Characterization and Pervaporation of Chlorinated Hydrocarbon–Water Mixtures with Fluoroalkyl Methacrylate-Grafted PDMS Membrane

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ABSTRACT: It is desirable to enhance the selectivity of a polydimethylsiloxane (PDMS) membrane for chlorinated hydrocarbons. In this study, the PDMS membranes were improved by graft polymerization of 1H,1H,9H-hexadecafluorononyl methacrylate (HD-FNMA), which has the effect of increasing the selectivity for chlorinated hydrocarbons. The PDMS membrane and HDFNMA were irradiated simultaneously by a ⁶⁰Co source. The grafted membranes had a microphase-separated structure, that is, a separated structure of PDMS and grafted HDFNMA. In the grafted PDMS membrane, a great separation performance for a TCE-water mixture was shown due to the introduction of the hydrophobic polymer, poly(HDFNMA). For the permeation of the grafted PDMS membrane, the permeability of molecules in the PDMS phase was significantly great. and that in the poly(HDFNMA) phase was too low to affect the whole permeation of the grafted PDMS membrane directly. However, the permeation of molecules at the interface of poly(HDFNMA) and PDMS played an important role because poly(HDFNMA) had a much stronger affinity for TCE than water. At a low feed concentration of the TCE solution, the diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. At a high concentration of TCE solution, TCE was sufficiently sorbed into the membrane so that the diffusion of water was prevented by TCE molecules; in turn, the permselectivity of TCE was increased significantly. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 273-287, 1999

Key words: graft polymerization; PDMS membrane; 1H,1H,1H-hexadecafluorononyl methacrylate; phase separation structure; selectivity for chlorinated hydrocarbons

INTRODUCTION

Chlorinated hydrocarbons represented by trichloroethylene (TCE) and tetrachloroethylene (PCE) have been widely used in detergents for metals and cleaning.^{1,2} Recently, it has been a social problem that ground water and soil are contaminated with chlorinated hydrocarbons. Their toxicity has been clarified for several years.^{1,2} Their discharge has been regulated, and the use of substitutes has been considered.^{1,2} The purification of groundwater and wastewater, which are contaminated with chlorinated hydrocarbons, is desired and has been studied.^{1,2} At present, various means of aeration, adsorption on activated carbon, photolysis, and ozonization are used in the removal of chlorinated hydrocarbons at very low concentrations from these contaminated waters.^{1,2}

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Pervaporation can be useful compared with these conventional methods because of the flexibility in design, the low energy cost, and the possibility of solvent recycling.^{1,2} In the removal of very low concentrations of chlorinated hydrocarbons from these contaminated water (<1000 g/m³), the use of pervaporation applications with membranes that allow chlorinated hydrocarbons to permeate preferentially has been considered for several years.^{1–19} The high selectivity of pervaporation makes it potentially very interesting for continuous recovery of volatile organic compounds under compatible conditions.

Polydimethylsiloxane (PDMS) has been well known as an excellent polymer membrane material for its high permeability to gases and liquids,²⁰ but the selectivity for organic compounds was not so excellent. Pervaporation performance of a membrane is determined by both the sorption and the diffusion characteristics of the permeating components in the membrane. The molecular size of TCE is larger than that of water; hence, it is desirable to enhance the selectivity of PDMS for chlorinated hydrocarbons by solubility rather than diffusivity. C. Dotremont et al.^{5,15} improved the solubility of the PDMS membrane for chlorinated hydrocarbons by incorporation of a filler (silicate).

Fluorinated polymers have been studied for their hydrophobicity based on their low surface energy.^{9,21,22}

The PDMS membranes were improved using fluoroalkylmethacrylates (FALMA) to enhance the affinity of PDMS for chlorinated hydrocarbons. For this improvement, blending of PDMS and poly(FALMA) is difficult due to the low affinity of PDMS for poly(FALMA). There is the 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 in that form.²³

Graft polymerization is a method of conducting the growth of the graft chain by polymerization, starting with reactive radicals produced in the membrane.^{24,25} Generally, a vinyl monomer has been used in graft polymerization. Irradiation by gamma rays, electron beams, ultraviolet (UV) light, and plasma has been well known as a means of radical formation.^{24,25} In a previous study,²⁶ the PDMS membranes were modified by sorbing FALMA using UV irradiation in order to increase the partition coefficient of chlorinated hydrocarbons into the membrane. However, in this method, the increase in the membrane weight by poly(FALMA) is about 1 wt %. A radiation source that has high energy and the possibility of industrial use has been studied.²⁷⁻⁴⁸ Compared with UV, gamma ray radiation has high energy and can control the degree of grafting in order to obtain compatible flux and selectivity. Preirradiation and simultaneous irradiation have been known as methods of radiation-induced graft polymerization.²⁴ Preirradiation is a method in which the monomer is reacted with the polymer, which has been irradiated in advance.²⁴ The preservation of radicals is necessary for this method. Simultaneous irradiation is a method in which the monomer and polymer are irradiated simultaneously.²⁴ In this study, simultaneous irradiation was studied.

