# Pervaporation of Volatile Organic Compounds/Water Mixtures Through Poly(1*H*,1*H*,9*H*-hexadecafluorononyl methacrylate)-Filled Poly(1-trimethylsilyl-1-propyne) Membranes

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**ABSTRACT:** Poly(1-trimethylsilyl-1-propyne) (PMSP) is a glassy polymer that contains many microvoids. The permselectivity of the PMSP membrane is controlled by the microvoids, and its permeation behavior is different from rubbery polymer membranes. PMSP membrane was filled with poly(1*H*,1*H*,9*H*-hexadecafluorononyl methacrylate) (PHDFNMA), and the solution-diffusion mechanism during pervaporation was investigated. Separation performance was increased due to the introduced hydrophobic polymer, PHDFNMA, as compared to the PMSP membrane. For the 62 wt % PHDFNMA-filled PMSP membrane, the permselectivity was significantly enhanced. The microvoids in the PMSP membrane play an important role in permselectivity. As the feed of ethyl butanoate (EBU) concentration increased and the EBU quantity sorbed into the PHDFNMA-filled PMSP membrane increased, the diffusion of water was prevented; in turn, the water flux decreased. At a low feed concentration, the diffusivity of the EBU molecule was much lower than that of water due to the larger molecular size of EBU. As EBU was sufficiently sorbed into the membrane, the diffusion of water was prevented by the EBU molecules; in turn, the permselectivity of EBU significantly increased. At a high-feed EBU concentration, the diffusion of water increased, and the diffusion of EBU decreased to a constant as the PHDFNMA-filled PMSP membrane was plasticized. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1054–1060, 2002

**Key words:** PMSP membrane; PHDFNMA filling; pervaporation

## INTRODUCTION

Recently, pervaporation separation has become an effective process for the separation and recovery of liquid mixtures in chemical industries.[1,2] Pervaporation is potentially useful when distillation is difficult, such as for the fractionation of azeotropic mixtures, close boiling components, thermal decomposition, and isomeric mixtures,

because of its energy-saving features.[3–16] Therefore, pervaporation is of growing interest for water treatment applications to remove volatile organic pollutants and for industrial applications such as wine or beer dealcoholization, juice concentration, and extraction of volatile organic compounds from various liquid media.[3–16]

The pervaporation membrane separation technique is a fractionation process that uses a dense polymeric membrane as a separation barrier between the liquid feed and permeate vapor. The permselectivity can be determined by the sorption–diffusion mechanism. The sorption of the

permeate component can be controlled by the affinity for the membrane material. The diffusion can be described as the permeation rate of the component through the membrane.

The poly(1-trimethylsilyl-1-propyne) (PMSP) membrane has the highest permeability of all polymeric membranes.[17] Therefore, this polymer has been expected to have potential utility in industrial applications. Its permeation properties and industrial applications have been studied.[17–29] The PMSP membrane has an extraordinary large free volume (microvoids) and excellent sorption properties. These are the main factors affecting its permeability.

In a previous study,[5] the polydimethylsiloxane (PDMS) membrane, which is a rubbery polymer membrane, was grafted by 1*H*,1*H*,9*H*-hexadecafluorononyl methacrylate (HDFNMA) with a ^{60}Co source and by a simultaneous irradiation method. In the pervaporation application of the grafted PDMS membrane, the selectivity for trichloroethylene (TCE) was enhanced due to introduction of the hydrophobic polymer, poly(1*H*,1*H*,9*H*-hexadecafluorononyl methacryate (PHDFNMA). At a high concentration of TCE solution, the diffusion of water was prevented by the TCE molecules sorbed in the membrane; in turn, the permselectivity of TCE significantly increased.

PMSP is a glassy polymer and has many microvoids.[17] The permselectivity of the PMSP membrane is controlled by the microvoids,[17] and its permeation behavior is different from rubbery polymer membranes. In this study, PMSP membrane was filled with PHDFNMA, and the solution-diffusion mechanism during pervaporation was investigated.

## EXPERIMENTAL

### Materials

PMSP (Shin-etsu Chemical Co., Ltd., Tokyo, Japan) was used throughout this work. HDFNMA (Daikin Fine Chemical Laboratory Corp., Tokyo, Japan), ethyl butanoate (EBU) (special grade, Wako Pure Chemical Industries, Ltd., Tokyo, Japan), and 2-propanol (Kanto Chemical Co., Inc., Tokyo, Japan) were used as received.

