# Removal of Benzene from an Aqueous Solution of Dilute Benzene by Various Cross-Linked Poly(dimethylsiloxane) Membranes during Pervaporation

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ABSTRACT: This paper focuses on the effects of cross-linkers of the cross-linked poly(dimethylsiloxane) membranes derived from poly(dimethylsiloxane) dimethyl methacrylate macromonomer (PDMSDMMA), and divinyl compound, on the pervaporation characteristics of the removal of benzene from an aqueous solution of dilute benzene. When an aqueous solution of 0.05 wt % benzene was permeated through the cross-linked PDMSDMMA membranes, they showed high benzene permselectivity. Both the permeability and benzene permselectivity of the membranes were enhanced with increasing divinyl compound content as the cross-linker and were significantly influenced by the kind of divinyl compound. PDMSDMMA membranes cross-linked with divinylsiloxane (DVS) showed very high membrane performance during pervaporation. The best normalized permeation rate, separation factor for benzene permselectivity, and pervaporation separation index of a PDMSDMMA−DVS membrane were $1.96 \times 10^{-5}$ m kg/(m$^2$ h), 2886, and 5657, respectively. These pervaporation characteristics are discussed from the viewpoint of the chemical and physical structure of the cross-linked PDMSDMMA membranes.

## Introduction

Recently, the environmental pollution caused by our economic activities has become a problem. In particular, water pollution due to volatile organic compounds (VOCs) is a concern because of their possible negative effect on ecology and the human body, directly and indirectly. Therefore, the development of technology to remove dilute VOCs from water is strongly desirable.

In general, the adsorption method using active carbon for the removal of dilute VOCs in water is used. However, since this method is expensive and not efficient, the development of an efficient removal technology is required. The membrane removal technique has great advantages in term of potential savings in energy costs. Therefore, many studies have reported on the permeation and separation characteristics for VOCs/water through various hydrophobic polymer membranes, mainly composed of poly(dimethylsiloxane) (PDMS),[1−5] composites or zeolite-filled PDMS,[6,7] and other materials.[8−10]

In previous papers,[11−17] we studied the relationship between the structure of multicomponent polymer membranes containing PDMS and their permselectivity for aqueous ethanol solutions during pervaporation. We demonstrated that the permselectivity of multicomponent polymer membranes was dependent on the morphology of their microphase separation. In further studies,[18,19] we elucidated that in graft copolymer membranes the microphase separation between poly(methyl methacrylate) and PDMS significantly influenced their permeability and permselectivity for the removal of VOCs from an aqueous solution of dilute VOCs and that a continuous PDMS phase in the microphase separation played an important role in the selective removal of VOCs. Since we found that the PDMS component of multicomponent polymer membranes is very important for VOCs permselectivity, we tried to prepare polymer membranes that consisted of only PDMS. However, it was very difficult to prepare PDMS membranes from a PDMS macromonomer.

Therefore, in this study, cross-linked PDMS membranes were prepared by the copolymerization of PDMS dimethyl methacrylate macromonomer (PDMSDMMA) as the PDMS component, with various divinyl compounds as cross-linkers which have a high affinity for benzene, thus improving the performance of the PDMS membrane. The removal of benzene from an aqueous solution of dilute benzene through the cross-linked PDMSDMMA membranes during pervaporation (PV) was investigated, and the benzene permselectivity of their membranes is discussed from the viewpoint of the chemical and physical structure of the membrane.

## Experimental Section

**Materials.** Poly(dimethylsiloxane) dimethyl methacrylate macromonomer (PDMSDMMA) (**1**) as the base polymer of the membrane matrix was supplied by Toray Dow Corning Silicone Co., Ltd. Divinylbenzene (DVB) (**2**), divinylsiloxane (DVS) (**3**), and ethylene glycol dimethyl methacrylate (EGDM) (**4**) were used as cross-linkers and were purified by distillation under a nitrogen atmosphere. 2,2-Azobis(2-methylpropionnitrile) (AIBN) recrystallized from methanol solution was used as the initiator. All other solvents and reagents were of analytical grade from commercial sources and were used without further purification.

**Preparation of Cross-Linked PDMSDMMA Membranes.** The cross-linked PDMSDMMA membranes (PDMSDMMA−DVB, PDMSDMMA−DVS, PDMSDMMA−EGDM) were prepared by the copolymerization of PDMSDMMA with the divinyl compounds as cross-linkers using AIBN as an initiator, in a mold plate between two glass plates at 80 °C for 24 h under a nitrogen atmosphere, as shown in Figure 1.[20] To remove any excess unreact monomers, the membranes were soaked in *n*-hexane for 24 h and dried under reduced pressure at room temperature. All of cross-linked PDMSDMMA membranes were rubbery.

