Synthesis of Poly[*p*-(1*H*,1*H*,2*H*,2*H*-perfluoroalkyl-oxyoligosiloxanyl)styrene]s and Oxygen Permselectivity of Their Membranes

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ABSTRACT: Comb-shaped polymers having both perfluoroalkyl groups and oligosiloxanylene groups with different length were synthesized by homopolymerization of *p*-(1*H*,1*H*,2*H*,2*H*-perfluoroalkyloxyoligosiloxanyl)styrene. These polymers contained a 38.3–71.7 wt% perfluoroalkyl chain and 10.2–38.8 wt% oligosiloxanylene chain and showed high oxygen permeabilities ($P_{O_2} = 0.3\text{--}1.7 \times 10^{-8}$ cc(STP) cm cm⁻² s⁻¹ cmHg⁻¹), and good oxygen permselectivities ($\alpha = P_{O_2}/P_{N_2} = 2.2\text{--}3.5$). In particular, poly[*p*-(1*H*,1*H*,2*H*,2*H*-perfluorohexyloxydimethylsilyl)styrene] and poly[*p*-(5-(1*H*,1*H*,2*H*,2*H*-perfluorododecyloxy)hexamethyltrisiloxanyl)styrene] showed the best results of these comb-shaped polymers ($P_{O_2} = 1.14 \times 10^{-8}$ cc(STP) cm cm⁻² s⁻¹ cmHg⁻¹, $\alpha = 2.96$ and $P_{O_2} = 8.05 \times 10^{-9}$ cc(STP) cm cm⁻² s⁻¹ cmHg⁻¹, $\alpha = 3.17$, respectively). As the siloxanylene chain in these polymers was extended, P_{O_2} increased and α decreased, whereas on extending the perfluoroalkyl chain, P_{O_2} decreased but α had a maximum value at a certain perfluoroalkyl chain length. This behavior was closely related to the state of aggregation and mobility of the perfluoroalkyl chains. The introduction of perfluoroalkyloxy groups to poly(*p*-oligosiloxanylstyrene) was effective for the simultaneous enhancement of α and P_{O_2} . Laminated membranes consisting of comb-shaped polymers and cross-linked polydimethylsiloxane showed good P_{O_2} and α .

KEY WORDS Perfluoroalkyl Group / Oligosiloxanylene Group / Comb-shaped Polymer / Membrane / Oxygen Permselectivity /

Since high gas affinity of perfluorinated and polyfluorinated organic compounds was applied to artificial blood, the fluorine-containing compounds have been expected to be oxygen permselective membrane materials. For example, Kajiyama *et al.*¹ reported a high oxygen permselective membrane consisting of perfluorotributylamine, a liquid crystalline compound, and poly(vinyl chloride). Recently two kinds of poly(1-trimethylsilylpropyne)(PMSP) based membranes modified by fluorine-containing compounds were reported to have very high oxygen permselectivity (α) and permeability (P_{O_2}): one was surface-modified by fluorine gas² and the other was modified by imbibing hexafluorobutyl methacrylate.³

However, in general it has not been reported that the introduction of a fluorine-containing group to a membrane polymer *via* covalent bonds shows good effect for enhancing oxygen permselectivity. In the case of introduction of a small amount of a fluorine-containing group such as a trifluoromethyl group, P_{O_2} increased but α decreased because of the bulkiness of the group,^{4–6} and in the case of a polymer having a large amount of fluorine-containing group such as polytetrafluoroethylene, P_{O_2} was very low and α was not high because of its high crystallinity. Moreover a polymer with a high fluorine content is apt to be insoluble and have poor membrane forming ability. Therefore, in order to make a membrane highly oxygen

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permselective, an appropriate chemical structure, which satisfies both high fluorine content and low crystallinity must be selected.

Perfluoroalkane-containing polymers usually have the following characteristics: high gas affinity, crystalline property, high melting point (T_m), and insolubility in ordinary solvents. On the other hand, siloxane-containing polymers have the following characteristics: high oxygen permeability, amorphous nature, low glass transition temperature (T_g), and high solubility in ordinary solvents. In order to obtain good oxygen permselective membrane materials having the advantages of both fluorine- and siloxane-containing polymers, we designed a polystyrene having a perfluoroalkyl group at *para* position via an oligosiloxanylene spacer and synthesized comb-shaped polymers having perfluoroalkoxyoligodimethylsiloxanes as the grafts.

This paper describes the synthesis of poly- $[p-(1H,1H,2H,2H$ -perfluoroalkoxyoligosiloxanyl)styrene]s having perfluoroalkyl and oligosiloxanylene chains with different length (Scheme 1) and good oxygen permselectivity of their membranes, and we discuss the effects

of the length of perfluoroalkyl and oligosiloxanylene chain of the polymers on α and P_{O_2} values.

EXPERIMENTAL

Materials

p-Chlorostyrene was supplied by Hokko Chemical Industry Co., Ltd. and distilled over calcium hydride. 1,5-Dichlorohexamethyltrisiloxane was synthesized from hexamethylcyclotrisiloxane.⁷ 1*H*,1*H*,2*H*,2*H*-Perfluoroalkylalcohols were purchased from Fluorochem Ltd., KE-42TS of Shin-etsu Silicone, Inc. was used for polydimethylsiloxane (PDMS).

Synthesis of p-(1H,1H,2H,2H-Perfluoroalkoxyoligosiloxanyl)styrene (Sn,m: n = 1, 2, and 3, m = 4, 6, 8, and 10) (Scheme 1)

The monomers were represented as **Sn,m** where **n** (= 1, 2, and 3) and **m** (= 4, 6, 8, and 10) designate the lengths of an oligodimethylsiloxanylene and a perfluoroalkyl chain, that is, the numbers of silicon and fluorocarbon atoms, respectively.

