

Characterization for Graft Polymerization of Alkyl Methacrylate onto Polydimethylsiloxane Membranes by Electron Beam and Their Permselectivity for Volatile Organic Compounds

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ABSTRACT: Polydimethylsiloxane (PDMS) membranes were improved by graft polymerization of fluoroalkyl methacrylates (FALMA) and alkyl methacrylates (AMA) by electron beam, and the effect of the solubility and diffusibility of a monomer on graft polymerization and the pervaporation through grafted membrane were investigated. The difference of the grafted amount was small for the monomers with various solubility parameters and $\log P_{ow}$ which is the logarithm of the octanol–water partition coefficient. Compared to each other in the same group of FALMA or AMA, the sorpted and grafted amount for a monomer that has low molecular volume was high, and the sorpted and grafted amount for a monomer that has high molecular volume was low. FALMA-grafted PDMS membranes showed high separation performance compared to PDMS membranes. Among them, 2,2,3,3,3-pentafluoropropyl methacrylate grafted PDMS membrane, which had a high grafted amount, and F/Si calculated by the grafted amount had high selectivity for trichloroethylene (TCE). The FALMA-grafted PDMS membranes that had the high TCE concentrations in the sorbed solution exhibited high permselectivity for TCE. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 203–213, 2001

Key words: graft polymerization by electron beam; polydimethylsiloxane membrane; fluoroalkylmethacrylate; pervaporation; volatile organic carbon

INTRODUCTION

Recently, the contamination of ground water and soil by volatile organic compounds (VOCs) has become a social problem. Their toxicity has been clear for several years. Several processes—i.e., aeration, adsorption on activated carbon, photolysis, and ozonization—have been proposed for the removal of VOCs from contaminated groundwater and wastewater.^{1,2} Pervaporation is attractive and potentially cost competitive compared to

these methods. The pervaporation of VOCs/water solution using organophilic polymers has been studied.^{3–24}

The polydimethylsiloxane (PDMS) membrane has been the most widely used and studied material to perform VOCs extraction because of its high permeability, ease of preparation into several shapes, and relatively slight thickness.^{10,11,25–27} To obtain the more useful membrane keeping the properties of the PDMS membrane, the synthesis of copolymers of PDMS and their improvement by the incorporation of fillers such as silicates and zeolites have been expected and studied.^{15,19} Fluorinated polymers are recognized as the practical membrane materials just

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like PDMS and have been studied as organic compounds by their hydrophobicity based on low surface energy.^{18,28–30} It is interesting to synthesize a more useful membrane material by combining the PDMS and fluorinated polymer. But the affinity of PDMS to fluorinated polymer is low. Graft polymerization is a useful method to combine the polymeric materials with incompatible chemical and physical properties. Graft polymerization can be achieved by ionizing radiation, γ -ray, electron beam, ultraviolet light, and plasma irradiation, and several papers have been reported on grafting.^{31–60} Electron beam has high energy and is able to effectively graft polymerize in quantity.^{31,32,38,39,47,48,51} The growth of the graft chain by polymerization started with reactive radicals caused in the membrane.^{31,32} Generally, the vinyl monomer has been used in graft polymerization. Preirradiation and simultaneous irradiation have been known as the method of radiation-induced graft polymerization.^{31,32} Preirradiation is a method in which a monomer is reacted with a polymer that had been irradiated in advance.^{41,42} In simultaneous irradiation, the monomer and polymer are irradiated simultaneously.^{31,32} We studied improving PDMS membranes by graft polymerization of fluoroalkylmethacrylates (FALMA) to enhance the affinity of PDMS to VOCs.^{3–5,7} These grafted membranes increased the selectivity for VOCs and showed effective separation performance.

The solubility and diffusibility of the monomer for the membrane are important for the preirradiation method. The solubility is affected by the chemical affinity of the monomer for the membrane. Also, the molecular volume is closely concerned with the diffusibility of organic compounds. Hence, for the preirradiation method, the solubility parameter, the octanol–water partition coefficient (P_{ow}), and the molecular volume are important. The solubility parameter (δ) by Hansen⁶¹ can be described as