### Membrane Preparation

HDFNMA in ampoules was degassed and sealed under vacuum. The ampoules were irradiated at dose rates of 0.1 mRad/h for 5 h with a ^{60}Co source at 25°C. After the irradiation was finished, the obtained polymer (PHDFNMA) was soaked, washed in acetone, and dried under vacuum. PHDFNMA was then ground into a powder by an autogrinder (Nitto Science Co., Ltd., Tokyo, Japan) and sieved with a JIS 28801 testing sieve with a 45 $\mu$ aperture (Tokyo Screen Co., Ltd., Tokyo, Japan).

PMSP was purified by the solution precipitation method with a toluene–methanol system. Purified PMSP was dissolved in toluene to 2.0 wt % and cast onto a glass plate. Sieved PHDFNMA powder was added to the cast solution, and then, the solution was dried under vacuum.

### Pervaporation Experiment

Pervaporation experiments were performed as in a previous study[3–6] with the continuous-feed-type equipment at 25°C. The feed solution was circulated through the cell and the feed tank. The grafted surface of the membrane was kept in contact with the feed solution in the cell. The effective membrane area in the cell was 19.6 cm$^2$. The pressure on the permeation side was kept below 10 Torr by vacuum pumps. When steady-state flow conditions were reached, the permeate was collected in traps cooled by liquid nitrogen ($-196$°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate of the solution, the total flux ($J$), was obtained with eq. (1):

$$J = Q/At \qquad (1)$$

where $Q$ is the amount of solution that permeated during the experimental time interval, $t$, and $A$ is the effective surface area. The EBU and water flux were calculated from $J$ and the permeate composition.

The concentration of EBU in the feed and permeate solution was determined by gas chromatography with a flame ionization detector. The EBU concentration in the permeate was high, which was far beyond its solubility limit in water. The phase separation took place in the permeate. 2-Propanol was then added to the permeate solution. The permeate solution was homogenized and analyzed to determine the EBU concentration. The separation factor during pervaporation, $\alpha_{pv}$, was calculated as:

$$\alpha_{pv} = [Y(1 - X)]/[(1 - Y)X] \qquad (2)$$

where $X$ and $Y$ denote the concentrations (wt %) of EBU in the feed and permeate solutions, respectively.
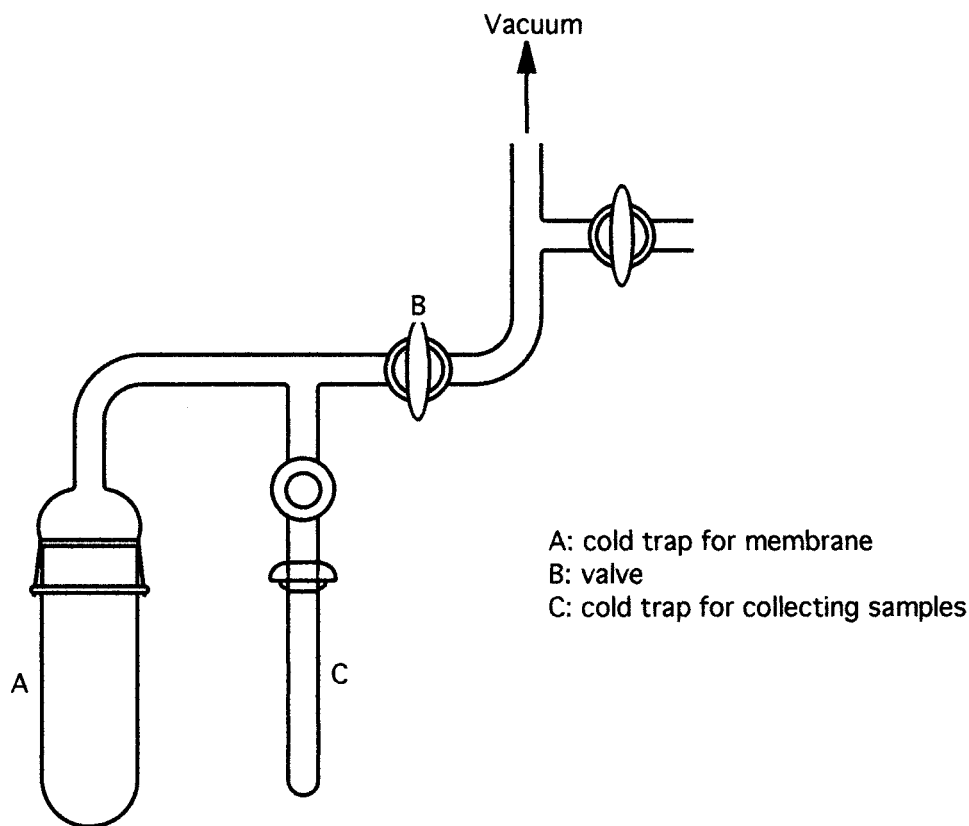
**Figure 1**   Apparatus for measurement of the composition of the membrane.