Scheme 1. Synthetic routes to **Sn,m** monomers ($m=4, 6, 8, \text{ and } 10$). **Sn,m**: **n** (= 1, 2, and 3) and **m** (= 4, 6, 8, and 10) designate the lengths of an oligodimethylsiloxanylene and perfluoroalkyl chain, that is, the numbers of silicon and fluorocarbon atoms, respectively. **a**, dichlorodimethylsilane; **b**, ammonia water; **c**, dichlorodimethylsilane; **d**, 1,5-dichlorohexamethyltrisiloxane; **e**, 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl alcohol = $\text{HOCH}_2\text{CH}_2(\text{CF}_2)_{m-1}\text{CF}_3$ ($m=4, 6, 8, \text{ or } 10$).

Synthesis of *p*-(1*H*,1*H*,2*H*,2*H*-perfluoroalkyloxydimethylsilyl)styrene (**S1**, *m*: *m* = 4, 6, 8, and 10) (Scheme 1)

These monomers were synthesized from *p*-vinylphenylmagnesium chloride via *p*-(chlorodimethylsilyl)styrene as reported previously.⁸

Synthesis of *p*-(1*H*,1*H*,2*H*,2*H*-perfluoroalkyloxytetramethyldisiloxanyl)styrene (**S2**, *m*: *m* = 4, 6, 8, and 10) (Scheme 1)

These new 4 monomers were synthesized from *p*-vinylphenyldimethylsilanol via *p*-(chlorotetramethyldisiloxanyl)styrene.

p-Vinylphenyldimethylsilanol. To a mixture of ether (50 ml) and 4*N* ammonia water (100 ml), *p*-(chlorodimethylsilyl)styrene⁹ 5.40 g (27.6 mmol) was added dropwise with vigorous stirring at 0°C. After the addition, the two layers mixture was stirred at room temperature for 1 h. The water layer was extracted with ether, which was combined with the ether layer. The solution was dried over anhydrous sodium sulfate overnight and the solvent removed completely. Yield 98.9%. ¹H NMR (CCl₄) δ 0.40 (6H, s, PhSi (CH₃)₂), 4.40 (1H, s, SiOH), 5.26 (1H, dd, *J*₁ = 2.0 Hz, *J*₂ = 11.0 Hz, CH=C-), 5.76 (1H, dd, *J*₁ = 2.0 Hz, *J*₂ = 18.0 Hz, CH=C-), 6.73 (1H, dd, *J*₁ = 11.0 Hz, *J*₂ = 11.0 Hz, CH=CH₂), and 7.43 ppm (4H, 2d, -C₆H₄-). IR (NaCl) 3376 (OH), 2968 (CH), 1602 (C=C), 1258 (SiC), and 1154 cm⁻¹ (SiO).

p-(Chlorotetramethyldisiloxanyl)styrene. To dichlorodimethylsilane 7.75 g (60.0 mmol) and dry triethylamine 3.29 g (32.6 mmol) in ether (40 ml), *p*-vinylphenyldimethylsilanol 5.80 g (32.6 mmol) was added dropwise, and the solution was stirred for 12 h at room temperature in nitrogen. After stirring, the ether was removed and dry hexane (40 ml) was added, and the formed triethylamine hydrochloride was filtered out in nitrogen. The solution was concentrated and purified by distillation. Yield 35.4%. bp 92.0°C (0.45 mmHg). ¹H NMR (CCl₄) δ 0.38 (6H, s, PhSi

(CH₃)₂), 0.63 (6H, s, ClSi (CH₃)₂), 5.26 (1H, dd, *J*₁ = 2.0 Hz, *J*₂ = 11.0 Hz, CH=C-), 5.76 (1H, dd, *J*₁ = 2.0 Hz, *J*₂ = 18.0 Hz, CH=C-), 6.73 (1H, dd, *J*₁ = 11.0 Hz, *J*₂ = 11.0 Hz, CH=CH₂), and 7.43 ppm (4H, 2d, -C₆H₄-).

p-(1*H*,1*H*,2*H*,2*H*-perfluorohexyloxytetramethyldisiloxanyl)styrene (**S2**, 4). To 1*H*,1*H*,2*H*,2*H*-perfluorohexan-1-ol 2.00 g (8.47 mmol) and dry pyridine 0.68 g (8.47 mmol) in ether (50 ml), *p*-(chlorotetramethyldisiloxanyl)styrene 2.28 g (8.47 mmol) was added dropwise, and the solution was stirred for 12 h at room temperature in nitrogen. After the formed pyridine hydrochloride was filtered out in nitrogen, the solvent was removed completely. Yield 72.1%. ¹H NMR (CCl₄) δ 0.13 (6H, s, OSi (CH₃)₂), 0.38 (6H, s, PhSi (CH₃)₂), 2.36 (2H, tt, *J*₁ = 7.40 Hz, *J*₂ = 18.6 Hz, CH₂CF₂), 3.92 (2H, t, *J* = 7.40 Hz, CH₂SiO), 5.20 (1H, dd, *J*₁ = 2.0 Hz, *J*₂ = 11.0 Hz, CH=C-), 5.68 (1H, dd, *J*₁ = 2.0 Hz, *J*₂ = 18.0 Hz, CH=C-), 6.68 (1H, dd, *J*₁ = 11.0 Hz, *J*₂ = 11.0 Hz, CH=CH₂), and 7.41 ppm (4H, 2d, -C₆H₄-). IR (NaCl) 2972 (CH), 1602 (C=C), 1258 (SiC), 1238 (CF), and 1136 cm⁻¹ (SiO).