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

$$\delta_d = (\Delta E_d/V)^{1/2} \quad (1a)$$

$$\delta_p = (\Delta E_p/V)^{1/2} \quad (1b)$$

$$\delta_h = (\Delta E_h/V)^{1/2} \quad (1c)$$

where δ_d , δ_p , and δ_h represent the solubility parameter of dispersion, polarization, and hydrogen bonding, and $\Delta E_d/V$, $\Delta E_p/V$, and $\Delta E_h/V$ repre-

sent the energy density of dispersion, polarization, and hydrogen bonding, respectively. Total heat of mixing of solvent and polymer (ΔH_m) is described using the solubility parameter as follows⁶¹:

$$\Delta H_m = V_m \cdot (\delta_{\text{solvent}} - \delta_{\text{polymer}})^2 \cdot \phi_{\text{solvent}} \cdot \phi_{\text{polymer}} \quad (2)$$

where V_m and ϕ represent the total molecular volume of the polymer solution and the volume fraction in the polymer solution, respectively. When ΔH_m is lower, that is, the difference of δ_{solvent} and δ_{polymer} is smaller, solvent and polymer are mixed more homogeneously. The hydrophobicity is used to indicate the physical property of the molecule that governs its partitioning into the nonaqueous partner of an immiscible or partially immiscible solvent pair.⁶² According to Nernst,⁶² the partition coefficient can be simply described as

$$P = C_o/C_w \text{ or } \log P = \log C_o - \log C_w \quad (3)$$

where C_o and C_w represent molar concentrations of the partitioned compound in the organic and aqueous phase, respectively. The octanol–water partition coefficient (P_{ow}) has been generally used in expressing hydrophobicity.^{62,63} In hydrophobicity, P_{ow} is closely concerned with the solubility of organic compounds.^{62,63}

In this study, we grafted PDMS membranes with FALMA and alkylmethacrylates (AMA) by the electron beam preirradiation method. We then investigated the effect of solubility and diffusibility of the monomer on graft polymerization and applied the grafted membrane to pervaporation.

EXPERIMENTAL

Materials

Commercial PDMS membranes (Fuji Systems Corporation), 50 μm thick, were used throughout this work. 2,2,3,3,3-pentafluoropropyl methacrylate (PFPMA), 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA), 2-(perfluorobutyl)ethyl methacrylate (PFBEMA), 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA) (Daikin Fine Chemical Laboratory Corporation), butyl methacrylate (BMA), and hexyl methacrylate (HMA) (Special grade, Tokyo Kasei Kogyo, Ltd.) were used as received to avoid homopolymerization. Trichloroethylene (TCE), 2-propanol, and acetone (Special grade,

Waco Pure Chemical Industries, Ltd.) were used as received. The abbreviation and physico-chemical properties of FALMA and AMA used in this study are given in Table I.

Graft Polymerization by Electron Beam

The graft polymerization was performed as reported by Ishigaki et al.^{47,48} The schematic diagram of the apparatus is shown in Figure 1.

Preirradiation

A PDMS membrane of 7×7 cm evacuated in advance was placed in a polyethylene bag under nitrogen. The bag was then placed on dry ice and irradiated by an electron beam of a total dose of 150 kGy. The membranes were then placed in contact with degassed FALMA or AMA monomer in the liquid phase under vacuum. After the polymerization was ended, the membranes were rinsed in acetone overnight to remove the homopolymers and the nonreacted monomers and dried for 48 h in an evacuated vessel.

Simultaneous Irradiation

A PDMS membrane of 7×7 cm and a FALMA or AMA monomer were simultaneously degassed. After reaching equilibrium, the membrane was taken off the monomer, the excess solution on the surfaces was wiped off with a filter paper and placed in a polyethylene bag under nitrogen. The membrane was then grafted by the same method as preirradiation. The degree of grafting was calculated as

$$\text{Degree of graft (\%)} = (W_1 - W_0)/W_0 \times 100 \quad (4)$$

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

Characterization of the Grafted PDMS Membrane

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an IPS-9000SX (JEOL, Ltd.) with $\text{MgK}\alpha$ 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 in a previous study^{3-5,7} using the continuous-feed

Table I Composition and Properties of Various FALMA and AMA Used in this Study

Compound	Abbreviation	Formula	M_w	bp
2,2,3,3,3-Pentafluoropropyl methacrylate	FALMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CF}_2\text{CF}_3$	218.11	55°C/100 mmHg
2,2,3,3,4,4-Hexafluorobutyl methacrylate	PFPMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CF}_2\text{CHF}_2\text{CF}_3$	250.13	74°C/100 mmHg
2-(Perfluorobutyl)ethyl methacrylate	HFBMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2(\text{CF}_2)_3\text{CF}_3$	332.15	61°C/5 mmHg
1H,1H,9H-Hexadecafluorononyl methacrylate	PFBEMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2(\text{CF}_2)_8\text{H}$	500.16	112°C/7 mmHg
	HDFNMA			
	AMA			
Butyl methacrylate	BMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{CH}_3$	142.20	164°C
Hexyl methacrylate	HMA	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_5\text{CH}_3$	170.25	70°C/5 mmHg

