Effects of Morphology of Multicomponent Polymer Membranes Containing Calixarene on Permselective Removal of Benzene from a Dilute Aqueous Solution of Benzene

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Received November 22, 2002; Revised Manuscript Received January 10, 2003

ABSTRACT: This paper focuses on the structural characteristics of membranes used in the removal of benzene from a dilute aqueous solution of benzene by pervaporation. Poly(methyl methacrylate)-*graft*-poly(dimethylsiloxane) (PMMA-*g*-PDMS) and poly(methyl methacrylate)-*block*-poly(dimethylsiloxane) (PMMA-*b*-PDMS) membranes containing *tert*-butylcalix[4]arene (CA), (CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS) were studied. When an aqueous solution of 0.05 wt % benzene was permeated through CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes, these membranes showed strong benzene permselectivity. Both the permeability and the benzene permselectivity of CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes were enhanced by increasing the CA content, due to the affinity of the CA for benzene. The permeability and the benzene permselectivity of CA/PMMA-*b*-PDMS membranes were much greater than those of CA/PMMA-*g*-PDMS membranes. Transmission electron microscope (TEM) observations revealed that both the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes had a microphase-separated structure consisting of a PMMA phase and a PDMS phase-containing CA. The microphase-separated structure of the latter membranes was much clearer than that of the former and was lamellar. The distribution of CA in the microphase-separated structure of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes was analyzed by differential scanning calorimetry.

Introduction

Pervaporation (PV) is a highly promising membrane technique for the separation of organic liquid mixtures.[1] Membrane processes have great advantages in terms of potential savings in energy costs for the separation of organic liquid mixtures such as alcohol/water, benzene/cyclohexane, and benzene/water. Many researchers have studied the permeation and separation of organic liquid mixtures through a variety of polymer membranes by PV.[2−10]

We have reported the relationship between the structure of multicomponent polymer membranes containing poly(dimethylsiloxane) (PDMS) and vinyl polymers such as poly(methyl metacrylate) (PMMA) and poly(styrene) (PSt) and their permselectivity for aqueous ethanol solutions during PV.[11−18] The permeability and permselectivity of the multicomponent polymer membranes depended on the morphology of their microphase-separated structure. Further studies[19] revealed that the microphase separation in graft copolymer (PMMA-*g*-PDMS) membranes prepared from PMMA and PDMS significantly influenced their permeability and permselectivity for the removal of VOCs from a dilute aqueous solution of VOCs and that a continuous PDMS phase in the microphase-separated structure played an important role in the selective removal of VOCs.

In a previous paper,[20] we also studied the permeation and separation characterictics for the removal of benzene from a dilute aqueous solution of benzene, a toxic VOC, using a PMMA-*g*-PDMS membrane containing *tert*-butylcalix[4]arene (CA).[21,22] The latter is a cyclic oligomer made of phenol units linked to alkylidene groups, and it has a cavity for the potential introduction of a variety of organic compounds. The CA/PMMA-*g*-PDMS membranes showed strong benzene permselectivity, and both the permeability and the benzene permselectivity of these membranes were enhanced with increasing CA content. This enhancement in the permeability and the benzene permselectivity could be attributed to the fact that CA was preferentially distributed in the PDMS phase rather than the PMMA phase of the microphase-separated structure of the CA/PMMA-*g*-PDMS membranes, and the benzene was preferentially sorbed into the PDMS phase due to strong interactions between CA and benzene.

We previously investigated the PV characteristics of an aqueous ethanol solution through graft (PMMA-*g*-PDMS) and block (PMMA-*b*-PDMS) copolymer membranes.[18] The continuous PDMS phase in the microphase-separated structure of the PMMA-*b*-PDMS membranes was more ordered than that in the PMMA-*g*-PDMS membranes. When CA was added to these two types of membranes, it was expected that CA would be preferentially distributed in the PDMS phase of the block copolymer membrane, and consequently, the benzene permselectivity would be enhanced.

Thus, in this study the PV characteristics for the removal of benzene from a dilute aqueous solution of benzene using CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes, which were prepared from graft and block copolymers with a similar PDMS content, were investigated. Their permeability and benzene permselectivity are discussed from the viewpoints of the morphology of the microphase-separated structure of the graft and block copolymer membranes and the CA distribution within these membranes.

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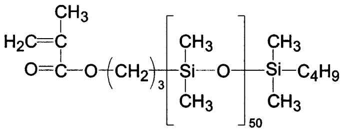
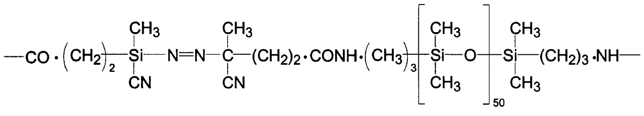
10.1021/ma025863m CCC: $25.00

Experimental Section

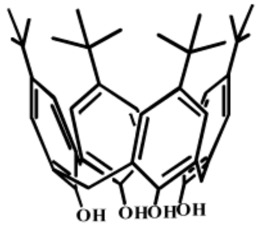
Materials. A poly(dimethylsiloxane) (PDMS) macromonomer (**1**) consisting of 51 units of PDMS was supplied by Toray Dow Corning Silicone Co., Ltd. PDMS macroazoinitiator[23−25] (**2**), which has 59 units of PDMS block subunit, was supplied by Wako Pure Chemical Industries, Ltd. Methyl methacrylate (MMA) was purified by distillation under reduced pressure. The 2, 2′-azobis(isobutyronitrile) (AIBN) recrystallized from methanol solution was used as an initiator. *tert*-Butylcalix[4]arene (CA) (**3**) was obtained from Aldrich Chem. Co., Ltd. All other solvents and reagents were of analytical grade, and they were obtained from commercial sources and used without further purification.