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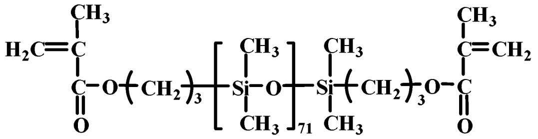
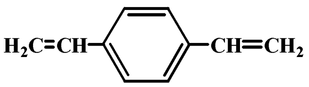
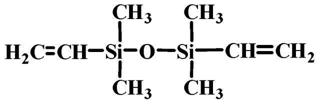


$H_2C{=}C(CH_3)-C(=O)-O-(CH_2)_3-[Si(CH_3)_2-O]_{71}-Si(CH_3)_2-(CH_2)_3-O-C(=O)-C(CH_3){=}CH_2$

PDMSDMMA macromonomer (**1**)

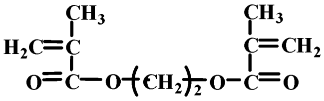


divinyl benzene, DVB (**2**)



$H_2C{=}CH-Si(CH_3)_2-O-Si(CH_3)_2-CH{=}CH_2$

divinyl siloxane, DVS (**3**)



$H_2C{=}C(CH_3)-C(=O)-O-(CH_2)_2-O-C(=O)-C(CH_3){=}CH_2$

ethyleneglycol dimethylmethacrylate, EGDM (**4**)

**PV Apparatus and Measurements.** The PV cell and PV apparatus have been described in a previous paper.[21] The effective membrane area was about 13.8 cm$^2$. The PV experiments were carried out under the following conditions: permeation temperature, 40 °C; pressure of permeate side, $1 \times 10^{-2}$ Torr. The feed solution, an aqueous solution of dilute benzene, was circulated between the PV cell and the feed tank to maintain a constant concentration of the feed solution in the PV cell. An aqueous solution of 0.05 wt % benzene was used as the fed solution for all of the PV study as well as the sorption and swelling studies. The permeation rate (kg/(m$^2$ h)) for the aqueous benzene solution during PV was determined from the weight (kg) of permeate collected in a cold trap, the permeation time (h), and the effective membrane area (m$^2$). To facilitate a comparison of the permeation rates of membranes with different thickness, the normalized permeation rate (m kg/(m$^2$ h)), which is the product of the permeation rate and the membrane thickness, was used. The results of the permeation of an aqueous benzene solution by PV were reproducible, and the errors inherent in these permeation measurements ranged within a few percent for the permeation tares through the membranes. Permeation results in this study were after the steady-state flux.

The benzene concentration in the feed and permeate was determined by a gas chromatograph (Shimadzu GC-14A) using a flame ionization detector (FID) and capillary column (Shimadzu Co. Ltd: PorapacQ) heated to 180 °C.

The separation factor, $\alpha_{sep.benzene/H_2O}$, was calculated from eq 1

$$\alpha_{sep.benzene/H_2O} = (P_{benzene}/P_{H_2O})/(F_{benzene}/F_{H_2O}) \tag{1}$$

where $F_{benzene}$ and $F_{H_2O}$ are the weight fractions of benzene and water in the feed solution and $P_{benzene}$ and $P_{H_2O}$ are those in the permeate, respectively.

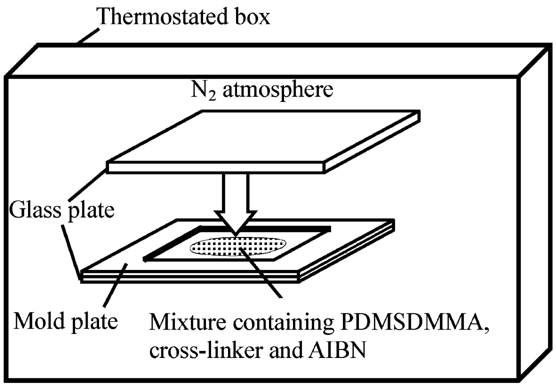


**Figure 1.** Schema of the preparation of the cross-linked PDMSDMMA membranes.

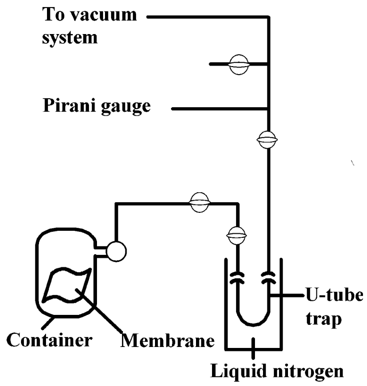


**Figure 2.** Diagram of the apparatus to determine the composition of the solution absorbed in the cross-linked PDMSDMMA membranes.

