Characterization of Graft Polymerization of Fluoroalkyl Methacrylate onto PDMS Hollow-Fiber Membranes and Their Permselectivity for Volatile Organic Compounds

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ABSTRACT: Polydimethylsiloxane (PDMS) hollow-fiber membranes grafted with 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA), which is a fluoroalkyl methacrylate, using a ^{60}Co irradiation source, were characterized and applied to pervaporation. The PDMS hollow-fiber membranes were filled with N_2 gas and sealed. The membranes and the HDFNMA solution were then irradiated simultaneously. In the HDFNMA solution, graft polymerization was performed. The degree of grafting of the outside surface of the hollow fiber was greater than that in the inside surface of the hollow fiber. In the grafted PDMS hollow-fiber membranes, the best separation performance was shown due to the introduced hydrophobic polymer, poly(HDFNMA). The grafted membrane had a microphase-separated structure, that is, a separated structure of PDMS and graft-polymerized HDFNMA. The permeability of molecules in the poly(HDFNMA) phase was so low that the diffusion of molecules was prevented in the active layer with many poly(HDFNMA) domains, as the feed solution was introduced through the inside of the hollow fibers and the outside was vacuumed. As the feed solution was introduced through the outside of the hollow fibers and the inside was vacuumed, the diffusion of molecules was not prevented in the active layer with few poly(HDFNMA) domains. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1573–1580, 2003

Key words: irradiation; graft copolymers; phase separation; diffusion

INTRODUCTION

Ground water contaminated with volatile organic compounds (VOCs) used widely in detergents for metals and cleaning, etc., has been a social problem.[1,2] The VOCs' toxicity has been clarified for several years.[1,2] Recently, their discharge has been regulated and the use of substitutes is considered. The purification of contaminated water has been extensively studied.[3,4] In recent years, the influence on the human body and the environment of various chemical compounds has been pointed out. Because the analysis operation to investigate the compounds is complex and time-consuming,[5] it becomes necessary to simplify the complex operation and to analyze at the same time. The organic compounds in environmental samples must be separated from the water and concentrated before detection by the analyzing equipment. In addition, recycling VOCs from waste water is important, especially, expensive VOCs involving aroma.

In the separation of very low concentrations of VOCs from these contaminated waters (<1000 g/m^3), the use of pervaporation applications with membranes that allow VOCs to permeate preferentially has been considered. The high selectivity of pervaporation makes it potentially very interesting for continuous recovery of VOCs under compatible conditions. The removal of VOCs using various membranes with permselectivity for organic compounds, for example, silicone rubber,[6–24] polyethyl-*block*-polyamide (PEBA),[15] crosslinked poly(acrylate-*co*-acrylic acid),[25–27] and poly[*n*-butyl acrylate-*co*-(trimethylsilyl)methyl methacrylate][28] were studied. Recently, various composite membranes have been developed.[1,4,29]

Polydimethylsiloxane (PDMS) has been well known as an excellent polymer membrane material for its high permeability to gases and liquids[30] and most widely used because of its ease of preparation into different shapes and relatively small thickness.[13–15,19] The pervaporation ability of the PDMS membrane to remove VOCs from water with very high separation factors has been recognized.[6–24] Recently, the enhancing of the selectivity of PDMS for VOCs is expected for efficiency. Therefore, the study of the pervaporation of VOCs from water has focused on the use of PDMS, its improvement,[17,21,22] and its copolymers.[9,13,14,31–37] Dotremont et al.[17,21,22] improved the solubility of the PDMS membrane for chlorinated hydrocarbons by incorporation of a filler (silicate).

Pervaporation is necessary for analytical use.[38–47] Pervaporation as an alternative to various analytical

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methods has been studied.[40–42,45–47] Luiz de Mattos and Zagatta,[39] studied the analytical pervaporation for the monitoring of ethanol in industrial fermentation. Papaefstathiou et al. studied the application of analytical pervaporation to various samples as food, medical, etc.[43,44,46]

Because the molecular volume of VOCs is larger than that of water and the penetrate quickly permeates a rubbery membrane like PDMS, permselectivity was not affected by the diffusivity.[20,32,34,36,37] Solubility significantly affects the permselectibity in pervaporation through a hydrophobic rubbery membrane.[20,32,34,36,37] Fluorinated polymers have also been studied as an organic aqueous mixture separation membrane expected to show excellent affinity for organic compounds due to their hydrophobicity based on their low surface energy.[48–50]

The enhancement of the affinity of PDMS for chlorinated hydrocarbons using fluoroalkyl methacrylates (FALMAs) is interesting. For this improvement, the blending of PDMS and poly(FALMA) is difficult due to the low affinity of PDMS for poly(FALMA).