Membranes that have a phase-separated structure in a composite with PDMS and the incompatible polymers have been reported.^{22,49–53} The articles reported on membranes, which were prepared by casting of the block copolymer and graft copolymer solutions or crosslinking them. The membranes were more hydrophobic at the airside surface than at the glass-side surface. The preparation of the membranes composed of a homogeneous mixture of incompatible polymer domains is difficult, while homogeneous membranes are better for evaluation of the permeation of the membrane and application to a membrane process.

Radiation-induced graft polymerization using the Gammacell ⁶⁰Co source has the possibility of radical reaction of the monomer absorbed in the membrane with excellent penetration and is expected to synthesize novel and useful membranes with a homogeneous composition of PDMS and poly(HDFNMA).







Figure 2 Apparatus for the graft polymerization by 60 Co.

In this study, the PDMS membranes were improved by graft polymerization of 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA), which had the effect of increasing the selectivity for chlorinated hydrocarbons, using a ⁶⁰Co source. PDMS is a silicone rubber, and the preservation of radicals is difficult. In this study, simultaneous irradiation was studied. We then characterized the grafted PDMS membrane and used it for pervaporation. This article reports the characterization and the permselectivity for chlorinated hydrocarbons of the grafted PDMS membranes.

EXPERIMENTAL

Materials

Commercial PDMS membranes (Fuji Systems Corporation), 50 μ m thick, were used throughout this work. The chemical structure of PDMS and HDFNMA is shown in Figure 1. HDFNMA (Daikin Fine Chemical Laboratory Corporation) was used as received to avoid homopolymerization. Methanol, acetone, and TCE (Special grade, Waco Pure Chemical Industries, Ltd.) were used as received.

Graft Polymerization of HDFNMA by a ⁶⁰Co Source

The procedure of graft polymerization was simultaneous irradiation as reported by G. Odian et al.²⁷ A schematic diagram of the apparatus is shown in Figure 2.

First, PDMS membranes $(7 \times 7 \text{ cm})$ and HDFNMA solution in ampoules were degassed and sealed under vacuum simultaneously. The ampoules were then irradiated from a ⁶⁰Co 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 an evacuated vessel. The degree of grafting was calculated as follows:

CHLORINATED HYDROCARBON-WATER MIXTURES

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

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

Poly(HDFNMA), a homopolymer polymerized by a 60 Co source was dissolved at a concentration of 5 g/100 mL in acetone. A glass viscometer was used to measure the kinematic viscosity at 25°C. The relative viscosity was calculated as follows:

Relative viscosity
$$\eta_{\rm rel} = \eta/\eta_{\rm o} = \rho t/\rho_{\rm o} t_{\rm o} = t/t_{\rm o}$$
 (2)

where η is the kinematic viscosity of 5 g/100 mL poly(HDFNMA) solution; $\eta_{\rm o}$ is the kinematic viscosity of acetone; ρ is the density of 5 g/100 mL poly(HDFNMA) solution; $\rho_{\rm o}$ is the density of acetone; t is the fluid time of 5 g/100 mL poly(HDFNMA) solution; and $t_{\rm o}$ is the fluid time of acetone.

Characterization of the Grafted PDMS Membrane

The Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectra were obtained by 1800 FTIR-ATR spectroscopy (Perkin-Elmer Co., Ltd.). The instrument was operated at a cycle equal to 50. The KRS-5 [TlBr-T(II)] internal refraction element (IRE) was used at an incident angle of 45°.

The wide-angle X-ray diffraction (WAXD) spectra were obtained with a 1200 X-ray diffractometer using a Cu anode (Rigaku-Denki Co., Ltd.). The instrument was operated at 40 kV, 20 mA, with λ equal to 1.54 at 20°C. The scan speed was $2\theta = 2.00^{\circ}/\text{min}$ for 3–50°.

The differential scanning calorimeter (DSC) curve was obtained using a DSC7 (Perkin–Elmer Co., Ltd.). The DSC scan starts from -150 °C and is measured up to 300 °C. The rate of temperature increase is usually 10 °C/min.

X-ray photoelectron spectroscopy (XPS) spectra were obtained with an IPS-9000SX (JEOL, Ltd.) $\,$

using MgK α exciting radiation (1253.6 eV). The X-ray gun was operated at 10 eV with a sample chamber vacuum of less than 5 × 10⁻⁹ Torr. The XPS spectra were recorded at two electron emission angles (θ) of 30 and 90°.

Pervaporation Experiment

The pervaporation experiments were performed as in the previous study²⁶ using the continuous feed type at 25°C. The feed solution was circulated through the cell and the feed tank. The effective membrane area in the cell was 19.6 cm². The pressure at the permeation side was kept below 10 Torr by a vacuum pump. Upon reaching steady-state flow conditions, 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 the following:

$$J = Q/At \tag{3}$$

where Q is the amount permeated during experimental time interval t, and A is the effective surface area. The TCE flux was calculated from the total flux and the permeate composition.

