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Communications to the Editor

Ethanol Permselectivity of Poly(dimethylsiloxane) Membranes Controlled by Simple Surface Modifications Using Polymer Additives

Takashi Miyata,* Yuichi Nakanishi, and Tadashi Uragami*

Chemical Branch, Faculty of Engineering,
and High-Tech. Research Center, Kansai University,
Suita, Osaka 564-80, Japan

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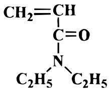
Pervaporation is a promising separation technique for azeotropic and close-boiling point mixtures, which cannot be adequately separated by distillation. Many papers have described the characteristics of permeation and separation for such organic liquid mixtures through various membranes by pervaporation.[1] During pervaporation, the permeants undergo a phase change from liquid to vapor through a membrane and are separated in their solution and diffusion processes in the membrane. Therefore, controlling the solubility of a permeant into the membrane is an effective method for improving the permselectivity of the membranes.

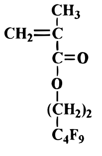
We have studied the relationship between the structure of multicomponent polymer membranes containing poly(dimethylsiloxane) (PDMS) and their permselectivity for aqueous ethanol solutions in order to develop excellent ethanol-permselective pervaporation membranes.[2−4] Our previous studies revealed that the phase structures of multicomponent polymer membranes strongly affect their permeability and permselectivity for aqueous ethanol solutions by pervaporation. Therefore, designing the phase structures of multicomponent polymer membranes is of great importance in enhancing membrane performance. For example, on the basis of the solution-diffusion theory, one approach to developing a high ethanol-permselective membrane is to design a membrane structure in which ethanol is more preferentially incorporated than water.

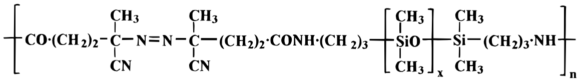
In general, the characteristics of the polymer surface are different from those of the polymer bulk.[5−20] For example, it is often observed that a more hydrophobic component is localized at the air contact side of two-component polymer membranes. The surface localization of a component is mainly governed by the surface free energy of the membrane. Therefore, a variety of polymer additives, which can be localized to the polymer surfaces, has been used for the surface modification of polymers. Such polymer additives are composed of a hydrophobic part for the surface modification plus an anchor part to introduce a strong affinity for the polymer matrix. Thus, polymer additives whose structures are well designed are very useful for the surface modification of pervaporation membranes.

In this study, we synthesized hydrophilic and hydrophobic polymer additives containing a PDMS component as the anchor part, in order to surface-modify an ethanol-permselective PDMS membrane. This paper describes the control of the ethanol permselectivity of PDMS membranes by surface modification using two types of polymer additives. Furthermore, we focus on the relationship between the surface characteristics of these surface-modified PDMS membranes and their permselectivity for aqueous ethanol solutions by pervaporation.

Hydrophilic and hydrophobic block copolymers containing a PDMS component were synthesized by polymerizing diethylacrylamide (DEAA) (**1**) or nonafluorohexyl methacrylate (NFHM) (**2**) *via* a PDMS macro-azo-initiator (PASA)[20−22] (**3**) (PDMS-*b*-PDEAA or PDMS-*b*-PNFHM, respectively) as follows. After the appropriate amount of DEAA or NFHM was dissolved together with PASA in benzene to make a 40 wt % solution in a glass tube, the polymerization was carried out at 60 °C for 6 h under nitrogen gas. Thus, the hydrophilic and hydrophobic block copolymers with varying amounts of PDMS were easily synthesized by using PASA as an initiator. In this study, we used the PDMS-*b*-PDEAA copolymer with a PDMS content of 53 mol % and PDMS-*b*-PNFHM copolymer with a PDMS content of 48 mol % as the hydrophilic and hydrophobic polymer additives, respectively.


(1)


(2)


$$\left[CO\cdot(CH_2)_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-(CH_2)_2\cdot CONH\cdot(CH_2)_3-\left[\underset{CH_3}{\overset{CH_3}{Si}}O\right]_x-\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3\cdot NH\right]_n$$
(3)

The surface-modified PDMS membranes were prepared by adding a small amount of hydrophilic PDMS-*b*-PDEAA or hydrophobic PDMS-*b*-PNFHM before the formation of PDMS networks on stainless plates. The appropriate amount of block copolymers was dissolved in tetrahydrofuran (THF) solutions of the PDMS base polymer (4 wt %), with tetraethyl orthosilicate as a cross-linker (excess to the PDMS base polymer) and stannous dibutyl diacetate as a catalyst (1.0 wt % relative to the PDMS base polymer) in the polycondensation reaction. After the resulting mixture was cast on a stainless steel plate, the PDMS network was formed by evaporating the THF at 25 °C for 8 h. The resulting PDMS-*b*-PDEAA/PDMS and PDMS-*b*-PNFHM/PDMS membranes were transparent, and their thickness was about 60 μm.

