Effects of Fluorine-Containing Graft and Block Copolymer Additives on Removal Characteristics of Dilute Benzene in Water by Microphase-Separated Membranes Modified with These Additives

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ABSTRACT: This paper focuses on the effects of the addition of fluorine-containing graft or block copolymer additives composed of 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acylate (perfluoroalkyl acylate, PFA) and poly(dimethylsiloxane) macromonomer (PDMS) or PDMS macro-azo-initiator to a microphase-separated membrane consisting of PDMS and poly(methyl methacrylate) (PMMA) on the benzene/water selectivity for an aqueous dilute benzene solution during pervaporation and the surface characteristics and structures of the surface-modified PMMA/PDMS membranes. The addition of the fluorine-containing copolymer additives, PFA-*g*-PDMS and PFA-*b*-PDMS, to a PMMA-*g*-PDMS membrane yielded hydrophobic surfaces at the air side of surface-modified membranes due to the localization of their additives on the air-side surface of these membranes. The addition of a small amount of the PFA-*g*-PDMS and PFA-*b*-PDMS enhanced both the benzene/water selectivity and the permeability for an aqueous dilute benzene solution during pervaporation because of the formation of their hydrophobic surfaces and the existence of the microphase-separated structures with a continuous PDMS phase in the inner of these membranes. When larger amounts of the PFA-*g*-PDMS and PFA-*b*-PDMS were added to a PMMA/PDMS, the latter additive could keep the microphase-separated structures with a continuous PDMS phase, but the former did not. The relationship between the permeation and separation characteristics for the removal of benzene from an aqueous benzene solution and the structures the PMMA-*g*-PDMS membranes surface-modified with PFA-*g*-PDMS and PFA-*b*-PDMS as fluorine-containing polymer additives is discussed in detail.

Introduction

Volatile organic compounds (VOCs) such as aromatic hydrocarbons and chlorinated hydrocarbons used as washing solvents in the chemical industry cause water and soil pollution. Such pollution contaminates subterranean water and consequently water in rivers and ponds. Recently, it has been pointed out that the removal of VOCs from watewater and the source of tap water is very important for our living.[1−3] An activated carbon method, ozone processing, and other methods have been developed to remove VOCs from water.[1] However, these methods do not efficiently remove VOCs and the cost of treatment is high. Membrane processes are greatly advantageous in terms of potential saving in energy coasts for the separation of organic liquid mixtures such as alcohol/water, benzene/cyclohexane, benzene/water, and so on.

Many workers have studied the permeation and separation of organic liquid mixtures by a variety of polymer membranes during pervaporation.[4−13] Pervaporation is a promising membrane technique for the separation of VOCs/water mixtures.[4,5,9−13]

We have reported the relationship between the structure of multicomponent polymer membranes containing poly(dimethylsiloxane) (PDMS) and poly(methyl methacrylate) (PMMA) and their permselectivity for aqueous ethanol solutions during pervaporation.[14−20] The permeability and permselectivity of the multicomponent polymer membranes are dependent on the morphology of their microphase-separated structure. Further studies[21,22] revealed that the microphase separation in graft copolymer (PDMA-*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,[23] we also studied the permeation and separation characteristics for the removal of benzene from a dilute aqueous solution of benzene using a PMMA-*g*-PDMS membrane surfaced-modified with a fluorine-containing graft copolymer additive composed of 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate (perfluoroalkyl acrylate, PFA) and PDMS (PFA-*g*-PDMS/PMMA-*g*-PDMS). The PFA-*g*-PDMS/PMMA-*g*-PDMS membranes showed strong benzene/water selectivity, and both the permeability and the benzene/water selectivity of these membranes were enhanced by addition of PFA-*g*-PDMS as a fluorine-containing polymer additive to the PMMA-*g*-PDMS membrane. This enhancement in the permeability and the benzene/water selectivity could be attributed to both their hydrophobic surfaces and microphase-separated structures of the PMMA-*g*-PDMS membranes.

We previously investigated the structure of graft (PMMA-*g*-PDMS) and block (PMMA-*b*-PDMA) copolymer membranes; 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. On the basis of these results, when block (PFA-*b*-PDMS) as a fluorine-containing polymer additive is added to the PMMA-*g*-PDMS membrane, it is expected that the fluorine components in the PFA-*b*-PDMS are arranged regularly and densely on the membrane surface, and consequently the surface of PFA-*b*-PDMS/PMMA-*g*-PDMS membranes becomes efficiently water-repellent.

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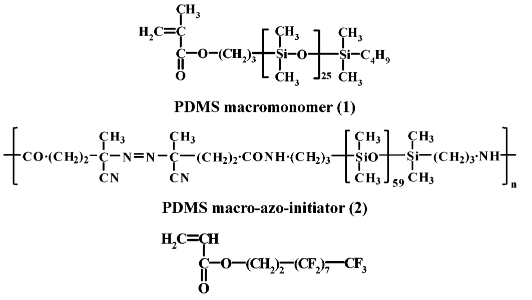
Chart 1


PDMS macromonomer (1)

PDMS macro-azo-initiator (2)

PFA (3)

Thus, in this study the pervaporation characteristics for the removal of benzene from a dilute aqueous solution of benzene using PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes, which were prepared by adding fluorine-containing graft and block copolymer additives to the PMMA-*g*-PDMS membrane, were investigated. Their permeability and benzene/water selectivity are discussed from the viewpoints of the morphology of the microphase-separated structure of the PMMA-*g*-PDMS membranes and the localization on the membrane surface of the PFA-*g*-PDMS and PFA-*b*-PDMS as polymer additives.

