Surface-Modified Polysulfone Hollow Fibers

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Synopsis

Controlled reactions on the inner side, outer side, and both sides of the surfaces of polysulfone ultrafiltration hollow fibers with propane sultone and Friedel-Crafts catalysts were developed. EPMA measurements and MTR spectra for the chemically modified fibers suggested existence of $-CH_2CH_2CH_2SO_3^-$ segments on the modified surfaces. The modified fibers were found to have smaller molecular weight cut-off than nonmodified fibers, and the fibers modified on the internal surfaces gave better rejection of polyethylene glycol 6000 than those modified on the external surfaces, although the fibers that reacted with solution of the propane sultone and $SnCl_4$ at 70°C and 80°C showed negative rejection of the polyethylene gylcol. Absorption of polyethylene glycol on the modified fibers is estimated to be less than the nonmodified fibers from the flux ratios of aqueous polyethylene glycol solution to pure water. This effect is attributed to the heparinlike active group of modified segments.

INTRODUCTION

Surface reactions of active reagents to membrane are useful modifications to introduce various functional groups such as SO_3H and COOH or active sites of enzymes. Surface-modified membranes may be obtained by a simple method, namely, being dipped into active reagents. Since only the surface is modified, they maintain their original characteristics of mechanical strength and thermal stability.[1,2] Sulfonation is one of the most common surface reaction reagents and the degree of sulfonation can be controlled by the reaction time.[2] Crassous et al.[3] recently reported a new chemical surface modification of styrene-isoprene-styrene block copolymer and succeeded in introducing $-SO_3H$, $-COOH$, and $-CONH_2$ on the membrane surfaces. This membrane was chemically modified by reaction with gaseous chlorosulfonyl-isocyanate and showed enhanced blood compatibility due to heparinlike structure. Fixing of heparin on the membrane surfaces by ionic coupling or covalent bonding was also investigated by several researchers.[4-7] Immobilized enzyme membrane prepared from covalently bonded enzyme on one face of the membrane[8-11] is another example of surface modification. In this case, economical use of expensive enzymes and improvement in the stability of an enzyme[10] are expected. Graft polymerization[12-16] provides another method of surface modification and can give several functional groups. It is, however, difficult to characterize exact structure of graft segments and to remove homopolymer from the surface. The latter case is especially difficult for hollow fiber.

The disadvantage of surface reaction to the membrane may be limiting examples of the reaction except as shown above. Loading the new functional groups on conventional membranes, a new concept of reaction, improves the fine values of the conventional membranes. A new functional group $-CH_2CH_2CH_2SO_3^-$ is introduced on the surface of polysulfone ultrafiltration membranes in this study. A hydrophilic sulfonate unit can be located to the polymer main chain having a joint segment of $(-CH_2-)_n$ in this reaction, while sulfonation directly introduces sulfonate unit on the main chain. Molecular design of the modified segment is that the long side chain will contribute to enhanced mobility of SO_3H moiety and to decrease pore sizes of ultrafiltration membranes. This could result in modified membranes having lower molecular weight cut-off than nonmodified membranes. There are also two possibilities that original thermal stability of the nonmodified membranes may remain in the membranes after the surface reaction, and that the functional groups introduced by the reaction are regarded as new modifications of heparin-active groups (e.g., $-OSO_3^-$, $-NHSO_3^-$, $-COO^-$).

This article describes the controlled reaction on one side or both sides of the surfaces of polysulfone ultrafiltration membranes with propane sultone and Friedel-Crafts catalysts. Characterization of the membranes performed from scanning electron microscopy (SEM), electrophoretic microanalysis (EPMA), Fourier transform infrared (FTIR), and ultrafiltration experiments are shown and discussed.

EXPERIMENTAL

Membranes

Membranes used for chemical modification were commercially available polysulfone hollow fibers (ultrafiltration membrane), SI-1 (Asahi Chemical Co., Ltd.). The fibers have internal and external skin layers and two layers of fingerlike macrovoids in their cross-section. The inside and outside diameter of the fibers are approximately 0.75 mm and 1.3 mm. Typical preparation and spinning of polysulfone hollow fibers were reported in the literature.[17-19] Water flux and rejection (R) of polyethylene glycol 20,000 for the fibers were observed to be 0.0317 cm^3/cm^2 s MPa (corresponds to 8.05 m^3/m^2 day at 3 kg/cm^2) and R = 0.126 at concentration of feed solution = 0.5 wt%. We found that there were no flux and rejection changes within experimental error for the fibers after immersion in methanol or hot water at 80°C for 12 h.

Chemical Modifications

The polysulfone hollow fiber was dipped in the solution of propane sultone and Friedel-Crafts catalyst ($SnCl_4$ or $AlCl_3$), at several conditions of temperature (35–100°C) and reaction time (10 s–60 min) as shown in Tables IA–IC. The reactive solution was injected into the hollow fiber with a 2.5 mL disposable syringe with a 21 G × 1 needle (Terumo Co.) as illustrated in Figure 1 when the internal surface of the fiber was intended to be modified. The hollow fiber, of which the bottom end was sealed, was inserted in a glass tube of 0.8 mm diameter and 30 cm in length filled with the reactive solution when the external surface of the fiber was modified. The above two procedures

TABLE IA
Surface-Modified Conditions and Characteristics of
Polysulfone Hollow Fibers: Catalyst = SnCl$_4$

