Poly[*p*-(1H,1H,2H,2H-perfluoroalkyloxydimethylsilyl)styrenes] as materials for ethanol-permselective membranes

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Several *p*-(1H,1H,2H,2H-perfluoroalkyloxydimethylsilyl)styrenes having perfluoroalkyl groups with different chain lengths were synthesized and polymerized. The polydimethylsiloxane-based blend membranes which contained a very small amount (1.0 wt%) of poly[*p*-(1H,1H,2H,2H-perfluoroalkyloxydimethylsilyl)styrene] had good ethanol permselectivity. All of their separation factors (α^{EtOH}) and permeation rates (P) were higher than those of polydimethylsiloxane. In particular, poly[*p*-(1H,1H,2H,2H-perfluorohexyloxydimethylsilyl)styrene] showed the best performance ($\alpha^{EtOH} = 22.3$, $P = 2.06 \times 10^{-2}$ g m m^{-2} h^{-1}). This was attributed to the characteristics of the fluorine-containing polymers which were accumulated at the membrane surface.

(**Keywords: perfluoroalkyl group; ethanol-permselective membrane; blend polymer membrane; pervaporation; poly(dimethylsiloxane); comb-shaped polymer**)

Introduction

Considerable attention has recently been paid to the concentration of aqueous ethanol solutions produced by the fermentation of biomass by a pervaporation process through polymeric membranes. In general, it is more economical to separate as small amount of permeating substance as possible. Since these solutions contain <10% ethanol and other substances such as sugar and inorganic compounds, it is more economical and practical to separate ethanol from water and other substances by using ethanol-permselective membranes. However, most of the polymeric membranes are water-permselective and only a few ethanol-permselective membranes have been reported, for example, poly(dimethylsiloxane) (PDMS)[1], poly(1-trimethylsilylpropyne) (PMSP)[2] and some fluorine-containing polymers[3]. The PDMS membrane has a low degree of ethanol permselectivity. Since fluorine-containing polymers show high water repellency, their membranes are anticipated to be highly ethanol-permselective. However, the fluorine-containing membranes tend to show low permeability owing to their high crystallinity, and moreover they are very expensive.

The permeation process of small molecules through non-porous membranes can be divided into dissolution in a membrane surface and diffusion through the membrane interior according to the solution-diffusion mechanism. In pervaporation of an ethanol–water mixture, diffusivity of water is higher than that of ethanol because of the smaller size of the water molecule. Therefore, if ethanol permselectivity is desired, a membrane of higher ethanol solubility should be used. Since ethanol solubility depends primarily on the nature of the membrane surfaces, we have been trying to prepare highly ethanol-permselective and highly permeable membranes by using PDMS-based membranes in which a fluorine-containing polymer is accumulated at the surface. Such a membrane can be prepared by casting a blend polymer solution which consists of a small amount of a fluorine-containing polymer (expensive), PDMS and a common solvent[4]. We have already reported an improved method of oxygen permselectivity by using a similar blend membrane which was made of a small amount of a fluorine-containing polymer and PDMS[5].

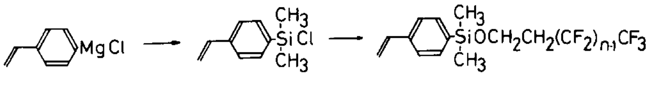
In this communication, we will describe the synthesis and polymerization of *p*-(1H,1H,2H,2H-perfluoroalkyloxydimethylsilyl)styrene(**Fn**)s, preparation of the surface-modified blend membranes consisting of poly(**Fn**) and PDMS by the above method[4], as well as the high ethanol permselectivity through these membranes in pervaporation.

Experimental

Materials. p-Chlorostyrene was supplied by Hokko Chemical Industry Co. Ltd and distilled over calcium hydride. 1H,1H,2H,2H-perfluoroalkylalcohols were purchased from Fluorochem Ltd., KE42-TS of Shin-etsu Silicone, Inc. was used for PDMS.

Synthesis of monomers. p-(1H,1H,2H,2H-perfluoroalkyloxydimethylsilyl)styrenes (**Fn**; $n = 4$, 6, 8 and 10) were synthesized via *p*-(chlorodimethylsilyl)styrene according to *Scheme 1*. *p*-(Chlorodimethylsilyl)styrene was prepared and distilled under nitrogen as reported previously[6,7].