The concentration of TCE in the feed and permeate solution was determined by gas chromatography using an flame ionization detection (FID) detector. The separation factor, α_{pv} , was calculated as

$$\alpha_{pv} = \{Y(1-X)\}/\{(1-Y)X\}$$
(4)

where *X* and *Y* denote the concentration of TCE in the feed and permeate solution, respectively.

Sorption Measurement

The dried and weighed membrane was immersed in TCE solution and sealed at 25°C until equilibrium was reached. The membrane was then taken out of the vessel, wiped quickly with filter paper, and weighed. The degree of sorption of TCE solution into the membranes was measured as follows:

Degree of sorption (%) =
$$(W_1 - W_0)/W_0 \times 100$$
 (5)

where W_0 and W_1 denote the weight of the dried membrane and the swollen membrane, respectively.



Figure 3 Apparatus for the composition measurement in the membrane.

The concentration of TCE solution soaked in the membrane was determined using the apparatus in the schematic diagram shown in Figure 3. The membrane on reaching equilibrium was taken out of the vessel, wiped quickly with filter paper, and placed in trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, cock B was closed, and the TCE solution soaked in the membrane and vaporized by heating with a drier was collected in cooled traps. The concentration of TCE solution in the feed and the soaked membrane was determined by gas chromatography. The separation factor, α_s , was calculated as

$$\alpha_s = \{Y'(1-X)\}/\{(1-Y')X\}$$
(6)

where X and Y' denote the concentration of TCE in the feed solution and the swollen membranes, respectively.

RESULTS AND DISCUSSION

Graft Polymerization of HDFNMA by a ⁶⁰Co Source

The effect of irradiation time on the degree of grafting at a fixed HDFNMA content or irradiation source strength was investigated. Various

Dose Rate of Irradiation (Mrad/h)	HDFNMA (wt % in MeOH)	Degree of Grafting (wt %)/Irradiation Time (h)					
		1	2	3	4	5	
0.5	30	17.8		69.9		46.7	
0.1	30	21.3	98.1	98.4	131	96.6	
0.1	50	85.1		a		a	
0.1	75	142		220		a	
0.1	100	105	138	133	136	143	

 Table I
 The Degree of Grafting Under Various Conditions in Simultaneous Irradiation

^a Grafted too much and unsuitable for use as membranes.

conditions in simultaneous irradiation and the degree of grafting are given in Table I. The membranes grafted at a dose rate of 0.5 Mrad/h were brittle and unsuitable for use as membranes.

The membranes grafted at dose rates of 0.1 Mrad/h were not so brittle. For the PDMS membranes soaked in 30 or 100 wt % HDFNMA and irradiated at 0.1 Mrad/h, HDFNMA was grafted equally in the whole membrane, and the grafted PDMS membrane was semipermeable; while in 50 or 75 wt %, the membranes were grafted too much and were unsuitable for use as membranes.

The dependence of the degree of grafting and membrane thickness on irradiation time is shown in Figure 4. The degree of grafting and membrane thickness at a fixed HDFNMA content, and a dose



Figure 4 Dependence of the degree of grafting and membrane thickness on irradiation time: (\Box) membrane irradiated in 30 wt % HDFNMA at 0.5 Mrad/h, (\bigcirc) in 30 wt % at 0.1 Mrad/h, (\triangle) in 100 wt % at 0.1 Mrad/h, and (\diamond) in MeOH at 0.1 Mrad/h.

rate of irradiation was increased with increasing irradiation time.

When the irradiation time or irradiation strength increase, the crosslinking between interor intrachains of individual polymers can take place significantly, compared to the grafting reaction. The crosslinking reaction contributes to membrane performance. When the membranes were grafted at a dose rate of 1 Mrad/h, the crosslinking reaction took place significantly, and the grafted membranes were not swelled in the solvent. In this study, the effect of irradiation time and HDFNMA content on the crosslinking reaction and grafting reaction were investigated.

The extent of the crosslinking reactions is a function of the thickness and HDFNMA composition of a membrane and would be different between membranes with different membrane thicknesses or between the grafted PDMS and homo-poly(HDFNMA) membranes under a given reaction condition. In this study, the thicknesses of the membranes before graft polymerization were constant, and the effect of the HDFNMA composition was investigated. The homopolymer, poly(HDFNMA), polymerized at 0.1 Mrad/h, was dissolved in acetone. Poly(HDFNMA) polymerized of 30 wt % HDFNMA was dissolved in acetone completely, while poly(HDFNMA) polymerized of 100 wt % HDFNMA did not dissolve completely and became a gel. Poly(HDFNMA) polymerized of 100 wt % HDFNMA was crosslinked because the HDFNMA content was high, and the density of the radicals produced by irradiation was high. The results show that the grafted HDFNMA of 100 wt % HDFNMA was crosslinked.