**Composition of the Solution Absorbed in Cross-Linked PDMSDMMA Membranes.** The PDMSDMMA−DVB, PDMSDMMA−DVS, and PDMSDMMA−EGDM membranes were dried completely under reduced pressure at room temperature and weighed. The dried membranes were immersed into an aqueous solution of 0.05 wt % benzene in a sealed vessel at 40 °C until equilibrium was reached. A large amount of the swollen cross-linked PDMSDMMMA membranes was placed in a container, as shown in Figure 2. The system in Figure 2 was vacuumed, and the container with the swollen membranes was heated. The solution absorbed in the swollen membranes was completely desorbed under reduced pressure and was collected in the U-tube cooled with liquid nitrogen. The compositions of the solutions in the cross-linked PDMSDMMA membranes were then determined by measuring the benzene concentration in the collected solution by gas chromatography (Shimazu GC-14A). The benzene/water composition in the cross-linked PDMSDMMA membranes and in the feed solution yielded the sorption selectivity, $\alpha_{sorp.benzene/H_2O}$, as expressed in eq 2

$$\alpha_{sorp.benzene/H_2O} = (M_{benzene}/M_{H_2O})/(F_{benzene}/F_{H_2O}) \tag{2}$$

where $F_{benzene}$ and $F_{H_2O}$ are the weight fractions of benzene and water in the feed solution and $M_{benzene}$ and $M_{H_2O}$ are those in the membrane, respectively.

**Measurement of Contact Angle.** The contact angles for water on the surfaces of the PDMSDMMA−DVB, PDMSDMMA−DVS and PDMSDMMA−EGDM membranes were measured by a contact angle meter (Erma, model G-I) at 25 °C. The contact angle, $\theta$, was calculated from eq 3[22,23]

$$\theta = \cos^{-1} [(\cos \theta_a + \cos \theta_r)/2] \tag{3}$$

where $\theta_a$ and $\theta_r$ are the advancing contact angle and the receding contact angle, respectively.

**Degree of Swelling of Membranes.** The dried PDMSDMMA−DVB, PDMSDMMA−DVS, and PDMSDMMA−EGDM membranes were weighed and immersed into an aqueous solution of 0.05 wt % benzene in a sealed vessel at 40 °C until equilibrium was reached. The membranes were then taken out of the vessel, wiped quickly with a filter paper, and weighed. The degree of swelling (DS) of the cross-linked PDMSDMMA

**Table 1. Relationship between the Membrane Thicknesses, the Practical Permeation Rates, and the Benzene Concentration in the Permeates**

| membrane | benzene concn in the permeate (wt %) | membrane thickness ($\mu$m) | permeation rate ($10^{-2}$ kg/(m$^2$h)) | normalized permeation rate ($10^{-5}$ m kg/(m$^2$h)) | separation factor |
|---|---|---|---|---|---|
| PDMSDMMA | 48 | 270 | 5.14 | 1.39 | 1853 |
| DVB (80 mol %) | 60 | 314 | 4.55 | 1.43 | 3099 |
| DVS (90 mol %) | 59 | 276 | 7.09 | 1.96 | 2886 |
| EGDM (70 mol %) | 50 | 357 | 4.96 | 1.77 | 2011 |

membranes was then determined from eq 4,

$$\mathrm{DS} = W_s/W_d \qquad (4)$$

where $W_s$ is the weight of the membrane swollen in an aqueous solution of 0.05 wt % benzene and $W_d$ is the weight of the dried membrane.

**Membrane Density.** The density of the cross-linked PDMSDMMA membranes was determined by measuring their weights in methanol with an electric gravity meter (Mirage Boeki, SD-120L) at 25 °C.

**Cross-Linking Density of Cross-Linked PDMSDMMA Membranes.** The cross-linking density, $\rho$, of the cross-linked PDMSDMMA membranes was calculated from the network theory of rubber elasticity given in eq 5[24−26]

$$\rho = E'/3d\phi RT \qquad (5)$$

where $E'$ is determined from the measurement with a dynamic mechanical analyzer (Rheogel-E4000 F3, U.B.M) under the following conditions: frequency, 1, 2, 4, 10 Hz; temperature, 40 °C; $d$ is membrane density, $\phi$ is the front factor (where $\phi = 1$), $R$ is the gas constant, and $T$ is the absolute temperature.

## Results and Discussion

**Permselectivity of Cross-Linked PDMSDMMA Membranes.** Table 1 summarizes the membrane thicknesses, the practical permeation rates, and the benzene concentrations in the permeates. It was very difficult to prepare the membranes with a same thickness in the method of the membrane preparation in this study. Therefore, the permeation rates were normalized for the membrane thickness to easily discuss the permeation and separation characteristics between the cross-linked PDMSDMMMA membranes with different membrane thicknesses.

Figure 3 shows the effects of the cross-linker content on the benzene concentration in the permeate and the normalized permeation rate through the PDMSDMMA−DVB, PDMSDMMA−DVS, and PDMSDMMA−EGDM membranes during PV. The normalized permeation rate in this figure is the product of the permeation rate and the membrane thickness. The benzene concentration in the permeate through all of the cross-linked PDMSDMMA membranes was higher than that in the feed concentration. These results suggest that all membranes had very high benzene permselectivity for an aqueous solution of 0.05 wt % benzene. Furthermore, all of the cross-linked PDMSDMMA membranes increased both their benzene permselectivity and their permeability with increasing DVB, DVS, and EGDM contents as cross-linkers. In particular, when DVB and DVS were used as cross-linkers, the benzene permselectivity was enhanced significantly. On the other hand, the normalized permeation rates through all of the cross-linked PDMSDMMA membranes were higher than that of the cross-linked PDMSDMMA membrane prepared from only PDMSDMMA without any cross-linker such as DVB, DVS, and EGDM.

