Polymers with Oligoorganosiloxane Side Chains as Material for Oxygen Permeable Membranes

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ABSTRACT: Styrene and methacrylate type monomers having oligoorganosiloxane substituents were synthesized, and the properties of the polymers therefrom as material for oxygen permeable membranes were evaluated by gas chromatographic method. Homopolymers with short siloxane chains were found to be better than those with long branches in selectivity in permeation and mechanical strength. Introduction of fluorine atoms into polymer structure did not improve the selectivity in permeation.

KEY WORDS Oligosiloxane / Ultrasonic Irradiation / Macromer / Fluoro Siloxane / Ring-Opening Polymerization / Vinyl Polymerization / Comb Polymer / Graft Copolymer / Oxygen Permeation / Permselective Membrane /

Recently, much attention has been paid to the selective gas permeable membranes. As material for oxygen permselective membrane, at least three basic requirements must be satisfied: 1) high permeability coefficient (P_{O_2}) 2) high selectivity $[\alpha = (p_{O_2,2}/p_{N_2,2})/(p_{O_2,1}/p_{N_2,1}) \simeq P_{O_2}/P_{N_2}]$, and 3) self-supporting property. We have reported poly(p-disiloxane substituted styrene)s as good self-supporting material for oxygen permeable membranes of considerably high separation factor [$\alpha = 2.8$ for poly(p-pentamethyldisiloxanylstyrene)].[1] We have been also interested in polydimethylsiloxane (PDMS) graft copolymers as surface modifying material of hydrophilic polymers.[2-5] Such polymers might be also of interest as oxygen permeable membrane material, because PDMS has high P_{O_2} although the selectivity in permeation and mechanical strength are low. The disadvantage about the mechanical strength has been overcome by putting the PDMS chain into block[6] or crosslinked[7] copolymers; however, the selectivity α remained still low. Since the reason for the low selectivity was suspected to be because of the inherent nature of the rather long PDMS chains in these copolymers, experiments were carried out to study the effects of the length of oligoorganosiloxane side chains on back bone polymers on the film forming property, and permeability and selectivity in oxygen permeation.

Up till now, many perfluorinated compounds have been known to show high solubility of oxygen, and some of them are used as artificial blood substitutes.[8] In designing oxygen permeable membranes, the modification of polymer structure by fluorine atoms seems quite interesting.

In this article, the syntheses of oligoorganosiloxanes having various vinyl-polymerizable groups (including macromers) and the properties of the polymers therefrom as material for oxygen permselective membranes are reported.

EXPERIMENTAL

The monomers were synthesized basically by reacting lithium silanolates with vinyl-polymerizable chlorosilane compounds. Lithium trimethylsilanolate (LTMS), lithium 3,3,3-trifluoropropyldimethylsilanolate (LFMS), p-dimethylchlorosilylstyrene (SSiCl), p-(3,3,3-trifluoropropyl)methylchlorosilyl styrene (FSiCl), 5-dimethylchlorosilylpentyl methacrylate (MSiCl) were synthesized according to reported methods.[1,2] Analyses of some new disiloxane monomers were reported.[1] The synthetic routes to styrenyl, methacrylyl, fluoro substituted styrenyl, and p-vinylbenzyl monomers are shown in Schemes 1—4.

Other monomers used in this study are 3-[3'-bis(trimethylsiloxy)methylsilylpropoxy]-2-hydroxypropyl methacrylate (MS3) and 2-perfluoroalkylethyl acrylate (FA) having the structure $CH_2=CHCO_2CH_2CH_2(CF_2)_n$-$CF_3(n=8.6)$. The chemical shifts are given as δ value in ppm unit using TMS as an internal standard. Vinyl and aromatic protons of S3, S4, S5, S8, and p-(5-chlorohexamethyltrisiloxanyl)styrene appeared at identical positions with those of S1. The signals of methacrylyl protons and methylene protons not linking directly to silicon atom of M5 and M8 were observed at identical positions with those of M2. Benzyl methylene, vinyl, and aromatic protons of B2, B3, B4, B5 were found at identical positions with those of B1.

Polymerizations were carried out typically in tetrahydrofuran (THF) using α,α'-azobisisobutyronitrile (AIBN) as an initiator. The polymers were purified by reprecipitation from THF into methanol. The molecular weights and molecular weight distribution were determined on GPC correlating to standard polystyrene. When necessary, some modifications were made for the solvent systems.

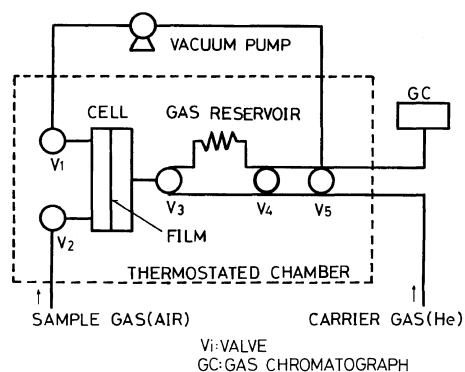T_gs were measured on a Perkin-Elmer model DSC-2 differential scanning calorimeter.

Figure 1. The schematic diagram of gas permeation rate apparatus.