p-(1*H*,1*H*,2*H*,2*H*-perfluorooctyloxytetramethyldisiloxanyl)styrene (**S2**, 6). A reaction and purification similar to those above were run with 1*H*,1*H*,2*H*,2*H*-perfluorooctanol 2.50 g (8.47 mmol). Yield 78.1%. ¹H NMR (CCl₄) δ 0.13 (6H, s, OSi (CH₃)₂), 0.38 (6H, s, PhSi (CH₃)₂), 2.38 (2H, tt, *J*₁ = 7.40 Hz, *J*₂ = 18.6 Hz, CH₂CF₂), 3.92 (2H, t, *J* = 7.40 Hz, CH₂SiO), 5.21 (1H, dd, *J*₁ = 2.0 Hz, *J*₂ = 11.0 Hz, CH=C-), 5.68 (1H, dd, *J*₁ = 2.0 Hz, *J*₂ = 18.0 Hz, CH=C-), 6.68 (1H, dd, *J*₁ = 11.0 Hz, *J*₂ = 11.0 Hz, CH=CH₂), and 7.40 ppm (4H, 2d, -C₆H₄-). IR (NaCl) 2972 (CH), 1600 (C=C), 1258 (SiC), 1236 (CF), and 1136 cm⁻¹ (SiO).

p-(1*H*,1*H*,2*H*,2*H*-perfluorodecyloxytetramethyldisiloxanyl)styrene (**S2**, 8). A reaction and purification similar to those above were run with 1*H*,1*H*,2*H*,2*H*-perfluorodecan-1-ol 5.29 g (8.47 mmol). Yield 93.5%. mp 26.0–28.0°C. ¹H NMR (CCl₄) δ 0.16 (6H, s, OSi (CH₃)₂),

0.38 (6H, s, $\text{PhSi}(\text{CH}_3)_2$), 2.38 (2H, tt, $J_1=7.40$ Hz, $J_2=18.6$ Hz, CH_2CF_2), 3.91 (2H, t, $J=7.40$ Hz, CH_2SiO), 5.20 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C}-$), 5.68 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C}-$), 6.68 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.42 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$). IR (NaCl) 2972 (CH), 1602 (C=C), 1258 (SiC), 1230 (CF), and 1136 (SiO).

p-(1*H*,1*H*,2*H*,2*H*-perfluorododecyloxytetramethyldisiloxanyl)styrene (**S2,10**). A reaction and purification similar to those above were run with 1*H*,1*H*,2*H*,2*H*-perfluorododecan-1-ol 6.13 g (8.47 mmol). Yield 87.4%. mp 37.0–42.0°C. ^1H NMR (CCl_4) δ 0.16 (6H, s, $\text{OSi}(\text{CH}_3)_2$), 0.38 (6H, s, $\text{PhSi}(\text{CH}_3)_2$), 2.40 (2H, tt, $J_1=7.40$ Hz, $J_2=18.6$ Hz, CH_2CF_2), 3.90 (2H, t, $J=7.40$ Hz, CH_2SiO), 5.22 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C}-$), 5.70 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C}-$), 6.68 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.42 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$). IR (KBr) 2974 (CH), 1600 (C=C), 1258 (SiC), 1230 (CF), and 1138 cm^{-1} (SiO).

Synthesis of p-(1*H*,1*H*,2*H*,2*H*-perfluoroalkyloxyhexamethyltrisiloxanyl)styrene (**S3,m**; $m=4, 6, 8$, and 10) (Scheme 1)

These new monomers were synthesized from *p*-(5-chlorohexamethyltrisiloxan-1-yl)styrene using 1,5-dichlorohexamethyltrisiloxane.

1,5-dichlorohexamethyltrisiloxane was prepared from hexamethylcyclotrisiloxane 22.2 g (100 mmol) and thionyl chloride 72.3 g (620 mmol) using triphenylphosphine 0.95 g (3.62 mmol) according to a reported method.⁷ Yield 75.3%. bp 80.0°C (20.0 mmHg). ^1H NMR (CDCl_3) δ 0.18 (6H, s, $\text{OSi}(\text{CH}_3)_2$) and 0.47 ppm (12H, s, $\text{ClSi}(\text{CH}_3)_2$).

p-(5-chlorohexamethyltrisiloxan-1-yl)styrene was synthesized from *p*-vinylphenylmagnesium chloride (36.0 mmol) and 1,5-dichlorohexamethyltrisiloxane 30.0 g (108 mmol) according to a reported method.¹⁰ Yield 47.9%. bp 108°C (0.22 mmHg). ^1H NMR (CDCl_3) δ 0.13 (6H, s, $\text{OSi}(\text{CH}_3)_2$), 0.37 (6H, s, $\text{PhSi}(\text{CH}_3)_2$),

0.43 (6H, s, $\text{ClSi}(\text{CH}_3)_2$), 5.30 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C}-$), 5.80 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C}-$), 6.80 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.50 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$).

p-(1*H*,1*H*,2*H*,2*H*-perfluorohexyloxyhexamethyltrisiloxanyl)styrene (**S3,4**). To 1*H*,1*H*,2*H*,2*H*-perfluorohexan-1-ol 2.00 g (8.47 mmol) and dry pyridine 0.68 g (8.47 mmol) in ether (50 ml), *p*-(5-chlorohexamethyltrisiloxan-1-yl)styrene 2.92 g (8.47 mmol) was added dropwise slowly, and the solution was stirred for 12 h at room temperature in nitrogen. After the formed pyridine hydrochloride was filtered out in nitrogen, the solvent was removed completely. Yield 54.1%. ^1H NMR (CDCl_3) δ 0.06 (12H, s, $\text{OSi}(\text{CH}_3)_2$), 0.34 (6H, s, $\text{PhSi}(\text{CH}_3)_2$), 2.33 (2H, tt, $J_1=7.40$ Hz, $J_2=18.6$ Hz, CH_2CF_2), 3.93 (2H, t, $J=7.40$ Hz, CH_2SiO), 5.30 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C}-$), 5.77 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C}-$), 6.74 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.46 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$). IR (NaCl) 2968 (CH), 1602 (C=C), 1264 (SiC), 1238 (CF), and 1044 cm^{-1} (SiO).