### Sorption Measurement

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

$$\text{Degree of Sorption } (\%) = (W_2 - W_1)/W_1 \times 100 \quad (3)$$

where $W_1$ and $W_2$ denote the weights of the dried membrane and the swollen membrane, respectively.

The concentration of the EBU solution soaked into the membrane was determined with the apparatus shown in Figure 1. When equilibrium was reached, the membrane was removed from the vessel, quickly wiped with filter paper, and placed in cold trap A. The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, valve B was closed, and we vaporized the EBU solution soaked in the membrane by heating

it with a drier. The solution was then collected in cold trap C.

The concentrations of EBU solution in the feed and the soaked membrane were determined by gas chromatography as in the pervaporation experiment. The separation factor during sorption, $\alpha_s$, was calculated as
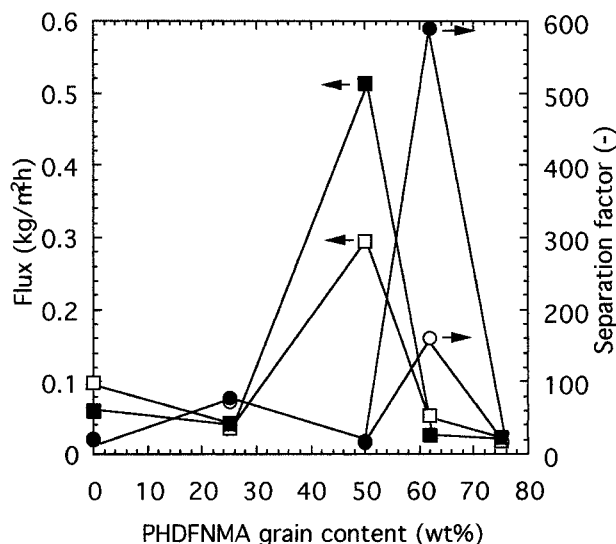
$$\alpha_S = [Y'(1 - X)]/[(1 - Y')X] \quad (4)$$

where $X$ and $Y'$ denote the concentrations (wt %) of EBU in the feed solution and the swollen membranes, respectively.

## RESULTS AND DISCUSSION

### Pervaporation of the PHDFNMA-Filled PMSP Membrane

The effect of PHDFNMA powder content on flux and $\alpha_{pv}$ the EBU/water mixture through the PHDFNMA-filled PMSP membrane is shown in Figure 2.

**Figure 2** Effect of the PHDFNMA powder contents on flux and $\alpha_{pv}$ for the EBU/water mixture through the PHDFNMA-filled PMSP membrane: 0.01 wt % feed solution (□) flux and (■) $\alpha_{pv}$ and 0.02 wt % feed solution (○) flux and (●) $\alpha_{pv}$.

In a previous study,[5] a PDMS membrane was grafted to HDFNMA with a $^{60}$Co source and by a simultaneous irradiation method. The permeation behavior of the grafted PDMS membrane during pervaporation was investigated. At a low feed concentration of TCE solution, the diffusivity of the TCE molecule was much lower than that of water due to the larger molecular size of TCE. As TCE was sufficiently sorbed into the membrane at a high concentration of TCE solution, the diffusion of water was prevented by the TCE molecules; in turn, the permselectivity of TCE significantly increased.