Polymer films were prepared by casting the polymer solution in THF (5%) on clean glass surface and evaporating the solvent under controlled conditions; the solvent was usually evaporated at 20°C during 48 h. The formed films were detached from the glass surface by immersing in water, and dried between filter papers under vacuum for 48 h. The polymer films, whose T_g is higher than 50°C, were annealed at 50°C for 24 h. The thickness of the films was about 80 μm. The permeability and selectivity in permeation were evaluated for supplied air by gas chromatographic method at 25°C. The flow diagram is shown in Figure 1.
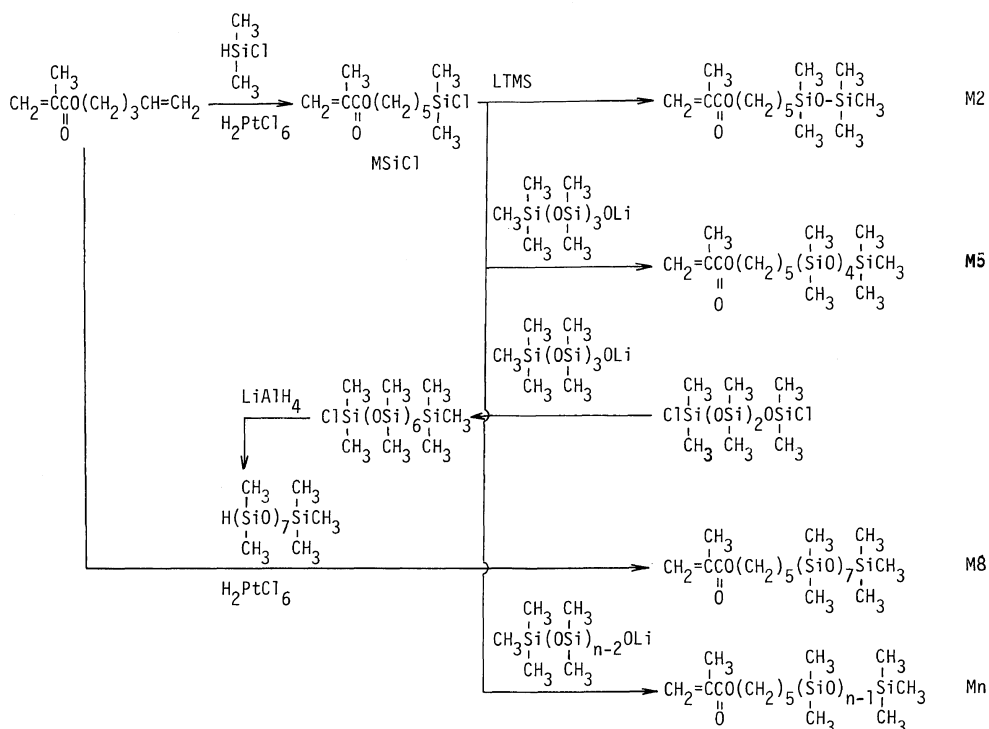
p-Trimethylsilylstyrene (S1)

To p-vinylphenylmagnesium chloride prepared from Mg (13.6 g, 148 mmol) and p-chlorostyrene (10.5 g, 75 mmol) in THF (85 ml), a slight excess of trimethylchlorosilane was added dropwise at 0°C. The usual work-up, distillation, and purification by silica gel column chromatography gave the product in 81% yield. bp 55—57°C (0.2 mmHg). ^{1}H NMR (CCl$_4$) $\delta = 0.23$ (s, 9H, SiCH$_3$), 5.16 (q, 1H, $J_1 = 1.6$ Hz, $J_2 = 10.8$ Hz, C=C), 5.65 (q, H 1H, $J_1 = 1.6$ Hz, $J_2 = 18.0$ Hz, C=C), 6.63 (q, H
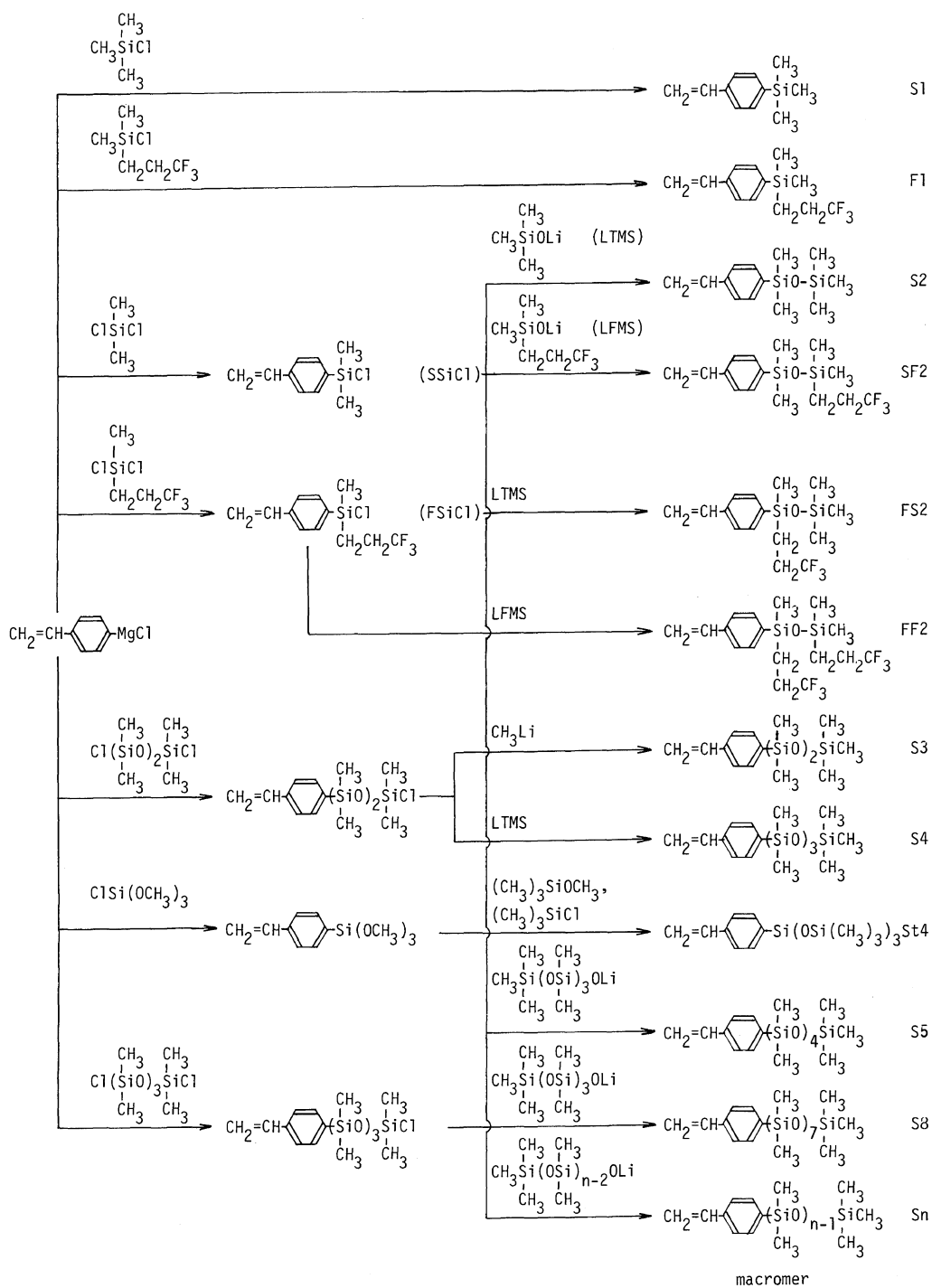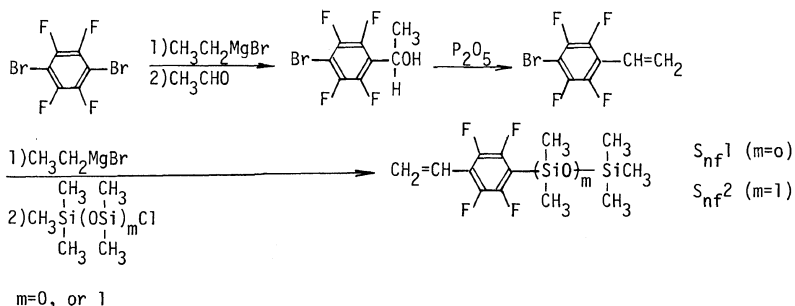
Scheme 1. Synthetic routes to styrene type oligosiloxane monomers.