p-(1*H*,1*H*,2*H*,2*H*-perfluorooctyloxyhexamethyltrisiloxanyl)styrene (**S3,6**). A reaction and purification similar to those above were run with 1*H*,1*H*,2*H*,2*H*-perfluorooctanol 2.50 g (8.47 mmol). Yield 60.0%. ^1H NMR (CDCl_3) δ 0.06 (12H, s, $\text{OSi}(\text{CH}_3)_2$), 0.34 (6H, s, $\text{PhSi}(\text{CH}_3)_2$), 2.42 (2H, tt, $J_1=7.40$ Hz, $J_2=18.6$ Hz, CH_2CF_2), 3.93 (2H, t, $J=7.40$ Hz, CH_2SiO), 5.30 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C}-$), 5.77 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C}-$), 6.73 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.43 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$). IR (NaCl) 2972 (CH), 1603 (C=C), 1258 (SiC), 1135 (CF), and 1033 cm^{-1} (SiO).

p-(1*H*,1*H*,2*H*,2*H*-perfluorodecyloxyhexamethyltrisiloxanyl)styrene (**S3,8**). A reaction and purification similar to those above were run with 1*H*,1*H*,2*H*,2*H*-perfluorodecan-1-ol 5.29 g (8.47 mmol). Yield 69.9%. ^1H NMR (CDCl_3) δ 0.06 (12H, s, $\text{OSi}(\text{CH}_3)_2$), 0.34 (6H, s, $\text{PhSi}(\text{CH}_3)_2$),

2.42 (2H, tt, $J_1=7.40$ Hz, $J_2=18.6$ Hz, $\text{CH}_2\text{-CF}_2$), 3.93 (2H, t, $J=7.40$ Hz, CH_2SiO), 5.20 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C-}$), 5.73 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C-}$), 6.73 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.40 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$). IR (NaCl) 2972 (CH), 1603 (C=C), 1258 (SiC), 1230 (CF), and 1033 cm^{-1} (SiO).

p-(1*H*,1*H*,2*H*,2*H*-perfluorododecyloxyhexamethyltrisiloxanyl)styrene (**S3**, **10**). A reaction and purification similar to those above were run with 1*H*,1*H*,2*H*,2*H*-perfluorodecan-1-ol 6.13 g (8.47 mmol). Yield 72.6%. ^1H NMR (CDCl_3). δ 0.06 (12H, s, $\text{OSi}(\text{CH}_3)_2$), 0.34 (6H, s, $\text{PhSi}(\text{CH}_3)_2$), 2.44 (2H, tt, $J_1=7.40$ Hz, $J_2=18.6$ Hz, CH_2CF_2), 3.90 (2H, t, $J=7.40$ Hz, CH_2SiO), 5.20 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C-}$), 5.73 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C-}$), 6.73 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.40 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$). IR (NaCl) 2972 (CH), 1600 (C=C), 1258 (SiC), 1230 (CF), and 1033 cm^{-1} (SiO).

Synthesis of p-(1*H*,1*H*,2*H*,2*H*-perfluorodecyldimethylsilyl)styrene (**S1'**, **8**). (Scheme 2)

p-Vinylphenylmagnesium chloride (2.43

Scheme 2. Chemical structures of the silicon-containing styrenes synthesized.

mmol) in tetrahydrofuran (THF) was added dropwise to chloro(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)dimethylsilane prepared from 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decene and chlorodimethylsilane and purified by vacuum distillation ($78^\circ\text{C}/20\text{ mmHg}$) according to the reported method.¹¹ The solution was stirred for 12 h at room temperature and concentrated. The product was isolated by silica-gel column chromatography using hexane as eluent. Yield 18.4%. $R_f=0.63$, ^1H NMR (CCl_4). δ 0.33 (6H, s, $\text{PhSi}(\text{CH}_3)_2$), 1.06 (2H, t, SiCH_2), 1.86 (2H, tt, CH_2CF_2), 5.20 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C-}$), 5.70 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C-}$), 6.70 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.38 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$).

Synthesis of p-(hexyloxydimethylsilyl)styrene (**S1**, **Hx**) (Scheme 2)

Dry pyridine 0.55 g (6.88 mmol), ether (50 ml), and 1-hexanol 0.702 g (6.88 mmol) were added dropwise to *p*-(chlorodimethylsilyl)styrene 2.28 g (8.47 mmol), and the solution was stirred for 16 h at room temperature in nitrogen. After water was added to dissolve and remove the formed pyridine hydrochloride, the ether layer was dried over anhydrous sodium sulfate and concentrated. The product was purified by distillation. Yield 66.3%. bp 85.0°C (0.20 mmHg). ^1H NMR (CCl_4) δ 0.41 (6H, s, $\text{PhSi}(\text{CH}_3)_2$), 0.88 (3H, t, CH_3CH_2), 1.34 (8H, m, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 3.46 (2H, t, $J=6.0$ Hz, OCH_2), 5.26 (1H, dd, $J_1=2.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{C-}$), 5.77 (1H, dd, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\text{CH}=\text{C-}$), 6.74 (1H, dd, $J_1=11.0$ Hz, $J_2=11.0$ Hz, $\text{CH}=\text{CH}_2$), and 7.42 ppm (4H, 2d, $-\text{C}_6\text{H}_4-$). IR (NaCl, cm^{-1}): 2966 (CH), 1600 (C=C), 1256 (SiC), and 1068 cm^{-1} (SiO).

Synthesis of 1,3-bis(p-vinylphenyl)tetramethyldisiloxane(**S22**) (Scheme 2)

This crosslinking agent was prepared according to the reported method.¹²

Polymerization of *p*-(1*H*,1*H*,2*H*,2*H*-perfluoroalkoxyoligosiloxanyl)styrene (**Sn,m**) (Table I)

Poly(**Sn,m**)s were obtained by the conventional radical polymerization of **Sn,m** and reprecipitation in methanol. The results are summarized in Table I.