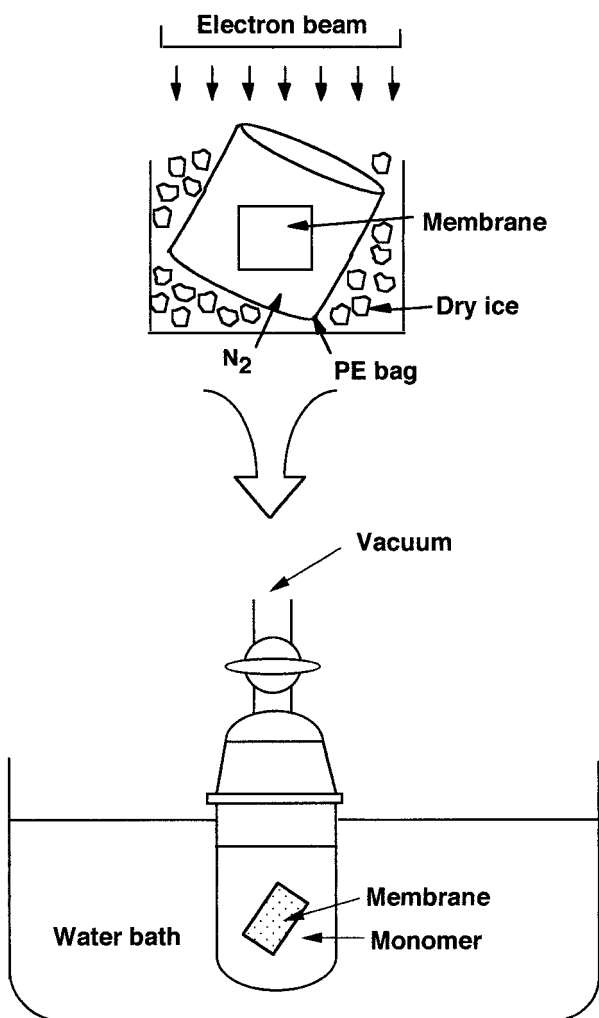


Figure 1 Apparatus for the graft polymerization by electron beam.

type at 25°C. The feed solution was circulated through the cell and the feed tank. The grafted surface of the membrane was kept in touch with the feed solution in the cell. The effective membrane area in the cell was 19.6 cm². The pressure on the permeation side was kept below 10 Torr by vacuum pumps. 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 of solution, total flux (J), was obtained using eq. (5),

$$J = Q/At \quad (5)$$

where Q is the amount that permeated during the experimental time interval t and A is the effective surface area. The TCE and water flux were cal-

culated from the total flux, which is the permeation rate of solution (J) and the permeate composition.

The concentration of TCE in the feed and permeate solution was determined by gas chromatography using a flame ionization detector. The TCE 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 TCE concentration. The separation factor during pervaporation α_{pv} was calculated as

$$\alpha_{pv} = \{Y(1 - X)\}/\{(1 - Y)X\} \quad (6)$$

where X and Y denote the concentrations of TCE in the feed and permeate solutions, respectively, and their concentration unit is weight percent (wt %).

Sorption Measurement

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

$$\text{Degree of sorption (\%)} = (W_3 - W_2)/W_2 \times 100 \quad (7)$$

where W_2 and W_3 denote the weights of the dried membrane and the swollen membrane, respectively.

The concentration of the TCE solution soaked into the membrane was determined using the apparatus shown in Figure 2. Upon reaching equilibrium, the membrane was removed from the vessel, quickly wiped with filter paper, and placed in cold trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, valve B was closed, and the TCE solution soaked in the membrane was vaporized by heating with a drier and collected in cold trap C.

The concentration of TCE solution in the feed and the soaked membrane was determined by gas chromatography, the same as in the pervaporation experiment. The separation factor during sorption α_s was calculated as