Scheme 2. Synthetic routes to methacrylate type oligosiloxane monomers.

Scheme 3. Synthetic route to fluoro-substituted styrene type oligosiloxane monomers.

1H, $J_1 = 10.8$ Hz, $J_2 = 18.0$ Hz, C=C̲H̲), 7.23 (d,

2H, $J = 8.5$ Hz, ⬡—Si), and 7.40 ppm (d, 2H,

$J = 8.5$ Hz, ⬡—Si).
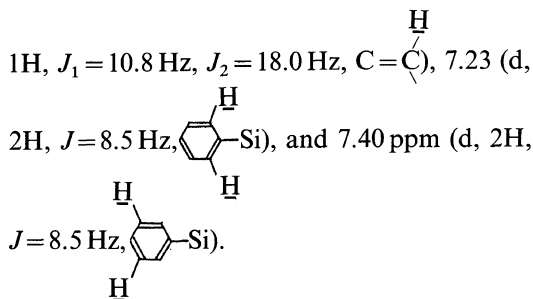
p-(3,3,3-Trifluoropropyl)dimethylsilylstyrene (F1)

p-Vinylphenylmagnesium chloride was similarly reacted with 3,3,3-trifluoropropyldimethylchlorosilane. 70% yield. ^{1}H NMR (CCl$_4$) $\delta = 0.32$ (s, 6H, SiCH̲$_3$), 0.77—1.17 (m, 2H, SiCH̲$_2$), 1.30—2.38 (m, 2H, CH̲$_2$CF$_3$), 5.21 (q, 1H, $J_1 = 10.6$ Hz, $J_2 = 1.5$ Hz, C=C),

CH₃SiCl (with CH₃ groups) → CH₂=CH—⟨benzene⟩—CH₂SiCH₃(CH₃)₂ **B1**

ClSiCl (with CH₃ groups) → CH₂=CH—⟨benzene⟩—CH₂SiCl(CH₃)₂ → (LTMS) → CH₂=CH—⟨benzene⟩—CH₂SiO-SiCH₃ **B2**

CH₂=CH—⟨benzene⟩—CH₂MgCl

Cl(SiO)₂SiCl (with CH₃ groups) → CH₂=CH—⟨benzene⟩—CH₂(SiO)₂SiCl → (CH₃Li) → CH₂=CH—⟨benzene⟩—CH₂(SiO)₂SiCH₃ **B3**

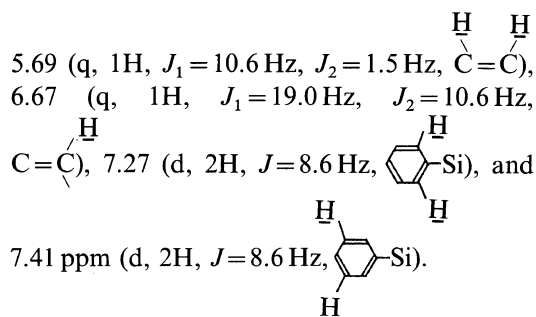(LTMS) → CH₂=CH—⟨benzene⟩—CH₂(SiO)₃SiCH₃ **B4**

