

Surface Modified Polysulfone Hollow Fibers.

III. Fibers Having a Hydroxide Group

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Synopsis

Polysulfone ultrafiltration hollow fibers were chemically modified on the surfaces with propylene oxide and Friedel-Crafts catalysts. A peak at 1.6 ppm was observed in H^1 -NMR spectrum of the modified fibers at 45°C, while the peak was not observed at 27°C measurements. The peak was attributed to a hydroxide group from the peak shift at high temperature. Micro ATR spectra of the modified fibers also suggested existence of $CH(CH_3)CH_2OH$ segments on those surfaces. The modified fibers showed 10–80% rejection of polyethylene glycol 6000 at feed concentration of 0.5 wt %, depending on the conditions of surface reaction, and were found to have smaller molecular cut-off than nonmodified fibers. The fibers were also compared with modified fibers with propane sultone reported previously [A. Higuchi et al., *J. Appl. Polym. Sci.*, **36**, 1753 (1988)], which had negatively charged segments of $CH_2CH_2CH_2SO_3^-$. Absorption of bovine serum albumin on the modified fibers was estimated to be less than the nonmodified fibers from permeation measurements. It is suggested that fibers having hydrophilic surfaces show better results of anti-absorption of solutes than the nonmodified fibers.

INTRODUCTION

Surface reactions of active reagents to membrane are useful modifications to introduce various functional groups such as SO_3H , $COOH$, or active sites of enzymes.^{1–3} Surface modification of hydrophobic membranes that introduce hydrophilic segments on their surfaces can present advantages of both hydrophilic and hydrophobic membranes. Thermal stability and mechanical strength are maintained in the membranes from the hydrophobic nature of polymer backbones,^{2,4} while transport characteristics such as less absorption of solutes and lower molecular cut-off are generally governed by the hydrophilic skin layers in the membranes.

In our previous study,^{2,5} we introduced a negatively charged group, $-CH_2CH_2CH_2SO_3^-$, on the surfaces of polysulfone hollow fibers from the reaction of polysulfone, propane sultone, and Friedel–Crafts catalysts. We found that the novel modified fibers with propane sultone showed excellent results for antiabsorption of solutes compared to the nonmodified and conventionally sulfonated fibers.^{2,5}

This article describes surface reaction of polysulfone hollow fibers with propylene oxide and Friedel–Crafts catalyst by a one-step reaction that gives hydrophilic surface without the use of charged segments (“hydroxide type”).

EXPERIMENTAL

Membranes

The membranes used for chemical modification in this study were commercially available polysulfone hollow fibers (ultrafiltration membrane), SI-1 (Asahi Chemical Co., Ltd.), the same grade of fibers used in previous studies.^{2,5} The inside and outside diameters of the fibers were approximately 0.75 mm and 1.3 mm. Water flux and rejection (R) of polyethylene glycol (PEG) 20,000 for the fibers were observed to be $14.5 \text{ m}^3/\text{m}^2 \text{ day}$ at $3 \text{ kg}/\text{cm}^2$ and $R = 0.126$ at feed concentration (C_f) of 0.5 wt % in this study.

Chemical Modifications

The polysulfone hollow fiber was dipped in the solution of propylene oxide, hexane, and Friedel-Crafts catalyst (AlCl_3) at 5°C for several reaction times (30 sec–10 min), as shown in Table I. Apparatus for the chemical modification of the fibers was described in the previous study;² the same procedures for the chemical modification were employed in this study.