The flux increased until a maximum was reached for the 50 wt % HDFNMA-filled PMSP membrane and then decreased with increasing PHDFNMA powder content. The separation factor increased due to introduction of the hydrophobic polymer PHDFNMA. Because the PMSP layer was thin in the 50 wt % PHDFNMA-filled PMSP membrane, the flux increased. However, as the PHDFNMA powder content increased, the filled PHDFNMA prevented permeation, and the flux decreased.
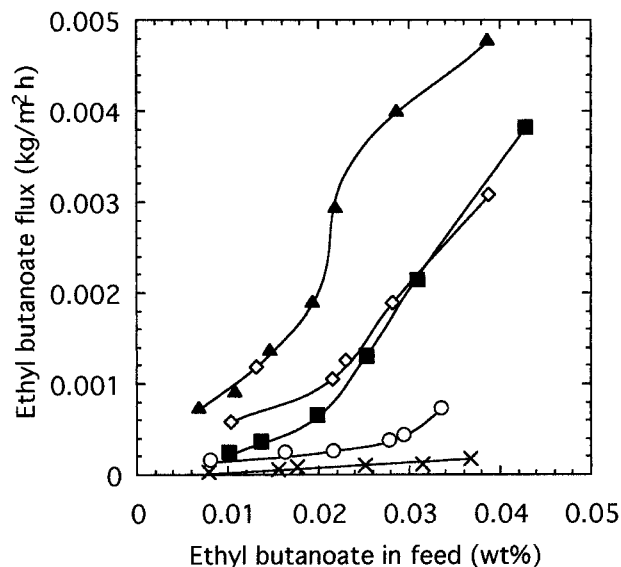
The water flux as a function of EBU concentration in the feed solution is shown in Figure 3 for the PHDFNMA-filled PMSP membranes. The water flux increased with the feed concentration for the 25 and 50 wt % PHDFNMA-filled PMSP membranes. For the 62 and 75 wt % PHDFNMA-

filled PMSP membranes and the PMSP membrane, the water flux decreased with feed concentration. The water flux for the 62 wt % PHDFNMA-filled PMSP membrane significantly decreased. The EBU flux as a function of EBU concentration in the feed solution is shown in Figure 4 for the PHDFNMA-filled PMSP membranes. For all the membranes, the EBU flux increased with the feed concentration, and for the 62 wt % PHDFNMA-filled PMSP membrane, this tendency was significant. The microvoids in the PMSP membrane play an important role in its permselectivity. As the EBU quantity sorbed into the PMSP membrane increased with the feed EBU concentration, the diffusion of water was prevented; in turn, the water flux decreased. For the 25 and 50 wt % PHDFNMA-filled PMSP membranes, because the PMSP layer was thin and the sorbed EBU was high, the PHDFNMA-filled PMSP membranes were plasticized, and the flux increased. For the 62 wt % PHDFNMA-filled PMSP membrane, because the EBU quantity sorbed into the PHDFNMA-filled PMSP membrane significantly increased with the feed EBU concentration due to the hydrophobic PHDFNMA, the diffusion of water was prevented; in turn, the flux decreased. For the 75 wt % PHDFNMA-filled PMSP membrane, because the filled PHDFNMA prevented the permeation, the fluxes of water and EBU were low.

The relationships between EBU concentration in the feed and permeate are shown in Figure 5
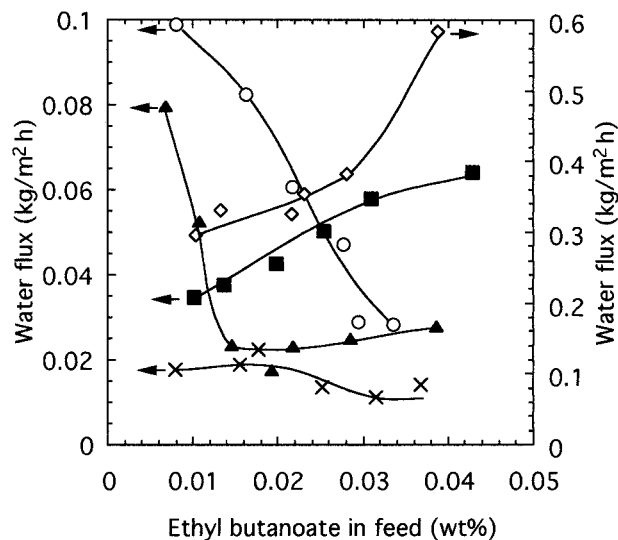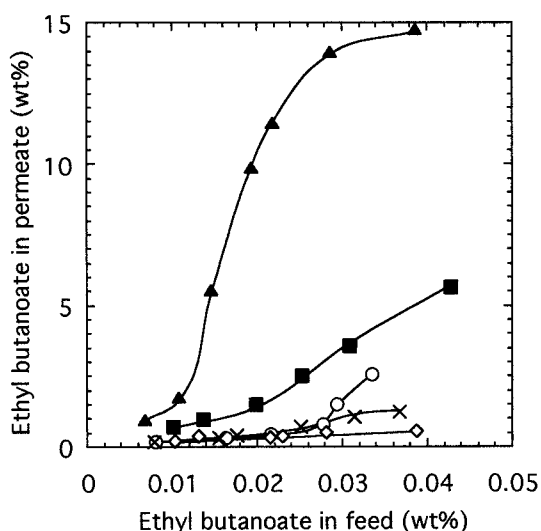