PDMS macromonomer (1)



PDMS macro-azo-initiator (2)



***tert*-butylcalix [4] arene (3)**

Syntheses of Graft and Block Copolymers Consisting of PMMA and PDMS. A graft copolymer consisting of PMMA and PDMS (PMMA-*g*-PDMS) was synthesized by copolymerization of PDMS macromonomer with MMA, using the methods described in previous reports.[11,14,17−20] A block copolymer consisting of PMMA and PDMS (PMMA-*b*-PDMS) was synthesized by copolymerization of MMA with a PDMS macroazoinitiator according to methods described in previous papers.[18]

The average molecular weights of the resultant PMMA-*g*-PDMS and PMMA-*b*-PDMS were determined by gel permeation chromatography (GPC) (Waters Associate Inc., R-400) with a TSK-GEL column (Tosoh Co., Ltd., G2000HXL, G3000HXL, G5000HXL) and ultraviolet spectrophotometry (Shimadzu Co. Ltd., SPD-2A). Tetrahydrofuran was used as an eluant, and the calibration was performed with polystyrene standards. The composition of the PMMA-*g*-PDMS and PMMA-*b*-PDMS (dissolved in chloroform-*d*) was determined by 270 MHz ^{1}H nuclear magnetic resonance (^{1}H NMR) (JEOL, GSX-270) spectra, obtained by measuring the integrals of the peaks assigned to the methyl protons (3.5 ppm) of PMMA and the dimethylsiloxane protons (0 ppm) of PDMS. The number-average molecular weights (M_n) and the composition of the resultant PMMA-*g*-PDMS and PMMA-*b*-PDMS are summarized in Table 1.

In this study, PMMA-*g*-PDMS with a DMS content of 74 mol % and PMMA-*b*-PDMS with a DMS content of 71 mol % were used as the matrix polymer for preparing membranes. These membranes showed the highest benzene permeability and benzene/water permselectivity among a family of PMMA-*g*-PDMS and PMMA-*b*-PDMS membranes with variable DMS content.

Table 1. Results of the Copolymerization of MMA with a PDMS Macrmonomer and PDMS Macroazoinitiator

copolymer	feed DMS units (mol%)	mol wt			polymer DMS units (mol%)
		10^5M_w	10^5M_n	M_w/M_n	
PMMA-*g*-PDMS	80	1.18	0.76	1.55	74
PMMA-*b*-PDMS	80	1.12	0.55	2.05	71

[a] Determined by GPC calibrated with a polystyrene standard. [b] Determined by ^{1}H NMR.

Preparation of PMMA-*g*-PDMS and PMMA-*b*-PDMS Membranes Containing CA. After the PMMA-*g*-PDMS or PMMA-*b*-PDMS was dissolved in benzene at 25 °C to a concentration of 4 wt %, CA was added to this benzene solution for preparation of the casting solution. The PMMA-*g*-PDMS and PMMA-*b*-PDMS containing CA (CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDM) membranes were prepared by pouring the casting solution onto a rimmed glass plate, and then allowing the solvent to evaporate completely at 25 °C. The thickness of the resultant membranes was about 160 μm.

Composition of the Solution Sorbed into the Membranes. The CA/PMMA-*g*-PDM and CA/PMMA-*b*-PDMS membranes were completely dried under reduced pressure at room temperature. The dried membranes were immersed in 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 and wiped quickly with a filter. The solution absorbed into the swollen membranes was completely desorbed under reduced pressure and was collected in a cold trap. The composition of the solution in the membrane was determined by measuring the benzene concentration in the collected solution using gas chromatography (Shimazu GC-14A).

The composition of the solution sorbed into the membranes and that of the feed solution yielded the sorption selectivity, $\alpha_{\mathrm{sorp\cdot benzene/H_2O}}$, as expressed in eq 1

$$\alpha_{\mathrm{sorp\cdot benzene/H_2O}} = (M_{\mathrm{benzene}}/M_{\mathrm{H_2O}})/(F_{\mathrm{benzene}}/F_{\mathrm{H_2O}}) \qquad (1)$$

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

Membrane Density. The density of CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes was determined by measuring their weights in air and water with an electric specific weight measure (Mirage Boeki, SD-120L) at 25 °C.

Transmission Electron Microscopy (TEM). The CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes were vapor-stained with an aqueous solution of 0.5 wt % RuO_4 in a glass-covered dish.[26] The stained membranes were then embedded in epoxy resin and cut into thin films (thickness: approximately 60 nm) with a microtome (Leica, Reichert Ultracut E). The morphological features that were highlighted by our staining procedure were observed by transmission electron microscopy (TEM) (JEOL JEM-1210) at an accelerating voltage of 120 kV.

Glass Transition Temperature (T_g) Measurements. The glass transition temperatures (T_gs) of the dry CA/PMMA-*g*-PDMS and CA/PMMA-*g*-PDMS membranes and the wet membranes immersed in the feed solution were determined by differential scanning calorimetry (DSC) (Rigaku, TAS-200). The specimens were heated from about −150 to +150 °C at a heating rate of 20 °C/min.