There is a possibility of preparing graft or block copolymers of them. Graft and block copolymers, compared to mixtures of the corresponding polymers, often make it possible to join incompatible polymers.[51] Graft polymerization is a method of conducting the growth of the graft chain by polymerization, starting with reactive radicals produced in the membrane.[52,53] Generally, a vinyl monomer has been used in graft polymerization. Irradiation by gamma rays, electron beams, ultraviolet light, and plasma has been well known as the means of radical formation.[52,53] A radiation source which has high energy and the possibility of industrial use has been noted and studied.[54–62] Preirradiation and simultaneous irradiation have been known as methods of radiation-induced graft polymerization.[52] Preirradiation is a method in which a monomer is reacted with a polymer which has been irradiated in advance.[52] The preservation of radicals is necessary for this method. Simultaneous irradiation is a method in which the monomer and the polymer are irradiated simultaneously.[53] In previous studies,[31–35] PDMS sheet membranes were grafted by various irradiation methods, and it was clarified that gamma rays had high energy and that a simultaneous irradiation method by gamma rays could produce a phase-separated structure and control the degree of grafting to obtain compatible permeability.

Hollow-fiber membranes have a wider membrane surface area and a more useful shape for separating VOCs than have sheet membranes and have been studied.[6–8,10,11,18,19,23,24,29] Yamaguchi et al.[29] synthesized alkyl acrylate plasma-grafted porous polyethylene hollow fibers and reported their permeability.

In this study, the PDMS hollow-fiber membranes, which have useful shapes, were grafted with 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA), which is effective for permselectivity using a ^{60}Co irradiation source. The grafted PDMS hollow-fiber membranes, which have an interesting structure, were characterized, and the permeability in the pervaporation of ethyl butanoate, which involves aroma and a water mixture, was investigated.

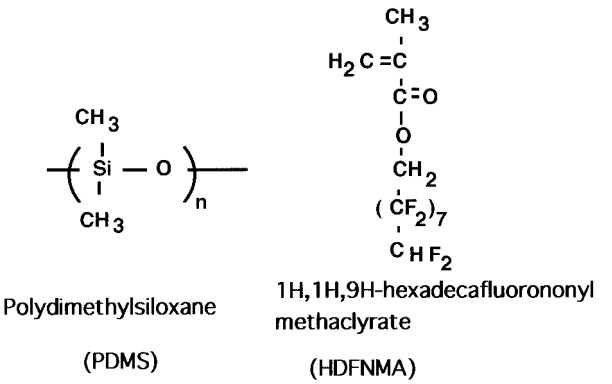

Figure 1 Structures of PDMS and HDFNMA.

EXPERIMENTAL

Materials

Commercial PDMS hollow-fiber membranes (Fuji Systems Corp., Tokyo, Japan), of 1-mm i.d. and 1.5-mm o.d., were used throughout this work. The chemical structures of PDMS and HDFNMA are shown in Figure 1. HDFNMA (Daikin Fine Chemical Laboratory Corp., Tokyo, Japan) was used as received to avoid homopolymerization. Ethyl butanoate (EBU), methanol, and acetone (special grade, Wako Pure Chemical Industries, Ltd., Tokyo, Japan) were used as received.

Graft polymerization of HDFNMA by a ^{60}Co source

The procedure for graft polymerization was simultaneous irradiation as reported by Odian et al.,[62] and the schematic diagram of the apparatus is shown in Figure 2.