Experimental Section

Materials. The poly(dimethylsiloxane) macromonomer (**1**), which has 25 units of pendant PDMS, was supplied by Toray Dow Corning Silicone Co., Ltd. PDMS macro-azo-initiator (**2**),[24−26] which has 59 units of the PDMS block subunit, was supplied by Wako Pure Chemical Industries Ltd. 1*H*,1*H*,2*H*,2*H*-Heptadecafluorodecyl acrylate (perfluoroalkyl acrylate: PFA) (**3**) (Clariant (Japan) K.K.) was used as received. Methyl methacrylate (MMA) as a comonomer was purified by distillation under reduced pressure in nitrogen gas. 2,2-Azobis(isobutyronitrile) (AIBN) recrystallized from benzene solution was used as an initiator. All other solvents and reagents were of analytical grade and were obtained from commercial sources and used without further purification.

Copolymerization of PDMS Macromonomer with MMA or PFA. Graft copolymers consisting of PMMA and PDMS (PMMA-*g*-PDMS) were synthesized by the copolymerization of a PDMS macromonomer with MMA by the methods reported in previous paper as follows:[14,15,21,22] The PDMS macromonomer was copolymerized with MMA using AIBN in benzene at 60 °C for 6 h under nitrogen gas. The resulting PMMA-*g*-PDMS was isolated by slow precipitation with a 1:2 mixture of *n*-hexane and ethanol and was purified by reprecipitation from benzene solution into a 1:2 mixture of *n*-hexane and ethanol. In this study, PMMA-*g*-PDMS with a DMS content of 74 mol % was used as a matrix polymer because its membrane showed the highest permeability and selectivity for a dilute aqueous solution of benzene in PMMA-*g*-PDMS membranes with various DMS contents. The highest permeability and selectivity were due to the fact that the membrane with a DMS content of 74 mol % had a microphase separation consisting of a continuous PDMS phase to allow benzene to permeate preferentially, as reported in a previous paper. A graft copolymer consisting of PFA and PDMS (PFA-*g*-PDMS) was obtained by the copolymerization of a PDMS macromonomer with PFA by the method reported in a previous paper as follows:[23] PDMS macromonomer and PFA in a typical composition were dissolved together with AIBN (0.5 wt % relative to the monomers) in benzene to make a 40% solution. The mixture was then transferred to a glass tube. The copolymerization was carried out at 60 °C for 6 h under nitrogen gas. The resulting PFA-*g*-PDMS was isolated by slow precipitation with a 1:2 mixture of *n*-hexane and ethanol. It was purified by reprecipitation from benzene solution into a 1:2 mixture of *n*-hexane and ethanol and dried at 40 °C in vacuo.

A block copolymer composed of PFA and PDMS (PFA-*b*-PDMS) was prepared as followed: PDMS macro-azo-initiator and MMA in a typical composition were dissolved in benzene to create a 40 wt % solution, and the mixture was them transferred to a glass tube. The polymerization, the isolation, and purification of the resulting PFA-*b*-PDMS were similar procedures to PFA-*g*-PDMS.

Average molecular weights of PFA-*g*-PDMS were determined by gel permeation chromatography (GPC) (Waters Associates, Inc., R-400), equipped with a TSK-GEL column (Tosoh Co., Ltd.; G2000HXL, G5000HXL), and ultraviolet spectrophotometry (Shimadzu Co., Ltd., SPD-2A).

Tetrahydrofuran was used as an eluent, and calibration was done with polystyrene standards. The number-average molecular weight of PFA-*g*-PDMS and PFA-*b*-PDMS were 182 000 and 203 000 g/mol, respectively, and the ratio of the weight-average molecular weight to the number-average molecular weight (M_w/M_n) was about two. The compositions of the resultant PFA-*g*-PDMS and PFA-*b*-PDMS were determined from 270 MHz ^{1}H nuclear magnetic resonance (NMR) (JEOL; EX-270) spectra by measuring the integrals of the peaks assigned to methylene protons (2.5 and 4.5 ppm), and the PFA and DMS contents in the resulting PFA-*g*-PDMS and PFA-*b*-PDMS were about 90 mol %. In this study, therefore, PFA-*g*-PDMS and PFA-*b*-PDMS with a PFA content of 10 mol % were used as fluorine-containing polymer additives.

Membrane Preparation. Prescribed amounts of PMMA-*g*-PDMS were dissolved in benzene at 25 °C at a concentration of 4 wt % for the preparation of casting solutions. Furthermore, the prescribed amounts of PFA-*b*-PDMS (PFA-*b*-PDMS/PMMA-*g*-PDMS membranes) were prepared by pouring the casting solutions onto rimmed stainless steel plates and allowing the solvent to evaporate completely at 25 °C in dry air. The resulting membranes were transparent, and their thickness was about 150 μm.

A membrane taken off the stainless steel plate has two surfaces that were formed under a different environment: A surface of the membrane was formed in contact with the dried air, and another surface was formed in contact with the stainless steel plate. In this study, we call them the air-side surface and the stainless steel-side surface of the membrane.

Permeation Measurements. Pervaporation was performed using the apparatus described in previous studies.[14−23] The experimental conditions were as follows: permeation temperature, 40 °C; pressure of permeate side, 1×10^{-2} Torr. The effective membrane area was 13.8 cm^2. An aqueous solution of 0.05 wt % benzene was used as a feed solution. The feed solution was circulated between the pervaporation cell and the feed tank to maintain the concentration of the feed solution in the pervaporation cell constant during pervaporation. After the permeate was dissolved in a definite amount of ethanol for mixing water with benzene, its composition was determined using a gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector (FID) and a capillary column (Shimadzu Co., Ltd., Porapak Q) heated to 180 °C. The permeation rates of an aqueous benzene solution in pervaporation were determined from the weight of the permeate collected in a cold trap, the permeation time and effective membrane area. The results of the permeation of an aqueous benzene solution by pervaporation were reproducible, and the errors inherent in the permeation measurements are of the order of a few percent.