In general, when the permselectivity of a membrane is increased by modifying the membrane, the permeability of membrane is decreased.[27,28] In this study, however, both the permselectivety and the permeability of PDMSDMMA−DVB, PDMSDMMA−DVS, and PDMSDMMA−EGDM membranes were enhanced with increasing cross-linker content. Therefore, we investigated in detail the chemical and physical structures of the PDMSDMMA−DVB, PDMSDMMA−DVS, and PDMSDMMA−EGDM membranes to elucidate the benzene permeation behavior for an aqueous dilute benzene solution during PV.

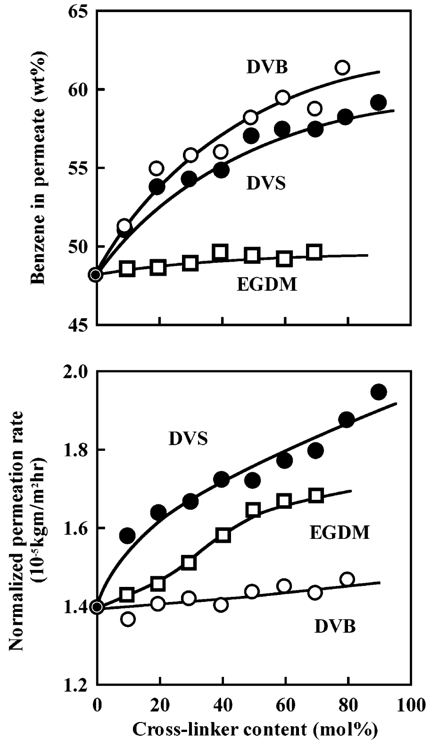


**Figure 3.** Effects of the DVB (○), DVS (●), and EGDM (□) content on the normalized permeation rate and the benzene concentration in the permeate for an aqueous solution of 0.05 wt % benzene through cross-linked PDMSDMMA membranes during PV.

**Chemical Structure of the Cross-Linked PDMSDMMA Membranes.** In general, the separation and permeation characteristics for organic liquid mixtures through polymer membranes by PV are based on the solubility of the permeants into the polymer membrane (sorption process), and the diffusivity of the permeants in the polymer membrane (diffusion process).[23,29−31] The solubility and diffusivity of the permeants are significantly influenced by the chemical and physical structures of the polymer membranes. Therefore, we characterized the cross-linked PDMSDMMA membranes from the viewpoint of the chemical and physical structure of the polymer membranes.

In Figure 4, the contact angles for water on the surface of the cross-linked PDMSDMMA−DVB, PDMSDMMA−DVS, and PDMSDMMA−EGDM membranes are shown as a function of the cross-linker content. The

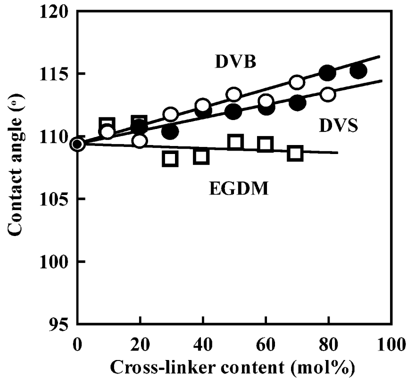


**Figure 4.** Effects of the DVB (○), DVS (●), and EGDM (□) content on the contact angles for water of cross-linked PDMSDMMA membranes.

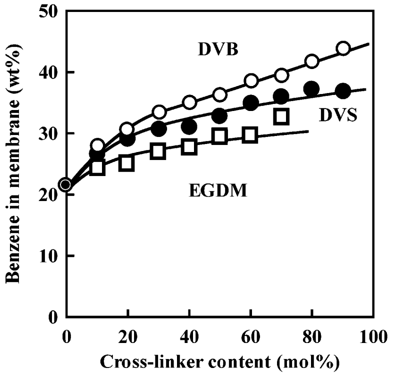


**Figure 5.** Effects of the DVB (○), DVS (●), and EGDM (□) content on the benzene concentration in cross-linked PDMSDMMA membranes immersed in an aqueous solution of 0.05 wt % benzene.

contact angles for water on the surface of the PDMSDMMA−DVB and PDMSDMMA−DVS membranes obviously increased with increasing DVB and DVS content, whereas the contact angle for the PDMSDMMA−EGDM membrane decreased very slightly with increasing EGDM content. These contact angle measurements suggest that, with increasing cross-linker content, the surface of PDMSDMMA−DVB and PDMSDMMA−DVS membranes became more hydrophobic, but the PDMSDMMA−EGDM membrane became minutely more hydrophilic.