PDMS hollow-fiber membranes were filled with N_2 gas and sealed. The fiber membranes and HDFNMA solution in ampules were degassed and sealed under a vacuum simultaneously. The ampules were then irradiated at dose rates of 0.1 Mrad/h for 5 h from a ^{60}Co source at 25°C. After the irradiation was ended, the membranes were washed and soaked in acetone for 24 h to remove the monomer and homopolymer with acetone. The membranes were then dried for 48 h in a vacuum oven at 25°C. The degree of grafting was calculated as follows:

$$\text{Degree of grafting (\%)} = (W_1 - W_0)/W_0 \times 100 \quad (1)$$

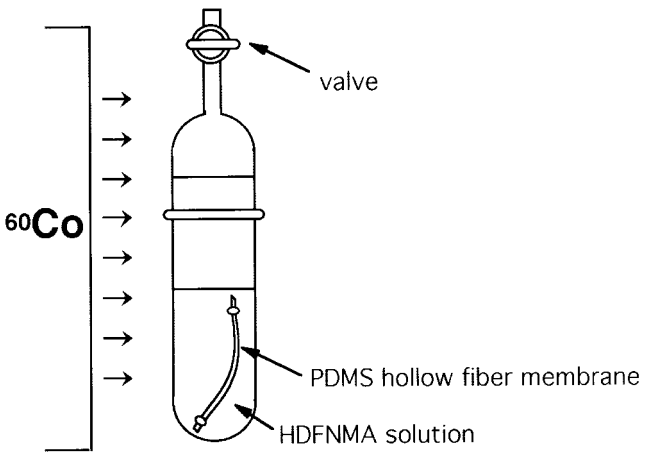

Figure 2 Apparatus for the graft polymerization by ^{60}Co.

where W_0 and W_1 denote the weight of the PDMS membrane and the grafted PDMS membrane, respectively.

Characterization of the grafted PDMS hollow-fiber membranes

The surface morphologies of the grafted PDMS hollow-fiber membranes were analyzed by a microscope (Olympus SZ × 12). The grafted PDMS hollow-fiber membranes were placed on a black plate and analyzed.

Pervaporation experiment

The experimental setup is shown schematically in Figure 3. The feed solution was introduced through the inside [Fig. 3(a)] or the outside [Fig. 3(b,c)] of the hollow fibers. The effective membrane length in the cell was 13.5 cm. Pervaporation is expected to have application to various uses. The pervaporation experiment was operated at 25°C as the analysis is usually operated at normal temperature. The feed solution was circulated or passed one-way through the cell and the feed tank. Yamada reported that suitable results had been obtained below 10 Torr.[63] The pressure at the permeation side was kept below 10 Torr by a vacuum pump. The permeate was collected in traps cooled by liquid nitrogen (− 196°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate, flux (J), was obtained by eqs. (2a) and (2b):