Permeation Measurements. Pervaporation (PV) was performed using the apparatus described in previous studies.[11−20] The experimental conditions were as follows: permeation temperature, 40 °C; pressure on the permeate side, 1×10^{-2} Torr. The effective membrane area was 13.8 cm^2. In all PV experiments in this study, the air-side surface of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes faced the feed side of the permeation cell. An aqueous solution of 0.05 wt % benzene was used as the feed solution. The feed solution was circulated between the PV cell and the feed tank

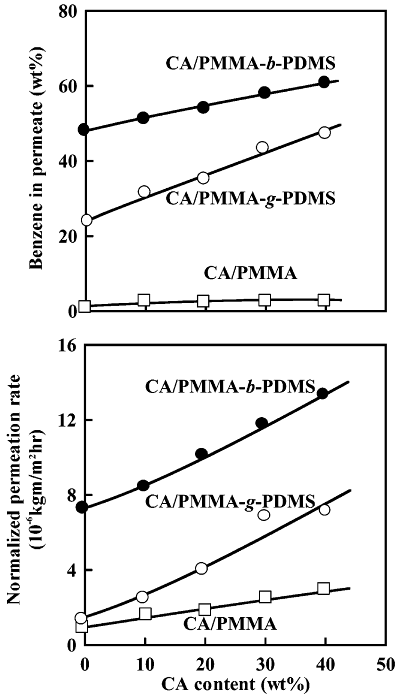


Figure 1. Normalized permeation rates and benzene concentrations in the permeate for PV of an aqueous solution of 0.05 wt % benzene through CA/PMMA-*g*-PDMS (○), CA/PMMA-*b*-PDMS (●), and CA/PMMA (□) membranes as a function of CA content.

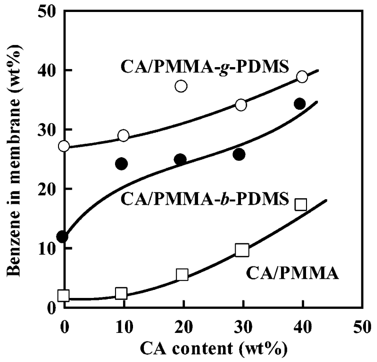


Figure 2. Effect of CA content on benzene concentration in the CA/PMMA-*g*-PDMS (○), CA/PMMA-*b*-PDMS (●) and CA/PMMA (□) membranes immersed in an aqueous solution of 0.05 wt % benzene.

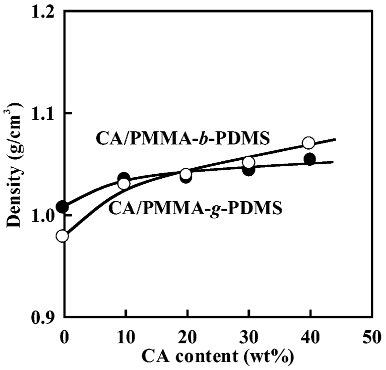


Figure 3. Relationship between the CA content and the density of CA/PMMA-*g*-PDMS (○) and CA/PMMA-*b*-PDMS (●) membranes.

to maintain a constant concentration of feed solution in the PV cell. After the feed and permeate containing benzene and water were dissolved in a specific amount of ethanol, the compositions of the feed solution and the permeate were determined by a gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector (FID) and a capillary column (Shimadzu Co., Ltd., PorapacQ) heated to 180 °C. The permeation rate for the aqueous benzene solution during PV was determined from the weight of the permeate collected in a cold trap, the permeation time and the effective membrane area. 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 rates through the membranes. Permeation results in this study were after the steady-state flux.

The composition of the benzene and water mixtures in the feed and permeate yielded the separation factor, $\alpha_{\text{sep}\cdot\text{benzene/H}_2\text{O}}$, as expressed by eq 2,

$$\alpha_{\text{sep}\cdot\text{benzene/H}_2\text{O}} = (P_{\text{benzene}}/P_{\text{H}_2\text{O}})/(F_{\text{benzene}}/F_{\text{H}_2\text{O}}) \qquad (2)$$

where F_{benzene} and $F_{\text{H}_2\text{O}}$ are the weight fractions of benzene in the feed and water and P_{benzene} and $P_{\text{H}_2\text{O}}$ are those in the permeate, respectively.

Losses of dissolved CA from CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes were not observed.

Results and Discussion

Permeation and Separation Characteristics of Graft and Block Copolymer Membranes Containing Calixarene. In Figure 1, the normalized permeation rates and the benzene concentrations in the permeate for an aqueous solution of 0.05 wt % benzene partitioned through CA/PMMA-*g*-PDMS, CA/PMMA-*b*-PDMS, and CA/PMMA membranes by PV are shown as a function of the CA content. The normalized permeation rate in Figure 1 is the product of the permeation rate and the membrane thickness. The fact that the benzene concentrations in the permeates of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes were much higher than in the feed suggests that these membranes were highly benzene permselective. Both the benzene concentration in the permeates and the normalized permeation rates of these graft and block copolymer membranes containing CA increased with increasing CA content. These results indicate that the addition of CA to PMMA-*g*-PDMS, PMMA-*b*-PDMS membranes can enhance both permselectivity and permeability. In general, most modifications of PV membranes cannot improve permselectivity without lowering permeability. Therefore, it is unusual that the addition of CA enables the membrane selectivity to increase without lowering the permeability.

On the other hand, the CA/PMMA membrane showed an increase in the normalized permeation rate and a very slight increase in benzene concentration in the permeate with increasing CA content. However, the increase in the permeability and the benzene permselectivity of the CA/PMMA membrane was much smaller than those of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes, and there is an obvious difference in the permeability and benzene permselectivity between the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes. These facts suggest that the morphology of these membranes significantly influences both permeability and permselectivity.

To clarify the effect of CA on the affinity of benzene for CA/PMMA-*g*-PDMS, CA/PMMA-*b*-PDMS, and CA/PMMA membranes, the benzene concentrations in these membranes were examined. Figure 2 shows the benzene concentrations of the CA/PMMA-*g*-PDMS, CA/PMMA-*b*-PDMS, and CA/PMMA membranes immersed in an