Laminated Membrane Preparation

A toluene solution of polydimethylsiloxane (PDMS) was cast on a poly(tetrafluoroethylene) sheet, and the solvent was evaporated for 24 h at room temperature. The membrane was dried *in vacuo* for 24 h to make it tough and the thickness of PDMS ($=L_p$) was measured. On this PDMS membrane a 1,3-bis(trifluoromethyl)benzene solution of poly(**Sn,m**) was cast and the solvent was evaporated for 24 h at room

temperature to yield a laminated membrane, which was then dried *in vacuo* for 24 h. The thickness of the laminated membrane ($=L_L$) was measured and that of poly(**Sn,m**) ($=L_s$) was calculated from $L_s = L_L - L_p$.

Estimation of Oxygen Permeability

Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2} ; cc(STP) cm cm⁻² s⁻¹ cmHg⁻¹) from upstream at atmospheric pressure to downstream *in vacuo* were measured by gas chromatography using YANACO GTR-10. Diffusion constants (D_{O_2} and D_{N_2} ; cm² s⁻¹) were determined by time-lag method using the same apparatus. Solubility coefficients (S_{O_2} and S_{N_2} ; cc(STP) cm⁻³ cmHg⁻¹) were calculated using $S = P/D$. In the case of a laminated membrane, P and D were estimated by a series model

Table I. Homopolymerization of **Sn,m**^a and characterization of poly(**Sn,m**)

No.	Mono- mer ^b	Solv ^c	Yield %	M_w^d × 10 ⁴	M_w/M_n^d	F% ^e wt%	Si% ^f wt%	T_g^g °C	T_m^g °C	ΔH_m^g kcal mol ⁻¹	Membrane ^h forming ability
1	S1, 4	THF	52.0	9.5	1.8	51.6	17.4	5.5	—	—	s
2	S1, 6	THF	58.0	2.0	1.7	60.9	14.1	22.4	—	—	b
3	S1, 8	BTB	42.0	5.0	1.1	67.1	11.9	91.4	27.9	1.1	b
4	S1, 10	BTB	24.0	4.7	2.5	71.7	10.2	171.5	80.8	2.5	b
5	S2, 4	THF	36.7	1.7	2.6	44.0	29.7	-51.1	—	—	s
6	S2, 6	THF	67.2	6.8	2.5	53.3	24.7	12.4	—	—	f
7	S2, 8	BTB	38.2	4.7	2.8	60.0	21.2	43.5	—	—	f
8	S2, 10	BTB	22.4	3.3	2.0	65.0	18.5	—	42.5	0.78	b
9	S3, 4	THF	31.0	1.2	2.1	38.3	38.8	—	—	—	s
10	S3, 6	THF	49.8	3.2	2.1	47.5	33.0	-50.1	—	—	s
11	S3, 8	BTB	26.9	1.6	2.0	54.3	28.8	9.3	—	—	f
12	S3, 10	BTB	18.5	5.2	3.4	59.5	25.5	39.3	—	—	f
13	S1, Hx	THF	41.0	7.9	1.8	0	23.0	—	—	—	b
14	S1', 8	BTB	35.7	0.71	1.2	68.9	0	—	25.4	30	b
15	S1	THF	71.7	3.0	3.4	0	41.5	136 ⁱ	—	—	b
16	S2	THF	67.2	5.8	1.9	0	58.8	36 ⁱ	—	—	f
17	S3	THF	—	—	—	0	68.0	-10 ⁱ	—	—	s

^a Polymerized by 0.20 mol% AIBN at 60°C.

^b For the code see Schemes 1 and 2.

^c THF=tetrahydrofuran; BTB=1,3-bis(trifluoromethyl)benzene.

^d Determined by GPC correlated to standard polystyrene.

^e The weight percent of (CF₂)_{m-1}CF₃ in the polymer.

^f The weight percent of (SiOMe₂)_{n-1} in the polymer.

^g Determined by DSC.

^h f=flexible, S=soft, and b=brittle.

ⁱ From ref 10.

equation.¹³

Measurements

For GPC measurements, a Hitachi 655A-11 Liquid Chromatograph was used. ¹H-NMR spectra were recorded on a JNM-PMX60 (60MHz) NMR spectrometer. Thermal analysis was made on a Shimadzu DSC-50. Elongations at a break were measured at a strain rate of 5 mm min⁻¹ by using a TOM-5 of Minebea Co.

RESULTS AND DISCUSSION

Synthesis and Polymerization of *p*-(1*H*,1*H*,2*H*,2*H*-perfluoroalkyloxyoligosiloxanyl)styrene (**S_n, m**)

12 types of *p*-substituted styrenes having a perfluoroalkyl chain and an oligodimethylsiloxanylene chain with different length were synthesized according to Scheme 1. **S1,4** and **S1,6** were colorless liquid and the others were white solids. In order to investigate the effects of a perfluoroalkyl group and Si-O bond, a perfluoroalkyl substituted styrene (**S1',8**) having no Si-O bond and an alkylsilyl substituted styrene (**S1,Hx**) having a hexyl chain instead of a 1*H*,1*H*,2*H*,2*H*-perfluorohexyl chain were synthesized for comparison with **S1,8** and **S1,4**, respectively (Scheme 2).

Comb-shaped polymers were synthesized from the homopolymerization of **S_n,ms**. The results of radical homopolymerization of **S_n,m** and characterization of poly(**S_n,m**) are listed in Table I. All poly(**S_n,m**)s were white solids and had *M_w* of about 10⁴. Since these polymers contain SiOC bonds, they can be cleaved by hydrolysis. However, no hydrolysis product was detected after the polymer was mixed with water for 24 h. Therefore, these polymers are stable enough to be used as oxygen separation membranes in air.