$$J = Q/At \tag{2a}$$

$$A = 2\pi l r_1^{1/2} r_2^{1/2} \tag{2b}$$

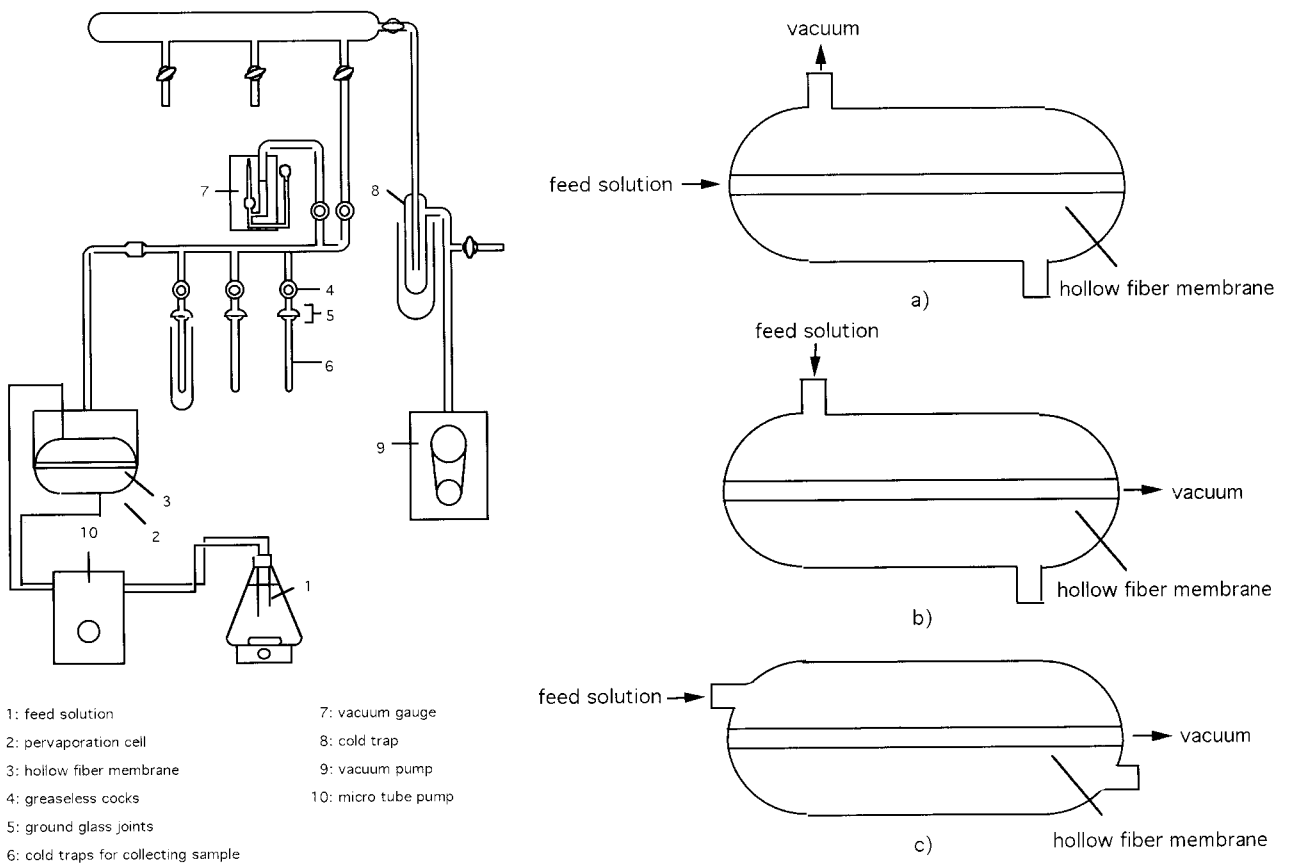

Figure 3 Pervaporation apparatus.

TABLE I
Degree of Grafting Under Various Conditions in Simultaneous Irradiation

HDFNMA (wt % in MeOH)	Degree of grafting (wt %)
30	34
100	33

Dose rate of irradiation: 0.1 Mrad/h; irradiation time: 5 h.

where Q is the amount permeated during experimental time interval t; A, the effective surface area; $r_1^{1/2}$, the i.d.; $r_2^{1/2}$, the o.d., and l, the effective membrane length in the cell. The EBU flux was calculated from the total flux and the permeate composition. The concentration of EBU in the feed and permeate solution was determined by a gas chromatograph with an FID detector [Hewlett–Packard (HP) 5890 Series II]. The gas chromatograph was operated using an HP PLOT Q column (0.32-mm i.d., 15-m length with a 20-mm liquid phase). The EBU concentration in the permeate was high, which is far beyond its solubility limit in water. The phase separation took place in the permeate. Isopropanol was added to the permeate solution. The permeate solution was homogenized and analyzed to determine the EBU concentration. The enrichment factor during pervaporation, β, was calculated as follows:

$$\beta = Y/X \tag{3}$$

where X and Y denote the concentrations of EBU in the feed and permeate solutions, respectively.

RESULTS AND DISCUSSION

Characterization of the grafted PDMS hollow-fiber membrane

Various conditions in the simultaneous irradiation and the degree of grafting are given in Table I. The degree of grafting for a PDMS hollow-fiber membrane grafted in a 30 wt % HDFNMA/MeOH solution was as much as that in 100 wt % HDFNMA.

The morphologies of the grafted PDMS hollow-fiber membranes were analyzed by a microscope. The micrographs are shown in Figure 4. The dark parts are the PDMS phase. The white parts are the grafted PHDFNMA phase. In a 30 wt % HDFNMA/MeOH solution, the graft polymerization reached the inside surface of the hollow fiber due to the swelling effect by MeOH. In 100 wt % HDFNMA, the graft polymerization did not reach the inside surface of the hollow fiber.

Pervaporation of the grafted PDMS hollow-fiber membrane

Figure 5 shows the concentration of EBU in the feed tank as a function of time at various flow rates of the feed solution introduced through the inside of the PDMS hollow-fiber membranes. The feed solution was circulated through the cell and the feed tank. The total volume of the feed solution was 300 mL. The removal rate of EBU became much greater as the flow rate was increased.

