Removal of volatile organic compounds from dilute aqueous solutions by pervaporation

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Removal of volatile organic compounds (VOCs) from aqueous solutions through poly(methyl methacrylate) (PMMA)-polydimethylsiloxane (PMMA-g-PDMS), poly(ethyl methacrlyrate)-PDMS (PEMA-g-PDMS) and poly(n-buthyl methaclyrate)-PDMS (PBMA-g-PDMS) graft copolymer membranes by pervaporation (PV) were investigated. When an aqueous solution of dilute benzene was permeated through their membranes, they were benzene-permselective. Permeation and separation characteristics of the PMMA-g-PDMS and PEMA-g-PDMS membranes changed drastically at a DMS content of 40 and 70 mol%, respectively. However, the permselectivity and permeability of the PBMA-g-PDMS membrane were gradually increased with increasing DMS content. Furthurmore, the observations by the transmission electron microscope revealed that the PMMA-g-PDMS and PEMA-g-PDMS membranes have distinct microphase separation but the PBMA-g-PDMS membrane does not. The permeation and separation characteristics of their membranes in PV are discussed in detail from the viewpoint of the physical and chemical membrane structures of the graft copolymer membranes.

Key words: volatile organic compounds, graft copolymer membranes, pervaporation, dilute aqueous solution, microphase separation

INTRODUCTION

It is increasingly important to remove volatile organic compounds (VOCs) from water in drained factory waste and living waste. At present, VOCs are removed by absorbent. On the other hand, pervaporation is promising technique for removal of VOCs in water.

Poly(dimethysiloxane) (PDMS) membrane is known as a benzene-permselective, in the separation of the aqueous benzene solutions by pervaporation.[1] The benzene-permselectivity of the membrane is attributable to its stronger affinity for benzene than for water. An advantage of the PDMS membrane is high diffusivity of benzene in the membrane due to its low Tg. On the other hand, PDMS membranes have some disadvantages such as weak mechanical strength. Many researchers have introduced crosslinking structures into the PDMS membrane to improve its disadvantage. However, introducing cross-linking structures made the diffusivity of the permeants in the membrane low.

In this study, we have studied the relationship between the two-component polymer membranes consisting of PDMS and poly(alkylmethacrylate) and their permselectivity for an aqueous benzene solution to develop pervaporation membranes to remove benzene.

EXPERIMENTAL SECTION

Materials. PDMS macromonomer which has 81 units of pendant PDMS was supplied by Toray Dow Corning Silicone Co., Ltd. Methyl methacrylate (MMA), ethyl methacrylate (EMA) and n-buthyl methacrylate (BMA) as comonomers were purified by distillation under reduced pressure in nitrogen gas. 2,2-Azobis(isobutyronitrile) (AIBN) recrystallized from methanol solution was used as an initiator.
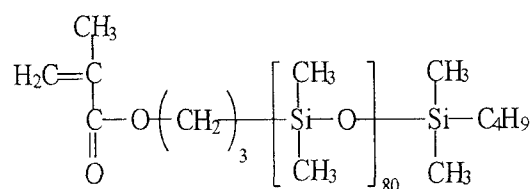
PDMS macromonomer

Copolymerization of PDMS macromonomer with MMA, EMA and BMA. PDMS macromonomer and methacrylate solutions in benzene to make a 40wt% with AIBN (0.5wt% relative to the monomers) were placed in a glass tube. Copolymerizations were performed for 6 hr to synthesize PMMA-g-PDMS, PEMA-g-PDMS and PDMS-g-PBMA under nitrogen gas. They were purified by reprecipitation from benzene solution into a 1:2 mixture of n-hexane and ethanol, and dried *in vacuo*. (The resulting copolymers were characterized by ^{1}H-NMR, JEOL; GSX-400 and GPC, Waters Associate Inc; R-400) The DMS content in PMMA-g-PDMS, PEMA-g-PDMS and PBMA-g-PDMS were determined from ^{1}H-NMR spectra by measuring the integrals of the peaks assigned to methyl protons (3.5 ppm) of the methacrylate and DMS protons (0 ppm) of the DMS macromonomer. Averages of molecular

Tab. 1. Result of the polymerization of MMA, EMA and
BMA with a PDMS macromonomer.