Contact Angle Measurement. Contact angles of water on the air-side and stainless steel-side surface of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes were measured using a contact angle meter (Erma model G-1) at 25 °C. The contact angles were determined from the advancing contact angle (θ_a), and the receding contact angle (θ_b) by eq 1.

$$\theta = \cos^{-1}\left(\frac{\cos\theta_a + \cos\theta_b}{2}\right) \tag{1}$$

In this study, the surface free energy was obtained from the contact angles of water and formamide with eq 2, which was propsed by

Owens et al.,[27] as follows:

$$\frac{(1 + \cos \theta)\gamma_1}{2} = (\gamma_s^{\ d}\gamma_1^{\ d})^{1/2} + (\gamma_s^{\ p}\gamma_1^{\ p})^{1/2} \qquad (2)$$

$$\gamma_s = \gamma_s^{\ d} + \gamma_s^{\ p}$$

where γ_s and γ_1 are the surface free energy of the solid and liquid, and $\gamma_s^{\ d}$, $\gamma_s^{\ p}$, $\gamma_1^{\ d}$, and $\gamma_1^{\ p}$ are the dispersion force components and polar force components of the surface free energy of the solid and the liquid, respectively. The dispersion force component and polar force component of the surface free energy of water are 21.8 and 51.0 erg/cm^2, respectively, and those of formamide are 39.5 and 18.7 erg/cm^2, respectively.[28,29]

X-ray Photoelectron Spectroscopy (XPS). Surfaces of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes were characterized with an X-ray photoelectron spectroscope (JEOL, JPS-9000MX). Typical operation conditions were as follows: Mg Kα radiation with 10 kV and 10 mA. The pressure in the instrumental chamber was less than 1×10^{-5} Pa. No radiation damage was observed during the data collection time. The charge correction in the binding energy scale was done by setting the $-CH_2-$ peak in the carbon spectra to 280.5 eV. Overlapping peaks were resolved into their individual components of the core-level spectra, which were well described by Gaussians. The full width at half-maximum (fwhm) of each individual peak was less than 2.0 eV.

Transmission Electron Micrographs (TEM). The PMMA-*g*-PDMS/PEMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes were vapor-stained with an aqueous solution of 0.5 wt % RuO_4 in glass-covered dishes.[30] The stained membranes were embedded in epoxy resin and cross sectioned into thin films (Leica; Reichert Ultracut E). The morphological features that can be brought out by our staining procedure were observed with a transmission electron microscope (TEM) (JEOL JEM-1210) at an accelerating voltage of 80 kV.

Atomic Force Microscopy (AMF). Shapes of the surface of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes were observed by an AMF (IIS SPA400). Measurements were carried out by trapping mode. The sensed lever was set up at 20 N m.

Results and Discussion

Permeation and Separation Characteristics. In Figure 1 are shown the effects of the PFA−PDMS content on the normalized permeation rate and the benzene concentration in the permeate for an aqueous solution of 0.05 wt % benzene through the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes during pervaporation. As can be seen from this figure, in all membranes the benzene/water selectivity of the PMMA-*g*-PDMS membranes containing PFA-*g*-PDMS or PFA-*b*-PDMS was greater than that of the PMMA-*g*-PDMS membrane without PFA-*g*-PDMS or PFA-*b*-PDMS. The benzene/water selectivity of the PFA-*b*-PDMS/PMMA-*g*-PDMS membranes containing a smaller amount of PFA-*b*-PDMS yielded an approximately similar benzene/water selectivity to the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes containing a larger amount of PFA-*g*-PDMS. This result suggests that the addition of PFA-*b*-PDMS is more effective for the water-repellent on the surface of the PMMA-*b*-PDMS membranes than that of PFA-*g*-PDMS. Thus, the contact angle for water of these membranes was measured to investigate the degree of water-repellency of their membranes.

Characterization of Membrane Surface. Figure 2 shows the effect of the PFA-PDMS (PFA-*g*-PDMA or PFA-*b*-PDMS) on the contact angle for water on the air-side and stainless steel-side surfaces of the PFA-*g*-PDMA/PMMA-*g*-PDMS or PFA-*b*-PDMS/PMMA-*g*-PDMS membranes. Even though the addition of either polymer additive, the contact angle for water on the air-side surface of the membranes increased significantly. These results suggest that the air-side surface of these membranes became more hydrophobic and was water-repellent. The addition of PFA-*b*-PDMS to the PMMA-*g*-PDMS yielded higher contact angles for water in comparison with that of the PFA-*g*-PDMS and was much more effective for the water-repellent. Thus, the surface free energies for the air-side and stainless steel-side surfaces of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes were determined from the contact angles for water and formamide on the air-side and stainless steel-side surfaces of these membranes. In Figure 3, the surface free energies for the air-side and stainless steel-side surfaces of these membranes are shown. As can be seen from this figure, the surface free energies for both surfaces of these membranes decreased drastically following the addition of PFA-*g*-PDMS and PFA-*b*-PDMS. In the surface free energies of the air-side surface of these membranes, those of the PFA-*b*-PDMS/PDMS membranes were lower than those of the PFA-*g*-PDMS/PDMS membranes. These results indicate that PFA-*b*-PDMS was more significantly concentrated at the air-side surface than PFA-*g*-PDMS. The surface free energies of the air-side surface of these membranes were lower than those of the stainless steel-side surface. These results suggest that the hydrophobic PFA-*g*-PDMS and PFA-*b*-PDMS were more preferentially concentrated at the air-side surface than at the stainless steel-side surface because air is much more hydrophobic than the stainless steel surface. The surface free energy of Teflon (poly(tetrafluoroethylene)), well-known as a typical hydrophobic material, is 22 erg/cm^2, and those of the PFA-*g*-PDMS and PFA-*b*-PDMS as polymer additives prepared in this study were lower than that of Teflon. From this fact, it is expected that the surface of the membranes can be very efficiently made water-repellent by addition of polymer additive with an extremely small amount. The addition of the PFA-*b*-PDMS to the PMMA-*g*-PDMS gave