$$\alpha_s = \{Y'(1 - X)\}/\{(1 - Y')X\} \quad (8)$$

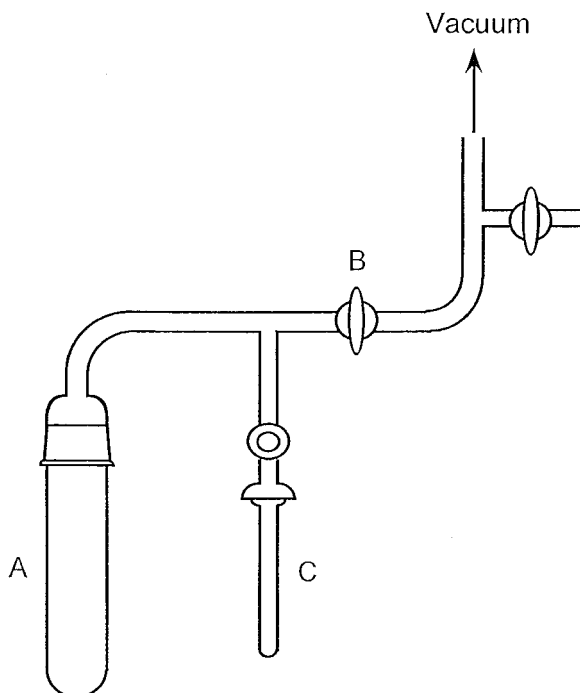


Figure 2 Apparatus for the composition measurement in the membrane: (A) cold trap for membrane, (B) valve, and (C) cold trap for collecting samples.

where X and Y' denote the concentrations of TCE in the feed solution and the swollen membranes, respectively, and their concentration unit is weight percent (wt %).

RESULTS AND DISCUSSION

Graft Polymerization by Electron Beam

Dependence of the degree of grafting on polymerization time (i.e. immersion time) for the HDFNMA-grafted PDMS membrane by preirradiation is shown in Figure 3. The degree of grafting was increased with increasing polymerization time and achieved equilibrium in 2 h. Therefore, the polymerization time was determined to be 2 h. The degree of grafting obtained was around 4.4 wt % for HDFNMA. The degree of sorption for PDMS with HDFNMA is 12.6 wt %. The grafted amount of HDFNMA was less than the sorpted amount. One part of the HDFNMA sorpted into the PDMS membrane was grafted onto the PDMS membrane.

Characterization of the Grafted PDMS Membrane

The surface morphologies of the grafted membranes were analyzed by XPS spectra. The ratios

of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for a few nm beneath the surface on the grafted membrane at 30° and 90° photoelectron emission angle and characterized in Table II. In this spectra, the composition of the atoms is determined up to 4.5- and 9-nm depth from the surface at the photoelectron emission angle of 30° and 90°, respectively.⁶⁴ As the ratio of the fluorine atom calculated by the degree of grafting increased, the ratio of the fluorine atom by XPS increased at the surface. The F/Si ratio on the reverse side of the grafted PDMS membranes was lower than the F/Si on the grafted surface by preirradiation. After the irradiation, the degassed FALMA was placed in the reactor, and the PDMS membranes were soaked and grafted. The graft polymerization was promoted in the grafted PDMS membrane.⁶⁴ The quantity of the radicals on the inside and reverse side of the grafted PDMS membrane was lower than that on the surface. Hence, the degree of grafting on the inside and reverse side of the grafted PDMS membrane was lower than that on the surface. By a simultaneous irradiation method that irradiates a membrane swollen by a monomer, the F/Si ratio on the reverse side of the grafted PDMS membranes was not so low compared to the F/Si on the grafted surface.

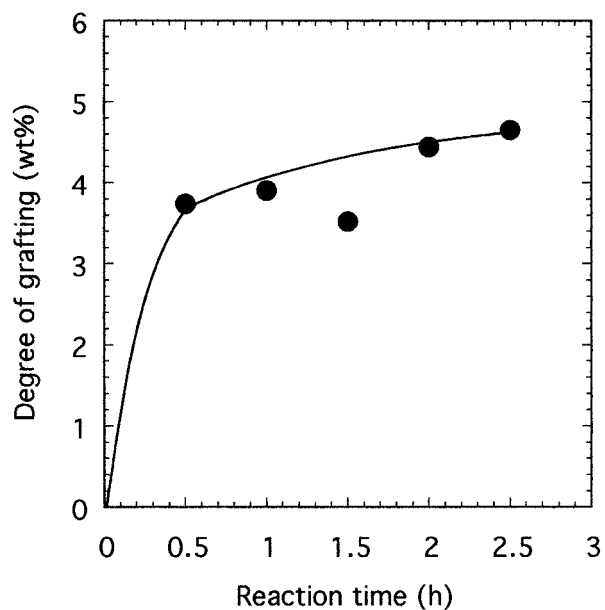


Figure 3 Dependence of the degree of grafting on polymerization time for HDFNMA-grafted PDMS membrane by preirradiation.