**Figure 3** Water flux as a function of the feed EBU concentration during pervaporation through (■) 25, (◇) 50, (▲) 62, and (×) 75 wt % PHDFNMA-filled PMSP membranes and (○) PMSP membrane.

**Figure 4**  EBU flux as a function of the feed EBU concentration during pervaporation through (■) 25, (◇) 50, (▲) 62, and (×) 75 wt % PHDFNMA-filled PMSP membranes and (○) PMSP membrane.

for the PHDFNMA-filled PMSP membranes. For all the membranes, the EBU concentration in the permeate increased with the feed concentration, and for the 62 wt % PHDFNMA-filled PMSP membrane, the increase was significant.



**Figure 5**  Relationships between the EBU concentration in the feed and permeate during pervaporation through (■) 25, (◇) 50, (▲) 62, and (×) 75 wt % PHD-FNMA-filled PMSP membranes and (○) PMSP membrane.
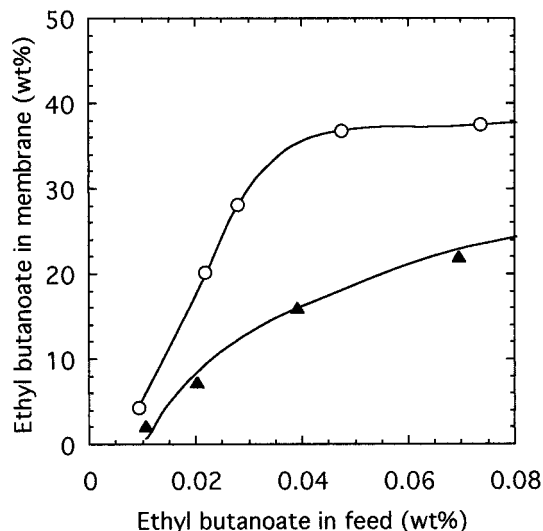


**Figure 6**  Sorption of EBU as a function of the feed concentration at equilibrium on the (▲) 62 wt % PHD-FNMA-filled PMSP membrane and the (○) PMSP membrane.

## Sorption of the PHDFNMA-Filled PMSP Membrane

The sorption isotherms for the 62 wt % PHD-FNMA-filled PMSP membranes and PMSP membrane are shown in Figure 6. For both membranes, the concentration of EBU solution soaked in the membrane linearly increased with feed concentration at low feed concentrations, but the increase was minor at high feed concentrations. The concentration of EBU solution soaked in the PHDFNMA-filled PMSP membrane was low compared to the PMSP membrane.

PMSP is a glassy polymer and has many microvoids. The sorption into the PMSP membrane was controlled by the microvoids. Because the PHDFNMA-filled PMSP membrane has few microvoids, the sorption of EBU was low compared to the PMSP membrane.
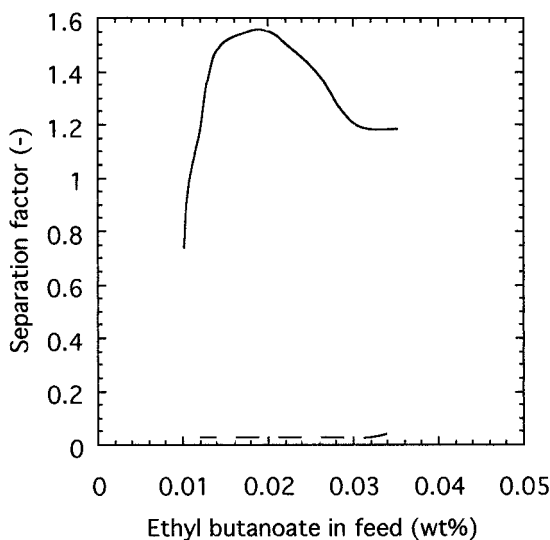
## Diffusion of the PHDFNMA-Filled PMSP Membrane