CH₃(SiO)₄Li → CH₂=CH—⟨benzene⟩—CH₂(SiO)₄SiCH₃ **B5**
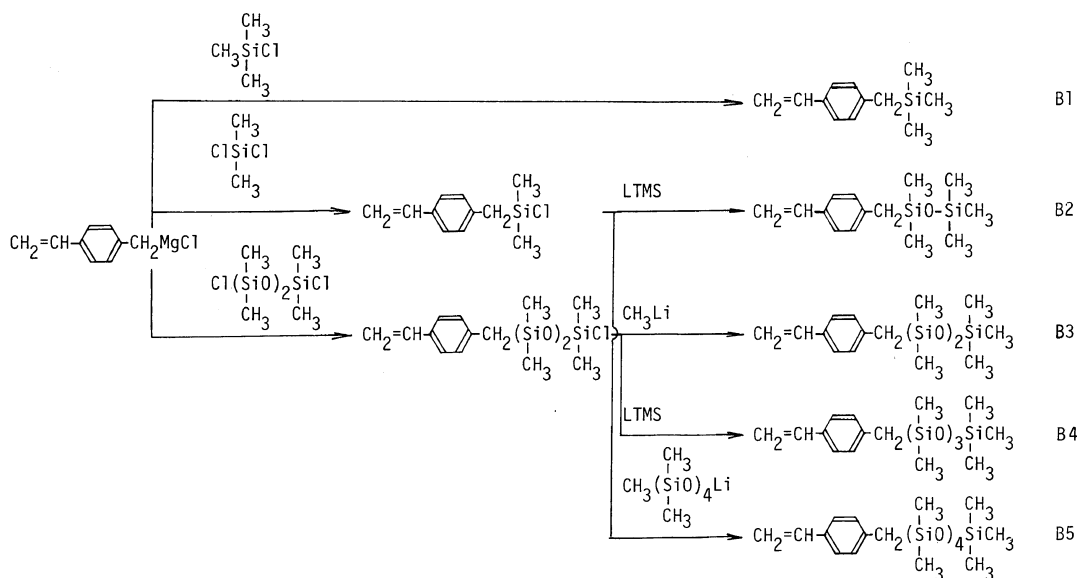
Scheme 4. Synthetic routes to p-vinylbenzyl type oligosiloxane monomers.

5.69 (q, 1H, $J_1 = 10.6\,\text{Hz}$, $J_2 = 1.5\,\text{Hz}$, $\overset{H}{\underset{}{C}} = \overset{H}{\underset{}{C}}$), 6.67 (q, 1H, $J_1 = 19.0\,\text{Hz}$, $J_2 = 10.6\,\text{Hz}$, $\overset{H}{\underset{}{C}} = \overset{}{\underset{}{C}}$), 7.27 (d, 2H, $J = 8.6\,\text{Hz}$, ⟨benzene⟩–Si), and 7.41 ppm (d, 2H, $J = 8.6\,\text{Hz}$, ⟨benzene⟩–Si).

p-(5-Chlorohexamethyltrisiloxanyl)styrene

p-Vinylphenylmagnesium chloride was added dropwise to 70% excess 1,5-dichlorohexamethyltrisiloxane[9] (35.5 g, 128 mmol) at 60°C during 1.5 h. After removing the formed salt, the product was isolated by distillation in 42% yield. bp 105°C (0.20 mmHg). ¹H NMR (CCl₄) $\delta = 0.15$ (s, 6H, OSi(CH₃)₂), 0.34 (s, 6H, ⟨benzene⟩–Si(CH₃)₂), and 0.50 ppm (s, 6H, ClSi(CH₃)₂).

p-Heptamethyltrisiloxan-1-ylstyrene (S3)

p-(5-Chlorohexamethyltrisiloxanyl)styrene (20 g, 58 mmol) was methylated with slight excess methyllithium or methylmagnesium

bromide in ethyl ether (150 ml) at -78—0°C. 95% yield. The product was purified by column chromatography. ¹H NMR(CCl₄) $\delta = 0.07$ (s, 9H, Si(CH₃)₃), 0.09 (s, 6H, OSi(CH₃)₂), 0.33 ppm (s, 6H, ⟨benzene⟩–Si (CH₃)₂).
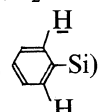
p-Nonamethyltetrasiloxan-1-ylstyrene (S4)

p-(5-Chlorohexamethyltrisiloxanyl)styrene (20 g, 58 mmol) was reacted with a slight excess of LTMS. Usual work-up and column chromatography afforded the product in 85% yield. ¹H NMR(CCl₄) $\delta = 0.08$ (s, 21H, OSiCH₃) and 0.33 ppm (s, 6H, ⟨benzene⟩–Si(CH₃)₂). S4 could be synthesized alternatively by methylation of p-(7-chlorooctamethyltetrasiloxanyl)styrene by methyllithium or methylmagnesium bromide.
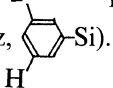
p-Trimethoxysilylstyrene

Trimethoxychlorosilane (8.5 g, 54 mmol) was added dropwise at 50°C during 20 min to p-vinylphenylmagnesium chloride (36 mmol) in THF (40 ml). The reaction mixture was warmed to 60—65°C, and reacted for 3 h. After evaporating the solvent, dry ethyl ether (90 ml) was added, and the formed salt was

removed by filtration under N_2. Distillation gave the product in 36% yield. bp 61°C (0.15 mm Hg). ^{1}H NMR(CCl$_4$) $\delta = 3.40$ (s, 9H, C$\underline{H}_3$), 5.05 (q, 1H, $J_1 = 10.8$ Hz, $J_2 = 1.5$ Hz,

$\overset{/}{\underset{\underset{\underline{H}}{\overset{\underline{H}}{|}}}{C}}=C$), 5.60 (q, 1H, $J_1 = 17.2$ Hz, $J_2 = 1.5$ Hz,