Figure 5 shows the effects of the cross-linker content on the benzene concentration in the cross-linked PDMSDMMA membranes immersed in an aqueous solution of 0.05 wt % benzene. The benzene concentrations in the PDMSDMMA−DVB, PDMSDMMA−DVS, and PDMSDMMA−EGDM membranes were much higher than those in the cross-linked PDMSDMMA membrane prepared from only PDMSDMMA. Furthermore, with increasing cross-linker content, the benzene concentrations in the cross-linked PDMSDMMA membranes with cross-linker increased significantly. With increasing cross-linker content, the increase in the benzene concentration of the PDMSDMMA−DVB and PDMSDMMA−DVS membranes is supported by the contact angle measurements in Figure 4, but this is not the case for the PDMSDMMA−EGDM membrane.

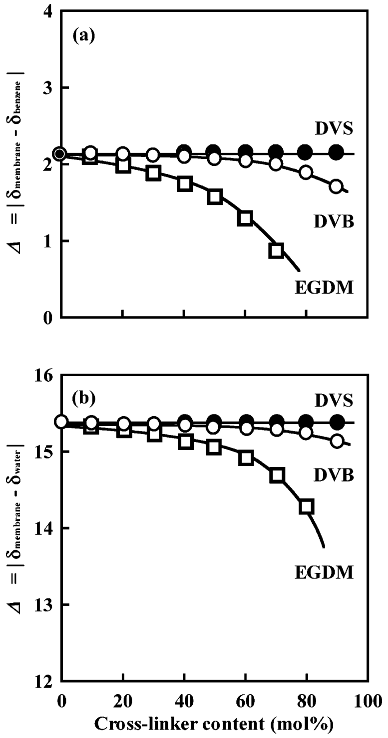


**Figure 6.** Difference in the solubility parameters between benzene and the cross-linked PDMSDMMA membranes (a) and between water and these membranes (b) as a function of the DVB (○), DVS (●), and EGDM (□) content.

**Table 2. Hansen Solubility Parameters for Benzene, Water, and PDMS**

| | solubility parameters [(MPa)$^{1/2}$] | | | |
|---|---|---|---|---|
| material | $\delta_d$ | $\delta_p$ | $\delta_h$ | $\delta$ |
| benzene | 18.4 | 0 | 2.0 | 18.6 |
| $H_2O$ | 15.5 | 16.0 | 42.4 | 47.9 |
| PDMS | 15.9 | 0.10 | 4.7 | 16.5 |

To clarify the relationship between the contact angle for water of the PDMSDMMA−EGDM membranes and the benzene concentrations in the PDMSDMMA−EGDM membranes with a change in the EGDM content, the affinity between the polymer membranes and the permeants was investigated in more detail using the solubility parameters of the polymer membranes and the permeants. The effects of the cross-linker content on the differences in the solubility parameter between benzene and the cross-linked PDMSDMMA membranes, and between water and these membranes, are shown in parts a and b of Figure 6, respectively. The difference in the solubility parameter, Δ, was calculated from the solubility parameter of benzene ($\delta_{\text{benzene}}$) or water ($\delta_{\text{water}}$) and the membrane ($\delta_{\text{membrane}}$) using eqs 6 and 7:

$$\Delta = | \delta_{\text{membrane}} - \delta_{\text{benzene}} | \qquad (6)$$

$$\Delta = | \delta_{\text{membrane}} - \delta_{\text{water}} | \qquad (7)$$

The solubility parameter, $\delta_{\text{membrane}}$, of each cross-linked PDMSDMMA membrane was calculated from the solubility parameters and the volume ratios of PDMSDMMA and the cross-linker, based on the atomic group contribution method.[32−37] The solubility parameters of the PDMSDMMA homopolymer, benzene, and water are summarized in Table 2. A small Δ means that the membrane has a strong affinity for benzene and water. In the PDMSDMMA−DVB and PDMSDMMA−EGDM membranes, it is clear that the affinity between the membranes and benzene was enhanced with increasing cross-linker content, as shown in Figure 6a. However, the affinity between these membranes and water also increased with the cross-linker content. In particular,

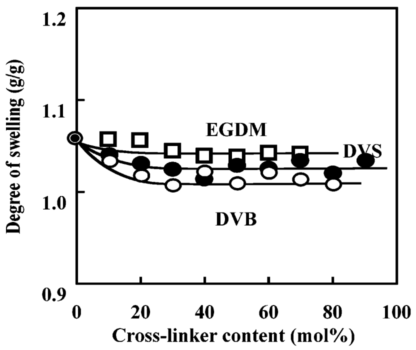


**Figure 7.** Effects of the DVB (○), DVS (●), and EGDM (□) content on the degree of swelling of cross-linked PDMSDMMA membranes immersed in an aqueous solution of 0.05 wt % benzene.

the PDMSDMMA−EGDM membranes showed high affinities for both benzene and water with increasing EGDM content. The fact that the contact angle for water of the PDMSDMMA membranes cross-linked with EGDM in Figure 4 became slightly hydrophilic may be attributed to the high affinity between the PDMSDMMA−EGDM membranes and water. This is related to the fact that the PDMSDMMA−EGDM membranes had lower benzene permselectivity despite the fact that the PDMSDMMA−EGDM membranes had a higher affinity for benzene in comparison to the PDMSDMMA−DVB and PDMSDMMA−DVS membranes.