Transport Measurements

Ultrafiltration apparatus and procedures were described in the previous paper.² The trans-pressure drop at the fiber, Δp , was fixed at $3 \text{ kg}/\text{cm}^2$, and speed of feed solution at the inlet of the fiber was fixed at $6 \text{ cc}/\text{min}$ throughout the experiments. The ultrafiltration measurements were performed at $20 \pm 0.5^\circ\text{C}$. The standard deviations for flux (J) and rejection measurements were found to be 3 and 5%.²

RESULTS AND DISCUSSION

Characterization

The skin layer of the modified fiber (HP-4) was carefully separated from the fiber with a sharp knife and was dissolved in CDCl_3 for measurement of

TABLE I
Surface-Modified Conditions and Characteristics of Polysulfone Hollow Fibers

Membrane	Reaction temp ($^\circ\text{C}$)	Reaction time (min)	Modified side ^a	Components of reaction solution			R^b (%)	J^b (m/day)
				AlCl_3 (g)	PO (g)	Hexane (g)		
SI-1	—	—	—	—	—	—	0.0	3.96
HP-1	5.0	10.0	I	1.6	0.58	26.6	9.8	2.07
HP-2	5.0	5.0	I	1.6	3.0	26.6	23.8	1.12
HP-3	5.0	1.0	B	3.9	17.0	22.4	46.7	1.37
HP-4	5.0	0.5	B	3.9	17.0	11.2	83.3	0.26

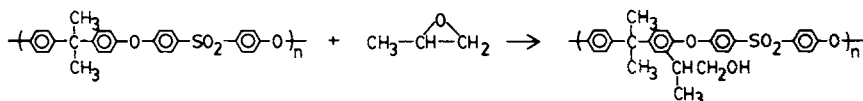
^a B stands for the condition that both surfaces of the fibers are modified. I stands for the condition that the internal surface of the fibers is modified.

^b Feed solution = 5000 ppm, PEG 6000.

$^1\text{H-NMR}$ (400 MHz, JNM GX-400, JEOL Ltd.). $^1\text{H-NMR}$ spectra of the skin layer region are shown in Figure 1. A main peak at 1.7 ppm is attributed to the methyl group of bisphenol A. A peak at 1.6 ppm was observed in the spectrum at 45°C, while it is not observed at 27°C measurement. The peak is, therefore, attributed to a hydroxide group from the peak shift at high temperature.

Micro ATR (FT-IR model 1600, Perkin-Elmer Co.) spectra of modified fiber (*a*, HP-4), nonmodified fiber (*b*) and a difference spectrum between (*a*) and (*b*) are shown in Figure 2. The difference spectrum 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. The difference spectrum shows absorptions at 3400 cm^{-1} , corresponding to a hydroxide group and 2850 and 2930 cm^{-1} , corresponding to CH_2 and CH_3 groups.

An estimated product of the reaction between polysulfone, propylene oxide, and AlCl_3 is postulated from similar Friedel-Crafts reaction between benzene, toluene, and propylene oxide reported by Inoue et al.,⁶ and is shown in Scheme 1:



Scheme 1

$^1\text{H-NMR}$ and micro ATR spectra suggest that the surface reaction probably occurs according to the scheme under the present conditions.

Transport Experiments

Typical conditions of chemical modification of the fibers and transport characterization of the fibers are summarized in Table I. The rejection of PEG 6000 is found to increase (i.e., 10–80%) with the increase of propylene oxide and AlCl_3 in the reaction solution, while the nonmodified fiber (SI-1) cannot reject

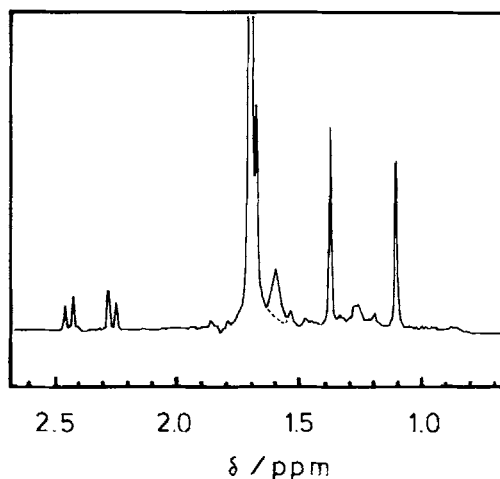


Fig. 1. $^1\text{H-NMR}$ spectra of modified polysulfone (solid line = spectrum at 45°C; dashed line = spectrum at 27°C).