The poly(HDFNMA) made of 30 wt % HDFNMA by irradiation was viscous and dissolved in acetone completely. The grafted HDFNMA of 30 wt % HDFNMA was not crosslinked. The relative



Figure 5 Dependence of viscosity of poly(HDFNMA) on irradiation time.

viscosity of poly(HDFNMA) polymerized of 30 wt % HDFNMA at 0.1 Mrad/h as a function of the irradiation time is shown in Figure 5. The viscosity was increased with irradiation time. The results showed that the degree of polymerization was increased with irradiation time.

Characterization of the Grafted PDMS Membrane

The FTIR–ATR of the grafted PDMS membranes is shown in Figure 6. After the PDMS was grafted with HDFNMA, a characteristic new peak was observed near 1150 and 740 cm⁻¹. The peaks are characteristic peaks of poly(HDFNMA). The intensity of these peaks was increased with the grafted amount.

Figure 7 shows the WAXD patterns of the grafted PDMS membrane. As reported by Nakamae,⁵⁴ the lower 2θ of the inner halo is assigned to the intersegmental distance of the polymer, and the larger 2θ of the outer halo is assigned to the intrasegmental distance of the polymer. The halo for PDMS was observed at $2\theta = 12$ and 21° . The halo for poly(HDFNMA) was observed at 2θ = 17 and 40° . Intersegmental and intrasegmental distances of poly(HDFNMA) were narrower than those for PDMS. For the grafted membrane, 2θ = 17 and 40° values of the halo were observed in addition to $2\theta = 12$ and 21° for PDMS, and the intensity of the halo for poly(HDFNMA) increased with an increasing degree of grafting. Furthermore, no new halo was observed for the grafted PDMS membranes. PDMS and poly(HDFNMA) existed individually in the grafted PDMS membranes. The semipermeable grafted PDMS membrane is considered to have a microphase-separated structure; that is, a separated structure of PDMS and grafted HDFNMA.⁵⁴ PDMS is a rubbery polymer, and it clearly has no crystalline structure based on the diffraction patterns. From the diffraction patterns of the region of poly-(HDFNMA), no crystalline structure was observed in the membrane. In the separation processes in nonporous membranes, it has been



Figure 6 FTIR-ATR spectra of PDMS membranes before and after graft polymerization of HDFNMA: membrane irradiated at (a) 0.1 Mrad/h for 5 h in 100 wt % HDFNMA and (b) for 1 h in 30 wt % HDFNMA; (c) PDMS.



Figure 7 Wide-angle X-ray diffraction patterns of PDMS and grafted PDMS membranes: membrane irradiated in 30 wt % HDFNMA at 0.1 Mrad/h for (a) 5, (b) 3, and (c) 1 h; (d) PDMS; (e) poly(HDFNMA).

found that both sorption and diffusion depend on the degree of crystallization. Gas and liquid can permeate the amorphous regions preferentially compared with the crystal regions.⁵⁵ Furthermore, the intersegmental and intrasegmental distances of the polymer also affect the permeability.⁴

The DSC curves of the grafted PDMS membranes are shown in Figure 8. For the membrane after grafting with HDFNMA, the endothermic peak of the internal friction energy between the macromolecular chains for PDMS was observed at -124° C. The peak for the homopolymer of HDFNMA polymerized by irradiation was not observed in the range of $-150-300^{\circ}$ C.

Figure 9 shows the correlation between the internal friction energy for the macromolecular chains (J/g) at -124°C and the degree of grafting for the grafted PDMS membranes.

The internal friction energy between molecular chains (J/g) for the grafted PDMS membranes was decreased with increasing degree of grafting.

The peak of the internal friction energy between the macromolecular chains (J/g) for the grafted PDMS membranes was obtained at the same temperature for PDMS; hence, it is considered that the grafted PDMS membranes have the microphase-separated structure of PDMS and grafted HDFNMA.⁵⁶

The linear relationship between the internal friction energy between macromolecular chains (J/g) and the degree of grafting is better for membranes soaked in 100 wt % HDFNMA and irradiated at 0.1 Mrad/h. Because the quantity of PDMS in a unit volume of the grafted PDMS membranes, which was soaked in 100 wt % HDFNMA and irradiated at 0.1 Mrad/h, is constant, the internal friction energy between macromolecular chains for the membranes irradiated in 100 wt % HDFNMA was in inverse proportion to the degree of grafting. The poly-(HDFNMA) regions in the membranes soaked in 100 wt % HDFNMA and irradiated at 0.1 Mrad/h were dispersed quite homogeneously.

The surface morphologies of the grafted PDMS membranes were analyzed by X-ray photoelectron



Figure 8 DSC curve of PDMS and grafted PDMS membranes: membrane irradiated at (a) 0.1 Mrad/h for 5 h in 100 wt % HDFNMA and (b) for 1 h in 30 wt % HDFNMA; (c) PDMS; (d) poly(HDFNMA).