$\overset{\underline{H}}{\underset{\overset{/}{C}}{\overset{\backslash}{C}}}=C$), 6.50 (q, 1H, $J_1 = 10.8$ Hz, $J_2 = 17.2$ Hz,

$C = \overset{/}{\underset{\underline{H}}{C}}$ 7.08 (d, 2H, $J = 7.8$ Hz, ⟨⟩–Si), and

7.40 ppm (d, 2H, $J = 7.8$ Hz, ⟨⟩–Si).
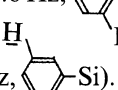
p-[Tris(trimethylsiloxy)silyl]styrene (St4)

The mixture of *p*-trimethoxysilylstyrene (0.9 g, 4 mmol), trimethylchlorosilane (1.3 g, 12 mmol), and trimethylmethoxysilane (1.3 g, 12 mmol) was added dropwise to water (4.4 ml) and diethyl ether (4.2 ml) mixture at 15°C during 1 h, and reacted over night. The product was extracted with ether, and purified by column chromatography. 25% yield. The compound tended to adsorb on silica gel. ^{1}H NMR(CCl$_4$) $\delta = 0.20$ (s, 27H, SiC$\underline{H}_3$), 5.25 (q,

1H, $J_1 = 10.8$ Hz, $J_2 = 1.5$ Hz, $\overset{/}{\underset{\underline{H}}{C}}=C$), 5.73 (q,

1H, $J_1 = 17.2$ Hz, $J_2 = 1.5$ Hz, $\overset{/}{\underset{\underline{H}}{C}}=\overset{\underline{H}}{\underset{}{C}}$), 6.72 (q,

1H, $J_1 = 10.8$ Hz, $J_2 = 17.2$ Hz, $C = \overset{/}{\underset{\underline{H}}{C}}$), 7.33 (d,

2H, $J = 7.8$ Hz, ⟨⟩–Si), and 7.51 ppm (d, 2H,

$J = 7.8$ Hz, ⟨⟩–Si).

p-Undecamethylpentasiloxan-1-ylstyrene (S5)

To LTMS (3.17 g, 32 mmol) in THF (80 ml), hexamethylcyclotrisiloxane (D$_3$) (6.68 g, 33 mmol) in THF (40 ml) was added at −78°C. After the addition, the reaction system

was warmed up to 0°C, and reacted for further 16 h. To this reaction mixture, SSiCl^2 (5.90 g, 30 mmol) in THF (20 ml) was added and reacted for 12 h. The usual work-up and column chromatography gave the product in 92% yield. ^{1}H NMR(CCl$_4$) $\delta = 0.07$ (s, 9H, Si(C$\underline{H}_3$)$_3$), 0.09 (s, 18H, OSi(C$\underline{H}_3$)$_2$), and 0.33 ppm (s, 6H, ⟨⟩–Si(C$\underline{H}_3$)$_2$).

p-(7-Chlorooctamethyltetrasiloxanyl)styrene

similarly to the synthesis of *p*-(5-chlorohexamethyltrisiloxanyl)styrene. The product was obtained in 39% yield. bp 111°C (0.15 mmHg). ^{1}H NMR $\delta = $(CDCl$_3$) 0.12 (s, 12H, OSi(C $\underline{H}_3$)$_2$), 0.33 (s, 6H, ⟨⟩–Si(C $\underline{H}_3$)$_2$), and 0.50 ppm (s, 6H, ClSi(C $\underline{H}_3$)$_2$).

p-Heptadecamethyloctasiloxan-1-ylstyrene (S8)

This monomer was synthesized similarly to S5 using *p*-(7-chlorooctamethyltetrasiloxanyl)styrene in place of SSiCl. 95% yield. ^{1}H NMR(CDCl$_3$) $\delta = 0.06$ (s, 9H, Si(C$\underline{H}_3$)$_3$), 0.09 (s, 36H, OSi(C$\underline{H}_3$)$_2$), and 0.33 ppm (s, 6H, ⟨⟩–Si(C$\underline{H}_3$)$_2$).

p-Polydimethylsiloxan-1-yl-styrene (Sn) (macromer)

To the polymerization product of D$_3$ (15.58 g, 70 mmol) initiated by LTMS (0.385 g, 4 mmol) at −78°C in THF and reacted for 24 h at 0°C, THF (20 ml) solution of SSiCl (1.18 g, 6 mmol) was added dropwise at the temperature. After the usual work-up and purification by column chromatography, the macromer Sn was obtained in 85% yield. $M_n = 7.1 \times 10^3$ ($\overline{DP} = 94$), $M_w = 7.5 \times 10^3$, $M_w/M_n = 1.06$. This macromer is abbreviated as S94.

Comments will be made on the order of the introduction of double bond and oligosiloxane side chain in results and discussion section.

5-Pentamethyldisiloxanylpentyl methacrylate (M2)

LTMS (0.24 g, 2.5 mmol) was reacted· with

MSiCl[2] (0.63 g, 2.5 mmol) at room temperature in THF (5 ml). The usual work-up and purification by column chromatography gave the product in 91% yield. ^{1}H NMR(CCl$_4$) $\delta = 0.14$ (s, 15H, SiCH$_3$), 0.33—0.82 (broad, 2H, CH$_2$Si), 1.00—1.83 (m, 6H, (CH$_2$)$_3$), 1.92 (s, 3H, CH$_3$), 4.03 (t, 2H, $J=6.1$ Hz, OCH$_2$), 5.60 (m, 1H, CH=), and 6.08 ppm (m, 1H, CH=).

5-(Undecamethylpentasiloxan-1-yl)pentyl methacrylate (M5)

This monomer was synthesized similarly to S5 using MSiCl as the terminating agent in place of SSiCl. The usual work-up and purification gave the product in 85% yield. ^{1}H NMR(CCl$_4$) $\delta = 0.15, 0.17, 0.19$ (three s, 33H, SiCH$_3$), and 0.33—0.73 ppm (m, 2H, SiCH$_2$).

