# Temperature-sensitive ethanol permselectivity of poly(dimethylsiloxane) membrane by the modification of its surface with copoly(*N*-isopropylacrylamide/1H,1H,2H,2H-perfluorododecyl acrylate)

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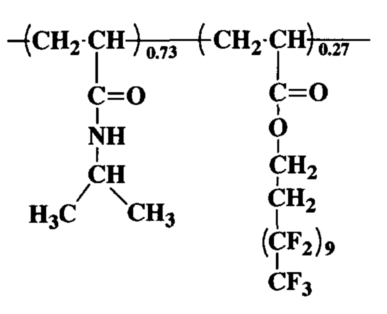
A blend membrane consisting of 5.3 wt% copoly(*N*-isopropylacrylamide/1H,1H,2H,2H-perfluorododecyl acrylate) and poly(dimethylsiloxane) showed a high ethanol permselectivity ($\alpha^{EtOH} = 19.7$ at 24°C) in pervaporation of 2.5 wt% aqueous ethanol solution. The value of $\alpha^{EtOH}$ had a maximum at about 36°C. This behaviour was due to the water repellency and thermal transition of the copolymer accumulated at the membrane surface.

**(Keywords: temperature sensitivity; copoly(*N*-isopropylacrylamide/1H,1H,2H,2H-perfluorododecyl acrylate); membrane; poly(dimethylsiloxane); ethanol permselectivity; pervaporation)**

## *Introduction*

Ethanol-permselective membranes are required for the concentration of dilute aqueous ethanol solutions produced from biomass, but there are few examples of such membranes. Although poly(dimethylsiloxane) (PDMS) membrane is one example, its ethanol permselectivity ($\alpha^{EtOH}$) is low. We have reported[1] the efficient enhancement of the $\alpha^{EtOH}$ of PDMS membrane by adding a small amount of poly(1H,1H,2H,2H-perfluoroalkylethoxydimethylsilylstyrene) ($\alpha^{EtOH} = 22.3$, $[EtOH]_{Feed} = 2.70$ wt% at 25°C). This was attributed to the accumulation of the fluorine-containing polymer at the membrane surface. As was demonstrated by this example, the property of the membrane surface is very important in pervaporation.



**Copoly(IPAA/FA)**

In this study, copoly(*N*-isopropylacrylamide/1H,1H, 2H,2H-perfluorododecyl acrylate) (copoly(IPAA/FA)) was used as a surface modifier in order to give temperature sensitivity to the permselectivity ($\alpha^{EtOH}$). Poly(*N*-isopropylacrylamide (PIPAA) has a thermal transition temperature of 32°C, i.e. it is soluble in water below 32°C and insoluble above 32°C; in other words, the extent of hydrophobicity of PIPAA changes drastically at this temperature. The thermal transition of the polymer[2] and its application[3,4] have recently been studied. Although the change was applied to controlling water or aqueous solution permeation rate of a microfiltration membrane[5] and an ultrafiltration membrane[6], there have been no examples of controlling permselectivity by utilizing the thermal change.

We report that temperature-sensitive ethanol permselectivity was given to PDMS membrane by adding a small amount of copoly(IPAA/FA).

## *Experimental*

*Materials.* *N*-isopropylacrylamide (IPAA) was kindly supplied by Kohjin Co. The mixture of 1H,1H,2H,2H-perfluoroalkyl acrylates having different fluorocarbon lengths ($n = 5$–$18$) was kindly supplied by Asahi Glass Co., Ltd and fractionated by distillation. The fraction with b.p. = 85°C (1.7 mmHg) was collected and used for (co)polymerization. The mean length ($n$) of the fluorocarbon in this fraction was 10.22, which was estimated by $^1H$ n.m.r. using 1,3-bis(trifluoromethyl)benzene (BTB) as an internal standard. Therefore, the fraction was called 1H,1H,2H,2H-perfluorododecyl acrylate (FA) ($n \approx 10$) in this paper. KE-42TS from Shin-etsu Silicone, Inc. was used as PDMS membrane.