The relationship between $\alpha_{pv}$, $\alpha_S$, and the apparent separation factor during diffusion ($\alpha_D$) is given by eq. (5):

$$\alpha_{pv} = \alpha_S \alpha_D \tag{5}$$

$\alpha_D$ can be described by eq. (6), which uses eqs. (2) and (4):

**Figure 7** Effect of feed concentration on $\alpha_D$ through the (—) 62 wt % PHDFNMA-filled PMSP membrane and the (– – –) PMSP membrane.

$$\alpha_D = [Y(1 - Y')]/[(1 - Y)Y'] \qquad (6)$$

where $Y$ and $Y'$ denote the concentration of EBU in the permeate solution and swollen membranes for the same feed solution, respectively. $\alpha_D$ was calculated by eq. (6) with the sorption isotherm in Figure 6 and the pervaporation in Figure 5. $\alpha_D$ as a function of the EBU concentration in the feed solution is shown in Figure 7. $\alpha_D$ of the PMSP membrane was constant with increasing feed concentration. For the PHDFNMA-filled PMSP, it significantly increased with the feed concentration until a maximum was reached, and then it decreased and became constant.

The sorption and diffusion of EBU and water molecules during pervaporation through the PHDFNMA-filled PMSP membrane were considered as follows: At a low feed concentrations, the diffusivity of the EBU molecule was much lower than that of water due to the larger molecular size of EBU. As EBU was sufficiently sorbed into the membrane, the diffusion of water was prevented by the EBU molecules; in turn, the permselectivity of EBU significantly increased. At a high feed EBU concentrations, the diffusion of water increased and the diffusion of EBU decreased to a constant as the PHDFNMA-filled PMSP membrane was plasticized.

## CONCLUSIONS

In this study, the glassy PMSP membrane was filled with PHDFNMA, and the sorption-diffusion

mechanism during pervaporation was investigated and compared to the grafted rubbery PDMS membranes.

The separation performance increased due to introduction of the hydrophobic polymer PHDFNMA, as compared to the PMSP membrane. For the 62 wt % PHDFNMA-filled PMSP membrane, the permselectivity was significantly enhanced.

The water flux for the 62 wt % PHDFNMA-filled PMSP membrane significantly decreased. For all the membranes, the EBU flux increased with the feed concentration, and for the 62 wt % PHDFNMA-filled PMSP membrane, this tendency was significant. The microvoids in the PMSP membrane play an important role in the permselectivity. As the EBU quantity sorbed into the PHDFNMA-filled PMSP membrane increased with the feed EBU concentration, the diffusion of water was prevented; in turn, the water flux decreased.

The concentration of the EBU solution soaked in the PHDFNMA-filled PMSP membrane was slight compared to the PMSP membrane. PMSP had many microvoids. The permeate molecule was mainly sorbed in the microvoids. As the PHDFNMA-filled PMSP membrane had few microvoids, the sorption of EBU was low compared to the PMSP membrane.

The sorption and diffusion of EBU and water molecules during pervaporation through the PHDFNMA-filled PMSP membrane were considered as follows by calculation of $\alpha_D$: At a low feed concentrations, the diffusivity of the EBU molecule was much lower than that of water due to the larger molecular size of EBU. As EBU was sufficiently sorbed into the membrane, the diffusion of water was prevented by the EBU molecules; in turn, the permselectivity of EBU significantly increased. At a high feed EBU concentrations, the diffusion of water increased, and the diffusion of EBU decreased to a constant as the PHDFNMA-filled PMSP membrane was plasticized. The permeation behavior of the PHDFNMA-filled PMSP membranes were different from the grafted rubbery PDMS membranes.

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