1-Hydroheptadecamethyloctasiloxane

To lithium nonamethyltetrasiloxanolate prepared from LTMS (0.96 g, 10 mmol) and D$_3$ (2.23 g, 10 mmol) in THF (35 ml) at $-78°$C, was added dropwise 1,7-dichlorooctamethyltetrasiloxane (5.22 ml, 15 mmol) in THF (20 ml) at room temperature during 1 h. After the reaction mixture was cooled down to dry-ice temperature, lithium aluminum hydride (0.88 g, 22 mmol) in THF (20 ml) was added dropwise during 1 h. The reaction mixture was allowed to warm up gradually to room temperature. After evaporating the solvent, n-hexane was added, and the formed salt was removed by centrifugation. Distillation after removal of n-hexane gave the product in 38% yield. bp 99°C (0.12 mmHg). ^{1}H NMR (CDCl$_3$) $\delta = 0.07$ (s, 45H, OSiCH$_3$), 0.10 (s, 6H, HSi(CH$_3$)$_2$), and 4.67 ppm (hept, 1H, SiH).

5-(Heptadecamethyloctasiloxan-1-yl)pentyl methacrylate (M8)

To chloroplatinic acid (H$_2$PtCl$_6$·6H$_2$O, 0.05 g) dissolved in 2-propanol (0.3 ml), 4-pentenyl methacrylate (1.85 g, 12 mmol) was added, and the mixture was warmed to 60°C.

Small amounts of 1-hydroheptadecamethyloctasiloxane were added to the mixture, and the reaction system was warmed to 100°C. Immediately after the activation of chloroplatinic acid occurred, which could be judged by the change in its color from brown to black, the system was cooled down again to 60°C, and the rest of 1-hydroheptadecamethyloctasiloxane (62 g, 10.4 mmol) was added dropwise at the temperature, and reacted for 6 h. After removal of 2-propanol by evacuation, the product was isolated by chromatography. 76% yield. ^{1}H NMR(CCl$_4$) $\delta = 0.10$ (s, 51H, SiCH$_3$), and 0.33—0.67 ppm (m, 2H, SiCH$_2$).

5-(Polydimethylsiloxan-1-yl)pentyl methacrylate (Mn)

Methacrylate macromer Mn was synthesized similarly to Sn using MSiCl as the terminating agent in the polymerization of D$_3$. Terminating reactions were carried out under ultrasonic irradiation.

Pentafluorostyrene (S$_{nf}$)

Bromopentafluorobenzene (4.20 g, 17 mmol) was added dropwise to THF (16 ml) solution of ethylmagnesium bromide (30 mmol) at 0°C, and reacted for 1 h at room temperature. After removal of THF, the reaction system was diluted with ether (56 ml), and reacted with acetaldehyde (2.5 ml, 45 mmol) in ethyl ether (17 ml) at 15°C for 16 h. After decomposing the reaction mixture with 1 N HCl (30 ml), the product was extracted with ethyl ether and the crude product, after evaporating the solvent, was dehydrated with phosphorus pentoxide (1.90 g) in the presence of hydroquinone (0.14 g) at 160°C to give the product. bp 72.0°C (87.5 mmHg). 71.1% yield. ^{1}H NMR was identical with the authentic sample.

4-Bromo-2,3,5,6-tetrafluorostyrene

To THF (130 ml) solution of 1,4-dibromotetrafluorobenzene (13.3 g, 43 mmol), ethylmagnesium bromide (48 mmol) in THF (25 ml)

was added dropwise at room temperature, and reacted for 1 h at the temperature. After removal of THF, the reaction system was diluted with ethyl ether (150 ml), are reacted with acetaldehyde (9.54 g, 275 mmol) in ethyl ether (30 ml) at 16°C for 16 h. A similar procedure with the synthesis of S_{nf} gave the product in 51% yield. bp 49.2°C (2.1 mmHg). ^{1}H NMR(CCl$_4$) $\delta = 5.78$ (q, 1H, $J_1 = 1.0$ Hz,

$J_2 = 11.0$ Hz, $\underset{H}{C} = \overset{/}{C}$), 6.12 (q, 1H, $J_1 = 1.0$ Hz,

$J_2 = 18.0$ Hz, $\overset{H}{C} = \overset{/}{C}$), and 6.73 ppm (q, 1H,

$J_1 = 11.0$ Hz, $J_2 = 18.0$ Hz, $C = \underset{H}{C}$).

4-Trimethylsilyl-2,3,5,6-tetrafluorostyrene ($S_{nf}1$)

To THF (64 ml) solution of ethylmagnesium bromide (12 mmol), 4-bromo-2,3,5,6-tetrafluorostyrene (2.79 g, 11 mmol) was added dropwise at 0°C, and reacted for 10 min at room temperature. The reaction was quenched with trimethylchlorosilane (3.4 ml, 27 mmol). After the usual work-up, distillation gave the product in 51% yield. bp 64.5°C (0.5 mmHg). ^{1}H NMR(CCl$_4$) $\delta = 0.49$ (s, 9H, SiCH$_3$), 5.77

(q, 1H, $J_1 = 2.0$ Hz, $J_2 = 11.0$ Hz, $\underset{H}{C} = \overset{/}{C}$), 6.17

(q, 1H, $J_1 = 2.0$ Hz, $J_2 = 17.8$ Hz, $\underset{H}{C} = C$), and

6.82 ppm (q, 1H, $J_1 = 11.0$ Hz, $J_2 = 17.8$ Hz,

$C = \underset{H}{\overset{/}{C}}$).