Table II Fluorine to Silicon Atomic Ratio for Surface of PDMS and Grafted PDMS Membranes by XPS Analysis

Grafted Membranes	Electron Emission Angle (°)	F/Si by XPS	Degree of Grafting (wt %)	F/Si Calculated by Degree of Grafting
PFPMA-grafted-PDMS (preirradiation)	30	0.463	10.1	0.1716
	90	0.456		
HFBMA-grafted-PDMS (preirradiation)	30	0.0567	5.6	0.09957
	90	0.0107		
PFBEMA-grafted-PDMS (preirradiation)	30	0.0703	5.9	0.1185
	90	0.113		
HDFNMA-grafted-PDMS (preirradiation) (Reverse side)	30	0.226	4.4	0.1067
	90	0.347		
	30	0.106		
	90	0.142		
HDFNMA-grafted-PDMS (simultaneous irradiation) (Reverse side)	30	0.355	4.5	0.1091
	90	0.260		
	30	0.381		
	90	0.167		

The Diffusibility of FALMA and AMA Through the PDMS Membrane in Graft Polymerization by Electron Beam

We investigated the effect of solubility and diffusibility of the monomer on graft polymerization according to solubility parameter, octanol–water partition coefficient (P_{ow}) and the molecular volume of the monomer.

The sorption amount and grafted amount are shown in Table III. The sorption amount of AMA in the PDMS membrane was 10 times as much as the sorpted FALMA amount. The grafted amount of AMA was about the same as the grafted FALMA amount. The grafted amount/sorpted amount for each FALMA and AMA is shown in Figure 4. Around 33% of FALMA sorpted in PDMS membrane was grafted, and around 2% of

AMA sorpted in PDMS membrane was grafted. The ratio of the grafted amount to the sorpted amount of monomer in the same group of FALMA or AMA was almost the same. The relationships between the solubility parameter and the grafted amount or sorpted amount are shown in Figure 5. The solubility parameter of PDMS is 15.11, low value compared to FALMA and AMA. The sorpted amount for AMA that has a high solubility parameter was high. The sorpted amount for FALMA that has a low solubility parameter was low. The difference of δ_{FALMA} and δ_{PDMS} is small, but the sorpted FALMA amount in PDMS membrane was low. The grafted amount was not so affected by the difference in the solubility parameter. The relationships between the $\log P_{ow}$ and grafted amount or sorpted amount are shown in

Table III Sorption and Solubility Data of Various FALMAs and AMAs for PDMS Membrane

Compound	Degree of Sorption in PDMS Membrane (mol/PDMS-100 g)	Degree of Grafting in PDMS Membrane (mol/PDMS-100 g)	Molecular Volume (cm ³ /mol)	Solubility Parameter ([J/m ³] ^{1/2} 10 ⁻³)	$\log P_{ow}$
PFPMA	0.152	0.046	170	16.18	2.74
HFBMA	0.062	0.022	187	16.70	2.82
PFBEMA	0.055	0.018	240	15.84	2.84
HDFNMA	0.025	0.0089	325	16.25	3.61
BMA	0.840	0.017	158	18.04	2.88
HMA	0.649	0.013	193	17.95	3.75
PDMS				15.11	

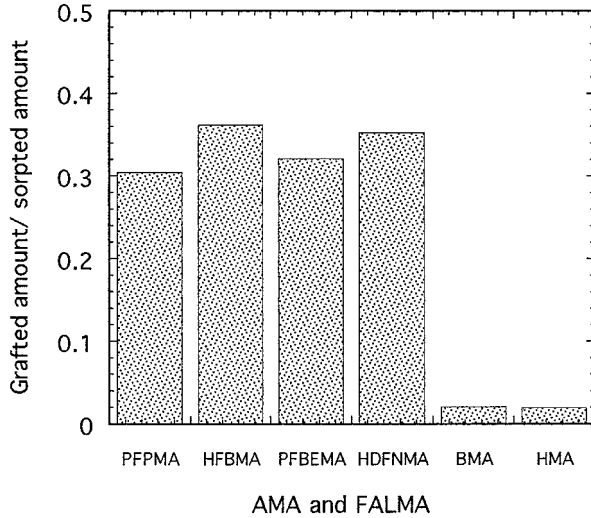


Figure 4 The grafted amount/sorted amount for each FALMA and AMA in PDMS membrane.

Figure 6. The sorted amount and the grafted amount was not so affected by the difference in the $\log P_{ow}$. The relationships between the molecular volume and the grafted amount or sorted amount are shown in Figure 7. The sorted amount for AMA was high because of the low molecular volume. The sorted amount for FALMA was low because of the high molecular volume. In this study, the PDMS membrane was grafted with FALMA and AMA. Comparing monomers in the same group of FALMA or AMA,