Thermal Analysis of Poly(**S_n,m**)

In all series, *i.e.*, poly(**S1,m**), poly(**S2,m**), and poly(**S3,m**) series, with increasing F% their *T_g*s increased. Since the *T_g*s are due to the

segmental motion of the polystyrene type backbone, the main chain mobility was suppressed by the bulkiness and aggregation of the perfluoroalkyl side chains. On the other hand, with increasing Si% their *T_g*s decreased owing to a plasticizing effect by the siloxanylene groups. In summary, the increasing orders of the *T_g*s were as follows:

$$\begin{aligned} \text{poly}(\mathbf{S_n}, 4) &< \text{poly}(\mathbf{S_n}, 6) < \text{poly}(\mathbf{S_n}, 8) \\ &< \text{poly}(\mathbf{S_n}, 10), \\ \text{poly}(\mathbf{S3}, \mathbf{m}) &< \text{poly}(\mathbf{S2}, \mathbf{m}) < \text{poly}(\mathbf{S1}, \mathbf{m}) \end{aligned}$$

Poly(**S1,8**) and poly(**S1,10**) in the poly(**S1,m**) series and poly(**S2,10**) in the poly(**S2,m**) series had a *T_m*, and in the poly(**S3,m**) series between *m*=4 to 10, the polymers did not have any *T_m*s, that is, poly(**S_n,m**)s with '*n*' less than 3 and '*m*' more than 6 had a *T_m* (Table I). Since only poly(**S_n,m**)s with long perfluoroalkyl chains had a *T_m* and perfluoroalkyl side chains were reported to be able to crystallize easily,¹⁴ these *T_m*s may be ascribed to the melting of crystalline part of their perfluoroalkyl side chains. The heat of melting (*ΔH_m*) of poly(**S1',8**) was much higher than that of poly(**S1,8**) (Table I, No. 3 and No. 14). This finding shows that the SiO bond in a poly(**S_n,m**) functions as a suppressor of the crystallization of the side chains.

Membrane Forming Ability of Poly(**S_n,m**)

Figure 1 shows the appearance of the poly(**S_n,m**) membranes prepared by solvent casting method. In the figure flexible (++), soft (-), and brittle (+) indicate membranes with more than 50%, 10–50%, and less than 10% in elongation at a break, respectively. The polymeric membranes with high oligodimethylsiloxane content (Si%) were soft (-), while those with high perfluoroalkyl content (F%) were brittle (+). Polymers containing balanced amounts of Si% and F%, that is, poly(**S2,6**) (No. 6 in Figure 1), poly(**S2,8**) (No. 7), poly(**S3,8**) (No. 11), and poly(**S3,10**) (No. 12), formed flexible membranes (++).

Estimation of Oxygen Permeability Coefficient Using Series Model Equation

Since most of the polymeric membranes obtained had strength not enough to resist an 1 atm pressure difference, oxygen permeability of the single membranes prepared from a pure poly(Sn, m) could not be measured directly. Therefore, the laminated membranes consisting of a cross-linked polydimethylsiloxane mem-

brane (PDMS) and poly(Sn, m) membrane were prepared and used for measurement of oxygen permeability. The permeability coefficient (P_s) of a poly(Sn, m) was calculated from that of PDMS (P_p) and that of the laminated membrane (P_L) using eq 1:

$$L_L/P_L = L_p/P_p + L_s/P_s, \quad L_L = L_p + L_s \quad (1)$$

where ' L ' designates a membrane thickness, ' P ' a permeability coefficient, suffix 'L' a laminated membrane, suffix 'p' a polydimethylsiloxane, suffix 's' a poly(Sn, m). P_s was an unknown value and the others were determined by experiment.

In order to confirm the reliability of P_{O_2} values calculated by the above method, an experimental P for copoly(S1, 4/S₂2) (For S₂2 see Scheme 2) membrane, which itself had strength enough to resist an 1 atm pressure difference, was compared with a calculated P value from a composite membrane consisting of a PDMS membrane and a copoly(S1, 4/S₂2) membrane (Table II). Good agreement between experimental and calculated values was observed in the range of 16.5–50.1% of a relative copoly(S1, 4/S₂2) membrane thickness. Therefore, in

Figure 1. Membrane forming ability of poly(Sn, m). The numbers in the figure correspond to those in Table I. (+ +), flexible; (+), brittle; (–), soft; F%, the weight % of $(CF_2)_{m-1}CF_3$ in poly(Sn, m); Si%, the weight % of $(SiOMe_2)_{n-1}$ in poly(Sn, m).

Table II. Estimation of oxygen permeability coefficient (P_{O_2}) and oxygen separation factor (α) using a laminated membrane^a

No.	Membrane thickness			Oxygen permeation of poly(S1, 4/S ₂ 2)	
	PDMS (L_p)	laminated membrane ($L_L = L_s + L_p$)	$100L_s^b$	$P_{O_2}^c$ (P_s)	α
	μm	μm	%		
1	0	—	100	2.09	2.48
2	207	415	50.1	2.13	2.47
3	350	558	37.3	2.10	2.46
4	740	948	21.9	1.98	2.46
5	1050	1258	16.5	1.92	2.46
6	1512	1720	12.1	1.26	2.30

^a For the codes see eq 1, and the text.

^b The thickness of poly(S1, 4/S₂2) membrane (L_s) was 208 μm .

^c In $\times 10^{-8}$ cc(STP) cm/cm² s⁻¹ cmHg⁻¹. The value for No. 1 was measured directly for pure poly(S1, 4/S₂2) membrane,¹² and the other values were calculated from that of a poly(S1, 4/S₂2)/PDMS laminated membrane ($= P_L$) and that of a PDMS membrane ($= P_p = 7.19 \times 10^{-8}$) using eq 1.