Four new monomers, **F4**, **F6**, **F8** and **F10**, were synthesized and identified as follows.



Fn

n = 4,6,8,10

Scheme 1 Synthetic route to *p*-(1H,1H,2H,2H-perfluoroethoxydimethylsilyl)styrene

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p-(1H,1H,2H,2H-perfluorohexyloxydimethylsilyl)-styrene(**F4**): To *p*-1H,1H,2H,2H-perfluorohexan-1-ol (1.80 g, 6.88 mmol) and pyridine (0.55 g, 6.88 mmol) in dry ethyl ether (30 ml), *p*-(chlorodimethylsilyl)styrene (1.35 g, 6.88 mmol) was added dropwise, and the mixture was stirred for 12 h at room temperature under nitrogen. After removing the formed pyridine hydrochloric acid and the solvent, the colourless liquid product was isolated by distillation in 54.2% yield (b.p. 76°C (0.3 mmHg)). ^{1}H n.m.r. (CCl_4) δ (ppm): 0.30 (s, 6H, $Si(CH_3)_3$), 2.36 (tt, 2H, $J_1 = 18.6$ Hz, $J_2 = 7.4$ Hz, $CH_2CH_2CF_2$), 3.87 (t, 2H, $J = 7.4$ Hz, $SiOCH_2CH_2$), 5.24 (dd, 1H, $J_1 = 10.4$ Hz, $J_2 = 1.6$ Hz, $HC{=}CH$), 5.73 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 1.6$ Hz, $HC{=}CH$), 6.72 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 10.4$ Hz, $H_2C{=}CHPh$), 7.33, 7.67 (2d, 4H, phenyl proton). I.r. (NaCl) (cm^{-1}): 2972, 1602 (C=C), 1258 ($SiCH_3$), 1238 (C–F), 1136 (Si–O).

p-(1H,1H,2H,2H-perfluorooctyloxydimethylsilyl)-styrene(**F6**): A reaction similar to that described above gave a colourless liquid product in 34.4% yield (b.p. 83°C (0.2 mmHg), m.p. −80 to −85°C). The ^{1}H n.m.r. and i.r. spectra were almost identical with those of **F4**.

p-(1H,1H,2H,2H-perfluorodecyloxydimethylsilyl)-styrene(**F8**): A reaction similar to the above gave a colourless liquid product in 76.8% yield ($R_f = 0.45$, (hexane); m.p. 42°C). The ^{1}H n.m.r. and i.r. spectra were almost identical with those of **F4**.

p-(1H,1H,2H,2H-perfluorododecyloxydimethyl-silyl)styrene(**F10**): A reaction similar to the above was followed. The usual work-up gave a solid white product in 91.7% yield ($R_f = 0.53$; (chloroform/hexane = 2/8); m.p. 64–74°C). ^{1}H n.m.r. ($C_2F_2Br_2$) δ (ppm): 0.36 (s, 6H, $Si(CH_3)_3$), 2.36 (tt, 2H, $J_1 = 18.6$ Hz, $J_2 = 7.4$ Hz, $CH_2CH_2CF_2$), 3.93 (t, 2H, $J = 7.4$ Hz, $SiOCH_2CH_2$), 5.20 (dd, 1H, $J_1 = 10.4$ Hz, $J_2 = 1.6$ Hz, $HC{=}CH$), 5.70 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 1.6$ Hz, $HC{=}CH$), 6.75 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 10.4$ Hz, $H_2C{=}CHPh$), 7.29, 7.45 (2d, 4H, phenyl proton). I.r. (NaCl) (cm^{-1}): 2968, 1602 (C=C), 1258–1206 ($SiCH_3$, C–F), 1154 (Si–O).

Polymerization. Polymers were obtained by conventional radical polymerization and reprecipitation in methanol. The results are shown in *Table 1*.