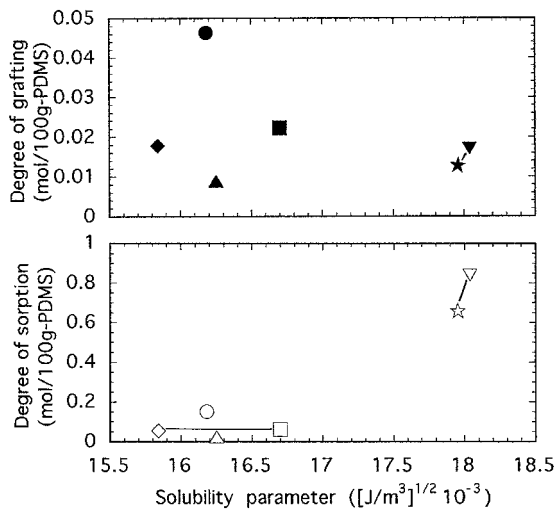


Figure 5 Relationship between the solubility parameter of monomer and the grafted amount or the sorted amount in PDMS membrane: (○) PFPMA, (□) HFBMA, (◇) PFBEMA, (△) HDFNMA, (▽) BMA, and (☆) HMA. Closed: grafted amount; open: sorted amount.

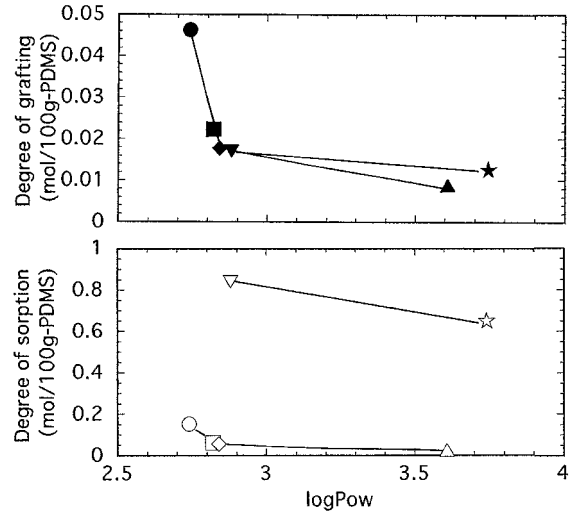


Figure 6 Relationship between the $\log P_{ow}$ of monomer and the grafted amount or the sorted amount in PDMS membrane: (○) PFPMA, (□) HFBMA, (◇) PFBEMA, (△) HDFNMA, (▽) BMA, and (☆) HMA. Closed: grafted amount; open: sorted amount.

the sorted and grafted amount was high for the monomer that has low molecular volume, and the sorted and grafted amount was low for the monomer that has high molecular volume.

Pervaporation of the Grafted PDMS Membrane

The pervaporation results of dilute TCE solution through the grafted PDMS membranes are shown

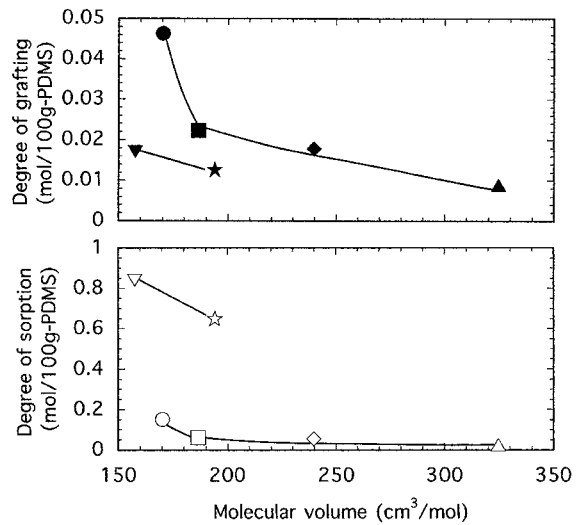


Figure 7 Relationship between the molecular volume of monomer and the grafted amount or the sorted amount in PDMS membrane: (○) PFPMA, (□) HFBMA, (◇) PFBEMA, (△) HDFNMA, (▽) BMA, and (☆) HMA. Closed: grafted amount; open: sorted amount.

Table IV Permeation Selectivity for TCE-Water Mixture Through PDMS Membrane and Grafted PDMS Membrane at 25°C