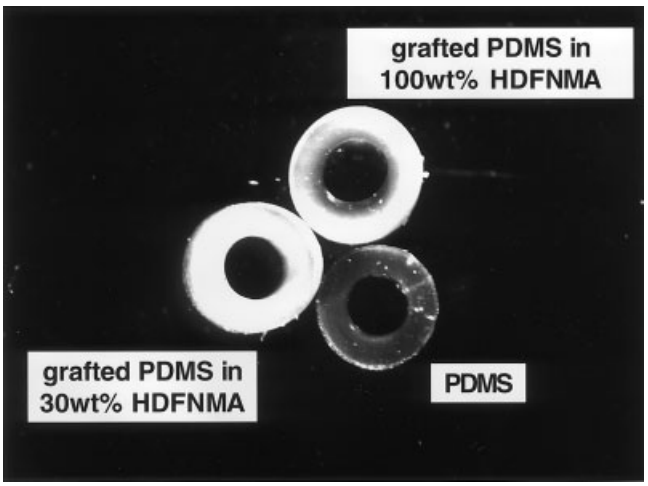

Figure 4 Micrographs of the grafted PDMS hollow-fiber membranes.

Figures 6 and 7 show the concentration of EBU in the feed tank as a function of time at various flow rates of the feed solution introduced through the outside of the PDMS hollow-fiber membranes. The results by the cell shown in Figure 3 (b) are shown in Figure 6. The results by the cell shown in Figure 3 (c) are shown in Figure 7. The solution was fed vertically to the hollow fibers in the cell shown in Figure 3 (b). The feed

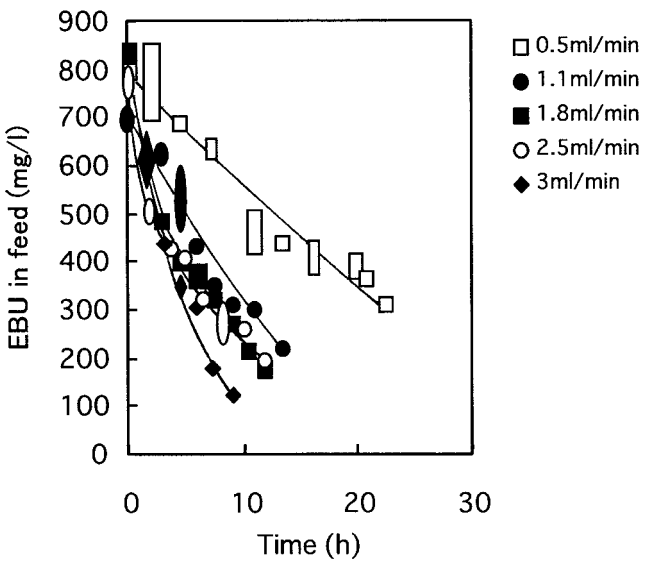

Figure 5 Concentration of EBU in the feed tank as a function of time at various flow rates of the feed solution introduced through the inside of the PDMS hollow-fiber membranes. The size of the marker indicates the uncertainty of the measurement.

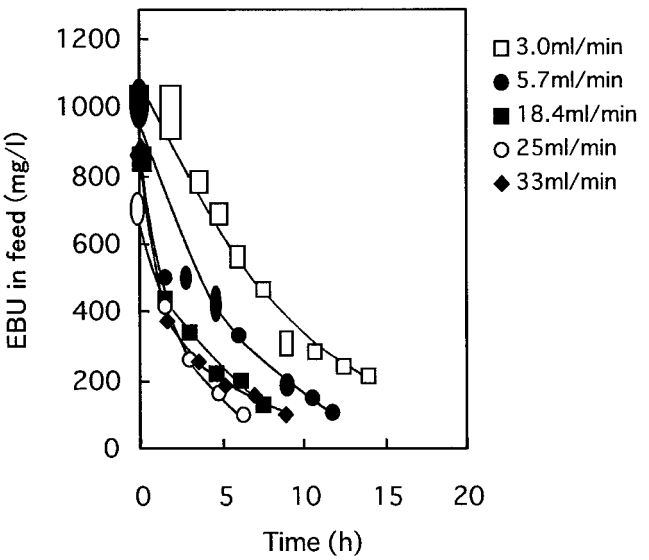

Figure 6 Concentration of EBU in the feed tank as a function of time at various flow rates of the feed solution introduced through the outside of the PDMS hollow-fiber membranes by the cell shown in Figure 3 (b). The size of the marker indicates the uncertainty of the measurement.