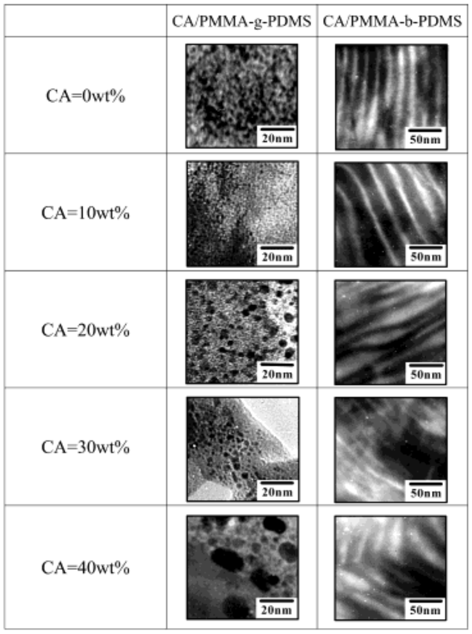


Figure 4. Transmission electron micrographs of cross sections of CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes with various CA contents. The dark region stained by RuO_4 represents PDMS and CA.

aqueous solution of 0.05 wt % benzene as a function of CA content. The benzene concentrations in all of these membranes increased with increasing CA content. These results indicate that the addition of CA to the PMMA-*g*-PDMS, PMMA-*b*-PDMS, and PMMA membranes can enhance the preferential absorption of benzene into these membranes. It is well-known that CA can form a complex with benzene.[21] Thus, enhancement of the benzene concentration in the CA/PMMA-*g*-PDMS, CA/PMMA-*b*-PDMS, and CA/PMMA membranes may be due to specific interaction between benzene and CA in the membranes. The preferential absorption of benzene following the addition of CA is an important factor for high benzene permselectivity of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes.

If the addition of CA is exclusively responsible for the enhancement of the affinity between benzene and CA, the benzene concentration absorbed into the various membranes should be equal. However, as can be seen in Figure 2, the benzene concentration in these membranes differed markedly between the various membranes. This difference in benzene concentration is dependent on differences in the affinity of the membrane matrix polymer for benzene. As shown in Figure 1, despite the fact that CA/PMMA-*b*-PDMS membranes showed higher benzene permselectivity than CA/PMMA-*g*-PDMS membranes, the benzene concentration in CA/PMMA-*g*-PDMS membranes was greater than that in the CA/PMMA-*b*-PDMS membranes. This difference in the affinity for benzene between the CA/PMMA-*g*-PDMS and the CA/PMMA-*b*-PDMS membranes may also be due to differences in the affinity of the polymer matrix portion for benzene.

Structure of Graft and Block Copolymer Membranes Containing Calixarene. It is well-known that the permeation and separation of organic liquid mixtures through polymer membranes generally depend on the chemical and physical structure of the membrane. This section focuses mainly on the physical structure of the membrane to elucidate the effects of CA on the permeability and permselectivity of CA/PMMA-*g*-PDMS and CA/PMMA-*b* PDMS membranes.

Figure 3 shows the effects of CA content on the density of CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS

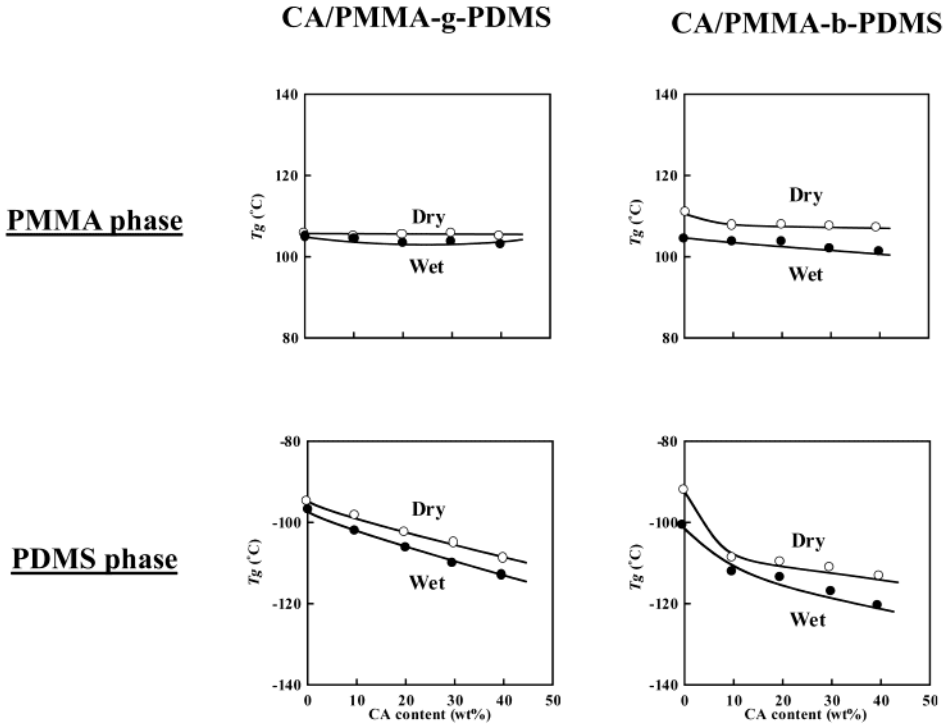


Figure 5. Effects of CA content on T_gs of the PMMA phase and the PDMS phase in the microphase separated CA/PMMA-*g*-PDMS membranes: (○) the dried membranes; (●) the membranes immersed in an aqueous solution of 0.05 wt % benzene. Higher and lower T_gs observed in DSC of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes were assigned to the PMMA and PDMS phases, respectively.

membranes. The addition of CA to the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes increases membrane density. Generally, increasing the membrane density lower of permeability is due to lower diffusivity of the penetrants in a high-density matrix. Although the membrane density increased in the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes with increasing CA content, both the permeability and benzene permselectivity of these membranes was enhanced. Enhancement of the benzene permselectivity following an increase in membrane density cannot be due to the physical structure of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes because the benzene molecules are much larger than water molecules. Therefore, the fact that both the normalized permeation rate and the benzene permselectivity increased in the CA/PMMA-*g*-PDMS and CA/PMMA-*b* PDMS membranes suggests that the permeation and separation mechanisms in CA/PMMA-*g*-PDMS and CA/PMMA-*b* PDMS membranes are quite different from the usual PV mechanism.