4-Pentamethyldisiloxanyl-2,3,5,6-tetrafluorostyrene($S_{nf}2$)

4-Vinyltetrafluorophenylmagnesium bromide, synthesized from 4-bromo-2,3,5,6-tetrafluorostyrene (2.49 g, 9.8 mmol) similarly in the synthesis of $S_{nf}1$, was reacted with pentamethylchlorodisiloxane (2.05 g, 11 mmol) at room temperature for 2 h. The usual work-

up and column chromatography gave the product in 72% yield. ^{1}H NMR(CCl$_4$) $\delta = 0.16$ (s, 9H, Si(CH$_3$)$_3$), and 0.51 ppm (t, 6H, $J_{FCSiCH} = 1.5$ Hz, OSi(CH$_3$)$_2$). Vinyl protons appeared at identical positions with $S_{nf}1$.

p-Trimethylsilylmethylstyrene (B1)

p-Vinylbenzyl-magnesium chloride, synthesized from activated magnesium (10.2 g, 240 mmol) by ethylene dibromide (1.0 ml) and p-chloromethylstyrene (7.0 g, 46 mmol) in ether (180 ml) at room temperature, was reacted with trimethylchlorosilane (12.3 ml, 97 mmol) under gentle reflux of the solvent. The reaction system was destroyed with aq. NH$_4$Cl, and the organic layer was collected. Column chromatography gave the product in 76% yield. ^{1}H NMR(CCl$_4$) $\delta = 0.14$ (s, 9H, SiCH$_3$), 2.16 (s, 2H, CH$_2$), 5.17 (q, 1H, $J_1 = 2.0$ Hz,

$J_2 = 11.0$ Hz, $\underset{H}{C} = \overset{/}{C}$), 5.67 (q, 1H, $J_1 = 2.0$ Hz,

$J_2 = 18.0$ Hz, $\underset{H}{C} = C$), 6.70 (q, 1H, $J_1 = 11.0$ Hz,

$J_2 = 18.0$ Hz, $\underset{H}{C} = \overset{H}{\overset{/}{C}}$), 6.99 (d, 2H, $J = 8.0$ Hz,

$\underset{H}{\overset{H}{\bigcirc}}$—CH$_2$), and 7.28 ppm (d, 2H, $J = 8.0$ Hz,

$\underset{H}{\overset{H}{\bigcirc}}$—CH$_2$).

p-Pentamethyldisiloxanylmethylstyrene (B2)

p-Vinylbenzylmagnesium chloride (240 mmol) was added dropwise to dimethyldichlorosilane (30 ml, 247 mmol) in THF (200 ml) during 4 h at room temperature to 40°C. After removal of excess dimethyldichlorosilane, the reaction product was again dissolved in THF (100 ml) and reacted with LTMS (240 mmol). The usual work-up and column chromatography gave the product in 70% yield. ^{1}H NMR $\delta = 0.13$ (s, 15H, SiCH$_3$), and 2.17 ppm (s, 2H, CH$_2$).

p-Heptamethyltrisiloxan-1-ylmethylstyrene (*B3*)

1,5-Dichlorohexamethyltrisiloxane (71.0 g, 256 mmol) was treated succesively with *p*-vinylbenzylmagnesium chloride (46 mmol) and methyllithium or methylmagnesium bromide (46 mmol), similarly to the synthesis of B2. The usual work-up and purification by column chromatography gave the product in 50% yield. ^{1}H NMR $\delta = 0.10$, 0.12, 0.13 (three s, 21H, SiC$\underline{H}_3$), and 2.17 ppm (s, 2H, C$\underline{H}_2$).

p-Nonamethyltetrasiloxan-1-ylmethylstyrene (*B4*)

End-capping the reaction mixture by LTMS in place of methyllithium or methylmagnesium bromide in the synthesis of B3 gave B4. 45% yield. ^{1}H NMR $\delta = 0.13$ (s, 27H, SiC$\underline{H}_3$), and 2.17 ppm (s, 2H, C$\underline{H}_2$).

p-Undecamethylpentasiloxan-1-ylmethylstyrene (*B5*)

End-capping the reaction product between LTMS and D$_3$ by the chlorosilane from *p*-vinylbenzylmagnesium chloride and dimethyl-dichlorosilane, similarly to the synthesis of S5, gave B5 in 48% yield. ^{1}H NMR $\delta = 0.13$ (s, 33H, SiC$\underline{H}_3$), and 2.17 ppm (s, 2H, C$\underline{H}_2$).

RESULTS AND DISCUSSION

The chain length of the monomers S5, Sn, M5, Mn, and B5 could be regulated by controlling the ring-opening reaction of D$_3$. However, monomers S8 and M8 could not be selectively synthesized by this method, because the ring-opening reaction of two moles of D$_3$ by LTMS gave a statistical product distribution. These monomers and S2, S3, S4, M2, SF2, FF2, FS2, S$_{nf}$2, B2, B3, and B4 were synthesized by stepwise coupling of suitable intermediates.