Figure 9 Dependence of the internal friction energy between molecular chains on the degree of grafting of the grafted PDMS membranes: membrane irradiated (\Box) in 30 wt % HDFNMA at 0.5 Mrad/h, (\diamond) in 30 wt % at 0.1 Mrad/h, and (\bigcirc) in 100 wt % at 0.1 Mrad/h.

spectroscopy (XPS) spectra. The XPS spectra are shown in Figure 10. By grafting with HDFNMA, the fluorine atom was detected, and the binding energy shift associated with the structure of fluorinated (CF, CF₂) and carbonyl (C=O) carbon species was shown.^{57,58} The ratios of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for a few nm beneath the surface on the grafted PDMS membrane at 30 and 90° photoelectron emission angles and are characterized in Table II. In these spectra, the composition of the atoms was determined up to 4.5 and 9 nm deep below the surface at photoelectron emission angles of 30° and 90°, respectively.⁵⁹ The ratios of fluorine and carbon on the grafted PDMS membranes were increased due to the introduction of HDFNMA by irradiation. The degree of grafting of the membrane, soaked in 100 wt % HDFNMA and irradiated at dose rates of 1 Mrad/h for 5 h, was 143 wt %, and the thickness increased about 1.3 times. According to the observation of silicon atoms on the grafted PDMS membrane surface, it is considered that the poly(HDFNMA) domains were dispersed in the entire PDMS membrane homogeneously by irradiation.

The degree of grafting of the grafted PDMS membrane was more than 100 wt %, while the degree of sorption of HDFNMA into PDMS membrane was 13 wt %. As a result, the following is considered. First, the graft polymerization starts with 1 region in the PDMS membrane. HDFNMA was then grafted more frequently on the poly(HDFNMA) domain than the PDMS domain due to the affinity of HDFNMA for poly(HDFNMA). The grafting on the poly(HDFNMA) region was promoted to extend the volume of PDMS, and, in turn, the grafted PDMS membrane had a microphase-separated structure.

The ratio of the fluorine atom at 30° was almost the same as that at 90° on the surface of the membrane. The ratio of the fluorine atom by the XPS spectra corresponded to that calculated by the degree of grafting. For the structure of the grafted PDMS membrane, a layer of poly(HDFNMA) was not formed on the surface of the PDMS membrane. The poly(HDFNMA) domains were dispersed into the entire PDMS membrane homogeneously by irradiation.

The domains of poly(HDFNMA) in the grafted PDMS membranes had a particle size that scattered natural light, and the domains were dispersed homogeneously, as expected.



Figure 10 XPS spectra of PDMS and grafted PDMS membranes: membrane irradiated in 100 wt % HDFNMA at 0.1 Mrad/h for (a) 5, (b) 3, and (c) 1 h; (d) PDMS.

HDFNMA in MeOH (wt %)	Irradiation Time (h) ^a	Electron Emission Angle (°)	Atomic Ratio ^b				
			F/Si	O/Si	C/Si	F/Si Calculated by Degree of Grafting	
100	1	30	2.71	1.41	2.82	2.50	
		90	1.61	1.50	2.72		
100	3	30	3.29	1.40	2.96	3.15	
		90	3.50	1.59	3.21		
100	5	30	5.54	1.41	3.61	3.39	
		90	5.62	1.83	4.07		
0	5	30	c	1.19	1.75		
		90	c	1.37	1.85		
PDMS		90	c	1.44	1.87		

 Table II
 Fluorine-to-Silicon, Oxygen-to-Silicon, and Carbon-to-Silicon Atomic Ratios

 for the Surface of PDMS and Grafted PDMS Membranes by XPS Analysis

^a Dose rate of irradiation was 0.1 Mrad/h.

^b F/Si is the fluorine atomic ratio (%) to silicon atomic ratio (%); O/Si is the oxygen atomic ratio (%) to silicon atomic ratio (%); C/Si is the carbon atomic ratio (%) to silicon atomic ratio (%).

° Not detected.

Pervaporation of Grafted PDMS Membrane

Figure 11 shows the effect of the irradiation time on the flux and the separation factor for TCE solution in pervaporation through a PDMS membrane irradiated in MeOH. The pervaporation of a PDMS membrane irradiated in MeOH was sub-



Figure 11 Effect of irradiation time on the flux and separation factor (α_{pv}) of TCE–water mixtures in pervaporation through irradiated PDMS membrane at 25°C: (\Box) 0.01 wt % and (\diamond) 0.025 wt % feed concentration.

stantially affected by irradiation. The effect of irradiation on the permeability of the PDMS membrane to gases was investigated by M. Minoura et al.⁶⁰ The results suggested that no remarkable difference except for crosslinking in the chemical structure between the unirradiated samples and irradiated samples could be seen, but the effects of irradiation on the transport of gases through the PDMS membranes were negligibly small.