We previously reported[11−14,17−19] that the morphology of microphase-separated multicomponent polymer membranes significantly influenced the permeation and separation of organic liquid mixtures by PV. In the selective removal of benzene from water, the continuity of the PDMS phase in the PMMA-*g*-PDMS membranes played a particularly important role.[19] The effects of CA content on the morphology of the CA/PMMA-*g*-PDMS membranes was also investigated.[20] A microphase separated structure with a PDMS continuous phase was observed in the CA/PMMA-*g*-PDMS membranes as well as in the PMMA-*g*-PDMS membranes without CA. The benzene permselectivity could be strongly attributed to the continuous PDMS phase containing CA. Therefore, investigating the effects of CA content on the morphology of the CA/PMMA-*b*-PDMS membranes is of great importance for clarifying the mechanism by which the addition of CA enhances both permeability and permselectivity.

Transmission electron micrographs of cross sections of CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes with variable CA content are shown in Figure 4. The PDMS and CA were stained by RuO_4, but the PMMA component was not. As can be seen in micrographs of PMMA-*g*-PDMS and PMMA-*b*-PDMS membranes without CA, their morphology was quite different. This difference significantly reflected the difference in permeability and benzene permselectivity of these membranes in Figure 1. These micrographs clearly demonstrate that all CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes, as well as the PMMA-*g*-PDMS membrane, had a distinct microphase separation. In the CA/PMMA-*b*-PDMS membranes especially, a change in the microphase-separated structure with increased CA content was almost undetectable, and a lamellar microphase separation structure was formed. The TEM micrographs of the CA/PMMA-*b*-PDMS membranes suggest that CA exists mainly in the continuous PDMS phase. In the CA/PMMA-*b*-PDMS membranes, the boundary layer between the PMMA phase and the PDMS phase was not well-defined with increasing CA content. Therefore, it is presumed that CA could not be distributed exclusively in the PDMS phase and consequently appears at the boundary layer between the PMMA phase and the PDMS phase. The clusters of CA observed in the TEM images of the CA/PMMA-*g*-PDMS membranes with a CA content of exceeding 20 wt % could be attributed to the formation of clusters of the PDMS phase, because the continuous PDMS phase in the CA/PMMA-*g*-PDMS membranes was smaller than in the CA/PMMA-*b*-PDMS membranes. The latter membranes also demonstrated microphase separation with a continuous PDMS phase containing CA. The high benzene permselectivity of the CA/PMMA-*b*-PDMS membranes can be attributed to the continuous PDMS phase containing CA and consisting of a clearly lamellar structure.

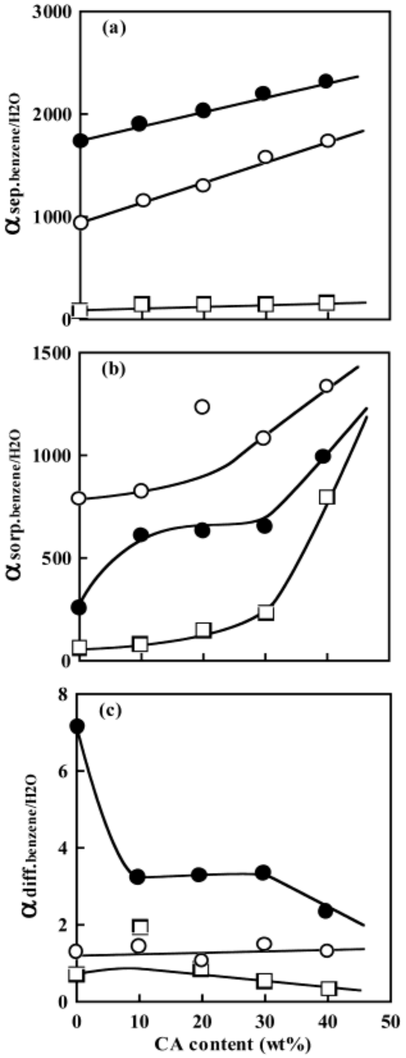


Figure 6. Effects of CA content in CA/PMMA-*g*-PDMS (○), CA/PMMA-*b*-PDMS (●), and CA/PMMA (□) membranes on their separation factor (a), sorption selectivity (b), and diffusion selectivity (c) for an aqueous solution of 0.05 wt % benzene.

To investigate the distribution of CA in the microphase separation, the effects of CA content on the T_gs of the PMMA phase and the PDMS phase were examined by DSC. The DSC measurements demonstrated that the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes had two T_gs, assigned to the PMMA phase and the PDMS phase, which were around +105 and −100 °C, respectively. In Figure 5, the T_gs of the PMMA and PDMS phases in dried CA/PMMA-*g*-PDMS and PMMA-*b*-PDMS membranes and membranes immersed in an aqueous solution of 0.05 wt % benzene are shown as a function of CA content. The T_g of the PMMA phase did not change with increasing CA content, but the T_g of the PDMS phase in both dried and wet CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes decreased.