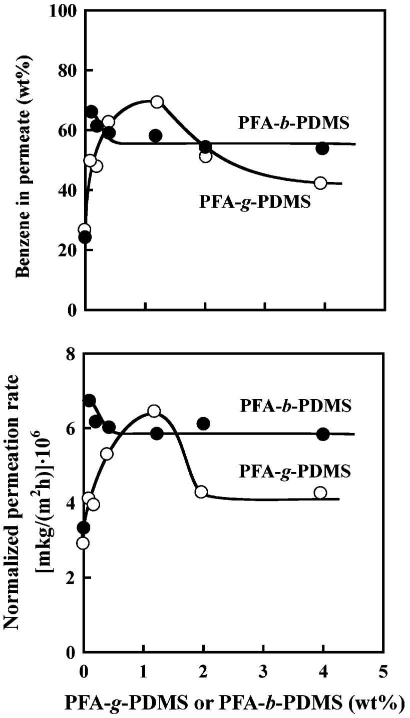


Figure 1. Effects of the PFA-*g*-PDMS or PFA-*b*-PDMS content on the normalized permeation rate and the benzene/water selectivity for an aqueous solution of 0.05 wt % benzene through the PFA-*g*-PDMS/ PMMA-*g*-PDMS (○) or PFA-*b*-PDMS/ PMMA-*g*-PDMS (●) membranes during pervaporation.

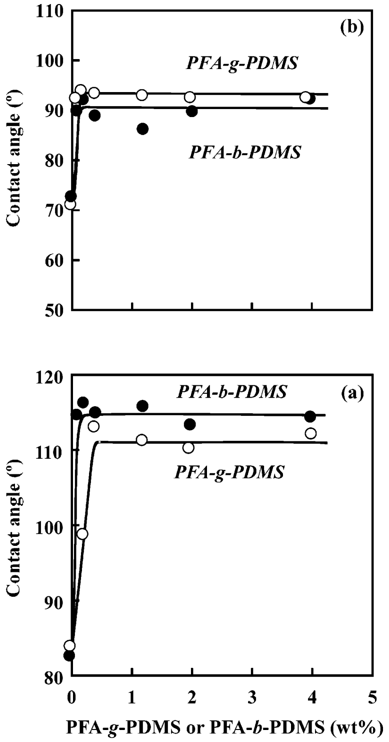


Figure 2. Effects of the PFA-*g*-PDMS or PFA-*b*-PDMS content on the contact angles for water on the air-side surface (a) and stainless steel-side surface (b) of the PFA-*g*-PDMS/PMMA-*g*-PDMS (○) or PFA-*b*-PDMS/PMMA-*g*-PDMS (●) membranes.

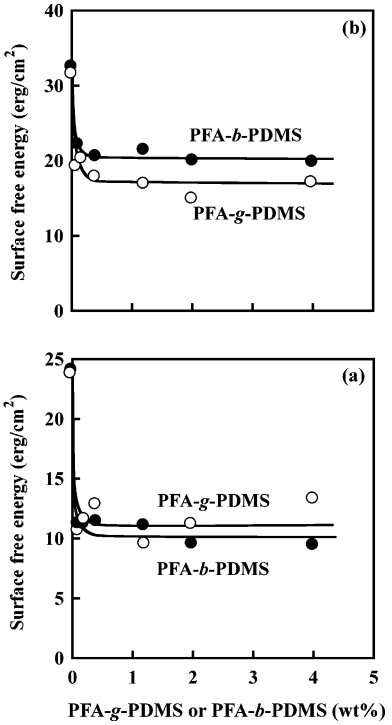


Figure 3. Effects of the PFA-*g*-PDMS or PFA-*b*-PDMS content on the surface free energy on the air-side surface (a) and stainless steel-side surface (b) of the PFA-*g*-PDMS/PMMA-*g*-PDMS (○) or PFA-*b*-PDMS/PMMA-*g*-PDMS (●) membranes.

much more lower surface free energy on the air-side surface of the membranes than that of PFA-*g*-PDMS. From this fact, it is presumed that the block copolymer (PFA-*b*-PDMS) is easily localized on the air-side surface of the membranes in comparison with the graft copolymer (PFA-*g*-PDMS).

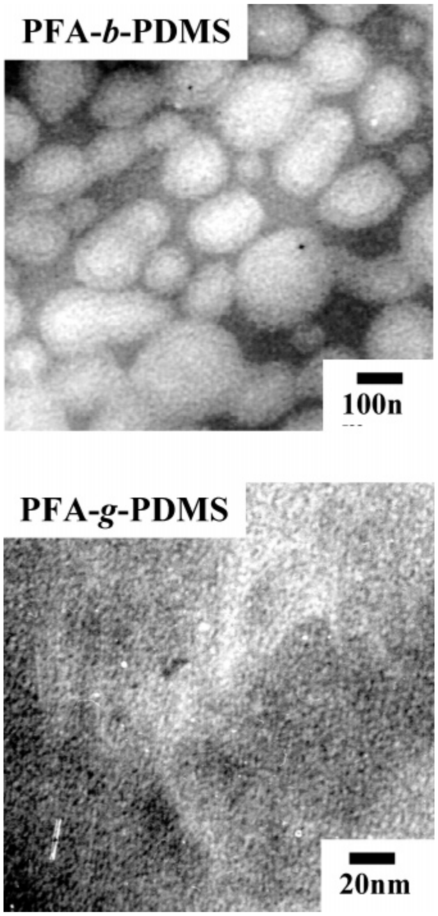


Figure 4. Transmission electron microscopy of the PFA-*g*-PDMS and PFA-*b*-PDMS.