Preparation of membranes. The binary blends of PDMS (0.20 g) and 0.5–2.0 wt% (based on PDMS) of one of the poly(**Fn**)s (0.002 g) were dissolved in tetrahydrofuran (4 ml) and the solutions (5 w/v%) were cast on poly(tetrafluoroethylene) (PTFE) sheets. The solvents were evaporated at room temperature for 24 h and dried *in vacuo* for 24 h. The thickness (l) of the membranes was in the range of 52–92 μm. The surfaces contacting with air and PTFE during casting were designated Air- and PTFE-side, respectively.

Pervaporation. Pervaporation of the aqueous ethanol solutions (2.70 wt%) through the blend polymer membranes was carried out by the usual method using a stainless steel cell at 25°C. The downstream pressure was kept at ~7 Pa. The permeation area (A) and time (t) were 18.1 cm^2 and 8–10 h, respectively. The pervaporation fluxes (Q, g) were determined by weighing the permeates collected in a cold trap in liquid nitrogen. The composition of the permeates was measured by means of a gas chromatograph. The pervaporation rate (P, g m m^{-2} h^{-1}) and ethanol separation factor (α^{EtOH}) were calculated from the following equations:

$$Q = P(A/lt)$$

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

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

Results and discussion

Characterization of polymers. All the poly(**Fn**)s ($\bar{M}_w \sim \times 10^4$) were white solids and had film-forming ability. However, the membrane from poly(**F4**) was somewhat soft and the membranes from poly(**F6**), poly(**F8**) and poly(**F10**) were brittle, so that they could not resist a 1 × 10^5 Pa pressure difference in the pervaporation. The brittle nature of poly(**F10**), poly(**F8**) and poly(**F6**) is ascribable to their high fluorine content (>60%). However, despite the still quite high fluorine content of poly(**F4**) (52%), this membrane was soft. This is probably due to the flexible Si–O bond connecting the perfluoroalkyl group with the benzene ring. Indeed, the glass transition temperature (T_g) of poly(**F4**) is 5.5°C, which is much lower than that of poly(perfluoropropyl-styrene), 107°C[8]. This fact suggests that the perfluoroalkyl substituents in poly(**F4**) can move more easily owing to the Si–O bonds.

Pervaporation. Table 2 shows that the pervaporation results of the ethanol–water (2.70/97.30 v/v) mixture through the binary blend polymer membranes, namely, poly(**F4**)–PDMS (1–4 in *Table 2*) and poly(**F10**)–PDMS (5 and 6) (0.5–2.0/100 w/w) membranes. In the case of permeation from the air-side, both α^{EtOH} and P of all the blend membranes were higher than those of

Table 1 Polymerization and copolymerization of *p*-(1H,1H,2H,2H-perfluoroalkyloxydimethylsilyl)styrenes[a]

Run no.	Monomer	Yield (%)	$\bar{M}_w$[b] (×10^4)	$\bar{M}_w/\bar{M}_n$[b]	$T_g[T_m]$[c] (°C)	F[d] (%)	Si[e] (%)	Membrane[f] appearance
1	**F4**	52.0	9.5	1.8	5.5	52	17	(+)
2	**F6**	13.0	2.0	1.7	–	61	14	(−)
3	**F8**	42.0	5.0	1.1	–	67	12	(−)
4	**F10**	24.0	4.7	2.5	(135)	72	10	(−)

[a] Polymerized in THF at 60°C with 0.2 mol% AIBN
[b] Determined by g.p.c.
[c] Determined by d.s.c.
[d] Weight per cent of $(CF_2)_nCF_3$ in the (co)polymer
[e] Weight per cent of $Si(CH_3)_2O_n$ in the (co)polymer
[f] (+) soft, (−) brittle

Table 2 Pervaporation of aqueous ethanol solution[a] through the PDMS-based blend membrane[b]

Run no.	Additive[c] polymer	Upstream[d] side	P^e	$P_{ethanol}{}^e$	$P_{water}{}^e$	α^{EtOH}	θ^f
1	poly(**F4**)	Air	20.6	7.85	12.7	22.3	110
2	poly(**F4**)	PTFE	8.61	1.17	7.43	5.52	103
3[g]	poly(**F4**)	Air	9.76	2.96	6.80	16.7	112
4[h]	poly(**F4**)	Air	11.4	3.91	7.53	19.4	114
5	poly(**F10**)	Air	13.5	2.71	10.8	8.93	111
6	poly(**F10**)	PTFE	19.9	3.18	16.8	6.61	102
7	None	Air	7.79	0.809	6.99	4.75	101