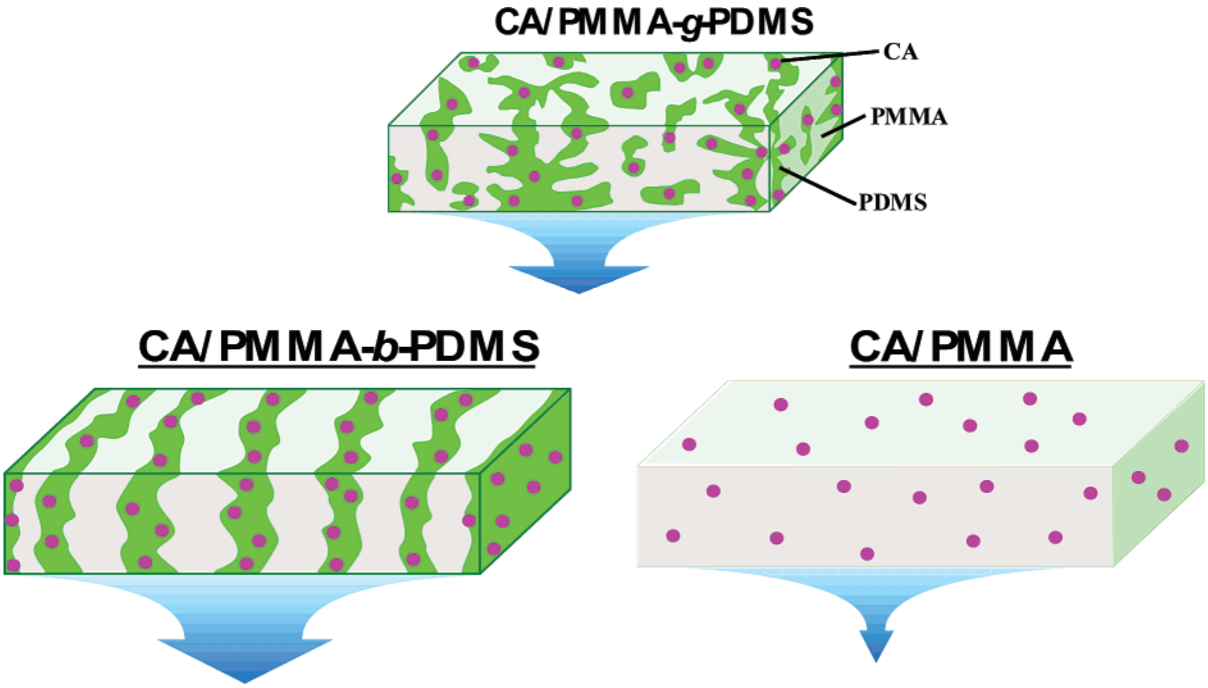


Figure 7. Structural models of CA/PMMA-*g*-PDMS, CA/PMMA-*b*-PDMS, and CA/PMMA membranes.

The decrease in the T_g of the PDMS phase suggests that the CA in the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes was present in the PDMS phase rather than in the PMMA phase. The DSC measurements revealed that the CA was preferentially distributed in the PDMS phase rather than in the PMMA phase. In addition, immersing the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes in an aqueous solution of 0.05 wt % benzene significantly decreased the T_g of the PDMS phase, but the T_g of the PMMA phase changed very little. This decrease in the T_g of the PDMS phase upon immersion of the membranes into an aqueous benzene solution can be attributed to the absorption of benzene into the PDMS phase containing CA. Consequently, since the CA in the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes was preferentially distributed in the PDMS phase rather than the PMMA phase, the benzene was preferentially absorbed into the former phase due to the strong interaction between CA and benzene. It is hypothesized that this preferential absorption of benzene into the PDMS phase containing CA is an important factor in the selective permeation of benzene over water. Therefore, the permselective removal of benzene from its dilute aqueous solution by both CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes may result from the fact that CA is preferentially distributed in the continuous PDMS phase.

In Figure 1, quite different slopes of the dependences were observed. These differences can be attributed to differences in T_gs of the PMMA phase and the PDMS phase in wet membranes.

Permselectivity Mechanism of Graft and Block Copolymer Membranes Containing Calixarene. In the solution-diffusion model,[27,28] differences in the solubility of the permeants in the polymer membranes and differences in the diffusivity of permeants in the polymer membranes are very significantly related to the permselectivity.[29] It is very important to determine the sorption selectivity and diffusion selectivity to elucidate the separation mechanism of a dilute aqueous solution of benzene through the graft and block copolymer membranes having a microphase-separated structure. Thus, to discuss the benzene permselectivity of a dilute aqueous solution of benzene through CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes from the viewpoint of the solution-diffusion mechanism, both the sorption selectivity and the diffusion selectivity must be determined. The sorption selectivity, $\alpha_{\mathrm{sorp\cdot benzene/H_2O}}$, was determined from eq 1 and the diffusion selectivity, $\alpha_{\mathrm{diff\cdot benzene/H_2O}}$, could be calculated from eq 3

$$\alpha_{\mathrm{diff\cdot benzene/H_2O}} = \alpha_{\mathrm{sep\cdot benzene/H_2O}}/\alpha_{\mathrm{sorp\cdot benzene/H_2O}} \quad (3)$$

In Figure 6, the separation factor, the sorption selectivity, and the diffusion selectivity for an aqueous solution of 0.05 wt % benzene through CA/PMMA-*g*-PDMS, CA/PMMA-*b*-PDMS, and CA/PMMA membranes are shown as a function of the CA content. The sorption selectivities of all of the membranes with various CA contents were greater than the diffusion selectivities. This observation suggests that the removal of benzene from a dilute aqueous solution of benzene using the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes is mainly governed by the sorption process. The fact that benzene was preferentially absorbed into these membranes rather than water also supports this conclusion. Furthermore, the sorption selectivity increased with increasing CA content. The increase in the benzene permselectivity with increased CA content was due to an increase in the solubility of benzene in the CA/PMMA-*g*-PDMS, PMMA-*b*-PDMS, and CA/PMMA membranes. The fact that the separation factor of the CA/PMMA-*b*-PDMS membranes was higher than that of the CA/PMMA-*g*-PDMS membranes and the sorption selectivities of the former membranes were lower than that of the latter, can be understood by both the sorption and diffusion selectivity, as summarized in Figure 6. Namely, the benzene permselectivity of the CA/PMMA-*g*-PDMS membranes was mainly dependent on the sorption selectivity, because the diffusion selectivity was very low. The benzene permselectivity of the CA/PMMA-