Membrane[a]	Reaction temp. (°C)	Reaction time (min)	Modified side[b]	Catalyst mole ratio	Rejection	Permeate flux (10^{-2} cm s^{-1} MPa^{-1})
HP-SB-1	50	5.0	B	0.22	0.788	0.0814
HP-SB-2	50	10.0	B	0.22	0.524	0.168
HP-SB-3	50	30.0	B	0.22	0.413	0.111
HP-SB-4	50	0.5	B	0.37	0.205	0.326
HP-SB-5	50	1.0	B	0.37	0.545	0.448
HP-SB-6	50	5.0	B	0.37	0.221	0.188
HP-SB-7	50	10.0	B	0.37	0.419	0.186
HP-SB-8	70	5.0	B	0.37	−0.162	0.0629
HP-SB-9	70	10.0	B	0.37	−1.063	0.0098
HP-SB-10	80	5.0	B	0.37	−0.237	0.0366
HP-SB-11	80	10.0	B	0.37	−0.541	0.0165
HP-SB-12	100	5.0	B	0.37	0.344	0.0165
HP-SB-13	50	1.0	B	0.50	0.395	0.313
HP-SB-14	50	5.0	B	0.50	0.260	0.280
HP-SB-15	50	10.0	B	0.50	0.291	0.328
HP-SB-16	80	10.0	B	0.78	0.690	0.281

[a] HP stands for propane sultone and Friedel-Crafts catalyst reaction, and SB stands for the conditions that catalyst is SnCl$_4$ and that both internal and external surfaces of the fibers are modified.

[b] B stands for the condition that the both surfaces of the fibers are modified.

TABLE IB
Surface-Modified Conditions and Characteristics of
Polysulfone Hollow Fibers: Catalyst = SnCl$_4$

Membrane[a]	Reaction temp. (°C)	Reaction time (min)	Modified side[b]	Catalyst mole ratio	Rejection	Permeate flux (10^{-2} cm s^{-1} MPa^{-1})
HP-SI-1	50	1.0	I	0.37	0.307	0.488
HP-SI-2	50	5.0	I	0.37	0.401	0.413
HP-SI-3	50	10.0	I	0.37	0.463	0.283
HP-SI-4	50	15.0	I	0.37	0.485	0.415
HP-SI-5	50	1.0	I	0.50	0.019	0.472
HP-SI-6	50	5.0	I	0.50	0.003	0.602
HP-SI-7	50	10.0	I	0.50	0.120	0.429
HP-SO-1	50	1.0	O	0.37	0.125	0.421
HP-SO-2	50	5.0	O	0.37	0.456	0.194
HP-SO-3	50	10.0	O	0.37	0.258	0.318
HP-SO-4	50	1.0	O	0.50	0.056	0.312
HP-SO-5	50	5.0	O	0.50	(−0.009)	0.688
HP-SO-6	50	10.0	O	0.50	0.005	0.559

[a] HP stands for propane sultone and Friedel-Crafts catalyst reaction. SI stands for the conditions that catalyst is SnCl$_4$ and that internal surface of the fibers is modified. SO stands for the conditions that catalyst is SnCl$_4$ and that external surface of the fibers is modified.

[b] I stands for the condition that the internal surface of the fibers is modified. O stands for the condition that the external surface of the fibers is modified.

TABLE IC
Surface-Modified Conditions and Characteristics of
Polysulfone Hollow Fibers: Catalyst = $AlCl_3$

Membrane[a]	Reaction temp. (°C)	Reaction time (min)	Modified side[b]	Catalyst mole ratio	Rejection	Permeate flux[c] (10^{-2} cm s^{-1} MPa^{-1})
HP-AB-1	70	1.0	B	0.025		n.p.
HP-AB-2	70	5.0	B	0.025		n.p.
HP-AB-3	70	10.0	B	0.025		n.p.
HP-AB-4	70	30.0	B	0.025		n.p.
HP-AB-5	70	60.0	B	0.025		n.p.
HP-AI-1	35	0.17	I	0.010	(−0.018)	0.850
HP-AI-2	35	1.0	I	0.010	0.0	0.445
HP-AI-3	50	0.17	I	0.010	(−0.017)	0.751
HP-AI-4	50	1.0	I	0.010	(−0.010)	0.657
HP-AI-5	70	0.17	I	0.010	(−0.017)	0.736
HP-AI-6	70	1.0	I	0.010	(−0.012)	0.732
HP-AI-7	70	1.0	I	0.025	0.336	0.186
HP-AI-8	70	5.0	I	0.025	0.001	0.606
HP-AI-9	70	10.0	I	0.025	0.051	0.456
HP-AO-1	70	1.0	O	0.025	0.190	0.153
HP-AO-2	70	5.0	O	0.025	0.228	0.0303
HP-AO-3	70	10.0	O	0.025		n.p.
HP-AO-4	70	30.0	O	0.025	0.441	0.0264
HP-AO-5	70	60.0	O	0.025		n.p.

[a] HP stands for propane sultone and Friedel-Crafts catalyst reaction. AB stands for the conditions that catalyst is $AlCl_3$ and that both internal and external surfaces of the fibers are modified. AI stands for the conditions that catalyst is $AlCl_3$ and that internal surface of the fibers is modified. AO stands for the conditions that catalyst is $AlCl_3$ and that external surface of the fibers is modified.

[b] B stands for the condition that the both surfaces of the fibers are modified. I stands for the condition that the internal surface of the fibers is modified. O stands for the condition that the external surface of the fibers is modified.

