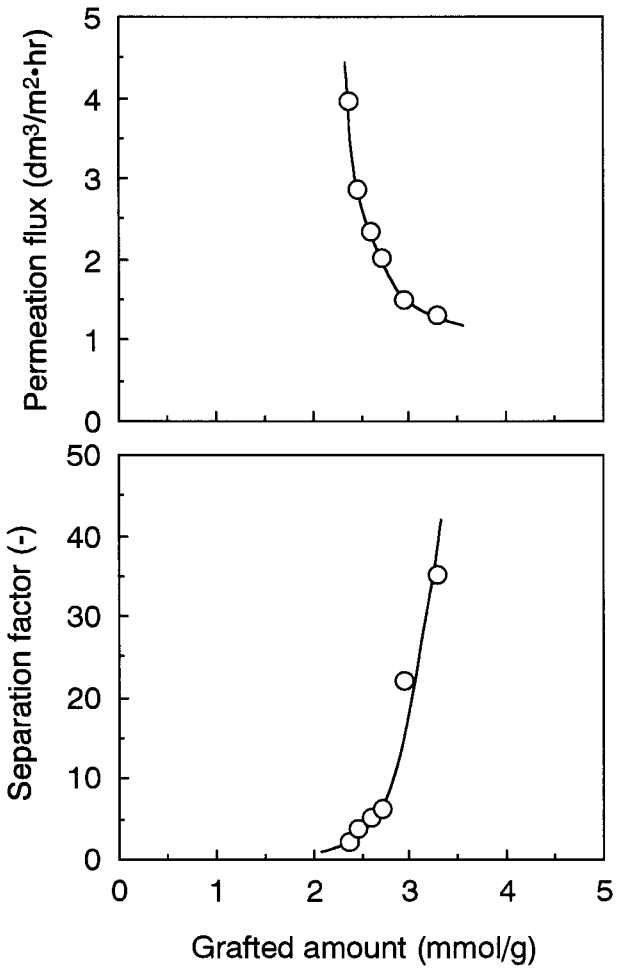

Figure 10 Change in permeation flux and apparent rejection with the grafted amount for grafted 0.5-ePFTE film in binary 40KDxt–15%40KqKDxt mixture systems in buffer solution of pH 6 at 25°C.

CONCLUSION

We pursued ultrafiltration properties of DMAEMA-grafted ePTFE films prepared by the combined use of plasma treatment and photografting using Dxt and qDxt. From the experimental results above, we can conclude the following:

- Water permeability is proportional to operating pressure below 2.0 kgf/cm^2. This confirms that both grafted 0.5-ePTFE and 3.0-ePTFE films undergo little structural change for operating pressures below 2.0 kgf/cm^2. Consequently, ultrafiltration experiments were carried out at an operating pressure of 2.0 kgf/cm^2.
- The apparent rejection to Dxt in water increases with an increase in the molecular weight of Dxt for both grafted ePTFE films, and the cutoff value decreases with an increase in the grafted amount for grafted 0.5-ePTFE films. A 40KDxt solute is selectively separated from the binary 40KDxt/250KDxt mixture system by using the difference in their apparent rejection, and the separation

factor increases with an increase in the grafted amount.

- The apparent rejection of qDxt is higher than that of Dxt for grafted 0.5-ePTFE films, and the apparent rejection of qDxt increases with the degree of quaternization. 40KDxt can be selectively separated from 40KDxt/40KqDxt mixture solutions at pH 6, where the difference in their apparent rejections is the maximum, and the separation factor increases with an increase in the grafted amount.

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