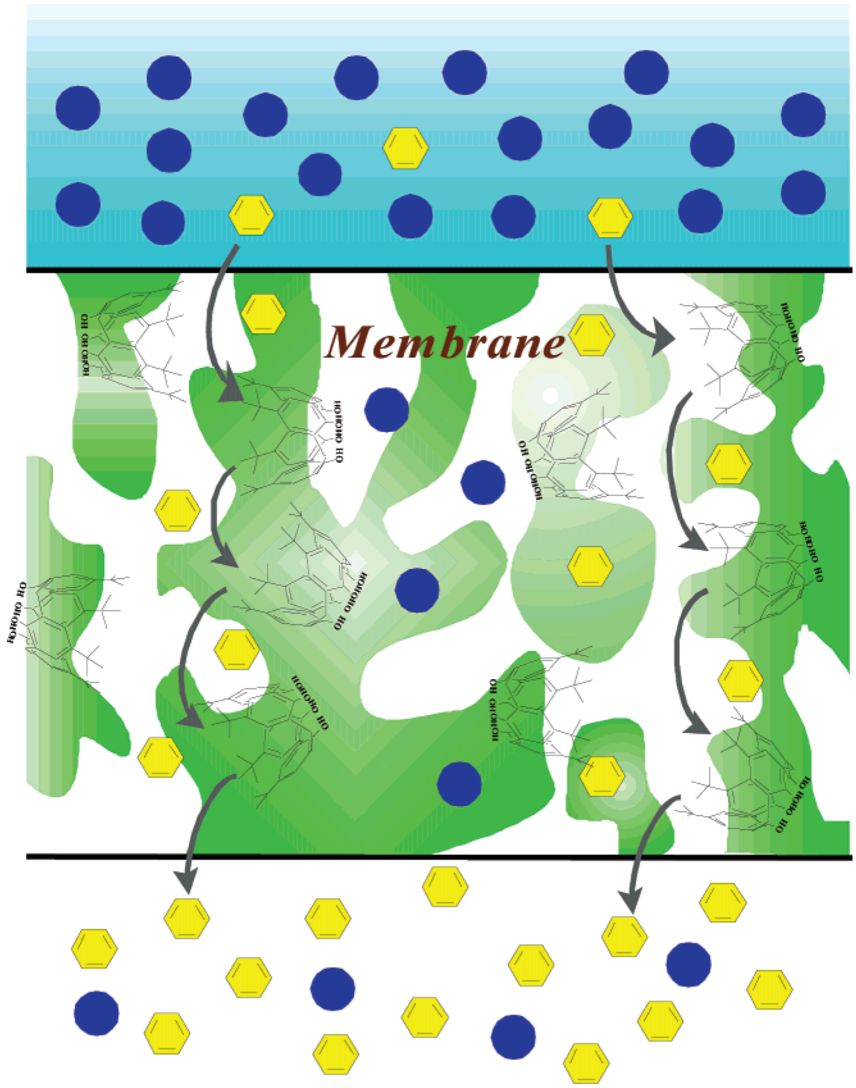


Figure 8. Tentative illustration of the permeation mechanism for benzene in a dilute aqueous solution of benzene through CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes on the basis of the solution-diffusion model: (●) water; (benzene ring) benzene.

b-PDMS membranes was governed by both the sorption and diffusion selectivity. The benzene permselectivity of the CA/PMMA membranes was exclusively due to the sorption selectivity.

Model of Permeation and Separation of Graft and Block Copolymer Membranes Containing CA. Structural models for the CA-containing membranes based on TEM observations and DSC measurements for the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes are shown in Figure 7. The affinity for benzene of the CA/PMMA membranes was enhanced with the addition of CA, but the benzene permeability was not particularly high, because these membranes did not have a PDMS phase. This observation suggests that the PDMS phase plays a very important role in the benzene permselectivity. The benzene permselectivities of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes differed, and it was presumed that the internal structures of these membranes significantly influenced the permeation and separation mechanisms. Namely, the PMMA-*b*-PDMS membranes clearly had a more continuous PDMS phase than the CA/PMMA-*g*-PDMS membranes, and consequently, the former membranes showed very high benzene permselectivity.

On the basis of the above results, a permselective mechanism for the partitioning of a dilute aqueous solution of benzene through CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes can be explained by the tentative model shown in Figure 8. As described in the previous section, the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes have a stronger affinity for benzene than for water because of the recognition function of CA. In the sorption process, therefore, the solubility of benzene in the membranes is enhanced by the addition of CA. On the other hand, the carrier transport mechanism implies that CA facilitated the transport of benzene in the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes. Thus, in the diffusion process, the benzene sorbed into the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes is preferentially transported over water by CA due to the specific interaction between CA and benzene. The continuous PDMS phase containing CA in the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes might act also as a path for the transport of benzene by CA. The high benzene permselectivity of the CA/PMMA-*b*-PDMS membranes having a continuous PDMS phase and consisting of a clearly lamellar structure is due to the fact that both the sorption and diffusion selectivity effectively contributed to the permeation and separation of a dilute aqueous solution of benzene. Thus, the strong enhancement of the benzene permselectivity of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes can be attributed to both CA functioning as a carrier to selectively transport benzene and the continuity of the PDMS phase in the microphase separation.