[c] n.p. stands for the condition that the no permeate flux was observed.

were performed at the same time for the fiber modified on both surfaces. After the reaction, the modified fibers were washed in water for 1 h, methanol for 1 h, and finally in water for 4 h, and stored in water until transport measurements took place. Deionized water by Milli-Q system (Millipore Corp.) was used throughout the experiments.

Characterization

ATR (MTR) spectrum of the polysulfone hollow fibers was measured from FTIR model 1800 (Perkin-Elmer Corp.). SEM and EPMA measurements were performed with JEOL 255-II and EDX (Kevex Co.).

Transport Measurements

A schematic of the ultrafiltration apparatus is given in Figure 2. Teflon tubing for the connection of each of the parts and stainless steel components (SUS 316) for the construction of other parts were used in the apparatus. The apparatus can, therefore, withstand maximum pressure of 2.94 MPa. The
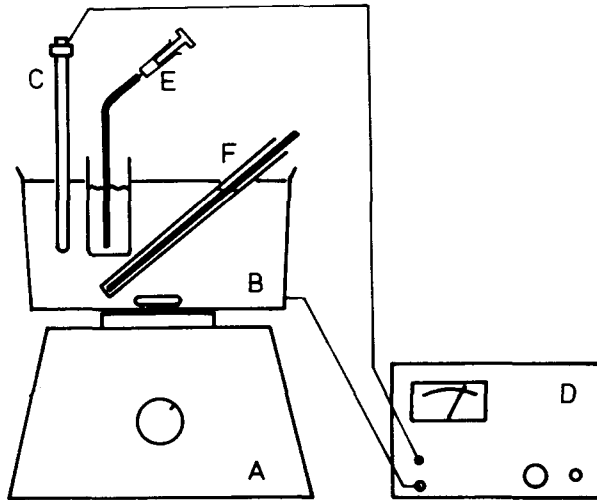
Fig. 1. Apparatus for chemical modification of the hollow fiber. A: magnetic stirrer, B: oil bath, C: magnetic adjustment thermostat, D: transistor relay, E: internal surface modification, F: external surface modification.

single hollow fiber (15 cm length) was jointed to a switching valve (G) with 1/16 FD ferrule (Gasukuro Kogyo Inc.). The rate of feed solution from a double-plunger pump of B (PUD-6, Gasukuro Kogyo Inc.) was kept at 6 cc/min in this study. Micro needle valve of I (MCV-1, Scientific Glass Engineering PTY, Ltd.) was used to adjust the transpressure drop at the fiber, Δp. Δp was fixed to be 0.294 MPa (3 kg/cm^2) throughout the experiments. Pressure shown in D_1 and D_2 was observed to correspond with each other within 0.01 MPa. Membrane area to calculate the flux was taken as equal to
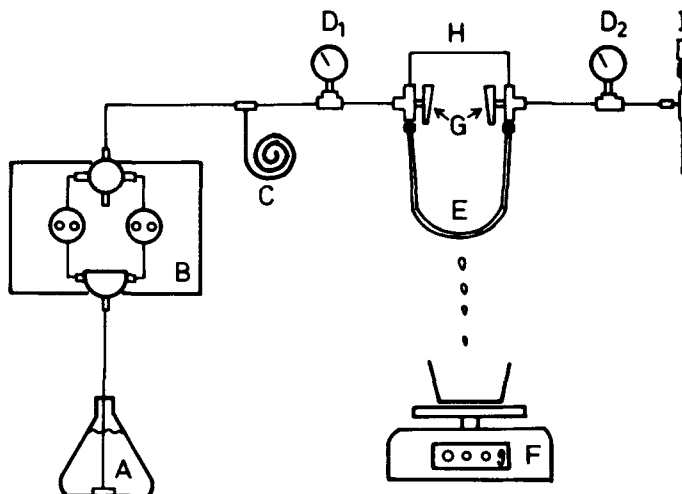
Fig. 2. Schematic representation of the ultrafiltration apparatus. A: feed solution, B: double-plunger pump, C: bourdon-tube dampener, D_1, D_2: pressure gauges, E: hollow fiber, F: electronic balance, G: switching valves, H: bypath, I: micro needle valve.

the internal active surface of the fibers. The rejection was calculated from the difference in the concentration of solute in the feed solution, C_f, and the concentration of solute in the permeate, C_p, by using eq. (1):
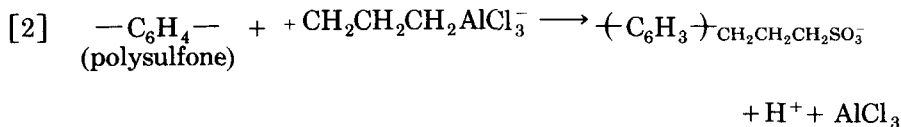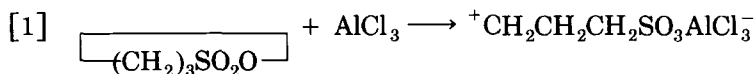
$$R = 1 - C_p/C_f \qquad (1)$$