The suface contact angles for water on the resulting membranes were then measured, and Figure 1 shows the relationship between the block copolymer content and the contact angle of water on the PDMS-*b*-PDEAA/PDMS and PDMS-*b*-PNFHM/PDMS membranes. The contact angle of water on the stainless steel side of the PDMS-*b*-PDEAA/PDMS membranes decreased following the addition of PDMS-*b*-PDEAA, but the air side contact angle did not change. With increasing PDMS-*b*-PNFHM content, however, the contact angle on the

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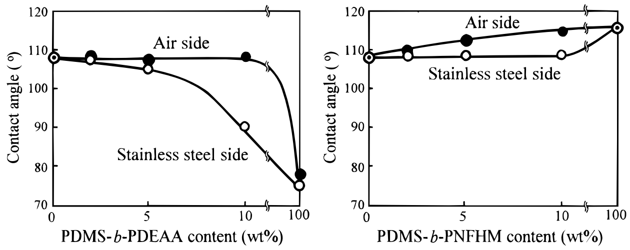

Figure 1. Relationship between the block copolymer content and the contact angles of water on the stainless steel side (○) and air side (●) surfaces of the PDMS-*b*-PDEAA/PDMS and PDMS-*b*-PNFHM/PDMA membranes.

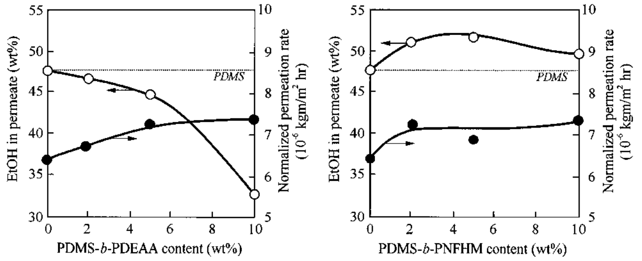

Figure 2. Effects of the block copolymer content on the ethanol concentration in the permeate (○) and the normalized permeation rate (●) of an aqueous solution of 10 wt % ethanol through the PDMS-*b*-PDEAA/PDMS and PDMS-*b*-PNFHM/PDMA membranes by pervaporation.

air side of the PDMS-*b*-PNFHM/PDMS membrane increased, but the stainless steel side contact angle remained constant. This can be attributed to the fact that the hydrophilic PDMS-*b*-PDEAA and hydrophobic PDMS-*b*-PNFHM copolymers are localized at the stainless steel and air side surfaces, respectively. Such surface localization of the block copolymers is caused by the minimization of the surface free energy of the membranes. The stainless steel side surface preferentially localizes the hydrophilic PDMS-*b*-PDEAA in order to minimize the interfacial free energy between the membrane and the stainless steel plate. In contrast, the air side surface does not localize this copolymer, because a PDEAA component in the PDMS-*b*-PDEAA/PDMS membrane is much more hydrophilic than the PDMS network itself. On the other hand, since a PNFHM component in the PDMS-*b*-PNFHM/PDMS membrane is very hydrophobic due to its fluorine-containing component, its localization to the air side makes the membrane surface more stable thermodynamically. Furthermore, since the amount of block copolymers added is very small and most of the block copolymer is concentrated at the membrane surface, the inner structure of the membranes is mainly constituted of the PDMS network without any block copolymer. Consequently, adding a small amount of hydrophilic or hydrophobic block copolymer enables a simple surface modification of the membrane without changing its inner structure.

Figure 2 shows the effect of the block copolymer content on the ethanol concentration in the permeate, and the normalized permeation rate for an aqueous solution of 10 wt % ethanol through the surface-modified PDMS membranes by pervaporation. In this figure, the normalized permeation rate is the product of the permeation rate and the membrane thickness. In these pervaporation experiments, the surface-modified PDMS membranes were set in a pervaporation cell with the modified surfaces facing the feed side. The ethanol concentration in the permeate passing through the PDMS-*b*-PDEAA/PDMS membranes decreased gradually with increasing PDMS-*b*-PDEAA content. However, adding a small amount of PDMS-*b*-PNFHM enhanced the ethanol permselectivity of the PDMS membranes without lowering their permeability.