Conclusions

To improve the permselectivity of membranes for the removal of benzene from a dilute aqueous solution of benzene, calixarene (CA) was introduced into PMMA-*g*-PDMS and PMMA-*b*-PDMS membranes. When an aqueous solution of 0.05 wt % benzene was permeated through CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes, their permeabilities and benzene permselectivities were enhanced with increased CA content. The benzene permselectivity of the CA/PMMA-*b*-PDMS membranes was greater than that of the CA/PMMA-*g*-PDMS membranes. The introduction of CA into PMMA-*g*-PDMS and PMMA-*b*-PDMS membranes increased the solubility of benzene in membranes because of the specific interaction between CA and benzene. In addition, TEM observations demonstrated that the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes were microphase separated having a discontinuous PMMA phase and a continuous PDMS phase, including CA. The phase separated structure of the CA/PMMA-*b*-PDMS membranes was more clearly lamellar in structure than that of CA/PMMA-*g*-PDMS membranes. Analysis of the permeation and separation characteristics of the CA/PMMA-*g*-PDMS and CA/PMMA-*b*-PDMS membranes for a dilute aqueous solution of benzene during PV by the solution-diffusion model confirmed that the improvements in both membrane permeability and permselectivity with the introduction of CA were dependent on the following: (i) preferential absorption of benzene into the CA/PMMA-*b*-PDMS and CA/PMMA-*b*-PDMS membranes and (ii) the high diffusivity of benzene in the continuous PDMS phase with CA in the CA/PMMA-*b*-PDMS membranes. We conclude that introducing molecular recognition devices like CA into microphase-separated graft and block copolymer membranes is very effective for improving both the permeability and the permselectivity of PV membranes for the removal of VOCs from water.

Acknowledgment. This research was supported financially by a Grant-in-Aid for Scientific Research on Priority Areas (B) “Novel Smart Membranes Containing Controlled Molecular Cavities” from the Ministry of Education, Science, Sports, and Culture, Japan, by Scientific Research (C) from the Japan Society for Promotion of Science (JSPS), and by the Kansai University Research Grants, Grant-in-Aid for Joint Research, 2001−2002.

References and Notes

(1) Haung, R. Y. M. *Pervaporation Membrane Separation Processes*; Elsevier: Amsterdam, 1991.
(2) Psaume, R.; Aurelle, Y.; Mora, J. C.; Bersillon, J. L. *J. Membr. Sci.* **1988**, *36*, 373.
(3) Blume, I.; Wijmans, J. G.; Baker, R. W. *J. Membr. Sci.* **1990**, *49*, 253.
(4) Nguyen, T. Q.; Nobe, K. *J. Membr. Sci.* **1987**, *36*, 11.
(5) Raghunath, B.; Hwang, S.-T. *J. Membr. Sci.* **1992**, *75*, 29.
(6) Schnabel, S.; Moulin, P.; Nguyen, Q. T.; Roizard, D.; Aptel, P. *J. Membr. Sci.* **1998**, *142*, 129.
(7) Mishima, S.; Kaneoka, H.; Nakagawa, T. *J. Appl. Polym. Sci.* **1995**, *103*, 195.
(8) Fang, Y.; Pham, V. A.; Matsuura, T.; Santerre, J. P.; Narbaitz, R. M. *J. Appl. Polym. Sci.* **1994**, *54*, 1937.
(9) Yang, D.; Majumdar, S.; Kovenklioglu, S.; Sirkar, K. K. *J. Membr. Sci.* **1995**, *103*, 195.
(10) Jian, K.; Pintauro, P. N. *J. Membr. Sci.* **1997**, *135*, 41.
(11) Miyata, T.; Takagi, T.; Kadota, T.; Uragami, T. *Macromol. Chem. Phys.* **1995**, *196*, 1211.
(12) Miyata, T.; Higuchi, J.; Okuno, H.; Uragami, T. *J. Appl. Polym. Sci.* **1996**, *61*, 1315.
(13) Miyata, T.; Takagi, T.; Uragami, T. *Macromolecules* **1996**, *29*, 7787.
(14) Miyata, T.; Nakanishi, Y.; Uragami, T. *Macromolecules* **1997**, *30*, 5563; *ACS Symp. Ser.* **1999**, *733*, 280.
(15) Uragami, T.; Doi, T.; Miyata, T. *ACS Symp. Ser.* **1999**, *733*, 263.
(16) Uragami, T.; Doi, T.; Miyata, T. *Int. J. Adhes. Adhes.* **1999**, *19*, 405.
(17) Miyata, T.; Takagi, T.; Higuchi, J.; Uragami, T. *J. Polym. Sci., Polym. Phys.* **1999**, *37*, 1545.
(18) Miyata, T.; Obata, S.; Uragami, T. *J. Polym. Sci., Polym. Phys.* **2000**, *38*, 584; *Macromolecules* **1999**, *32*, 3712; *Macromolecules* **1999**, *32*, 8465.
(19) Uragami, T.; Yamada, H.; Miyata, T. *Trans. Mater. Res. Soc. Jpn.* **1999**, *24*, 165; *J. Membr. Sci.* **2001**, *187*, 255.
(20) Uragami, T.; Meotoiwa, T.; Miyata, T. *Macromolecules* **2001**, *34*, 6806.
(21) Böhmer, V. *Angrew. Chem. Int. Ed. Engl.* **1995**, *34*, 713.
(22) Shinkai, S. *Tetrahedron* **1993**, *49*, 40, 8933.
(23) Inoue, H.; Ueda, A.; Nagai, S. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 1077.
(24) Inoue, H.; Ueda, A.; Nagai, S. *J. Appl. Polym. Sci.* **1988**, *35*, 2039.
(25) Inoue, H.; Matsumoto, A.; Matsukawa, K.; Ueda, A. *J. Appl. Polym. Sci.* **1990**, *40*, 1917.
(26) Trent, J. S.; Scheinbein, J. I.; Couchman, P. R. *Macromolecules* **1983**, *16*, 589.
(27) Binning, R. C.; Lee, R. J.; Jennings, J. F.; Martin, E. C. *Ind. Eng. Chem.* **1961**, *53*, 47.
(28) Aptel, P.; Cuny, J.; Jozefonvicz, J.; Morel, G.; Neel, J. *J. Appl. Polym. Sci.* **1974**, 18, 365.
(29) Uragami, T.; Takuno, M.; Miyata, T. *Macromol. Chem. Phys.* **2002**, *203*, 1162.

MA025863M