The concentration of polyethyleneglycol (PEG) 1000 (MW 950 ~ 1050), 2000 (MW 1800 ~ 2200), 3000 (MW 3000 ~ 3700), 6000 (MW 7800 ~ 9000) and 20,000 (MW approx. 15,000), and β-cyclodextrine (Nakarai Chemicals, Ltd.) was measured by RM102 differential refractometry (Union Giken Co., Ltd.). Viscosities of aqueous PEG 6000 solution were measured using an Ubbelohde viscometer at $20 \pm 0.02°C$. The concentration of vitamin B_{12} and NaCl (Nakarai Chemicals Ltd.) was measured by ultraviolet (UV) spectrophotometer model UVIDEC-100-V (Japan Spectroscopic Co., Ltd.) at $\lambda = 361$ nm and a conductometer of model CM-20S (TOA Electronics Ltd.). The ultrafiltration measurements were performed at $20 \pm 0.5°C$. The standard deviations for flux and rejection measurements were found to be about 3 and 5%.
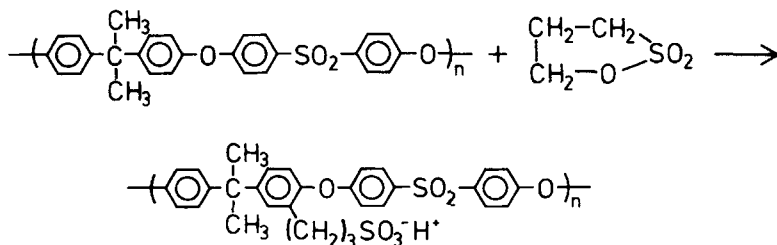
RESULTS AND DISCUSSION

Characterization

Polysulfone hollow fibers were chemically modified on the surface according to the conditions shown in Tables IA–IC. The anticipated product by Friedel–Crafts reaction is shown in Scheme 1. The mechanism of the reaction is postulated from that of alkylation of benzene using Friedel–Crafts catalyst:[20]

[1] $\underline{}_{(CH_2)_3SO_2O}$ + $AlCl_3$ $\longrightarrow$ $^{+}CH_2CH_2CH_2SO_3AlCl_3^{-}$

[2] $-C_6H_4-$ + $^{+}CH_2CH_2CH_2AlCl_3^{-}$ $\longrightarrow$ $+C_6H_3+_{CH_2CH_2CH_2SO_3^{-}}$
(polysulfone)

$$+ H^{+} + AlCl_3$$

The modified fibers prepared in this study were dyed deeply only on the side of the modified surface by 3.5 wt% brilliant blue in 10 wt% aqueous acetic acid solution while nonmodified fibers are slightly dyed. This evidence suggests
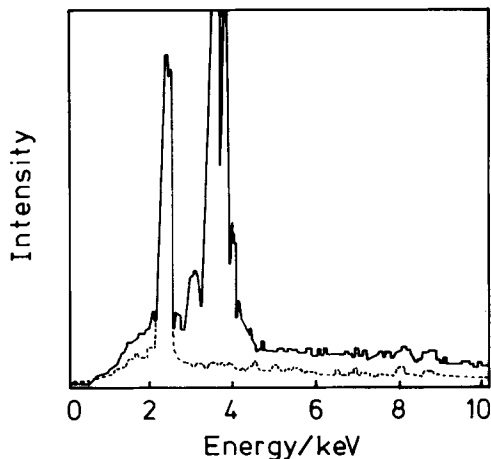

Scheme 1.

existence of an anion-charged group that originates from modified segments since brilliant blue has a quaternary ammonium in its structure.

EPMA spectra of modified (HP-SB-15) and nonmodified hollow fibers were investigated and as shown in Figure 3. HP-SB-15 is the fiber modified under the conditions where both surfaces were reacted for 10 minutes and $SnCl_4$/propane sultone (mole ratio) = 0.50. Both modified and nonmodified hollow fibers were immersed in 0.5 mol/L $AgNO_3$ aqueous solution for 12 h before EMPA measurements. Sulfur peak at about 2.3 keV, Ag peak at about 3.0 keV, and Sn peaks at about 3.4 keV and 3.7 keV were observed in the spectrum of the HP-SB-15, while only sulfur peak was found for the spectrum of the nonmodified hollow fiber. Sulfur peak in the spectrum of the nonmodified fiber is attributed to a sulfone group originated by a polysulfone backbone. Ag and Sn peaks found in the spectrum of HP-SB-15 also suggest existence of the anion-charged group in the modified fibers. Sn peak can be explained by the existence of a residual catalyst combined to sulfonate ion in HP-SB-15.

The MTR spectra of nonmodified (a), HP-SB-15 (b), and the difference spectrum between (a) and (b) are shown in Figure 4. The difference spectrum (c) was obtained under the condition that skeletal in plane vibration of aromatic rings (1580 cm^{-1} and 1490 cm^{-1}) showed minimum intensity in the difference spectrum that indicated the nearly equal contribution of the intensity of HP-SB-15 and the nonmodified fiber at the above wave numbers. The difference spectrum showed absorptions at 2850 cm^{-1} and 2930 cm^{-1} corresponding to $-CH_2-$ group and 1040 cm^{-1} and 1250 cm^{-1} due to $-SO_3^-$ group. The above results suggest that the surface reaction occurs according to Scheme 1 under the present conditions.