**Physical Structure of the Cross-Linked PDMSDMMA Membranes.** Figure 7 shows the degree of swelling of the PDMSDMMA−DVB, PDMSDMMA−DVS, and PDMSDMMA−EGDM membranes immersed in an aqueous solution of 0.05 wt % benzene as a function of the cross-linker content. The degree of swelling of all cross-linked PDMSDMMA membranes decreased with increasing cross-linker content. This decrease in the degree of swelling is due to the introduction of the cross-linking structure into the membrane matrix. Generally, polymer membranes with a strong affinity for the permeant are swollen in the feed solution. Although the cross-linked PDMSDMMA membranes have a strong affinity for benzene, the affinity for water is very low. Therefore, the degree of swelling of the cross-linked PDMSDMMA membranes was relatively low. This low degree of swelling can also be attributed to the strong benzene permselectivity of the cross-linked PDMSDMMA membranes.

In Figure 8, the effects of the cross-linker content on the density of the cross-linked PDMSDMMA membranes are shown. As can be seen in Figure 8, the density of the PDMSDMMA−DVB and PDMSDMMA−EGDM membranes increased with increasing DVB and EGDM content. In Figure 9, the elastic modulus, *E*′, of the cross-linked PDMSDMMA membranes is shown as a function of the cross-linker content. These values of elastic modulus can be applied to the estimation of the cross-linking density of the cross-linked PDMSDMMA membranes.

Figure 10 shows the effect of the cross-linker content on the cross-linking density of the cross-linked PDMSDMMA membranes which can be determined by applying the *E*′ value in Figure 9 to eq 5. As can be seen in Figure 10, with increasing DVB and EGDM content, the cross-linking density of the PDMSDMMA−DVB and PDMSDMMA−EGDM membranes also increased. Therefore, both the density and the cross-linking density of the PDMSDMMA−EGDM membranes were higher than those of the PDMSDMMA−DVB membranes. On the other hand, the density of the PDMSDMMA−DVS membranes increased with the DVS content very slightly. The cross-linking density of the PDMSDMMA−DVS membrane obviously decreased with increasing DVS content.

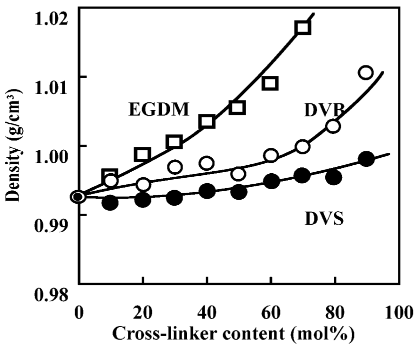


**Figure 8.** Membrane density of cross-linked PDMSDMMA membranes as a function of the DVB (○), DVS (●), and EGDM (□) content.

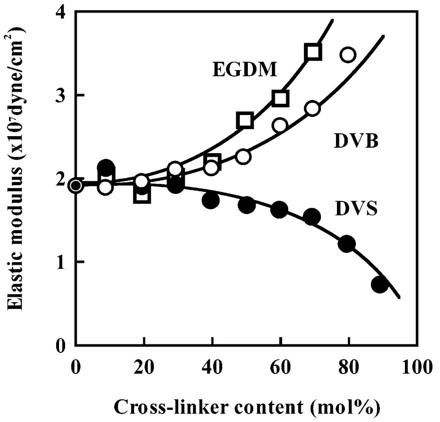


**Figure 9.** Relationship between the elastic modulus of the cross-linked PDMSDMMA membranes and the cross-linker content. DVB (○), DVS (●), and EGDM (□).

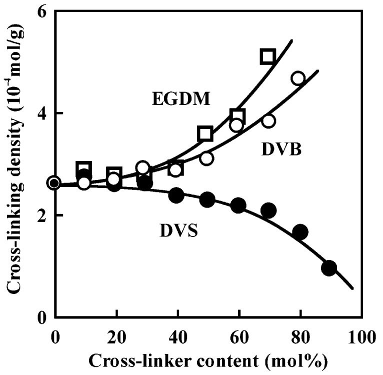


**Figure 10.** Cross-linking density of cross-linked PDMSDMMA membranes as a function of the DVB (○), DVS (●), and EGDM (□) content.