Membrane	Composition (wt %) Feed Permeate		Total Flux (10^{-3} kg/m ² · h)	Separation Factor α_p
PFPMA-grafted-PDMS	0.011	11	86	1100
(preirradiation)	0.023	20	120	1100
HFBMA-grafted-PDMS	0.012	5.0	120	450
(preirradiation)	0.024	9.1	130	410
PFBEMA-grafted-PDMS	0.0089	5.1	160	600
(preirradiation)	0.026	10	200	450
HDFNMA-grafted-PDMS	0.0083	3.2	210	400
(preirradiation)	0.024	11	100	520
HDFNMA-grafted-PDMS	0.010	1.5	190	150
(simultaneous irradiation)	0.023	2.9	130	130
BMA-grafted-PDMS	0.0099	3.7	140	390
(preirradiation)	0.025	8.3	140	350
HMA-grafted-PDMS	0.0091	2.2	140	240
(preirradiation)	0.025	6.1	140	260
EB irradiated-PDMS	0.011	0.53	490	51
(not grafted)	0.025	1.3	540	52
PDMS	0.010	4.8	63	500
	0.026	9.6	60	400

in Table IV. The pervaporation for the PDMS membrane, PDMS membrane irradiated by electron beam, grafted PDMS membranes by the preirradiation method, and simultaneous irradiation was investigated. The total flux for the PDMS membranes irradiated by electron beam was high compared to the unirradiated PDMS

membrane. It is thought that the PDMS membranes were made brittle by electron beam irradiation. By the preirradiation method, FALMA grafted PDMS membranes exhibited excellent separation performance. Among them, the PFPMA-grafted PDMS membrane, which had a high grafted amount and a high F/Si ratio, had high

Table V Sorption Selectivity for PDMS Membrane and Grafted PDMS Membrane

Membrane	TCE in Feed (wt %)	Degree of Swelling (wt %)	TCE in Membrane (wt %)	Separation Factor α_s
PFPMA-grafted-PDMS	0.011	2.6	13	1300
(preirradiation)	0.026	2.1	27	1400
HFBMA-grafted-PDMS	0.011	4.0	8.2	830
(preirradiation)	0.028	6.6	16	640
PFBEMA-grafted-PDMS	0.012	1.4	9.3	860
(preirradiation)	0.030	9.3	17	660
HDFNMA-grafted-PDMS	0.011	1.0	14	1500
(preirradiation)	0.026	1.1	18	840
HDFNMA-grafted-PDMS	0.011	1.2	3.9	360
(simultaneous irradiation)	0.028	2.5	21	930
BMA-grafted-PDMS	0.012	3.7	5.1	460
(preirradiation)	0.029	4.8	11	450
HMA-grafted-PDMS	0.012	1.3	3.9	340
(preirradiation)	0.028	4.5	11	430
EB irradiated-PDMS	0.0097	3.3	4.2	460
(not grafted)	0.029	1.0	14	550
PDMS	0.012	1.0	8.9	770
	0.032	1.8	14	530

selectivity for TCE. By the simultaneous irradiation method, the PDMS membrane swollen by HDFNMA was irradiated. The PDMS membrane was grafted and made brittle simultaneously. The HDFNMA-grafted PDMS membrane by the simultaneous irradiation method did not have high permselectivity for TCE.

The water and TCE flux as a function of the TCE concentration in the feed solution are shown in Figure 8 for the HDFNMA-grafted PDMS membranes by the preirradiation method and simultaneous irradiation method. For the PDMS membranes, the water flux was almost constant with increasing feed concentration. For the grafted PDMS membranes by the preirradiation method, the water flux decreased with increasing feed concentration. For all the membranes, the TCE flux was increased with increasing feed concentration, and for the grafted PDMS membranes by the preirradiation method, the tendency was significant.

The relationships between the TCE concentration in the feed and the permeate are shown in Figure 9 for the HDFNMA-grafted PDMS membranes by the preirradiation method and simultaneous irradiation method. For all the membranes, the TCE concentration in the permeate increased with increasing feed concentration, and for the grafted PDMS membranes by the preirradiation method, the tendency was significant.

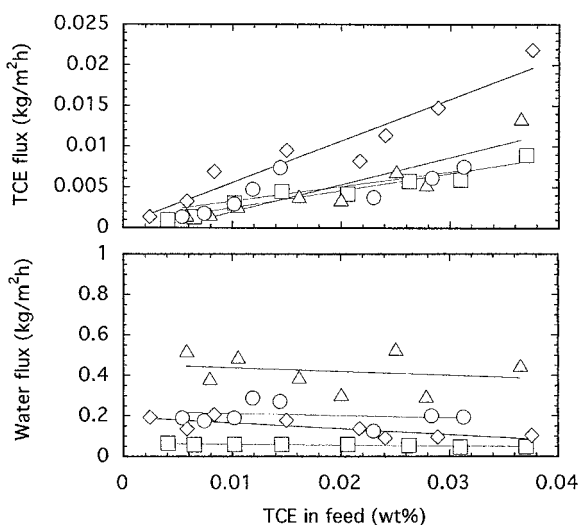


Figure 8 Effect of feed concentration on water and TCE flux for TCE–water mixture in pervaporation through PDMS membrane and grafted PDMS membrane by electron beam: (\diamond) grafted PDMS membrane by preirradiation method, (\circ) grafted PDMS membrane by simultaneous irradiation method, (\triangle) PDMS membrane irradiated by electron beam, and (\square) PDMS.