SEMs of cross-section of HP-SB-7 (a and b) and HP-AB-1 (c) are shown in Figure 5. Those of (b) and (c) show external skin layer regions of fibers. The modified fiber prepared from $SnCl_4$ catalyst (HB-SB-7) shows essentially no difference to the nonmodified one in ×50,000 SEM observations, while it is observed that the modified fiber prepared from $AlCl_3$ catalyst even at a
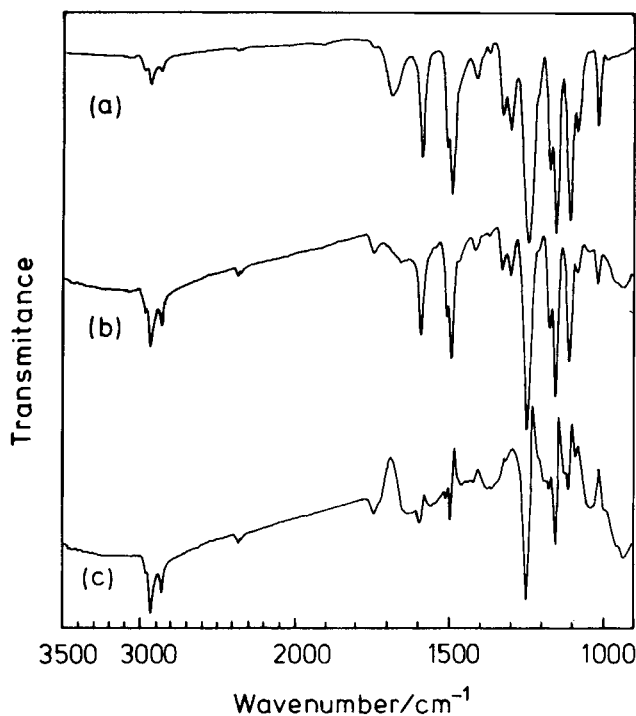
Fig. 4. MTR (ATR) spectra of the (a) nonmodified fiber, (b) modified fiber (HP-SB-15), and (c) difference spectrum.

reaction time of 1 minute shows slight degradation due to the melting of skin layers. Friedel–Crafts catalysts can essentially attack polysulfone in the long term and $AlCl_3$ is known to be a stronger catalyst than $SnCl_4$. $AlCl_3$, therefore, contributed to the melting of the skin layer even in as short a time as 1 minute. It is also observed that skin layers of the modified fibers prepared under the conditions of $SnCl_4$/propane sultone (mole ratio) = 0.50 and reaction time > 90 min showed SEMs similar to (c). We believe that $SnCl_4$ is a more desirable catalyst than $AlCl_3$ in the present reaction and that the modified fibers prepared on the conditions of reaction < 60 min and $SnCl_4$ catalyst have no degradation of skin layers from SEM observations.

Transport Experiments

Figure 6 shows dependence of rejection of vitamin B_{12} at C_f = 200 ppm on time for HP-SB-16. Rejection of the vitamin B_{12} at C_f = 200 ppm decreased as the time < 30 minutes and was observed to be almost constant at time > 30 minutes. Volume of filtrate by HP-SB-16 for 1 minute is 1.3 times higher than the fiber volume. It is remarkable that the steady state is reached after the volume of filtrate is about 40 times that of the fiber volume. This is because the diffusion of solutes is much less than that of water and it takes more time for the solutes to be absorbed on the surface and wall of the pores on the fiber. Concentration polarization and cake formation in ultrafiltration[21-27] are generally used to explain flux drop and decline of the observed rejection. Rejec-

tions and fluxes measured at time > 40 minutes are listed in Tables IA–IC. These can be regarded as steady-state values.

Figure 7 shows a relationship between flux and rejection of PEG 6000 in chemically modified and nonmodified hollow fibers at $C_f = 0.5$ wt%. These data and surface reaction conditions are shown in Tables IA–IC. The typical relationship that the fibers with high rejection give low flux are observed in the figure. The fibers prepared from $SnCl_4$ catalyst, however, show better
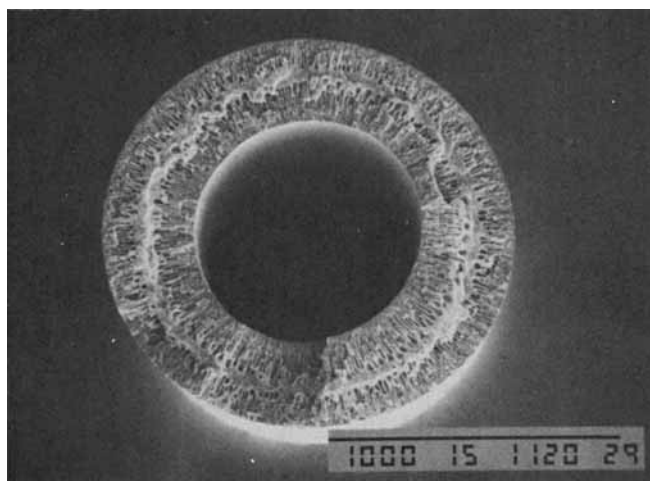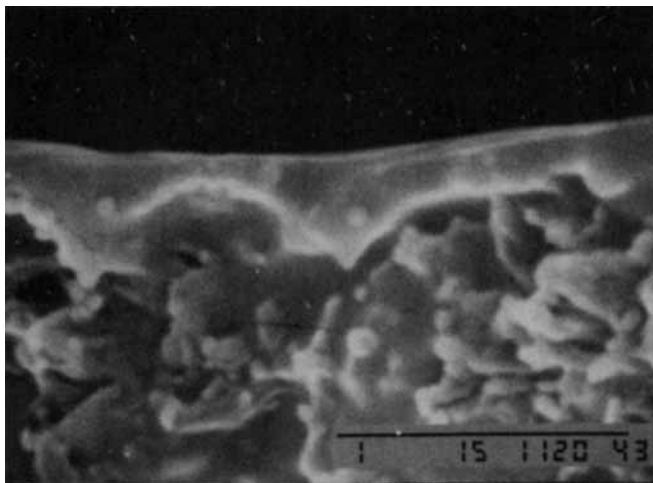