**Mechanism of Permselectivity in the Cross-Linked PDMSDMMA Membranes.** The packing density of the molecules within the membrane matrix significantly affects the diffusivity of the permeants. Membranes with an open structure (low packing density) yield a high diffusivity for the permeants and consequently a high permeability. The fact that the normalized permeation rates of the PDMSDMMA−DVS membranes in Figure 3 were the highest and increased

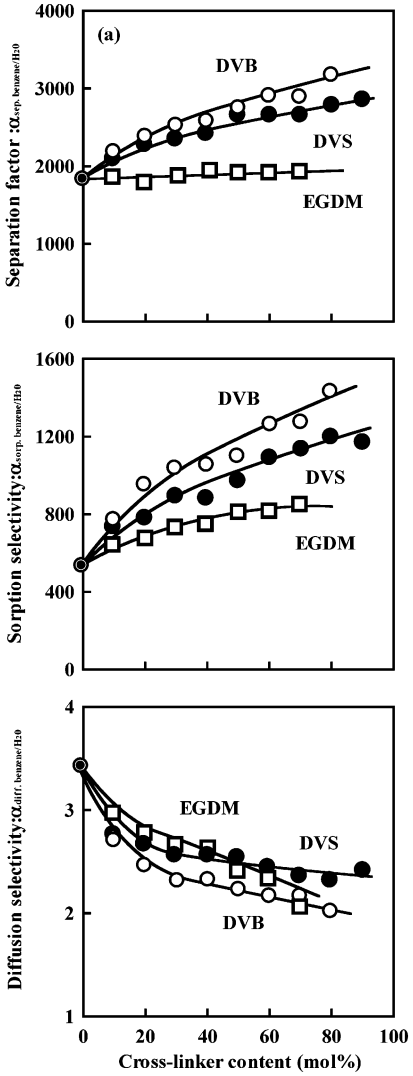


**Figure 11.** Effects of the cross-linker content on the separation factor, the sorption selectivity, and the diffusion selectivity for an aqueous solution of 0.05 wt % benzene through PDMSDMMA−DVB (○), PDMSDMMA−DVS (●), and PDMSDMMA−EGDM (□) membranes during PV.

with the DVS content can be attributed to the packing density of the membrane.

With respect to the separation and permeation characteristics for organic liquid mixtures through polymer membranes by PV, it is very important to determine the sorption selectivity and diffusion selectivity in order to elucidate the separation mechanism of an aqueous benzene solution through the cross-linked PDMSDMMA membranes. In general, the separation factor for mixtures of benzene and water in PV can be defined by eq 8:[38]

$$\alpha_{\mathrm{sep.benzene/H_2O}} = \alpha_{\mathrm{sorp.benzene/H_2O}}\alpha_{\mathrm{diff.benzene/H_2O}} \tag{8}$$

The diffusion selectivity, $\alpha_{\mathrm{diff.benzene/H_2O}}$, from eq 8 can be determined as shown in eq 9 using the separation factor, $\alpha_{\mathrm{sep.benzene/H_2O}}$, from eq 1 and the sorption selectivity, $\alpha_{\mathrm{sorp.benzene/H_2O}}$, from eq 2.

$$\alpha_{\mathrm{diff.benzene/H_2O}} = \alpha_{\mathrm{sep.benzene/H_2O}}/\alpha_{\mathrm{sorp.benzene/H_2O}} \tag{9}$$

In Figure 11, the separation factor, the sorption selectivity, and the diffusion selectivity for an aqueous solution of 0.05 wt % benzene are presented as a function of the cross-linker content in cross-linked PDMSDMMA membranes. As can be seen in Figure 11, with increasing cross-linker content, the increase in the separation factors of all cross-linked PDMSDMMA membranes was significantly dependent on the increase in the sorption selectivity. This change in the separation factors based on the kind of cross-linker also corresponds to that of the sorption selectivity due to the kind of cross-linker. The diffusion selectivity through all cross-linked PDMSDMA membranes decreased with increasing cross-linker content. This result suggests that the diffusivity of the benzene molecule, with its bigger molecular size, decreased with increasing cross-linker content. Thus, the introduction of the cross-linking structure into the membrane matrix leads to a remarkable decrease in the diffusion of benzene molecules as compared to the smaller water molecules. On the basis of the above results, we found that the benzene permselectivity of the cross-linked PDMSDMMA membranes and the increase in the benzene permselectivity of these membranes were governed mainly by the sorption selectivity.