In Figure 4, the transmission electron microscopy of the PFA-*g*-PDMS and PFA-*b*-PDMS is shown, in which TEM samples were prepared by casting the PFA-*g*-PDMS and PFA-*b*-PDMS on cupper meshes and drying them. The dark part is the PDMS component in the PFA-*g*-PDMS and PFA-*b*-PDMS. It is clear that both the PFA-*g*-PDMS and PFA-*b*-PDMS had a distinct microphase-separated structure, and the domain size of the PFA-*b*-PDMS was larger than that of the PFA-*g*-PDMS although a measure in the TEM images of the PFA-*g*-PDMS and PFA-*b*-PDMS was different. This result is due to higher cohesion of the fluorine component in the PFA-*b*-PDMS. Smaller microphase-separated structure in white particles of the PFA-*b*-PDMS was observed. This fact supports that the PFA-*b*-PDMS has a highly regular microphase-separated structure in comparison with the PFA-*g*-PDMS. On the other hand, the PFA-*g*-PDMS forms very small microphase separation in which the size of one domain is several nanometers. This fact suggests that only several molecules of the PFA or PDMS exist in one domain, a compatible state is formed, and consequently the regularity is not observed and the cohesion of the fluorine component is weaker in comparison with the PFA-*b*-PDMS. When the characterizations of the PFA-*g*-PDMS and PFA-*b*-PDMS are compared, the PFA-*b*-PDMS has a higher regularity, gives a denser cohesion of the fluorine component, and consequently shows a high water-repellency. From these characteristics of the PFA-*g*-PDMS and PFA-*b*-PDMS, the permeation and separation characteristics for an aqueous dilute benzene solution through the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes in Figure 1 are significantly influenced not only by the localization on the air-side surface of the fluorine-containing graft and block

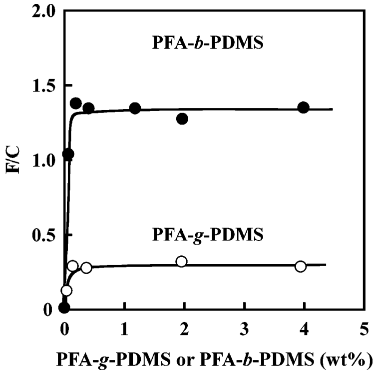


Figure 5. Effect of the PFA-*g*-PDMS or PFA-*b*-PDMS content on the F/C value on the air-side surface of the PFA-*g*-PDMS/PMMA-*g*-PDMS (○) or PFA-*b*-PDMS/ PMMA-*g*-PDMS (●) membranes.

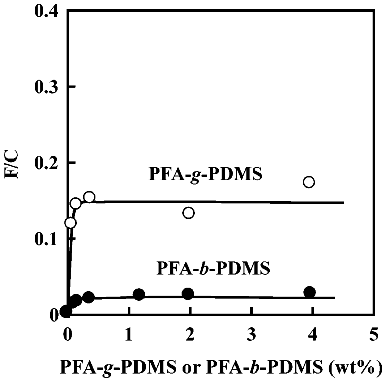


Figure 6. Effect of the PFA-*g*-PDMS or PFA-*b*-PDMS content on the F/C value on the stainless steel-side surface of the PFA-*g*-PDMS/ PMMA-*g*-PDMS (○) or PFA-*b*-PDMS/ PMMA-*g*-PDMS (●) membranes.

copolymer additives but also by the morphology of microphase-separated structure formed by the PFA-*g*-PDMS and PFA-*b*-PDMS.

The atomic ratios of fluorine and carbon (F/C) near the air-side surface of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes and those near stainless steel-side surface of these membranes are shown in Figures 5 and 6, respectively. In the air-side surface, the F/C values of the PFA-*b*-PDMS/PMMA-*g*-PDMS membranes were greater than those of the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes. This result supports that the fluorine component of the former membranes is preferentially localized on the air-side surface. On the other hand, in the stainless steel-side surface, the F/C value of the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes was higher than that of the PFA-*b*-PDMS/PMMA-*g*-PDMS membranes. Low F/C values of the latter membranes suggest that the fluorine component of the latter membranes was almost not localized on the stainless steel-side surface. The fact that the F/C values of the air-side surface of both the PFA-*g*-PDMS/ PMMA-*g*-PDMS and PFA-*b*-PDMA/PMMA-*g*-PDMS membranes were greater than those of the stainless steel-side surface of these membranes obviously supports that both the PFA-*g*-PDMS and PFA-*b*-PDMS as polymer additives were localized on the air-side surface.

It is very interesting to investigate the degree of an appearance of these polymer additives on the membrane surface. The PFA contents in the PFA-*g*-PDMS and PFA-*b*-PDMS used in this study were about 10 mol %. Carbon and fluorine numbers in the PFA molecule are 13 and 17, respectively. Carbon number in one unit of PDMS is 2. Therefore, when the ratio of PFA/PDMS is 1/9, the F/C value in the PFA is 0.548. The value of F/C in only PFA is 1.31 (=17/13). The F/C values on the air-side surface of the PFA-*b*-PDMS/PMMA-*g*-PDMS membranes were about 1.30, and those of the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes were about 0.33−0.41. The former result supports that the PFA-*b*-PDMS as a block copolymer additive is almost localized on the air-side surface of the PFA-*b*-PDMS/PMMA-*g*-PDMS membranes. On the other hand, the latter result is due to an infiltration to the inside of the membrane of a little fluorine component of the PFA-*g*-PDMS as a graft copolymer additive or the detection of PDMS component of the base polymer, PMMA-*g*-PDMS. From these results, it is supported that the addition of PFA-*b*-PDMS to the PMMA-*g*-PDMS preferentially localizes the fluorine components in the PFA-*b*-PDMS on the air-side surface.