(a)
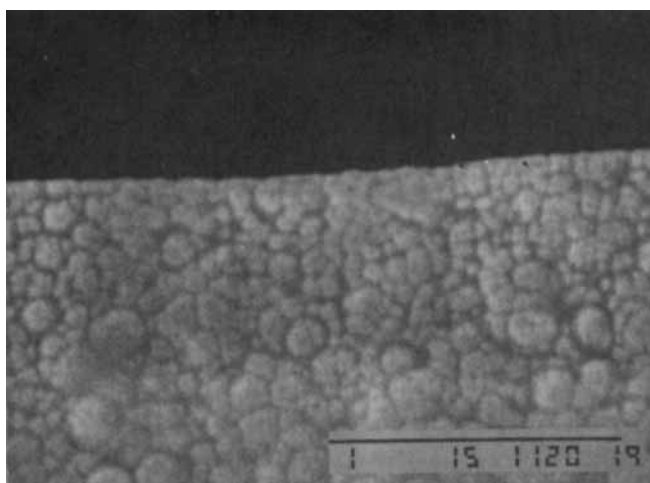
(b)

Fig. 5.   Scanning electron micrographs of cross-section of chemically modified hollow fibers. (a) Fiber modified with $SnCl_4$ catalyst, HP-SB-7 (50 × magnification), (b) fiber modified with $SnCl_4$ catalyst, HP-SB-7, external skin layer region (50,000 × magnification), (c) fiber modified with $AlCl_3$ catalyst, HP-AB-1, external skin layer region (50,000 × magnification).

(c)

Fig. 5. *(Continued from the previous page.)*

results than those from $AlCl_3$. The skin layer of the fibers prepared from $AlCl_3$ catalyst was observed to melt in SEM observation [see Fig. 5(c)]. $SnCl_4$ is, therefore, regarded as a preferable catalyst in the present reaction. Plots of HP-SB-5, HP-SB-16, HP-SI-1, HP-SI-2, and HP-SI-4 are observed to give higher rejection and higher flux than other fibers. Those fibers have chemically modified charged segments on the internal surface. The fiber modified on the external surface, however, gives less rejection than the above five fibers. This is because the original fibers have slightly larger pore sizes on the external surface than those on the internal surface, and the other reason is that the segments on internal surface of the fiber are pressed against the wall
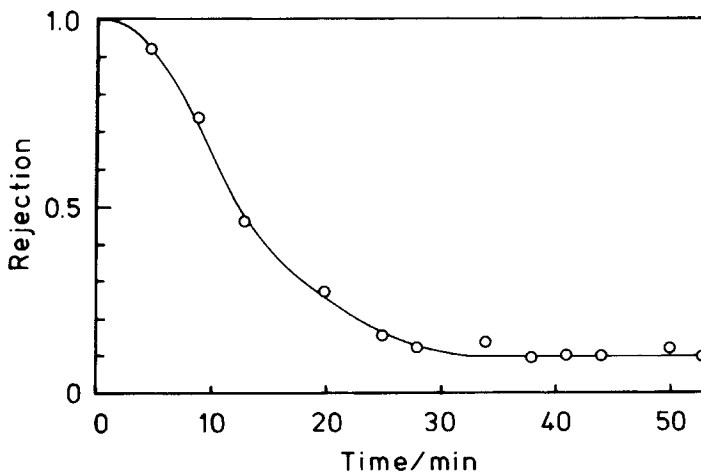

Fig. 6.   Dependence of rejection of vitamin B_{12} on time for HP-SB-16 at $C_f = 200$ ppm and 20°C.
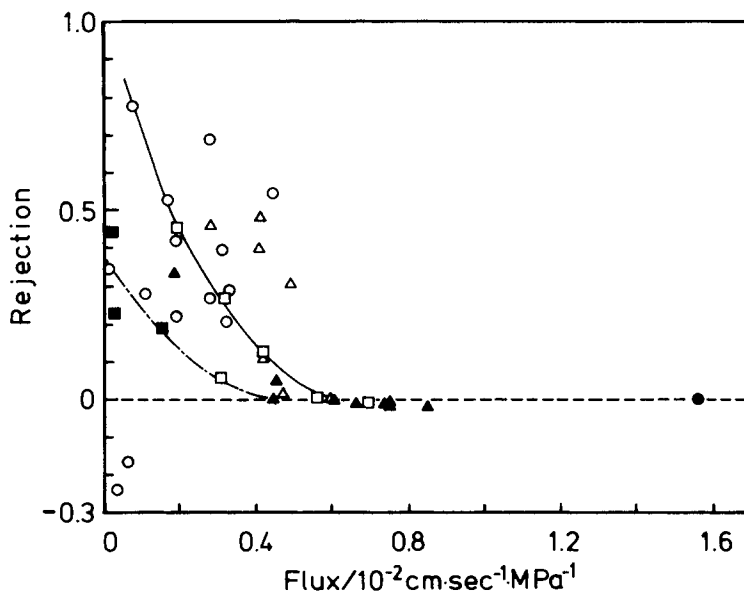
Fig. 7. Relationship between flux and rejection of PEG 6000 in chemically modified and nonmodified hollow fibers at $C_f = 0.5$ wt% and 20°C. ○: both the external and internal surfaces are modified with $SnCl_4$; △: the internal surface is modified with $SnCl_4$; □: the external surface is modified with $SnCl_4$; ▲: the internal surface is modified with $AlCl_3$; ■: the external surface is modified with $AlCl_3$; ●: the nonmodified fiber.

by pressure, while the segments on external surface are not perturbed by the pressure. These effects contribute to the smaller pore sizes on the internal surface and result in the higher rejection in the modified fibers.