Monomer		Moleculer weight[a]			Polymer[b]
Methacrylate	mol% of DMS units in feed	Mw×10⁻⁵	Mn×10⁻⁵	Mw/Mn	mol% of DMS units in copolymer
MMA	0	0.89	0.51	1.75	0
	50	1.74	0.66	2.62	34
	60	1.14	0.60	1.90	52
	70	1.52	0.74	2.04	68
EMA	0	2.82	2.21	1.28	0
	10	1.96	1.36	1.43	17
	30	2.11	1.46	1.43	56
	50	1.95	1.95	1.55	72
	60	1.94	1.94	1.50	75
	70	2.40	1.69	1.42	85
BMA	0	2.22	2.12	1.05	0
	10	1.67	1.24	1.35	16
	30	1.63	1.21	1.35	41
	60	2.05	1.76	1.17	73
	70	2.13	1.83	1.17	86

a) Determined by GPC

b) Determined by ¹H-NMR

weights of the copolymers were determined by GPC,
equiepped with on a TSK-GEL column (Tosoh Co. Ltd.;
G2000HXL, G3000HXL, G5000HXL). In Table 1,
characterizations of graft copolymers is summarized.

Membrane Preparation. A prescribed amount of graft
copolymer was dissolved in benzene at 25°C at a
concentration of 4 wt% for the preparation of casting
solutions. Their membranes were prepared by pouring the
solvent to evaporate completely at 25°C. (The resulting
membranes were transparent and their thickness were 80 -
200μm.)

Permeation Measurements. Pervaporation was
carried out using the apparatus as shown in Figure 1 under
the following conditions: permeation temperature, 40°C;
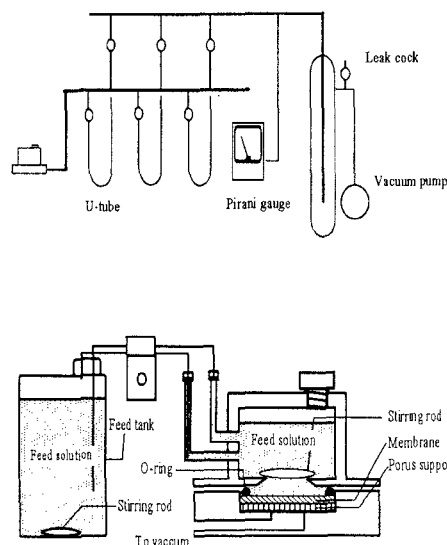pressure of permeate side, 1 x 10⁻² Torr. The effective

Fig.1. Pervaporation apparatus

membrane area was 13.8 cm². An aqueous solution of
0.05 wt% benzene was used as a feed solution. The
compositions of the feed solutions and permeate were
determined using a gas chromatography (Shimadzu GC-
17A) which have flame ionzation detector (FID) and
capillary column (Shimadzu Co. Ltd; PorapacQ) that
heated at 180°C.

Transmission Electron Micrographs (TEM). The
graft copolymer membranes were vapor-stained with an
aqueous solution of 5 wt% RuO₄. The stained membranes
embedded in epoxy resin were sliced into thin films
(thickness approximately 50nm) with a microtome (Leica;
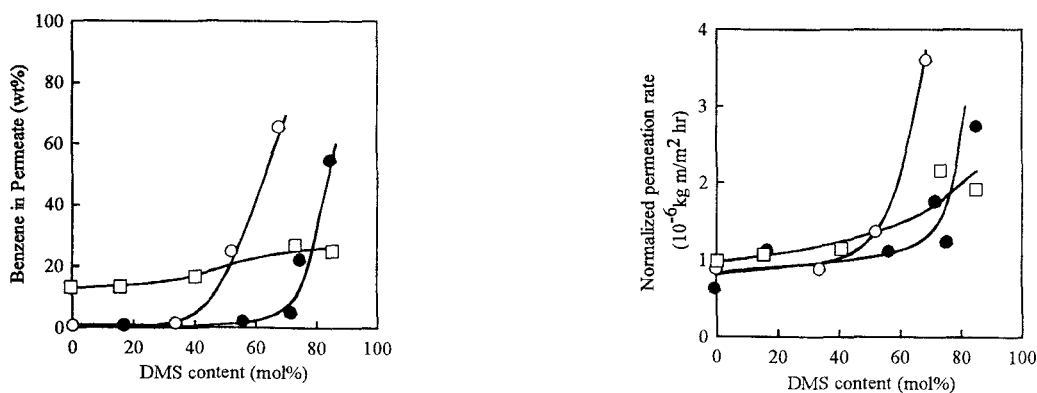Reichert Ultracut E). The structures of their membranes

Fig. 2. Effect of the DMS content on the benzene concentration in the permeate and normalized permeation rate
for an aqueous solution of 0.05wt% benzene through the PMMA-g-PDMS (○), PEMA-g-PDMS (●) and
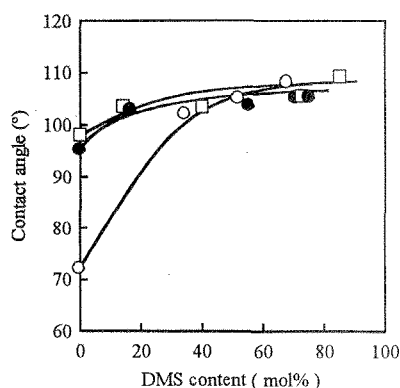PBMA-g-PDMS(☐) membranes by PV.