solution was circulated through the cell and the feed tank. The total volume of the feed solution was twice 300 mL, 600 mL, because the reduction rate of EBU was high and the difference was not clear at high flow rates of the feed solution introduced through the outside of the hollow fiber. The results clearly show that EBU in the feed solution using the cell shown in Figure 3 (b) is removed more efficiently as the flow rate is increased. The mass-transfer resistance of the

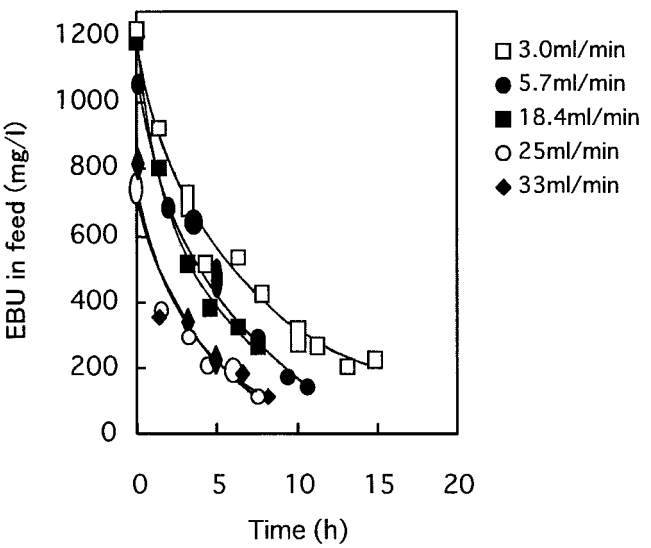

Figure 7 Concentration of EBU in the feed tank as a function of time at various flow rates of the feed solution introduced through the outside of the PDMS hollow fiber membranes by the cell shown in Figure 3 (c). The size of the marker indicates the uncertainty of the measurement.

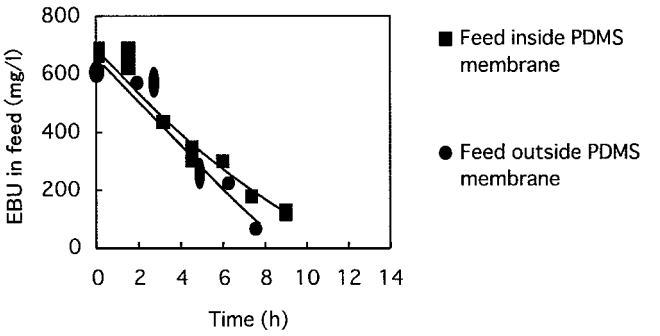

Figure 8 Concentration of EBU in the feed tank as a function of time for the PDMS hollow-fiber membranes. The feed solution was introduced through the inside [Fig. 3 (a)] or the outside [Fig. 3 (b)]. The size of the marker indicates the uncertainty of the measurement.

liquid boundary has a strong influence on the separation performance.[6–8,10,11] In addition, the efficiency was greater than that using the cell shown in Figure 3(c). The cell shown in Figure 3(b) was used in the following experiments.

The permeation behavior of the gradationally grafted membrane is interesting. The permeability of the grafted PDMS hollow fiber and the PDMS hollow fiber was investigated.

Figure 8 shows the concentration of EBU in the feed tank as a function of time for the PDMS hollow-fiber membranes. The feed solution was introduced through the inside [Fig. 3 (a)] or the outside [Fig. 3 (b)] of the hollow fibers circulating through the cell and the feed tank. The total volume of the feed solution was 300 mL and the flow rate was 3 mL/min. The EBU in the feed solution introduced through the outside of the hollow fiber was removed more efficiently than was the EBU in the feed solution introduced through the inside.

Figure 9 shows the concentration of EBU in the feed tank as a function of time for the grafted PDMS hollow-fiber membranes. The feed solution was intro-

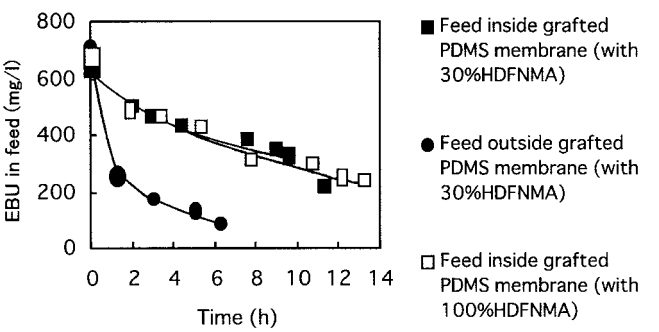

Figure 9 Concentration of EBU in the feed tank as a function of time for the grafted PDMS hollow-fiber membranes. The feed solution was introduced through the inside [Fig. 3 (a)] or the outside [Fig. 3 (b)]. The size of the marker indicates the uncertainty of the measurement.