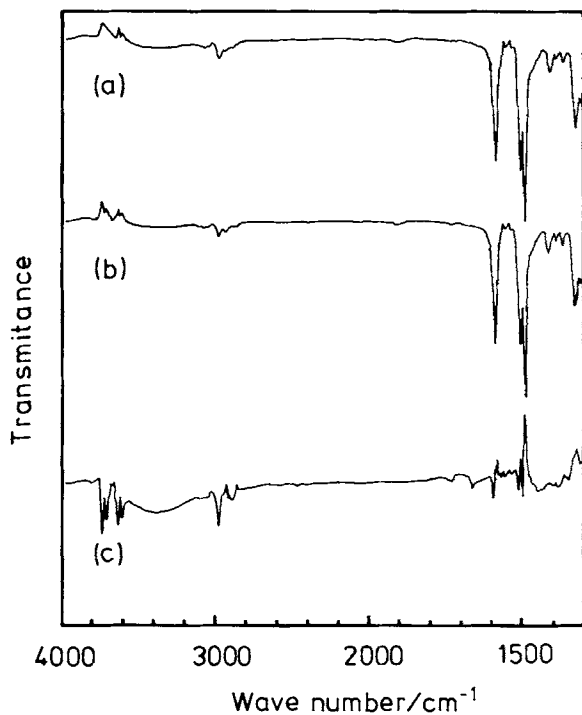


Fig. 2. Micro ATR spectra of the (a) modified fiber (HP-4), (b) nonmodified fiber, and (c) difference spectrum.

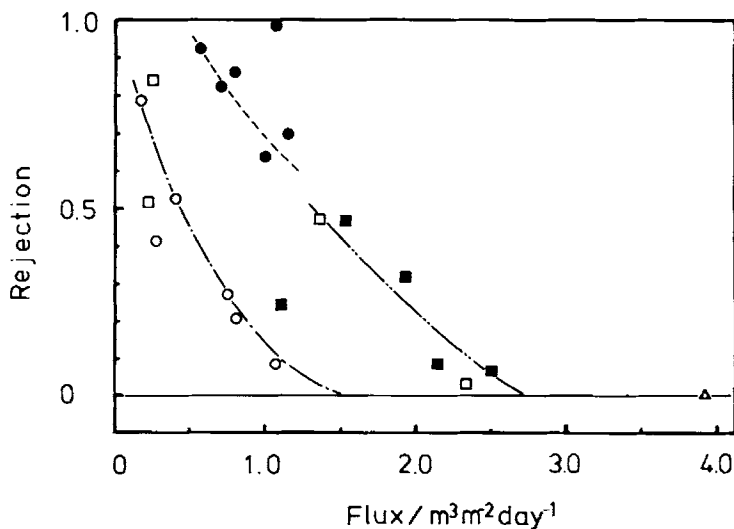
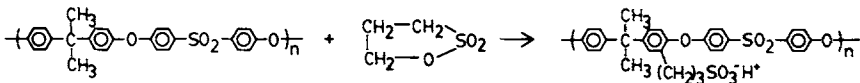


Fig. 3. Relationship between flux and rejection of PEG 6000 in chemically modified and non-modified hollow fibers at $C_f = 0.5$ wt % and 20°C: (■) internal surface is modified with propylene oxide; (□) both surfaces are modified with propylene oxide; (●) both surfaces are modified with propane sultone and immersed in 0.5 M HCl solution; (○) both surfaces are modified with propane sultone; (△) nonmodified fiber.

PEG 6000 in the present conditions. It is found that the molecular cutoff of the modified fibers can be controlled by the composition of the reaction solution.