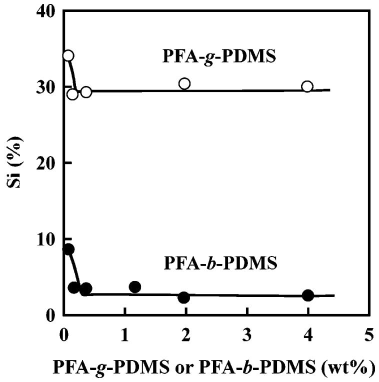


Figure 7. Effect of the PFA-*g*-PDMS or PFA-*b*-PDMS content on the Si concentration on the air-side surface of the PFA-*g*-PDMS/ PMMA-*g*-PDMS (○) or PFA-*b*-PDMS/ PMMA-*g*-PDMS (●) membranes.

Figure 7 shows the Si percentage in main elements such as Si, C, F, and O containing no H and N on the air-side surface of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/ PMMA-*g*-PDMS membranes. As can be seen from this figure, the Si content of on the air-side surface of the PFA-*b*-PDMS/ PMMA-*g*-PDMS membranes was much more lower than that of the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes, and Si was almost not contained on the air-side surface of the former membranes. The Si percentage on the air-side surface of the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes was higher than that in the PFA-*b*-PDMS as a polymer additive (19%). This is attributed to the detection of the PDMS component in the base polymer, PDMS-*g*-PDMS. This discussion supports the presumption in the measurements of the F/C value.

On the basis of the above results, it is found that the PFA-*b*-PDMS compared to the PFA-*g*-PDMS had a higher ability as a polymer additive for the selective removal of benzene from an aqueous dilute benzene solution and a higher water-repellency due to the addition of the former polymer additive could be attributed to the localization of a lot of fluorine components on the air-side surface of the PFA-*b*-PDMS/PMMA-*g*-PDMS membranes. Then, the shape of the air-side surface was observed by an atomic force microscopy (AMF) to visibly observe a cohesive state of the fluorine components. In Figure 8, the AMF images of the air-side surface of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes with different polymer additive content are shown. As can be seen from these images, the shape of the former membranes was approximately homogeneous, but the regularity was not observed. On the other hand, in the latter membranes patterns such as a tortoise shell was observed. The length and height of the domain of these patterns were about 50−100 nm and 3−5 nm, respectively, as shown in Figure 9. These results suggest that

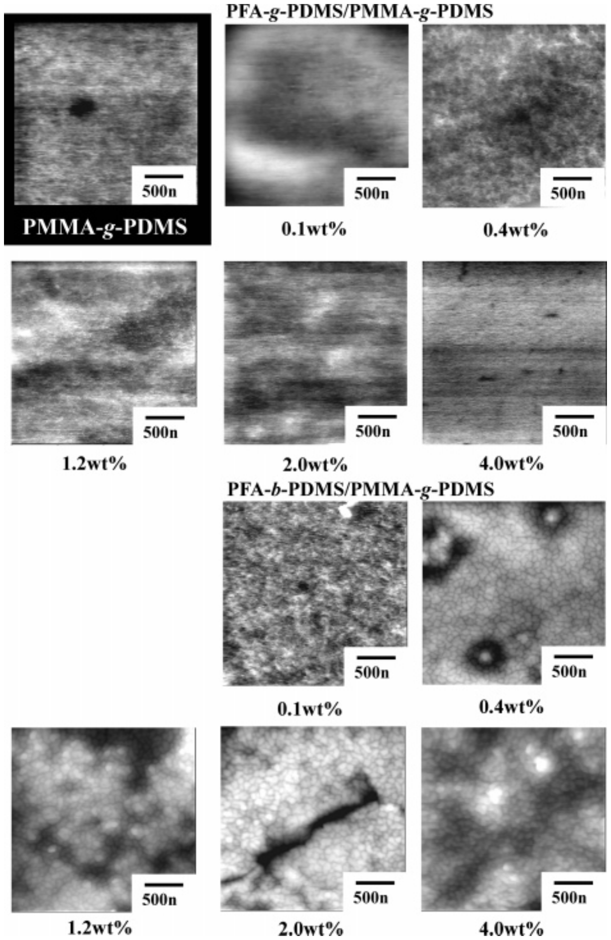


Figure 8. AMF images of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/ PMMA-*g*-PDMS membranes.

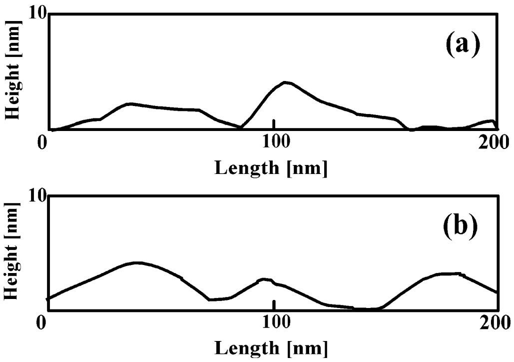


Figure 9. Cross-sectional profile of the PFA-*g*-PDMS/PMMA-*g*-PDMS (a) and PFA-*b*-PDMS/PMMA-*g*-PDMS (b) membranes.

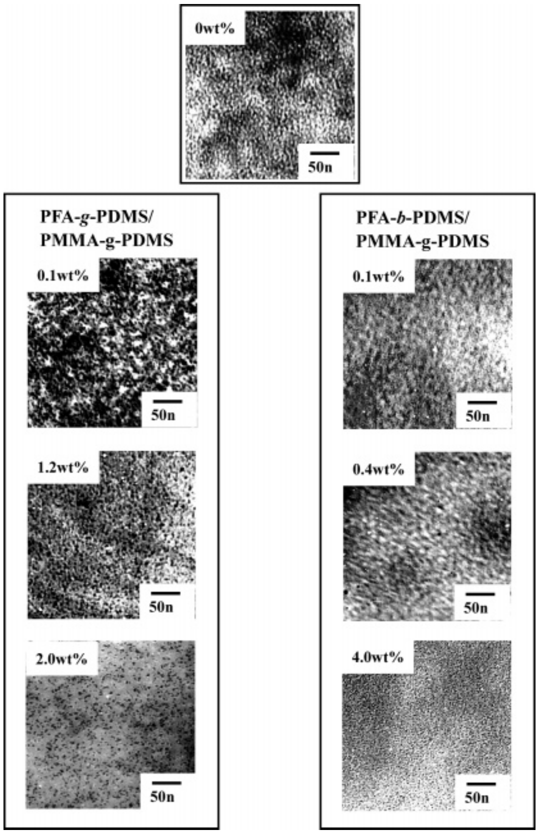


Figure 10. TEM images of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/ PMMA-*g*-PDMS membranes. The dark region stained by RuO_4 represents the PDMS component.

the PFA-*b*-PDMS is easily cohered and structured in comparison with the PFA-*g*-PDMS.