TABLE II
Pervaporation Data for PDMS Hollow-fiber and Grafted PDMS Hollow-fiber Membrane

Membrane	Pervaporation data					
	EBU in feed (mg L^{-1})	Flux			EBU in permeate (mg L^{-1})	Enrichment factor (β_{pv})
		Total	Water (10^{-3} kg $m^{-2}h^{-1}$)	EBU		
PDMS hollow-fiber irradiated in HDFNMA 30 wt % at 0.1 Mrad/h for 5 h	0.5	6.1	6.1	0.0054	880	1760
PDMS hollow fiber	0.5	5.0	5.0	0.0044	870	1740

duced through the inside [Fig. 3 (a)] or the outside [Fig. 3 (b)] of the hollow fibers circulating through the cell and the feed tank. The total volume of the feed solution was 300 mL and flow rate was 3 mL/min. The EBU in the feed solution introduced through the outside of the hollow fiber was removed more efficiently than was the EBU in the feed solution introduced through the inside. The removal rate of EBU in the feed solution introduced through the inside PDMS hollow-fiber membrane grafted in a 30 wt % HDFNMA/MeOH solution was as great as that in a 100 wt % HDFNMA.

The results in Figures 8 and 9 show two facts: One is that the removal rate of EBU in the feed solution introduced through the inside PDMS hollow-fiber membrane was more efficient than that through the inside of the grafted PDMS hollow-fiber membrane. Another is that the removal rate of EBU in the feed solution introduced through the outside of the grafted PDMS hollow-fiber membrane was more efficient than that through the outside of the PDMS hollow-fiber membrane.

The pevaporation results of a dilute EBU solution through the PDMS hollow-fiber membrane and the grafted PDMS hollow-fiber membrane are shown in Table II. The 500-ng/mL feed solution was passed one-way through the outside of the hollow fiber at a 3-mL/min flow rate. The grafted PDMS hollow-fiber membrane was affected by the irradiation and the flux was greater than that of the unirradiated PDMS fiber. The grafted PDMS membrane had a high selectivity for EBU and showed excellent performance in separating VOCs from water to utilize in water treatment and analysis.

The permeation mechanism for the PDMS hollow-fiber membrane grafted in a 30 wt % HDFNMA/MeOH solution and in a 100 wt % HDFNMA solution is shown in Figure 10. In this study, PDMS hollow-fiber membranes were filled with N_2 gas and sealed. The membranes and the HDFNMA solution were then irradiated simultaneously. The grafted amount in the outside surface of the hollow fiber was more than that in the inside surface. In a previous study,[9] we improved the PDMS sheet membrane by graft polymerization with HDFNMA, which had the effect of increasing the selectivity for chlorinated hydrocarbons, by a ^{60}Co source, and utilized it in pervaporation. In the grafted PDMS, the best separation performance was shown, due to introducing the hydrophobic polymer, poly(HDFNMA). The grafted membrane had a