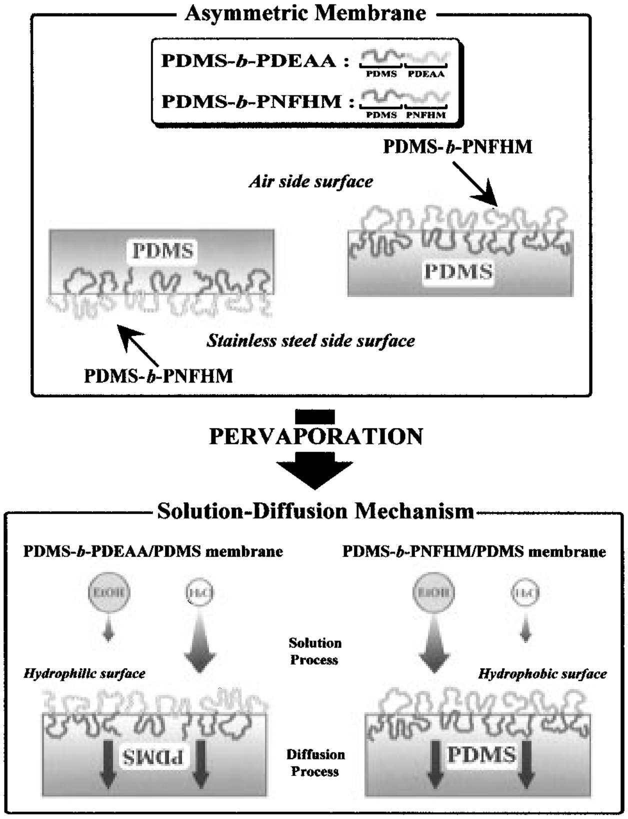

Figure 3. Tentative illustration of the structure of the PDMS-*b*-PDEAA/PDMS and PDMS-*b*-PNFHM/PDMA membranes, and the permeation mechanism of an aqueous ethanol solution through these membranes based on solution-diffusion theory.

When the block copolymer content was increased, the behavior of the ethanol concentration in the permeate corresponded to the contact angles, regardless of the kind of block copolymer used. This suggests that the permselectivity of the surface-modified PDMS membranes is strongly dependent on their surface characteristics. Therefore, the effects of adding block copolymers on the membrane permselectivity for an aqueous ethanol solution can be explained by the tentative model shown in Figure 3, as follows: Since the addition of the hydrophilic PDMS-*b*-PDEAA makes the stainless steel side surface of the PDMS membrane very hydrophilic, more water molecules are preferentially incorporated into the membrane surface than ethanol molecules due to their stronger affinity. On the other hand, the air side surface at which the very hydrophobic PDMS-*b*-PNFHM is localized prefers the predominant incorporation of ethanol molecules because of the lower hydrophilicity of ethanol. Furthermore, adding a small amount of block copolymer results in no detectable change in the inner structure of the rubbery PDMS membrane. Therefore, the surface modification of the PDMS membrane by block copolymers can control the selectivity of the solution process without changing the diffusion process in the permeation of an aqueous ethanol solution. Furthermore, since there are no changes in the inner structure of the membrane following the addition of the block copolymers, this enables maintenance of a high permeability similar to that of the PDMS membrane. Thus, increasing the hydrophilicity of the membrane surface lowers the ethanol permselectivity whereas increasing the hydrophobicity enhances the ethanol permselectivity. However, when PDMS-*b*-PNFHM was added, the ethanol concentration in the permeate began to decrease again with an increase in the PDMS-*b*-PNFHM content of more than 5 wt %. We also prepared a PDMS-*b*-PNFHM membrane with a PDMS content of 48 mol % without adding it into the PDMS membrane and performed the pervaporation experiments for an aqueous solution of 10 wt % ethanol. The PDMS-*b*-PNFHM membrane showed water permselectivity in spite of the high hydrophobicity of its surface. This water permselectivity was due to the lower diffusibility of the ethanol molecules in the rigid PNFHM component. Therefore, the addition of a large amount of PDMS-*b*-PNFHM into the PDMS membrane results in the formation of a water-permselective PDMS-*b*-PNFHM phase at the membrane surface, and thus the ethanol permselectivity of the PDMS-*b*-PNFHM/PDMS membrane with a PDMS-*b*-PNFHM content of 10 wt % is lower as compared to that with 5 wt %. Our findings suggest a novel concept for designing highly permselective membranes: an asymmetric membrane structure could be developed so that one side of the membrane has a strong affinity for the permeant, whereas the inner structure of the membrane is similar to the rubbery PDMS membrane.

Therefore, the permselectivity of the PDMS membrane can be simply controlled by the addition of various polymer additives. The addition of hydrophobic fluorine-containing copolymers improves the ethanol permselectivity of the PDMS membanes without lowering their permeability. The results of this study yield a novel concept for designing the structure of high-performance pervaporation membranes and enables us to prepare “a made-to-order membrane”.

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