Inner Structure of Membranes. The permeation and separation characteristics through polymer membranes are significantly influenced by the inner structure of membranes as reported in previous studies.[14,15,18−23] Thus, to reveal the inner structures of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes with different PMMA-*g*-PDMS and PFA-*b*-PDMS contents, respectively, the cross sections of these membranes were observed by TEM. These TEM images are shown in Figure 10. The PDMS component was stained by RuO_4, but the PMMA and PFA components were not. These micrographs clearly demonstrate that all PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes had distinct microphase-separated structure. As reported in previous papers,[14,15,19,21,22] the PMMA-*g*-PDMS membranes with a high DMS content had distinct microphase separation consisting of a continuous PDMS phase and a continuous PMMA phase. The continuous PDMS phase in the PMMA-*g*-PDMS membranes could preferentially permeate benzene in water.[21,22] As can be seen from Figure 10, the membranes containing PFA-*g*-PDMS or PFA-*b*-PDMS of a small amount have the morphology with a continuous PDMS phase. With increasing PFA-*g*-PDMS or PFA-*b*-PDMS content, a continuous PDMS phase changed a smaller dispersed morphology. In particular, the PFA-*g*-PDMS/PMMA-*g*-PDMS membrane containing PFA-*g*-PDMS of a larger amount had a discontinuous PDMS phase, but although the scale of the microphase-separated structure of the PFA-*b*-PDMS/PMMA-*g*-PDMS membrane containing PFA-*b*-PDMS of a larger amount became smaller, a discontinuous microphase separation was not formed. The result that the decrease in both the normalized permeation rate and the benzene/water selectivity of the PFA-*b*-PDMS/PMMA-*g*-PDMS membranes with increasing PFA-*g*-PDMS content was smaller than that of the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes could be attributed to the fact that the microphase-separated structure of the PFA-*b*-PDMS/PMMA-*g*-PDMS membrane containing PFA-*b*-PDMS of a larger amount was different from that of the PFA-*g*-PDMS/PMMA-*g*-PDMS with PFA-*g*-PDMS of a larger amount; i.e., with increasing PFA-*b*-PDMS content, the PFA-*b*-PDMS/PMMA-*g*-PDMS membrane did not form a clearly discontinuous microphase-separated structure.

Permeation Model. On the basis of the above results, the structures of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes modified with graft and block copolymer additives are shown by illustration in Figure 11. By the small addition of the PFA-*g*-PDMS and PFA-*b*-

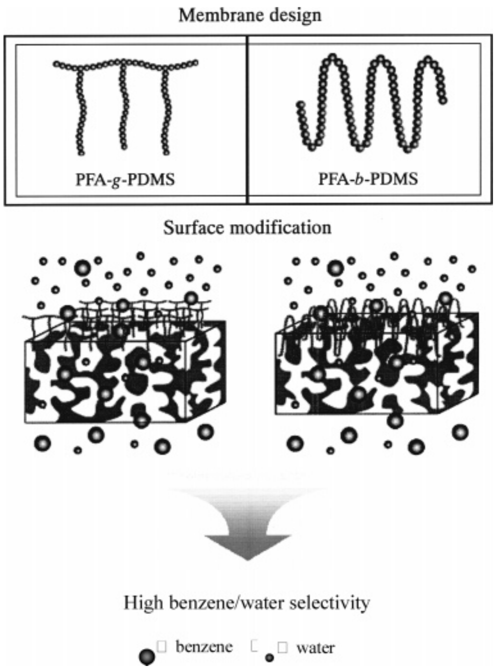


Figure 11. Illustration of the structure of the air-side surface and the permeation model of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes.

PDMS to the PMMA/PDMS membrane, the PFA-*g*-PDMS and PFA-*b*-PDMS are localized on the membrane surface, and only the membrane surface is water-repellent. As a result, in the permeation and separation of an aqueous dilute benzene solution through the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes during pervaporation, the solubility of water molecules in the sorption process is controlled, the relative solubility of benzene molecules is enhanced. Since a small addition of the fluorine-containing polymer additives does not change the microphase-separated structure of the PMMA-*g*-PDMS membrane, the benzene molecules predominantly diffuse through the continuous PDMS phase, and consequently the benzene/water selectivity is enhanced. Since the PFA-*b*-PDMS efficiently makes the the membrane surface water-repellent in comparison with the PFA-*g*-PDMS, a smaller addition of the former additive realizes a similar membrane performance to a larger addition of the latter one. The addition of the former does not remarkably affect the inner structure of the PFA-*b*-PDMS/PMMA-*g*-PDMS membrane, the PDMS phase in the base polymer, PMMA/PDMS, does not become a discontinuous phase and keeps predominant diffusion of the benzene molecules through the continuous PDMS phase, and consequently the benzene/water selectivity is not lowered following the increase of the additional amount of PFA-*b*-PDMS.