In this study of pervaporation through irradiated PDMS, almost the same results were obtained.

Figure 12 shows the effect of the irradiation time on the flux and the separation factor for TCE solution in pervaporation through a PDMS membrane irradiated in 30 and 100 wt % HDFNMA/MeOH. The flux of the grafted PDMS in 30 wt % HDFNMA membranes was increased with increasing irradiation time, and the separation factor was decreased with increasing irradiation time. The degree of grafting and membrane thickness was increased by irradiation. The poly(HDFNMA) region was increased and grown by graft polymerization to extend the volume of PDMS so that the flux of the grafted PDMS membranes was increased. The flux of the PDMS membrane grafted PDMS in 100 wt % HDFNMA was constant with increasing irradiation time, and the separation factor was increased with increasing irradiation time. By measurements of the ATR spectra of the grafted PDMS membranes,



Figure 12 Effect of irradiation time on the flux and separation factor (α_{pv}) of TCE–water mixtures in pervaporation through grafted PDMS membranes at 25°C: (\bigcirc) 0.025 wt % feed concentration through membrane irradiated at 0.1 Mrad/h in 30 wt % HDFNMA; (\triangle) 0.025 wt % feed concentration through membrane irradiated at 0.1 Mrad/h in 100 wt % HDFNMA.

no characteristic peak of crosslinking between inter- or intrachains of individual polymers was observed. However, the homo-poly(HDFNMA), polymerized of 100 wt % HDFNMA at 0.1 Mrad/h, was not dissolved in the solvent and became a gel. The crosslinking reactions affect both the sorption and permeation behavior. The more the crosslinking occurs, the less the permeants are sorbed into the membrane, and the slower they permeate through the membrane. The flux of the membranes grafted and crosslinked in 100 wt % HDFNMA was lower than that of the membranes grafted in 30 wt %. The grafted amount, the degree of crosslinking, and the permselectivity of the membrane grafted in 100 wt % HDFNMA was increased with increasing irradiation time.

The flux as a function of the TCE concentration in the feed solution is shown in Figure 13. For the PDMS and the membranes irradiated in MeOH, the flux was almost constant with increasing feed concentration. For the membranes grafted with HDFNMA, the flux was decreased with feed concentration.

The water flux and TCE flux as a function of the TCE concentration in the feed solution are shown in Figure 14 for the grafted PDMS membranes.

For the PDMS membrane irradiated in 100 wt % HDFNMA for 1 h, the water flux was almost

constant with increasing feed concentration, and for the more grafted PDMS membrane, especially that was irradiated in 100 wt % HDFNMA for 5 h, the water flux was still further decreased with an increase in the feed concentration.

For all the membranes, the TCE flux was increased with an increase in the feed concentration; and especially for the membrane irradiated in 100 wt % HDFNMA for 5 h, the tendency was significant.

In the previous study,²⁶ for the membranes modified using HDFNMA by UV irradiation, the flux was decreased with an increase in the feed concentration. Due to the introduction of the hydrophobic polymer, HDFNMA, the TCE quantity sorbed into the membrane was so high that the diffusion of water was prevented; in turn, the flux was decreased. In this study, similar phenomena were observed.

The relationships between the TCE concentration in the feed and permeate are shown in Figure 15. For all the membranes, the TCE concentration in the permeate was increased with an increase in the feed concentration; especially when the membranes were irradiated in 100 wt % HDFNMA for 5 h, the increase was significant.

The separation factor α_{pv} , as a function of the TCE concentration in the feed solution, is shown in Figure 16. α_{pv} was increased significantly with



Figure 13 Effect of feed concentration on flux for TCE-water mixtures in pervaporation through grafted PDMS membranes at 25°C: (\bigcirc) membrane irradiated in 100 wt % HDFNMA at 0.1 Mrad/h for 5 h; (\bigcirc) in MeOH at 0.1 Mrad/h for 5 h; (\bigcirc) PDMS.



Figure 14 Effect of feed concentration on flux for TCE-water mixtures in pervaporation through grafted PDMS membranes at 25°C: membrane irradiated in 100 wt % HDFNMA at 0.1 Mrad/h for (\bigcirc) 1, (\diamondsuit) 3, and (\Box) 5 h.

increasing feed concentration for the membrane irradiated in 100 wt % HDFNMA for 5 h.

In the grafted PDMS membrane, the best separation performance was shown due to the introduction of the hydrophobic polymer, poly(HDFNMA).

Pervaporation of Poly(HDFNMA) Membrane

The solution of poly(HDFNMA), a homopolymer polymerized at 30 wt % at 0.1 Mrad/h for 5 h, was cast. The membrane of poly(HDFNMA) polymerized for 5 h, a membrane with a thickness of 270 μ m, was used for pervaporation.

The flux as a function of the TCE concentration in the feed solution is shown in Figure 17. The total and water flux were almost constant with an increase in the feed concentration. TCE flux was increased with increasing feed concentration, and the rate was restrained at a high feed concentration.