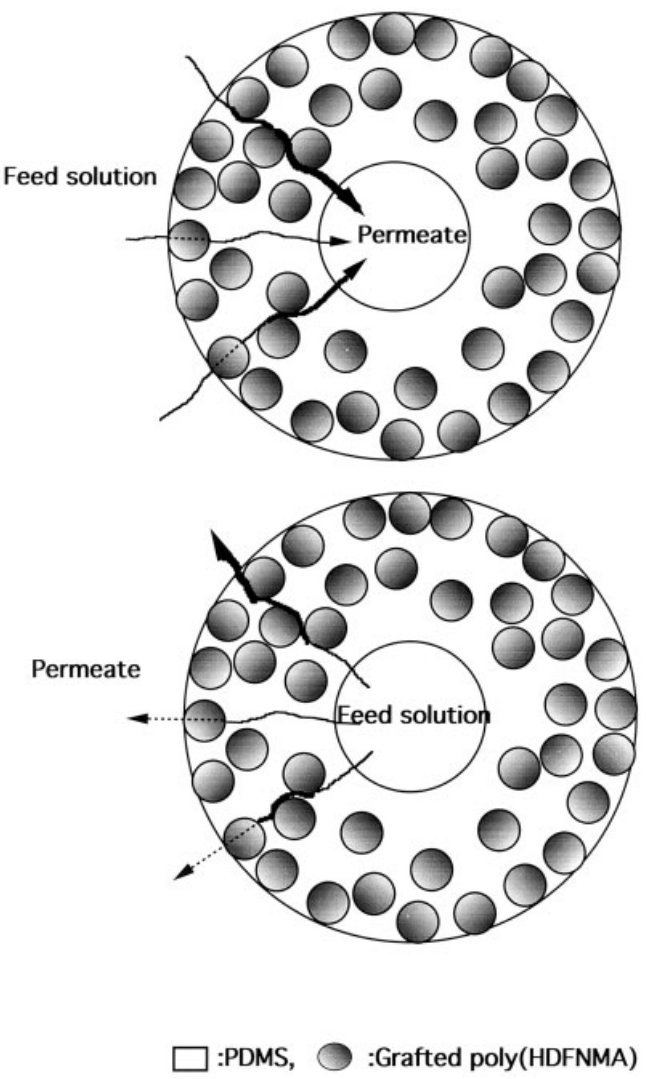

Figure 10 Tentative illustration of the permeation mechanism through the grafted PDMS hollow-fiber membrane.

microphase-separated structure, that is, a separated structure of PDMS and graft-polymerized HDFNMA. In gas permeation where the diffusion coefficient is not concentration-dependent, the permeation coefficient is given as follows:

$$P = 2\pi lDcV^{-1}[ln(r_1/r_2)]^{-1}\,[t - (r_1 - r_2)^2/6D] \quad (4)$$

where l is the effective membrane length in the cell; D, the diffusion coefficient; c, the feed concentration; V, the inside volume of the hollow fiber; $r_1^{1/2}$, the i.d.; $r_2^{1/2}$, the o.d., and t, the delayed time. In this case, the effective surface area (A) could be obtained by eq. (2b). In pervaporation, the permeation is influenced by the active layer. The permeability of molecules in the poly(HDFNMA) phase was so low that the diffusion of molecules was prevented in the active layer with an amount of poly(HDFNMA) domains, as the feed solution was introduced through the inside of the hollow fibers and the outside was vacuumed. As the feed solution was introduced through the outside of the hollow fibers and the inside was vacuumed, the diffusion of molecules was not prevented in the active layer with a small amount of poly(HDFNMA) domains.

CONCLUSIONS

In this study, PDMS hollow-fiber membranes were grafted with HDFNMA using a ^{60}Co irradiation source, characterized, and utilized in pervaporation. The mass-transfer resistance of the liquid boundary has a strong influence on the separation performance. EBU in the feed solution was removed more efficiently as the flow rate was increased and through the outside of the hollow fiber rather than the inside.

The inside surface of the PDMS hollow-fiber membranes was grafted due to the swelling effect. The grafted amount in the outside surface of the hollow fiber was more than that in the inside surface. The grafted membrane had a microphase-separated structure, that is, a separated structure of PDMS and graft-polymerized HDFNMA.

In the grafted PDMS hollow-fiber membranes, the best separation performance was shown due to introducing the hydrophobic polymer, poly(HDFNMA). The removal rate of EBU in the feed solution introduced through the inside PDMS hollow-fiber membrane was more efficient than that through the inside of the grafted PDMS hollow-fiber membrane. However, the removal rate of EBU in the feed solution introduced through the outside of the grafted PDMS hollow-fiber membrane was more efficient than that through the outside of the PDMS hollow-fiber membrane. The permeation in pervaporation differs from that in gas permeation. In pervaporation, the diffusion coefficient is concentration-dependent and the permeation is influenced by the active layer. The permeability of penetrates in the poly(HDFNMA) phase was so low that the diffusion of molecules was prevented in the active layer with an amount of the poly(HDFNMA) domains, as the feed solution was introduced through the inside of the hollow fibers and the outside was vacuumed. As the feed solution was introduced through the outside of the hollow fibers and the inside was vacuumed, the diffusion of molecules was not prevented in the active layer with a small amount of poly(HDFNMA) domains.

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