Figure 2. Oxygen permeation behavior of poly(**Sn,m**) membranes. The numbers in the figure correspond to those in Tables I and III. ●, poly(**Sn,m**); ○, Other silicon-containing polymers.

this study a composite membrane having a relative poly(**Sn,m**) thickness of 16.5–50.1% was used.

Oxygen Permeability (P_{O_2}) and Oxygen Permselectivity (α) of Poly(**Sn,m**)

P_{O_2} values for poly(**Sn,m**)s were plotted against α values (Figure 2). All poly(**Sn,m**)s showed good oxygen permselectivity. In particular, P_{O_2} and α for homopolymers of **S1,4** (No. 1 in Figure 2), **S1,6** (No. 2), **S2,6** (No. 6), **S2,8** (No. 7) and **S3,10** (No. 12) were $>4 \times 10^{-9}$ and >2.9 , respectively.

By substitution of CH_3 – in poly(*p*-trimethylsilylstyrene) (poly(**S1**), see Scheme 2) or poly(*p*-pentamethyldisiloxanylstyrene) (poly(**S2**), see Scheme 2) for $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{O}$ – or $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{O}$ –, P_{O_2} and α increased (No. 15 to No. 2 and No. 16 to No. 7). By substitution of $\text{CH}_3(\text{CH}_2)_5\text{O}$ – in poly(*p*-hexyloxydimethylsilylstyrene) (poly(**S1,Hx**)) for $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{O}$ –, both P_{O_2} and α also increased (No. 13 to No. 1). A simultaneous increase in P_{O_2} and α was also observed in case of the substitution of $-(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CF}_2$ – in poly(*p*-perfluorododecyldimethylsilylstyrene) (poly(**S1',8**)) for $-(\text{CH}_3)_2\text{SiOCH}_2\text{CH}_2\text{CF}_2$ – (No. 14 to No. 3). These facts indicate that perfluoroalkyl groups attached to the main chain via a SiOC bond in poly(**Sn,m**) are effective

for oxygen selective permeation.

As mentioned above, perfluoroalkoxysiloxanyl groups are good substituents for oxygen selective permeation. In order to investigate the reason for this, D_{O_2} was measured using the laminated equation similarly to the method for P_{O_2} and S_{O_2} was calculated from $S = P/D$. The results are shown in Table III. Increase in P_{O_2} and α was mainly due to increase in D_{O_2} and D_{O_2}/D_{N_2} , respectively. Therefore, the permeation is mainly ruled by the diffusion process.

Effects of the Length of Oligodimethylsiloxanylene Chain (n) and Perfluoroalkyl Chain (m) in Poly(**Sn,m**) on P_{O_2} and α

Figure 3 shows a plot of the P_{O_2} and α versus the perfluoroalkyl length (m) of each of poly(**S1,m**), poly(**S2,m**), and poly(**S3,m**) series. P_{O_2} decreased with increasing m . As shown in Table I, T_g increased with increase in m in poly(**Sn,m**). This T_g increase may be due to decrease in the main chain mobility caused by the aggregation of perfluoroalkyl side chains. The longer the perfluoroalkyl chain in poly(**Sn,m**), the higher the probability for aggregation of the chains may be. Therefore, longer perfluoroalkyl side chains of poly(**Sn,m**) led to a lower D_{O_2} and P_{O_2} .

α in Figure 3 shows a maximum value at a certain m value in each of the poly(**Sn,m**) series: $m=6$ in poly(**S1,m**), $m=8$ in poly(**S2,m**), and perhaps $m=10$ in poly(**S3,m**). These m values are consistent with the highest m of poly(**Sn,m**)s without T_m of the side chains in each of the three series as shown in Table I. This suggests that crystallinity of the side chains significantly affects α . When crystallization of the side chains begins at a certain m , denser and less dense regions come to be formed in the membranes. When perfluoroalkyl chains, which contribute to high α , partly from a crystalline region at a certain m , the region cannot participate in the oxygen permeation route resulting in decrease in α and P_{O_2} . This consideration is supported by the following

Table III. Oxygen permeability of the poly(Sn, m) membranes

No.	Polymer membrane ^a	P_{O_2} ^b	α	D_{O_2} ^c	D_{O_2}/D_{N_2}	S_{O_2} ^d	S_{O_2}/S_{N_2}
	mol%	$\times 10^{-9}$		$\times 10^{-8}$		$\times 10^{-3}$	
1	poly(S1, 4)	11.4	2.96	8.44	1.59	1.35	1.85
2	poly(S1, 6)	4.28	3.45	6.84	2.08	0.625	1.66
3-1	poly(S1, 8)	3.69	2.88	1.79	1.81	2.06	1.51
3-2 ^e	poly(S1, 8)	4.58	3.27	6.33	2.02	0.724	1.62
4	poly(S1, 10)	2.86	3.02	1.20	1.03	2.38	2.92
5	poly(S2, 4)	15.7	2.28	13.1	1.44	1.20	1.58
6	poly(S2, 6)	7.88	3.10	10.4	2.02	0.758	1.53
7	poly(S2, 8)	6.05	3.29	12.9	2.89	0.469	1.14
8	poly(S2, 10)	5.80	2.82	3.72	1.75	1.56	1.61
9	poly(S3, 4)	16.9	2.18	15.6	1.32	1.08	1.65
10	poly(S3, 6)	9.61	2.74	13.6	1.89	0.706	1.45
11	poly(S3, 8)	10.8	2.82	12.5	2.50	0.864	1.12
12	poly(S3, 10)	8.05	3.17	10.4	2.94	0.774	1.15
13	poly(S1, Hx)	9.66	2.29	2.78	1.31	3.47	1.76
14	poly(S1', 8)	2.55	2.48	0.430	2.11	5.90	1.18
15 ^f	poly (S1)	1.40	3.20	—	—	—	—
16 ^f	poly (S2)	4.00	3.00	1.80	1.64	2.20	1.69