The thickness of the poly(HDFNMA) membrane was 270 μ m, around five times as thick as grafted PDMS and PDMS membranes. The volume of the flux through the poly(HDFNMA) membrane was below 1 to 30 times the volume of the



Figure 15 Relationship between TCE concentration in feed and permeation in pervaporation through grafted PDMS membranes at 25°C: membrane irradiated in (\bigcirc) 100 wt % HDFNMA at 0.1 Mrad/h for 5 h and (\diamondsuit) in MeOH at 0.1 Mrad/h for 5 h; (\Box) PDMS.

flux through the grafted PDMS and PDMS membranes. The flux was inversely proportional to the membrane thickness.⁶¹ It is predicted that the flux of the poly(HDFNMA) membrane is one-fifth of the flux through the grafted PDMS and PDMS



Figure 16 Effect of feed concentration on separation factor (α_{pv}) in pervaporation through grafted PDMS membranes at 25°C: membrane irradiated in (\diamond) 100 wt % HDFNMA at 0.1 Mrad/h for 5 h and (\bigcirc) in MeOH at 0.1 Mrad/h for 5 h; (\Box) PDMS.



Figure 17 Effect of feed concentration on flux for TCE-water mixtures in pervaporation through poly-(HDFNMA) membranes at 25°C: (\Box) total flux; (\bigcirc) water flux; (\triangle) TCE flux.

membranes if the poly(HDFNMA) membrane had the same permeability as the grafted PDMS membranes. As we mentioned in the previous report, the intersegmental and intrasegmental distances in poly(HDFNMA) were narrower than those in PDMS. Hence, it is considered that the diffusion of the permeates was decreased, and a low flux was obtained for the poly(HDFNMA).

The diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. In the poly(HDFNMA) with low permeability to permeates, the TCE-permselectivity was restrained.

Miyata et al.^{52,53} reported the characteristics of permeation and separation for aqueous ethanol solutions through methyl methacrylate (MMA) dimethylsiloxane (DMS) copolymer membranes with microphase separation. They mentioned that, due to the high solubility and good diffusivity of ethanol molecules in the PDMS phase of the rubber state, the PDMS phase transports ethanol better than water.

Furthermore, the mass transport takes place solely in the amorphous polymer phase, not at all in the crystalline phase, and only part of the interface area is available for permeation in the semicrystalline phases.⁵⁵

The grafted PDMS membrane had a microphase-separated structure, that is, a separated structure of PDMS and graft-polymerized HD-FNMA. The permselectivity of TCE was high due to the introduction of the hydrophobic polymer, poly(HDFNMA). The permeation mechanism for the grafted PDMS membranes is shown in Figure 18.

For the pervaporation performance of the HDFNMA-grafted PDMS membrane, the following was considered. The permeability of the PDMS phase was significantly great, and that of the poly(HDFNMA) phase was too low to affect the total permeation directly. However, in the permeation at the interface of poly(HDFNMA) and PDMS, it played an important role in that poly(HDFNMA) had a much stronger affinity for TCE than for water.

Sorption of Grafted PDMS Membranes

The isotherms of sorption for grafted PDMS membranes are presented in Figure 19. Below 1 wt % TCE solution, the degree of swelling of the PDMS membrane with a thickness of 50 μ m was less than 1 wt %, too small a quantity of solution in the membrane to determine the composition. Hence, a PDMS membrane with a thickness of 200 μ m was used in this sorption measurement.



🔜 :PDMS, 🔇 (Grafted poly(HDFNMA)

Figure 18 Tentative illustration of the permeation through the grafted PDMS membrane for the TCE–water mixture.



Figure 19 Sorption of TCE on grafted PDMS membranes as a function of the feed concentration at equilibrium: membrane irradiated (\diamond) in 100 wt % HD-FNMA at 0.1 Mrad/h for 5 h and (\bigcirc) in MeOH at 0.1 Mrad/h for 5 h, (\times) PDMS, 50 μ m; (\Box) PDMS, 200 μ m.

For the PDMS membrane irradiated in MeOH and PDMS, straight lines can be fitted to the sorption isotherms. For the grafted PDMS membranes, the concentration of TCE solution soaked in the membrane was increased significantly with increasing feed concentration. It is effective for TCE sorption into the membrane to introduce the hydrophobic polymer, poly(HDFNMA). The membrane that had a high sorption selectivity for TCE showed great separation performance.

Diffusion of the Grafted Membrane

The relationship between the separation factor in permeation (α_{pv}) , the separation factor in sorp-

tion (α_s) , and the apparent separation factor in diffusion (α_D) is given by the following:

$$\alpha_{pv} = \alpha_s \cdot \alpha_D \tag{7}$$

 α_D can be described in eq. (8) using eqs. (4) and (6).

$$\alpha_D = \{Y(1 - Y')\} / \{(1 - Y)Y'\}$$
(8)

where Y and Y' denote the concentration of TCE in the permeate solution and the swollen membranes under the same feed solution, respectively.