[a] $[\mathrm{EtOH}]_{feed} = 2.70$ wt%
[b] Additive polymer/PDMS = 1/100 (w/w)
[c] See *Scheme 1*
[d] Air and PTFE mean the pervaporation from air- and PTFE-side, respectively
[e] In 10^{-3} g m m^{-2} h^{-1}
[f] Water droplet
[g] Additive polymer/PDMS = 0.5/100 (w/w)
[h] Additive polymer/PDMS = 2/100 (w/w)

PDMS itself (1, 3, 4 and 5 in *Table 2*). In poly(**F4**)–PDMS membrane, the addition of only 0.5 wt% poly(**F4**) was enough to improve the α^{EtOH} and P (3 in *Table 2*). In particular, poly(**F4**)–PDMS (1/100) membrane (1) showed the best results ($\alpha^{EtOH} = 22.3$, $P = 2.06 \times 10^{-2}$ g m m^{-2} h^{-1}). This performance is quite good, and better than that of a PDMS–PMSP graft copolymer[9] ($\alpha^{EtOH} = 28.3$, $P = 2.45 \times 10^{-3}$ g m m^{-2} h^{-1}), and comparable to that of an alkylsilylated PMSP ($\alpha^{EtOH} = 17.6$, $P = 2.36 \times 10^{-2}$ g m m^{-2} h^{-1})[10]. By using this membrane, the 2.70 wt% aqueous ethanol solution was concentrated to 38.2 wt%. The contact angles of water droplets on the membrane surfaces were measured. The angles for the air-side surfaces were 110, 112, 114 and 111° for 1, 3, 4 and 5, respectively, and therefore, these surfaces are more hydrophobic than that of PDMS (101° for 7). These results reveal that the pervaporation performance is improved by the poly(**Fn**) accumulated at the air-side surface. This idea is supported by the following experimental findings: the α^{EtOH} in the pervaporations from the PTFE-side are lower than those from the air-side for the same membrane (2 and 6) and nearer to those of PDMS itself except for no. 6. Moreover, the contact angles on the PTFE-side are very similar to that of PDMS (2 and 6). These facts indicate no enrichment of poly(**Fn**) on the PTFE-side.

In order to obtain more insight on α^{EtOH}, P was divided into $P_{ethanol}$ and P_{water}. It is apparent that the enhancements of α^{EtOH} values were due to the increase in $P_{ethanol}$ but not due to the decrease in P_{water}. This fact suggests that the fluorine-containing polymers endow PDMS membranes with ethanol affinity rather than water repellency.

Although the percentage of fluorine in poly(**F4**) is lower than that in poly(**F10**), the effect of the former on the enhancement of α^{EtOH} is superior to that of the latter. The reason is the difference in the compatibility: poly(**F10**) is less compatible with PDMS than poly(**F4**), resulting in partial bleeding of poly(**F10**) from the membrane surface. On the other hand, poly(**F4**) can form a more homogeneous surface owing to its better membrane-forming ability mentioned above and better compatibility with PDMS. Indeed, the poly(**F4**)–PDMS membrane was clear while the poly(**F10**)–PDMS membrane was opaque.

It is possible that Si–O–C bonds in poly(**Fn**)s are cleaved by hydrolysis in water during the pervaporation experiments. Nevertheless, it was confirmed that such undesirable cleavages did not take place, because the hydrolysed products, 1H,1H,2H,2H-perfluoroalkan-1-ols, were not detected by gas chromatography after poly(**Fn**)s were mixed with a large amount of water for 24 h and the high contact angle values were maintained after pervaporation experiments for > 8 h. This resistance to hydrolysis is accounted for by the water repellency of the perfluoroalkyl groups.

In conclusion, a good ethanol-permselective membrane was obtained by adding a very small amount of poly(**F4**) to PDMS. This is attributed to the poly(**F4**) being accumulated at the membrane surface.

Further research into the permeations of ethanol or oxygen through poly(**Fn**) membranes is now in progress.

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