Fig. 3. Relationship between the DMS content and the contact angle to water on the surface of the PMMA-g-PDMS(O), PEMA-g-PDMS (●) and PBMA-g-PDMS(☐) membranes.

Fig. 4. Effect of the DMS content on the density of the PMMA-g-PDMS (O), PEMA-g-PDMS (●) and PBMA-g-PDMS(☐) membranes.

were observed with a transmission electron microscope (TEM) (JEOL JEM-1210) at an accelerting voltage of 80kV.

RESULT AND DISCUSSION

Pervaporation Characteristics of PMMA-g-PDMS, PEMA-g-PDMS and PBMA-g-PDMS membranes.

Figure 2 shows the effect of DMS content on the benzene concentration in the permeate and normalized permeation rate for an aqueous solution of 0.05wt% benzene through the PMMA-g-PDMS, PEMA-g-PDMS and PBMA-g-PDMS membranes by pervaporation. The normalized permeation rate is the product of the permeation rate and the membrane thickness. All the graft copolymer membranes exhibited increases in benzene-permselectivity and permeability with increasing DMS content. Furthermore, the benzene-permselectivity of the PMMA-g-PDMS membrane increased dramatically at a DMS content of more than about 40 mol%, and that of the PEMA-g-PDMS membrane showed drastic changes in its benzene-permselectivity and permeability at more than about 70 mol%. On the other hand, the benzene-permselectivity of the PBMA-g-PDMS membrane was enhanced gradually with DMS content.

Generally, permselectivity of polymer membrane is strongly dependent upon chemical and physical structures. From the view point of chemical structure, it is apparent that PDMS has a stronger affinity for benzene than poly(alkyl methacrylate). Therefore, the membranes with a high DMS content have a stronger affinity for benzene. Since glass transition temperatures of PDMS and PMMA are about -127°C and 128°C, the diffusivity of benzene in the membranes is enhanced with increasing DMS content. These results lead to the speculation that both the physical
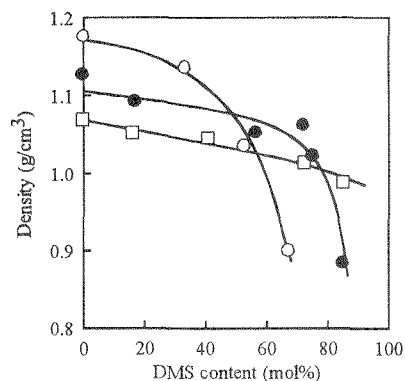
and chemical structures closely influence on the permselectivity of the membranes. We measured contact angle and membrane density, and observed the morphology by TEM to reveal the chemical and physical structures.

Contact angle. Figure 3, the contact angles to water on the surface of the PMMA-g-PDMS, PEMA-g-PDMS and PBMA-g-PDMS membranes shows as function of the DMS content in graft copolymers. Contact angles to water on the glass side of all the membranes increased with increasing DMS content. This is attributed to the fact that the hydrophobic PDMS component is localized at the air side surface of membranes. Contact angles to water become constant at a DMS content of about 50mol%. This suggests that the surfaces of their membranes were covered with PDMS component at more than 50mol%.

Membrane Density. Figure 4 shows the relationship between the DMS content on the density of the graft copolymer membranes. The densities of the PMMA-g-PDMS and PEMA-g-PDMS membranes decreased dramatically at a DMS content of about 40 and 70mol%, respectively, and that of the PBMA-g-PDMS membrane decreased gradually. Those changes correspond to the changes of normalized permeation rate (Figure 2). Figure 2 and Figure 4 reveal that the membrane density closely influences permeation rate of the membrane. In order to discuss the membrane structure more detail, morphologies of the graft copolymer membranes were observed by TEM.