 α_{pv} , α_s , and α_D are shown in Table III. α_D values calculated by eq. (6) using the sorption isotherms in Figure 19 and the pervaporation in Figure 15 as a function of the TCE concentration in the feed solution are shown in Figure 20.

The results show that α_D of the grafted PDMS membrane was significantly increased with increasing feed concentration.

The permeation of TCE and water molecules in pervaporation through the grafted PDMS membranes is concluded to be as follows. The mass transport takes place significantly in the PDMS phase. At the interface of poly(HDFNMA) and PDMS, a high solubility performance of TCE molecules was shown.

At a low feed concentration of TCE solution, the diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. At a high concentration of TCE solution, TCE was sufficiently sorbed into the membrane. The diffusion of water was prevented by the TCE molecules, and, in turn, the permselectivity of TCE was significantly increased.

In this study, the PDMS membranes were improved with graft polymerization of HDFNMA. The permeability of the PDMS phase was signif-

	Sorption Data			Pervaporation Data			
Membrane	TCE in Feed (wt %)	TCE in Membrane (wt %)	$\begin{array}{c} \text{Separation} \\ \text{Factor} \\ (\alpha_s) \end{array}$	TCE in Feed (wt %)	TCE in Membrane (wt %)	$\begin{array}{c} \text{Separation} \\ \text{Factor} \\ (\alpha_{pv}) \end{array}$	$\begin{array}{c} \text{Separation} \\ \text{Factor} \\ (\alpha_D) \end{array}$
PDMS irradiated							
wt % at 0.1	0.0123	19.9	2010	0.0104	6.63	684	0.340
Mrad/h for 5 h	0.0280	40.9	2470	0.0265	37.4	2250	0.912
PDMS	0.0131	6.90	564	0.0102	4.83	496	0.879
	0.0282	13.2	538	0.0263	9.55	402	0.747



Figure 20 Effect of feed concentration on the separation factor (α_D) in pervaporation through PDMS and grafted PDMS membrane at 25°C: (–) membrane irradiated in 100 wt % HDFNMA at 0.1 Mrad/h for 5 h; (---) PDMS.

icantly great, and that of the poly(HDFNMA) phase was too low to affect the whole permeation of the grafted PDMS membrane directly. However, in the permeation, at the interface of poly-(HDFNMA) and PDMS, poly(HDFNMA) showed excellent solubility performance for TCE. In order to enhance the selectivity of a rubber polymer membrane that has a high permeability, such as PDMS, it is effective to introduce a material that has a high solubility.

CONCLUSIONS

It is desirable to enhance the selectivity of PDMS for chlorinated hydrocarbons. In this study, we improved the PDMS membrane with graft polymerization of HDFNMA, which has the effect of increasing the selectivity for chlorinated hydrocarbons, by a ⁶⁰Co source and characterized the grafted PDMS membrane. Simultaneous irradiation is a method in which the monomer and polymer are irradiated simultaneously. PDMS is a rubbery polymer, and the preservation of radicals is difficult. In this study, simultaneous irradiation was studied.

The grafted PDMS membranes had a microphase-separated structure, that is, a separated structure of PDMS and grafted HDFNMA. For the graft polymerization, the following is considered. First, the graft polymerization starts with 1 region in the PDMS membrane. More HDFNMA was then grafted on the poly(HDFNMA) domain than on the PDMS domain due to the affinity of HDFNMA for poly(HDFNMA). The grafting on the poly(HDFNMA) region was promoted to extend the volume of PDMS, and, in turn, the grafted PDMS membrane has a microphase-separated structure.

The poly(HDFNMA) domains were dispersed into the entire PDMS membrane homogeneously by irradiation.

For the membranes soaked in 100 wt % HDFNMA and irradiated at 0.1 Mrad/h, the poly-(HDFNMA) domains were dispersed quite homogeneously.

In the grafted PDMS membranes, the best separation performance was shown with the introduction of the hydrophobic polymer, poly(HDFNMA).

The concentration of TCE sorbed into the membrane was high due to the introduction of the hydrophobic polymer, poly(HDFNMA). The membrane that had a high solubility selectivity for TCE showed great separation performance.

The permeability of the PDMS phase was significantly great, and that of the poly(HDFNMA) phase was too low to affect the whole permeation of the grafted PDMS membrane directly. However, in permeation on the surface of poly(HDFNMA) and PDMS, it played important role in that poly(HDFNMA) had a much stronger affinity for TCE than for water.

At a low feed concentration of TCE solution, the diffusivity of TCE molecules must be much lower than that of water due to the larger molecular size of TCE. At a high concentration of TCE solution, TCE was sufficiently sorbed into the membrane so that the diffusion of water was prevented by the TCE molecules; in turn, the permselectivity of TCE was increased significantly.

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