*Copolymerization and polymerization.* A tetrahydrofuran (THF) solution of IPAA and FA, whose feed ratio was 80:20 by weight (96:4 molar ratio), and 0.5 mol% AIBN was placed in a Pyrex tube, which was degassed and sealed. The solution in the tube was then heated at 50°C for 12 h. The mixture was poured into methanol. The THF solution of the resulting copolymer was reprecipitated to methanol and then to BTB in order to remove homopolymers of IPAA and FA, respectively. The copoly(IPAA/FA) was dried *in vacuo*. Yield 76.1%, $\eta_{inh}$ 0.21 dl g$^{-1}$ (THF), i.r. (NaCl, cm$^{-1}$): 1744 (C=O of

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FA), 1650 (C=O of IPAA). Composition of IPAA units and FA units in the copolymer was 34:66 by weight (73:27 molar ratio). It was soluble in THF and ethanol, and insoluble in benzene, BTB, 1,1,2-trichloro-1,2,2-trifluoroethane, dimethylsulfoxide, methanol and water (7–50°C).

Homopolymerization of FA was carried out in BTB in a similar manner. Yield 87.0%, $\eta_{inh}$ 0.22 dl g$^{-1}$ (BTB), soluble in BTB.

*Membrane preparation.* The binary blend of PDMS (toluene solution) and 5.3 wt% (based on PDMS) of copoly(IPAA/FA) was dissolved in THF and the solution was cast on a polytetrafluoroethylene (PTFE) sheet. The solvent was evaporated for 12 h and the resulting membrane was dried *in vacuo* for 24 h. In this paper the surface contacting with air during casting is designated as air-side.

PDMS-based blend membranes of homopolymers, i.e. polyFA or polyIPAA, were prepared in a similar manner.

*Pervaporation of aqueous ethanol solution.* Ethanol and water permeation rates ($P_{EtOH}$ and $P_{water}$: g m m$^{-2}$ h$^{-1}$) were measured by gas chromatography using Yanaco GTR-12L at 24–50°C (i.e. $3.10–3.37 \times 10^{-3}$ K$^{-1}$). A 2.5 wt% ethanol solution was fed from the air-side surface. Ethanol permselectivity ($\alpha^{EtOH}$) was expressed by the following equation:

$$\alpha^{EtOH} = (Y_{EtOH}/Y_{water})/(X_{EtOH}/X_{water})$$

where $X$ and $Y$ are the weight fractions of the feed and permeate, respectively.

## *Results and discussion*

*Table 1* shows the results of pervaporation from the air-side surface of the binary blend membrane and PDMS membrane. By adding 5.3 wt% (based on PDMS) of copoly(IPAA/FA) to PDMS, the $\alpha^{EtOH}$ value of PDMS membrane increased from 12.1 to 16.6 at 30°C. The contact angle values ($\theta$) of water on the air-side surface also increased. The increase in $\alpha^{EtOH}$ was ascribed to the decrease in $P_{water}$ without decrease in $P_{EtOH}$. These findings indicate that a hydrophobic surface was formed by copoly(IPAA/FA) and the $P_{water}$ was suppressed, and as a result $\alpha^{EtOH}$ increased. Therefore, the FA component in the copolymer was found to give a function as a surface-modifier to the copolymer. Moreover, since the FA component made the copolymer insoluble in water, the copolymer-containing membrane could be applied for the pervaporation of aqueous solution.

*Figure 1a* shows plots of $\alpha^{EtOH}$ of PDMS-based blend membranes containing 5.3 wt% of copoly(IPAA/FA) and 5.8 wt% of polyFA *versus* $1/T$. The $\alpha^{EtOH}$ of the former had a maximum at about $3.24 \times 10^{-3}$ K$^{-1}$ (about 36°C). Since the $\alpha^{EtOH}$ of the latter had no maximum and

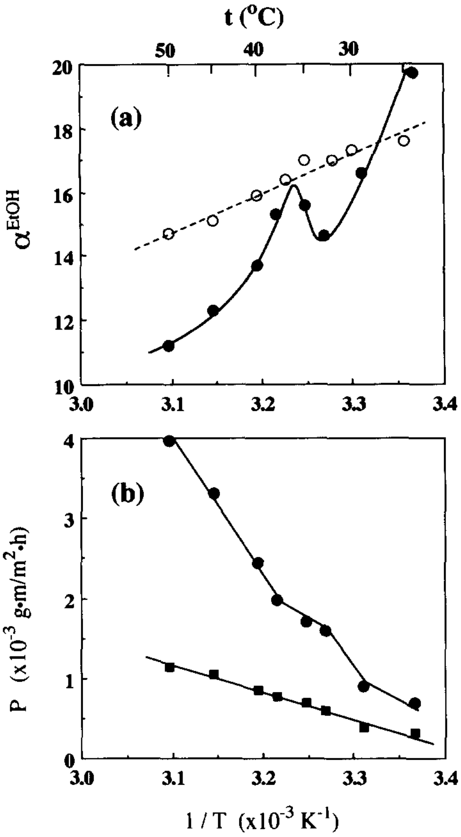

**Figure 1** Plots of (a) $\alpha^{EtOH}$ of PDMS-based blend membranes containing 5.3 wt% copoly(IPAA/FA) (●) and 5.8 wt% polyFA (○) and (b) $P_{water}$ (●) and $P_{EtOH}$ (■) of PDMS-based blend membrane containing 5.3 wt% copoly(IPAA/FA) *versus* $1/T$