**Estimation of Cross-Linked PDMSDMMA Membranes Performance.** We have been investigating methods to improve polymer membranes containing PDMS components for their ability to remove VOCs from water. We have previously reported the permeation and separation characteristics of an aqueous dilute benzene solution through graft copolymer membranes comprising poly(methyl methacrylate) (PMMA) and PDMS (PMMA-*g*-PDMS),[18,19] PMMA-*g*-PDMS membranes containing *tert*-butylcalix[4]arene (CA) (CA/PMMA-*g*-PDMS),[39] and PMMA-*g*-PDMS membranes surface-modified with a fluorine-containing graft copolymer consisting of 1*H*,1*H*,9*H*-hexadecafluorononyl methyl methacrylate (PFA) and PDMS (PFA-*g*-PDMS/PMMA-*g*-PDMS)[40] during PV. In Table 3, the permeation and separation characteristics of the PMMA-*g*-PDMS, the CA/PMMA-*g*-PDMS, the PFA-*g*-PDMS/PMMA-*g*-PDMS, the cross-linked PDMSDMMA−DVB, and the cross-linked PDMSDMMA−DVS membranes are presented under the same PV conditions: feed solution, an aqueous solution of 0.05 wt % benzene; permeation temperature, 40 °C; pressure of permeation side, $1 \times 10^{-2}$ Torr. PSI in this table is the pervaporation separation index,[41−43] which is the product of the permeation rate and the separation factor, and can be used as a measure of membrane performance during PV. As can be seen in Table 3, both the normalized permeation rate and the separation factor for the benzene permselectivity of the CA/PMMA-*g*-PDMS and PFA-*g*-PDMS/PMMA-*g*-PDMS membranes were improved as compared to the PMMA-*g*-PDMS membrane. Although the separation factors of the cross-linked PDMSDMMA−DVB and PDMSDMMA−DVS membranes were lower than that of the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes, the PSI of the former membranes was much greater than that of the latter one. On the basis of this result, we discovered that the introduction of a cross-linking structure into the membrane matrix using a suitable cross-linker with a high affinity for a permeant is a very effective method to give both a high permeation rate and a high permselectivity.

## Conclusions

The PDMSDMMA membrane was cross-linked by DVB, DVS, and EGDM. The permeation and separation characteristics of a dilute aqueous solution of benzene through the cross-linked PDMSDMMA−DVB, PDMS-

**Table 3. Membrane Performance of Various Polymer Membranes Containing PDMS Components**

| various PDMS membranes | $\alpha_{\mathrm{sep.benzene/H_2O}}$ | $\alpha_{\mathrm{sorp.benzene/H_2O}}$ | $\alpha_{\mathrm{diff.benzene/H_2O}}$ | NPR[a] | PSI[b] | ref |
|---|---|---|---|---|---|---|
| PMMA | 53 | 422 | 0.13 | 0.29 | 16 | 18, 29 |
| PMMA-*g*-PDMS[c] | 620 | 739 | 0.86 | 0.13 | 226 | 39 |
| CA/PMMA-*g*-PDMA[d] | 1772 | 1267 | 1.40 | 0.71 | 81 | 39 |
| PFA-*g*-PDMS/PMMA-*g*-PDMS[e] | 4492 | | | 0.64 | 2879 | 40 |
| PDMSDMMA-DVB[f] | 3171 | 1436 | 2.21 | 1.46 | 4627 | this study |
| PDMSDMMA-DVS[g] | 2886 | 1270 | 2.46 | 1.96 | 5657 | this study |

[a] Normalized permeation rate ($10^{-5}$ kg m/(m$^2$ h)). [b] Pervaporation separation index ($10^5$NPR × $\alpha_{\mathrm{sep.benzene/H_2O}}$). [c] PDMS content: 74 mol %. [d] PDMS content: 74 mol %; CA content: 40 wt %. [e] PDMS content: 74 mol %; PFA-*g*-PDMS content: 1.2 wt %. [f] DVB content: 80 mol %. [g] DVS content: 90 mol %.

DMMA−DVS, and PDMSDMMA−EGDM membranes during PV were investigated as a function of the cross-linker content. The cross-linked PDMSDMMA membranes showed high benzene permselectivity and permeability. With increasing cross-linker content, it was very interesting for note that both the permeability and the benzene permselectivity of all cross-linked PDMSDMMA membranes increased. The permeability and benzene permselectivity were significantly influenced by the kind of cross-linker. The above permeation and separation characteristics for a dilute aqueous solution of benzene during PV could be explained by the composition sorbed into the cross-linked PDMSDMMA membranes, the contact angle for water of the membrane surface, the difference in solubility parameters between the membrane and the permeants, the degree of swelling of these membranes, and the cross-linking density of these membranes. The permselectivity for a dilute aqueous solution of benzene during PV through the cross-linked PDMSDMMA membranes was analyzed by the solution-diffusion model. The benzene permselectivity of the cross-linked PDMSDMMA membranes was mainly governed by the sorption selectivity of the permeants. The pervaporation separation index of the PDMSDMMA−DVB and PDMSDMMA−DVS membranes were very high at 4627 and 5657, respectively.

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## Note Added after ASAP Posting

This article was released ASAP on 07/29/2003. The quality of Figure 1 has been enhanced. The correct version was posted on 11/13/2003.

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