Figure 3 shows a relationship between flux and rejection of PEG 6000 in chemically modified and nonmodified fibers at $C_f = 0.5$ wt %. Data of the modified fibers with propane sultone reported previously⁵ were also plotted in the same figure. The modified fibers with propylene oxide give higher rejection of PEG than the fibers modified with propane sultone (open circles in the figure) at the same flux, and show similar tendency of the fibers modified with propane sultone and immersed in HCl solution (closed circles in the figure) at $R \leq 50\%$. This indicates the fibers modified with propylene oxide show the tendency of high flux and rejection at $R \leq 50\%$, while the modified fibers with propylene oxide are reduced to give the same tendency of the modified fibers with propane sultone at $R > 50\%$. This is probably due to the fact that the length of modified segments of $\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ (Scheme 1) is shorter than that of $\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ (Scheme 2), and this effect may be contributing to the difficulty for the modified fiber with propylene oxide to give higher rejection than 50%:



Scheme 2

Figure 4 shows dependence of rejection of PEG on its molecular weight at $C_f = 0.5$ wt % for modified fiber with propylene oxide (HP-4), nonmodified fiber and modified fibers with propane sultone (HP-SB-1, HP-SI-4 and HP-SB-6) reported previously.² Any four modified fibers give more than 80% of the rejection for PEG 20,000 (approx. MW = 15,000) feed solution, while the rejection for the nonmodified fiber is found to be about 10%. HP-4 is found to

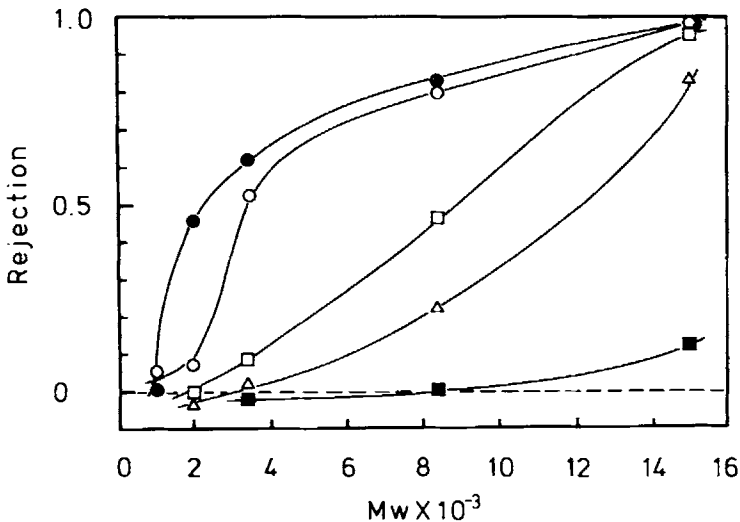


Fig. 4. Dependence of rejection of polyethylene glycol on the molecular weights at 20°C and $C_f = 0.5$ wt % for four modified fibers [(●) HP-4; (○) HP-SB-1; (□) HP-SI-4; (△) HP-SB-6] and SI-1 (■).

give similar rejection of PEG to HP-SB-1, while flux of HP-4 is 26% higher than HP-SB-1. The four modified fibers are found to have smaller molecular cut-off than nonmodified fibers.

Antiabsorption of Protein

$J\eta/J_0\eta_0$ is known to give a measure of the absorbed layer thickness of solutes on the pore wall, since $J\eta/J_0\eta_0$ is expressed as eq. (1) from the Hagen-Poiseuille law^{2,5}:

$$J\eta/J_0\eta_0 = r_s^4/r_0^4 \quad (1)$$

where r_0 is the pore radius at no absorption of the solutes, r_s is the effective pore radius where the solutes are absorbed on the pore wall, η_0 is the viscosity of pure water, and η is the viscosity of feed solution.

Absorption of bovine serum albumin (BSA) on the fibers was tested in this study. Figure 5 shows dependence of $J\eta/J_0\eta_0$ on running time at $C_f = 0.5\%$ of BSA in phosphate buffer solution at pH 7.0. Data for the modified fibers with propane sultone, conventionally sulfonated fiber, and nonmodified fiber reported previously⁵ are also plotted in the same figure. The figure suggests that the modified fiber with propylene oxide (HP-3) gives less absorption of BSA than the nonmodified and conventionally sulfonated fibers (S-PSF-1), although HP-3 is found to absorb more BSA than the fibers modified with propane sultone (HP-SI-4 and HP-SB-17H). The fibers modified with propane sultone probably show the best antiabsorption behavior due to the ionic repulsion, since isoelectric point of BSA is 4.7.⁷ HP-3 shows, however, less absorption of BSA than S-