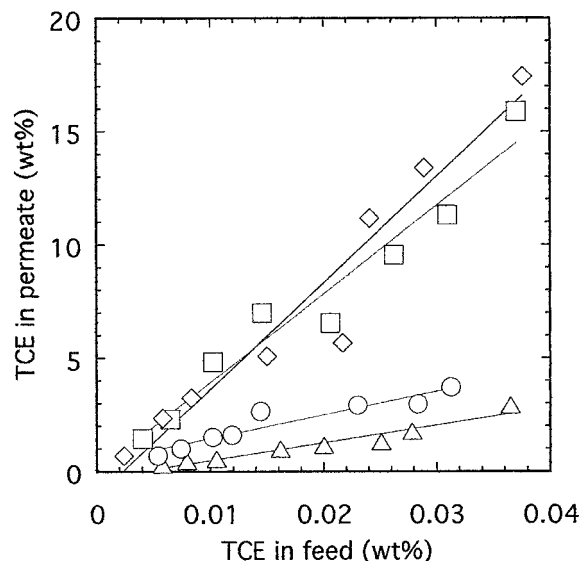


Figure 9 Relationship between TCE concentration in feed and permeation in pervaporation through PDMS and grafted PDMS membranes by electron beam: (\diamond) grafted PDMS membrane by preirradiation method, (\circ) grafted PDMS membrane by simultaneous irradiation method, (\triangle) PDMS membrane irradiated by electron beam, and (\square) PDMS.

In the FALMA-grafted PDMS membrane by the preirradiation method, the high separation performance was exhibited, due to the introduction of hydrophobic polymer, poly(FALMA).

Sorption of the Grafted PDMS Membrane

The sorption results of dilute TCE solution through the grafted PDMS membranes are shown in Table V. The sorption for the PDMS membrane, PDMS membrane irradiated by electron beam, grafted PDMS membranes by the preirradiation method and simultaneous irradiation was investigated. The solubility of TCE for the FALMA-grafted PDMS membranes by the preirradiation method was great compared with the PDMS membranes. Among them, the PFPMA-grafted PDMS membrane, which had a high grafted amount and a high F/Si ratio, had high sorption selectivity for TCE.

The FALMA-grafted PDMS membranes that had the high TCE concentrations in the sorbed solution exhibited high permselectivity for TCE.

CONCLUSIONS

We investigated the effect of solubility and diffusibility of a monomer on graft polymerization ac-

ording to solubility parameter, the octanol–water partition coefficient (P_{ow}) and the molecular volume of the monomer. Around 33% of FALMA sorpted in PDMS was grafted, and around 2% of AMA sorpted in PDMS was grafted. The difference of δ_{FALMA} and δ_{PDMS} is small but the sorpted FALMA amount in PDMS membrane was low. The difference in the grafted amount was little when considering the difference of the solubility parameter. The difference in the sorpted amount or grafted amount was little when considering the difference of the $\log P_{ow}$. The sorpted amount for AMA that has low molecular volume was high. The sorpted amount for FALMA that has high molecular volume was low. Compared to each other in the same group of FALMA or AMA, the sorpted and grafted amounts for the monomer that have low molecular volume was high, and the sorpted and grafted amounts for monomer that have high molecular volume was low.

The pervaporation for the PDMS membrane, PDMS membrane irradiated by electron beam, grafted PDMS membranes was investigated. The total flux for the irradiated PDMS membranes by electron beam was high compared to the unirradiated PDMS membrane. It is thought that the PDMS membranes were made brittle by electron beam irradiation. FALMA-grafted PDMS membranes showed excellent separation performance. Among them, the PFPMA-grafted PDMS membrane, which had a high grafted amount and F/Si ratio, had high permselectivity for TCE. In pervaporation through the PDMS and grafted PDMS membrane, the TCE concentration in the permeate were increased with increasing feed concentration, and for the grafted PDMS membranes by the preirradiation method, the tendency was significant. The TCE flux significantly increased with increasing feed concentration for the grafted PDMS membranes by the preirradiation method.

FALMA-grafted PDMS membranes exhibited high sorption performance. Among them, the PFPMA-grafted PDMS membrane, which had a high grafted amount and F/Si ratio, had high sorption selectivity for TCE. In the grafted PDMS membranes, the high permselectivity was shown, due to the introduction of the hydrophobic polymer poly(FALMA).

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