Microphase separation. Figure 5 shows the TEM images for cross-section of the graft copolymer membranes. The dark region represents the PDMS
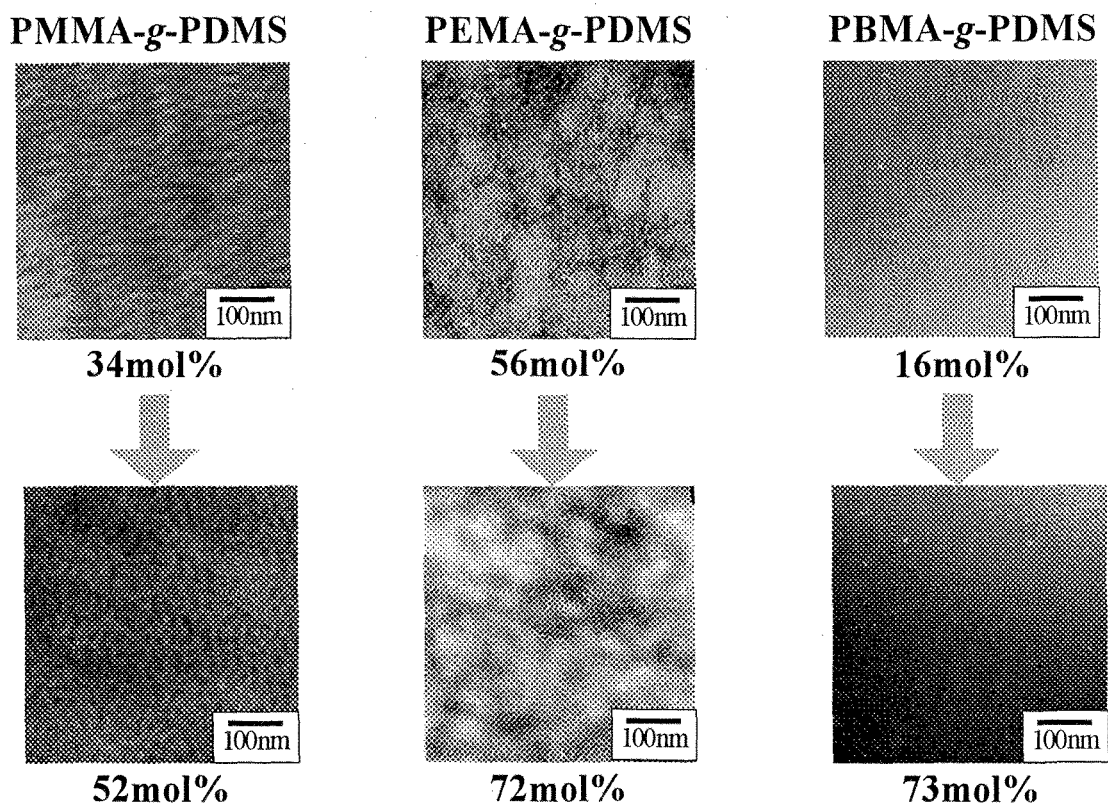
PMMA-*g*-PDMS   PEMA-*g*-PDMS   PBMA-*g*-PDMS

Fig. 5. TEM micrographs of the PMMA-*g*-PDMS, PEMA-*g*-PDMS and PBMA-g-PDMS membranes.

component stained by RuO_4. In the PMMA-g-PDMS and PEMA-*g*-PDMS membranes, distinct microphase separation was observed, but PBMA-g-PDMS membranes had no microphase separation. Furthermore, the PDMS component formed a continuous phase at a DMS content of more than 52 and 72mol% in PMMA-g-PDMS and PEMA-*g*-PDMS membranes, respectively. The benzene-permselectivity of the PMMA-g-PDMS and PEMA-*g*-PDMS membranes was dramatically improved at a DMS content of more than 52mol% and 72mol%. However benzene-permselectivity of PBMA-g-PDMS membranes was gently enhanced with increasing DMS content. These results suggest that the morphology of microphase separation in the graft copolymer membranes governs their benzene-permselectivity. Since benzene is mainly permeated through the continuous poly (alkyl methacrylate) phases in the graft copolymer membranes consisting of a discontiuos PDMS phase, the diffusivity of benzene is very low. After the PDMS component forms a continuous phase, the membranes show the high benzene-permselectity due to the high diffusivity of benzene in the continuous PDMS phase. This is the reason why the benzene-permselectivity

of the graft copolymer membranes is strongly enhanced by an increase in the DMS content.

CONCLUSION

The graft copolymer membranes showed benzene-permselectivity for an aqueous solution containing a slight amount of benzene. This permselectivity was enhanced with increasing DMS content in the graft copolymer membranes and influenced significantly by the microphase separated structure. In the graft copolymer membranes with the microphase separation, when the DMS component had a continuous phase, the benzene-permselectivity was remarkably increased. It was suggested that such a high benzene-permselectivity was dependent on a high diffusivity of benzene through the continuous DMS phase.

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