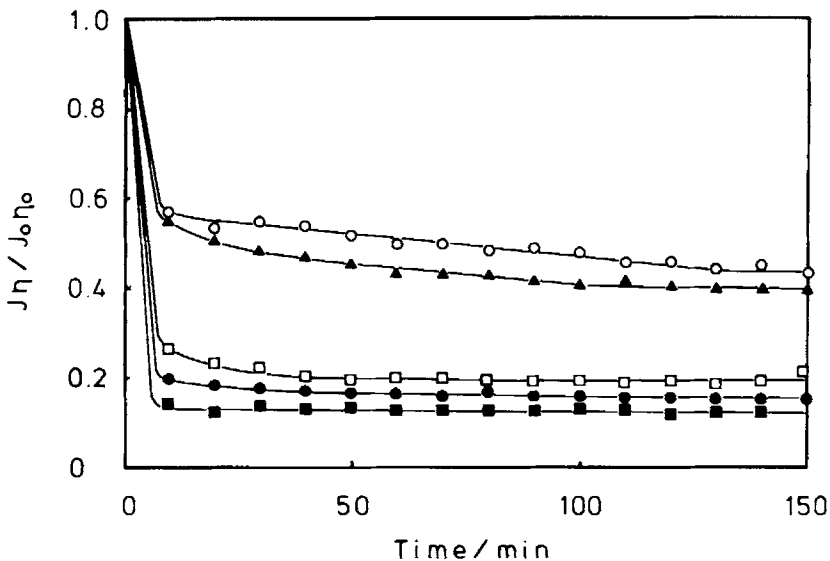


Fig. 5. Dependence of $J\eta/J_0\eta_0$ on running time for SI-1 (■), S-PSF-1 (●), HP-3 (□), HP-SI-4 (▲), and HP-SB-17H (○) at 20°C and $\Delta p = 3 \text{ kg/cm}^2$. Feed solution is 0.5 wt % BSA solution at pH 7.0.

TABLE II
Membrane Performance for Chemically Modified Hollow Fibers (HP-4)*

No.	Treatment	(J/m day ⁻¹)	R/%
1	Pure water	0.258	83.3
2	Hot water (80°C, 4 h)	0.373	74.5
3	0.5 M HCl (25°C, 4 h)	0.583	80.0
4	0.5 M NaOH (25°C, 4 h)	0.457	74.2

* Feed solution = 5000 ppm, PEG 6000 and $\Delta p = 3$ kg/cm².

PSF-1 shows. This effect can be attributed to the high flexibility of a hydrophilic group (i.e., hydroxide group) originated from the existence of a joint segment of CH(CH₃)CH₂ between polymer backbone and the hydrophilic group in HP-3, since conventionally sulfonated fiber does not have any joint segments. It is concluded that fibers having hydrophilic surfaces show better results of anti-absorption of solutes than the nonmodified fiber.^{2,3,5}

Membrane Performance

The membrane performance was tested for the modified fibers with propylene oxide (HP-4) and is shown in Table II. After HP-4 were kept standing in hot water at 80°C and 0.5 M HCl or 0.5 M NaOH solutions for 4 h. The rejections of PEG 6000 for HP-4 after the tests were found to show approximately same value to those for the original fibers before the tests, although fluxes were found to show 1.4–2.3 times higher than those before the tests. The results suggest that the surface modified fibers keep their thermal and chemical stabilities, which originate from the polysulfone backbone.

We are grateful to Mr. M. Yanase, N. Kubota, K. Watanabe, T. Yokoyama, K. Toyomoto, Y. Inai, T. Ichihashi and E. Wakita (Asahi Chem. Co., Ltd.) for their helpful suggestions.

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Received August 24, 1989

Accepted November 30, 1989