The modified fibers prepared at 70°C and 80°C (HP-SB-8, -9, -10, and -11) showed different rejection behavior from other fibers (see Table IA). Rejection of these fibers gives negative values from -0.162 to -1.063. Since all fibers prepared at 70°C and 80°C show negative values and HP-SB-9 gives high negative value (-1.063), the results cannot be considered to be experimental error. The color of reaction bath changes from light brown to dark brown when temperature of the reaction bath is elevated from 50°C to 70°C. The reaction bath becomes sticky in the temperature range of about 70°C to 80°C. Above 90°C, it becomes the bath having lower viscosity again, viscosity being similar to the solution at 50°C except in color. The chemical reaction on the surface of the fiber at 70°C and 80°C may bring about specific morphology of the charged segments on the surface, and the polyethylene glycol may prefer to absorb on the surface. We cannot explain the exact mechanism for the negative rejection found in HP-SB-8 ~ 11 at this moment because the same reaction of Scheme 1 is expected to occur on the surface at both 50°C and 70–80°C.

Three typical modified fibers which give rejection of PEG 6000 = 0.8, 0.5, and 0.2 at $C_f = 0.5$ wt% are chosen (HP-SB-1, HP-SI-4, and HP-SB-6). Dependence of rejection of polyethylene glycol on its molecular weight at $C_f = 0.5$ wt% for three modified and nonmodified fibers is shown in Figure 8. Any three modified fibers give more than 0.8 of the rejection for PEG 20,000
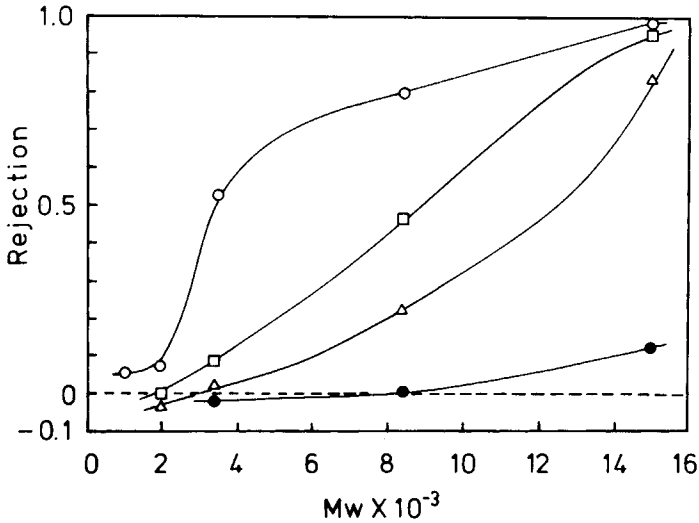
Fig. 8. Dependence of rejection of polyethylene glycol on the molecular weights at 20°C and $C_f = 0.5$ wt% for three modified fibers (○: HP-SB-1, □: HP-SI-4, △: HP-SB-6) and the nonmodified fiber (●).

feed solution, while the rejection for the nonmodified fiber is found to be about 0.1. The three modified fibers are found to have smaller molecular cut-off than nonmodified fibers. In Table II, rejection of linear solutes of polyethylene glycol is observed to be less than that of nonlinear solutes such as vitamin B_{12} ($C_f = 0.02$ wt%) and β-cyclodextrin ($C_f = 0.5$ wt%) in HP-SB-1, while molecular weights of PEG 1000 (MW 1000), vitamin B_{12} (MW 1357), and β-cyclodextrin (MW 1135) are almost the same. This results from the deformation and stretching of the polyethylene glycol,[28-30] and it is, therefore, able to pass more easily through the pore in the fibers than vitamin B_{12} or β-cyclodextrin. Although HP-SI-4 and HP-SB-6 cannot reject NaCl at $C_f = 50$ ppm, HP-SB-1, having the highest molecular cut-off among the three modified fibers, is observed to reject not only vitamin B_{12} and β-cyclodextrin, but also to reject NaCl for 5.2% at $C_f = 50$ ppm. Since the fiber did not reject NaCl at $C_f = 200$ ppm, Donnan exclusion of ions[31-33] will be responsible for the observation of the rejection for HP-SB-1. The charge density of HP-SB-1 is considered to be higher than that of HP-SI-4 and HP-SB-6.

The dependence of flux and rejection on feed concentration of PEG 6000 for HP-SI-4 is shown in Figures 9 and 10. It is observed that flux decreases

TABLE II
Rejection of Some Solutes on Chemically Modified Membranes

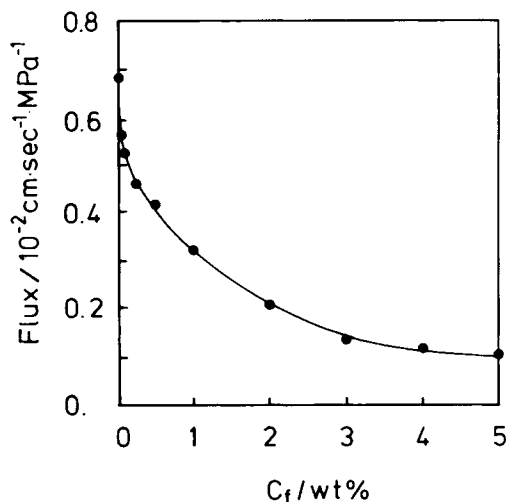|	Rejection				
Membrane	PEG 6000 (MW 8400)	PEG 1000 (MW 1000)	Vitamin B_{12} (MW 1357)	β-Cyclodextrin (MW 1135)	NaCl (MW 58.5)
HP-SB-1	0.788	0.067	0.130	0.194	0.052
HP-SI-4	0.485	(−0.006)	0.033	0.042	(−0.020)
HP-SB-6	0.211	(−0.025)	(−0.006)	(−0.033)	(−0.030)