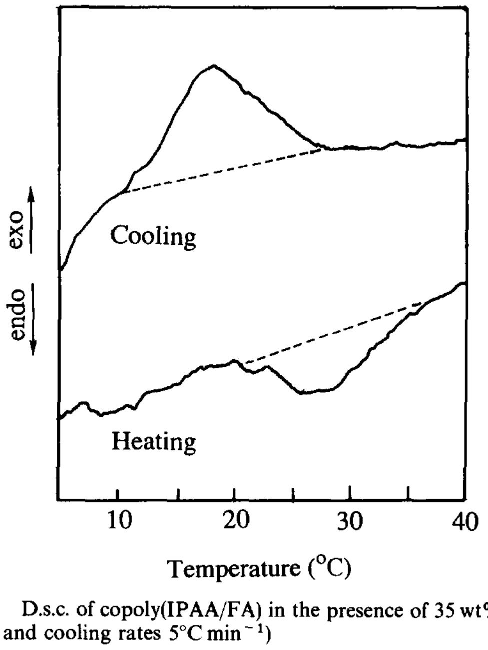

**Figure 2** D.s.c. of copoly(IPAA/FA) in the presence of 35 wt% water (heating and cooling rates 5°C min$^{-1}$)

**Table 1** Pervaporation of 2.5 wt% aqueous ethanol solution through the binary blend membrane[a] and PDMS membrane at 30°C

| Membrane | $\alpha^{EtOH}$ | $P_{water}$ (10$^{-3}$ g m m$^{-2}$ h$^{-1}$) | $P_{EtOH}$ (10$^{-3}$ g m m$^{-2}$ h$^{-1}$) | $\theta_{water}$[b] (deg) |
|---|---|---|---|---|
| Binary blend membrane[a] | 16.6 | 0.894 | 0.382 | 110 |
| PDMS membrane | 12.1 | 1.28 | 0.401 | 98 |

[a] PDMS-based blend membrane containing 5.3 wt% copoly(IPAA/FA)
[b] Contact angle of water droplet on the air-side surface

decreased monotonically with temperature increase, the phenomenon may be due to the thermal transition of the IPAA component in copoly(IPAA/FA). In fact this copolymer showed an endothermic peak at $3.41–3.25 \times 10^{-3}$ $K^{-1}$ (20–35°C) in the presence of water, as shown in *Figure 2*. This fact demonstrates that the change of $\alpha^{EtOH}$ *versus* temperature is due to the thermal transition of the copoly(IPAA/FA) at the membrane surface.

*Figure 1b* shows plots of $P_{water}$ and $P_{EtOH}$ of the same copoly(IPAA/FA)-containing membrane as in *Figure 1a versus* $1/T$. Although $P_{EtOH}$ increased monotonically with increasing temperature from 25 to 50°C, the increase in $P_{water}$ with increasing temperature was suppressed at $3.25–3.22 \times 10^{-3}$ $K^{-1}$ (35–38°C). This suppression is the reason for the increase in $\alpha^{EtOH}$ at this temperature. This finding suggests that the change of $\alpha^{EtOH}$ is caused by the change of hydrophobicity of the membrane surface.

In conclusion, a blend membrane consisting of 5.3 wt% of copoly(*N*-isopropylacrylamide/1H,1H,2H,2H-perfluorododecyl acrylate) and poly(dimethylsiloxane) showed a high ethanol permselectivity ($\alpha^{EtOH} = 19.7$ at 24°C) in pervaporation of 2.5 wt% aqueous ethanol solution. Moreover, the value of $\alpha^{EtOH}$ had a maximum at about 36°C. This behaviour was due to the change in the extent of hydrophobicity of the air-side surface (i.e. upstream surface) caused by thermal transition of the copolymer accumulated at the surface. Further research into the mechanism and precise method for controlling permselectivity by other parameters is now in progress.

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