^a For the codes see Schemes 1 and 2.^b In cc(STP) cm cm⁻² s⁻¹ cmHg⁻¹. Measured at 25°C.^c In cm² s⁻¹.^d In cc(STP) cm⁻³ cmHg⁻¹.^e Measured at 40°C which is higher than the T_m (=27.9°C) of poly (S1, 8).^f From ref. 10. **Figure 3.** Effects of the length of perfluoroalkyl chain (m) in poly(Sn, m) on oxygen permeation behavior. ' m ', (CF₂) _{$m-1$} CF₃ in poly(Sn, m); ○, ●, poly(S1, m); △, ▲, poly(S2, m); □, ■, poly(S3, m). **Figure 4.** Effects of the length of oligosiloxanylene chain (n) in poly(Sn, m) on oxygen permeation behavior. ' n ', (SiOMe₂) _{$n-1$} in poly(Sn, m); ○, ●, poly(Sn, 4); △, ▲, poly(Sn, 6); □, ■, poly(Sn, 8); ◇, ◆, poly(Sn, 10).

Figure 5. Imaginative schematic drawings of oxygen permeation mechanism through poly(Sn,m) membranes.

experimental fact: P_{O_2} and α of poly(S1,8) at 25°C, which is lower than its T_m (27.9°C), were lower than those at 40°C (Table III, No. 3-1 and No. 3-2). A maximum value of $D_{\text{O}_2}/D_{\text{N}_2}$ was also observed at the same m as that in the case of α vs. m in each of poly(Sn,m) series (Table III).

Figure 4 is a plot of P_{O_2} and α versus the oligosiloxanylene length (n) of poly(Sn,4), poly(Sn,6), poly(Sn,8) and poly(Sn,10). P_{O_2} increased with n . In poly(Sn,4) series whose perfluoroalkyl chains cannot crystallize, α decreased with increase in n , while in poly(Sn,8) series whose perfluoroalkyl chains can crystallize, α has a maximum value at $n=2$. In poly(Sn,6), and poly(Sn,10) series, it is very likely for α to have a maximum value at $n=1$ and 3, respectively.

From the above discussion, a schematic drawing (Figure 5) for oxygen selective permeation mechanism through a poly(Sn,m) membrane is proposed. When the siloxane length is long and perfluoroalkane length is short as shown in Figure 5(A), the oxygen permeation occurs mainly in the siloxane region of this membrane, the nature of which is similar to that of polydimethylsiloxane.

Therefore, P_{O_2} is high but α is low which are similar to those of polydimethylsiloxane. Examples are poly(S2,4) and poly(S3,4) (No. 5 and No. 9 in Figure 2). When the siloxane length is short and perfluoroalkane length is long as shown in Figure 5(C), perfluoroalkyl chains can crystallize. Since oxygen molecules cannot permeate a crystalline region, permeation occurs only in the amorphous region whose fraction is small and therefore P_{O_2} is very low. Poly(S1,8) and poly(S1,10) represent the above case (No. 3 and No. 4 in Figure 2). Finally, Figure 5(B) shows the best structure. In this case, since the balance of the siloxane length and perfluoroalkane length are good, both advantages are available for the permeation. Therefore, good performance of the oxygen permselective membrane was attained. This corresponds to poly(S1,6), poly(S2,8), and poly(S3,10).

Oxygen Permeability (P_{O_2}) and Oxygen Permselectivity (α) of Poly(Sn,m)/PDMS Laminated Membranes

Figure 6 shows the oxygen permeation behavior of the laminated membranes. These membranes were highly oxygen permselective.

Figure 6. Oxygen permeation behavior of poly(Sn, m)/PDMS laminated membrane. The numbers in the figure correspond to those in Tables I and III. ●, poly(Sn, m)/PDMS laminated membrane; ○, other silicon-containing polymers/PDMS laminated membrane.

In particular, laminated membranes consisting of cross-linked polydimethylsiloxane and poly- $[p-(1H,1H,2H,2H\text{-perfluorohexyloxydimethylsilyl})\text{styrene}]$ (No. 1) or poly $[p-\{3-(1H,1H,2H,2H\text{-perfluorodecyloxy})\text{tetramethyldisiloxanyl}\}\text{styrene}]$ (No. 7) showed the best result in all the laminated membranes ($P_{O_2} = 3.09 \times 10^{-8} \text{ cc(STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$, $\alpha = 2.69$ and $P_{O_2} = 2.41 \times 10^{-8} \text{ cc(STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$, $\alpha = 2.96$, respectively).

CONCLUSIONS

1. Homopolymerization of $p-(1H,1H,2H,2H\text{-perfluoroalkyloligosiloxanyl})\text{styrenes}$ (Sn, m) with different length of the perfluoroalkyl chain and oligosiloxanylene chain gave soluble comb-shaped polymers (poly(Sn, m)) which contain 38.3–71.7 wt% perfluoroalkyl unit and 10.2–38.8 wt% oligosiloxane unit.
2. Poly(Sn, m) membranes of a high perfluoroalkyl content were brittle, while those of a high oligosiloxane content were soft.
3. Poly(Sn, m) membranes showed relatively high α along with high P_{O_2} value.
4. Simultaneous introduction of oligosilox-

anylene and perfluoroalkyl chain to the side chain of polystyrene was effective for enhancing α without a drop in P_{O_2} .

5. P_{O_2} for poly(Sn, m)s increased with the length of oligosiloxanylene and decreased with increasing length of the perfluoroalkyl chain.

6. α for poly(Sn, m)s had a maximum value at a certain length of the perfluoroalkyl chain. This behavior was related to the mobility and aggregation state of the perfluoroalkyl chains.

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