Fig. 9.   Dependence of flux on feed concentration of PEG 6000 for HP-SI-4 at 20°C.

dramatically with the increase of the concentration. Flux was known to be in inverse proportion to the viscosity of feed solution (η) according to Darcy's law.[34] The inverse of the relative viscosity (η_0/η) of PEG 6000 and the ratios of flux of aqueous PEG solution at various concentration (J) to pure water flux (J_0) are summarized in Table III, where η_0 is the viscosity of pure water. The inverse of the relative viscosity is found to decrease with the increase of the concentration and it is, therefore, found that the tendency of flux decline at higher feed concentration is explained by increased viscosity of the feed solution to some extent. The flux decline, however, appears more steeply than the decrease of the viscosity ratio, η_0/η. This effect is explained by gel layer model[21-23] or osmotic pressure model[24,25] due to cake formation[27] and concentration polarization.[25] In Figure 10, rejection of PEG 6000 increases with

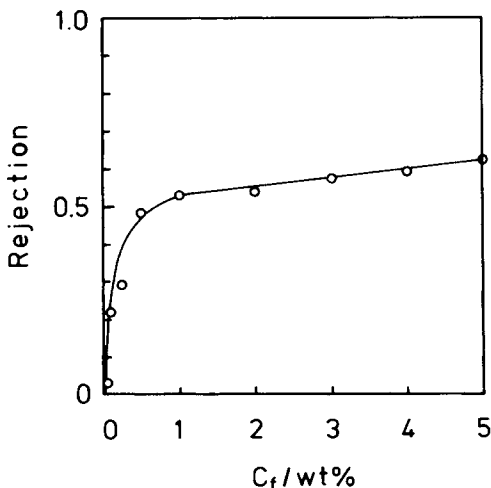Fig. 10.   Dependence of rejection of PEG 6000 on the feed concentration for HP-SI-4 at 20°C.

C (wt%)	η (cp)	η_0/η	J/J_0
0.0	1.002	1.00	1.00
0.10	1.021	0.981	0.77
0.25	1.057	0.948	0.67
0.50	1.113	0.903	0.61
1.00	1.240	0.808	0.47
2.00	1.515	0.661	0.30
3.00	1.831	0.547	0.20
4.00	2.188	0.458	0.17
5.00	2.627	0.381	0.16

the increase of the concentration dramatically at $C_f < 1$ wt% and the rejection is observed to be almost constant in the concentration range from 1 to 5 wt%. The relationship between the rejection and feed concentration in Figure 10 suggests that absorption of polyethylene glycol on pore walls in skin layers is almost accomplished at 1 wt% feed concentration and the cake on the surface of the fiber reduces effective pore radius and contributes to the higher rejection of PEG 6000 at $C_f > 1$ wt%. The reduced pore radius also causes the flux decline due to Hagen-Poiseuille's law.

$$J = n\pi r^4 \Delta p/8\eta d \qquad (2)$$

where r is the pore radius, n is the number of pores per unit area, d is the pore length. Equation (2) shows that flux decreases with the decrease of the pore radius by the factor of the fourth power of the pore radius.

Equation (2) is also applied for the estimation of relative absorption layer thickness of polyethylene glycol. It should be noted that the hollow fibers used in this study have two skin layers and fingerlike macrovoids in its morphology. The resistance of the fingerlike macrovoids for the water flux is, however, ignored for simplicity. The flux ratio of aqueous polyethylene glycol solution to pure water is given as eq. (3) under the conditions that n and d are assumed to be unchanged but the pore radius decreases when the polyethylene glycol is absorbed on the pore wall.

$$r_s^4/r_0^4 = J\eta/J_0\eta_0 \qquad (3)$$

where r_0 is the pore radius at nonabsorption of the polyethylene glycol, r_s is effective pore radius where polyethylene glycol is absorbed on the pore wall. $J\eta/J_0\eta_0$ therefore, gives a measure of the absorbed layer thickness on the pore. The flux times viscosity ratio, $J\eta/J_0\eta_0$, at $C_f = 0$ to $C_f = 0.5$ wt% is calculated to be 0.546 for nonmodified fiber and 0.673 for HP-SI-4. It should be considered that r_s^4/r_0^4 decreases dramatically for the modified fiber having smaller pore size than the nonmodified fiber, when the same thickness of absorbed layer occurred in the nonmodified and the modified fibers. It is satisfactory to consider that the modified fiber is absorbed to a lesser degree by the polyethylene glycol than the nonmodified fibers, since r_s^4/r_0^4 calculated for the modified fiber is greater than that for the nonmodified fiber. This is considered to be due to the heparinlike active group of modified segments ($-CH_2CH_2CH_2SO_3^-$).

The membrane performance was tested for the modified hollow fiber. After HP-SI-4 was kept standing in hot water at 80°C for 4 h, rejection of PEG 6000 and flux were found to be 0.545 and 0.00483 cm/s MPa at $C_f = 0.5$ wt%, while the rejection and flux before immersing in the hot water were observed to be 0.485 and 0.00415 cm/s MPa. Flux and rejection for HP-SI-4 were found to be unchanged or slightly improved after treatment of the fiber in the hot water. The results suggest that the surface-modified fibers keep their thermal stability that originates from the polysulfone backbone.

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