Conclusions

Fluorine-containing graft and block copolymer additives, PFA-*g*-PDMS and PFA-*b*-PDMS, were added to a microphase-separated PMMA/PDMS membrane with a continuous PDMS to improve the benzene/water selectivity and the permeability for an aqueous dilute benzene solution during pervaporation. The permeability and the benzene/water selectivity of the resulting PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes for an aqueous solution of 0.05 wt % benzene were investigated from the viewpoints of the surface characteristics and the microphase-separated structures of these membranes. Both the permeability and the benzene/water selectivity were enhanced upon the adding of PFA-*g*-PDMS and PFA-*b*-PDMS to a microphase-separated PMMA/PDMS membrane. This enhancement in the membrane performance could be attributed to the hydrophobicity of the air-side surface of the PFA-*g*-PDMS/PMMA-*g*-PDMS and PFA-*b*-PDMS/PMMA-*g*-PDMS membranes based on the localization of PFA-*g*-PDMS and PFA-*b*-PDMS at the air-side surface. The permeability and the benzene/water selectivity were dependent on the additional amount of PFA-*g*-PDMS and PFA-*b*-PDMS. The addition of a small amount of these fluorine-containing additives yielded the enhancement of both the permeability and the selectivity because the air-side surface of these membranes became more hydrophobic, and the microphase-separated structures with a continuous PDMS phase in the inner of these membranes were kept. On the other hand, in the addition of a large amount of these additives the PFA-*b*-PDMS/PMMA-*g*-PDMS membranes kept the microphase-separated structures with a continuous PDMS phase, but the PFA-*g*-PDMS/PMMA-*g*-PDMS membranes did not. The difference in the structure of these membranes significantly influenced the permeability and the selectivity.

In this study, we demonstrated that membranes with high permeability and high benzene/water selectivity can be designed by addition of fluorine-containing graft and block polymer additives, PFA-*g*-PDMS and PFA-*b*-PDMS, to a microphase-separated PMMA/PDMS membrane with a continuous PDMS phase, and the addition of the fluorine-containing copolymer additives to a microphase-separated base polymer offers potential for selective separation of benzene/water.

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References and Notes

(1) Baker, R. W. In *Membrane Separation Systems, Recent Developments and Future Directions*; Baker, R. W., Cussler. E. L., Eykamp, W., Koros, W. J., Riley, R. L., Strathmann, H., Eds.; Noyes Data Corp.: Park Ridge, NJ, 1991; p 151.
(2) Bravo, J. *Chem. Eng. Prog.* **1994**, *90*, 56.
(3) Kuzer, S.; Wintrich, H.; Mersmann, A. *Chem. Eng. Technol.* **1995**, *18*, 149.
(4) Psaume, R.; Aptel, P.; Aurelle, Y.; Mora, J. C.; Bersillon, J. L. *J. Membr. Sci.* **1988**, *26*, 373.
(5) Blume, I.; Wijmans, J. G.; Baker, R. W. J. *Membr. Sci.* **1990**, *49*, 253.
(6) Nguyen, T. Q.; Nobe, K. *J. Membr. Sci.* **1987**, *36*, 11.
(7) Rauhunath, B.; Hwang, S.-T. *J. Membr. Sci.* **1992**, *75*, 29.
(8) Schnable, S.; Moulin, P.; Nguyen, Q. T.; Roizard, D.; Aptel, P. *J. Membr. Sci.* **1998**, *142*, 129.
(9) Mishima, S.; Kaneka, H.; Nakagawa, T. *J. Appl. Polym. Sci.* **1995**, *103*, 1295.
(10) Fang, Y.; Pham, V. A.; Matsura, T.; Santerre, J. P.; Narbaitz, R. M. *J. Appl. Polym. Sci.* **1994**, *54*, 1937.
(11) Yang, D.; Majumdar, S.; Kovenklioglu, S.; Sirka, K. K. *J. Membr. Sci.* **1995**, *103*, 195.
(12) Lau, W. W. Y.; Finlayson, J.; Dickson, J. M.; Jiang, J.; Brook, M. A. *J. Membr. Sci.* **1997**, *134*, 209.
(13) Jim, K.; Pintanto, P. N. *J. Membr. Sci.* **1997**, *135*, 41.
(14) Miyata, T.; Takagi, T.; Kadota, T.; Uragami, T. *Macromol. Chem. Phys.* **1995**, *196*, 1211.
(15) Miyata, T.; Takagi, T.; Uragami, T. *Macromolecules* **1996**, *29*, 7787.
(16) Uragami, T.; Doi, T.; Miyata, T. *ACS Symp. Ser.* **1999**, *733*, 263.
(17) Uragami, T,; Doi, T.; Miyata, T. *J. Adhes. Adhes* **1999**, *19*, 405.
(18) Miyata, T.; Obata, S.; Uragami, T. *J. Polym. Sci., Polym Phys.* **2000**, *38*, 584.
(19) Miyata, T.; Obata, S.; Uragami, T. *Macromolecules* **1999**, *32*, 3712.

(20) Miyata, T.; Obata, S.; Uragami, T. *Macromolecules* **1999**, *32*, 8465.
(21) Uragami, T.; Yamada, H.; Miyata, T. *Trans. Mater. Res. Soc. Jpn.* **1999**, *24*, 165.
(22) Uragami, T.; Yamada, H.; Miyata, T. *J. Membr. Sci.* **2001**, *187*, 255.
(23) Miyata, T.; Yamada, H.; Uragami, T. *Macromolecules* **2001**, *34*, 8026.
(24) Inoue, H.; Ueda, A.; Nagai, S. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 1077.
(25) Inoue, H.; Ueda, A.; Nagai, S. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *35*, 2039.
(26) Inoue, H.; Matsumoto, A.; Matsukawa, K.; Ueda, A. *J. Appl. Polym. Sci.* **1990**, *40*, 1917.
(27) Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1741.
(28) Fowkes, S. M. *J. Phys. Chem.* **1962**, *66*, 382.
(29) Fowkes, S. M. *J. Phys. Chem.* **1963**, *67*, 2538.
(30) Trent, J. S.; Schenbeim, J. I.; Couchman, P. R. *Macromolecules* **1983**, *16*, 589.

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