In the synthesis of *p*-vinylphenylmagnesium chloride, it was realized that effective mixing is very important in smooth and efficient formation of the Grignard reagent. This was also found to be true in the synthesis of Mn macromer. Here, brief comments on ultrasonic irradiation on the syntheses of *p*-vinyl-

Table I. Effects of ultrasonic irradiation on the functionality of polysiloxane macromers[a]

No.[b]	D$_3$ mol l^{-1}	LTMS mol l^{-1}	Macromer				
			Yield %	M_n, calcd	M_n, UV $\times 10^3$	M_n, VPO	f^c
S-1	0.911	0.0633	79	3.0	2.8	3.0	1.07
S-2	0.613	0.0405	80	3.3	3.4	3.5	1.03
S-3	0.651	0.0217	85	6.3	6.7	5.9	0.88
S-3U[d]	0.651	0.0217	85	6.3	6.6	5.9	0.89
M-1	1.00	0.0289	94	8.0	7.6	5.5	0.72
M-2U	0.534	0.0328	76	3.9	3.7	3.8	1.03
M-3	1.04	0.0433	83	5.7	6.4	5.4	0.84
M-4U	0.779	0.0280	90	6.5	6.2	6.2	1.00
M-5	0.904	0.0768	60	2.9	3.9	3.5	0.90
M-6U	0.752	0.0278	90	5.6	5.6	5.6	1.00

[a] Polymerizations were carried out at 0°C in THF, and terminated with three-fold excess SSiCl (S-series) or MSiCl (M-series).

[b] U indicates the reaction under ultrasonic irradiation in the terminating step.

[c] $f = M_n$, VPO/M_n, UV.

[d] Functionalization by SSiCl was satisfactory as long as the concentration of LTMS was kept higher than about 0.03 mol l^{-1}, and no significant effect of ultrasonic irradiation was observed.

Scheme 5. Alternative route to S1—S4.
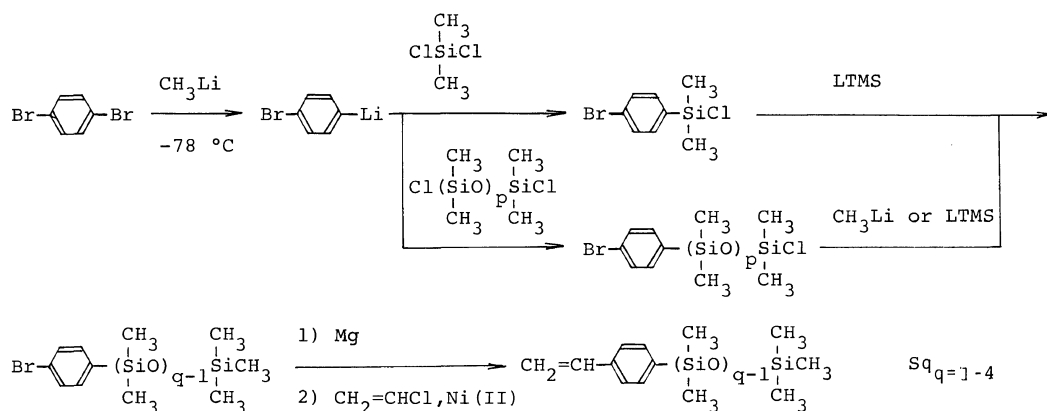
Table II. Polymerization and copolymerization of vinyl-polymerizable oligoorganosiloxane monomers[a]

No.	Feed		Yield	Composition[b]		$M_w{}^c$ $\times 10^4$	M_w/M_n	Siloxane[d]	Silicon[e] number	Appear-ance[f]
	M_1/wt%	M_2/wt%	%	M_1/wt%	M_2/wt%			wt%		
1	S1, 100	—	96	S1, 100	—	21.7	2.11	41	1.0	s
2	S1, 73	S5, 27	96	S1, 75	S5, 25	28.1	2.73	50	1.4	s
3	S1, 53	S5, 47	94	S1, 53	S5, 47	49.0	3.77	58	2.0	s
4	S1, 70	S94, 30	91	S1, 75	S94, 25	30.8	2.14	58	2.0	s
5	S1, 53	S94, 47	94	S1, 56	S94, 44	55.2	2.95	67	2.8	s
6	S2, 100	—	90	S2, 100	—	21.7	2.67	59	2.0	s
7	S2, 40	SF2, 60	80	S2, 41	SF2, 59	26.2	1.86	64	2.0	w
8	S2, 50	S_{nf}, 50	98	S2, 50	S_{nf}, 50	29.6	2.05	30	0.9	s
9	S2, 79	St4, 21	70	S2, 76	St4, 24	16.0	2.45	62	2.5	s
10	S2, 74	FA, 26	71	S2, 73	FA, 26	2.5	2.80	43	1.7	w
11	S2, 55	FA, 45	50	S2, 54	FA, 45	7.5	2.83	32	1.4	w
12	S2, 24	FA, 76	80	S2, 33	FA, 67	16.5	2.47	19	1.0	w
13	S3, 100	—	71	S3, 100	—	78.1	2.14	68	3.0	w
14	S3, 90	St, 10	40	S3, 91	St, 9	68.3	1.90	62	2.3	w
15	S3, 79	St, 21	68	S3, 76	St, 24	53.3	1.93	52	1.5	s
16	St4, 100	—	67	St4, 100	—	14.0	3.26	74	4.0	s
17	S5, 100	—	94	S5, 100	—	34.9	3.64	78	5.0	w
18	S5, 75	St, 25	64	S5, 74	St, 26	15.6	2.14	58	2.0	w
19	S5, 53	St, 47	73	S5, 53	St, 47	31.7	4.90	41	1.0	s
20	S5, 50	FA, 50	78	S5, 53	FA, 47	6.6	3.14	41	3.0	w
21	S8, 100	—	90	S8, 100	—	12.8	2.00	85	8.0	o
22	S8, 69	St, 31	38	S8, 67	St, 33	5.1	1.88	57	1.8	w
23	S8, 49	St, 51	58	S8, 50	St, 50	13.4	2.51	43	1.0	s
24	S94, 59	St, 41	69	S94, 57	St, 43	60.1	2.67	57	1.8	s
25	S94, 42	St, 58	11	S94, 39	St, 61	23.7	2.66	39	0.9	s
26	S_{nf}, 100	—	56	S_{nf}, 100	—	11.8	1.57	—	—	s
27	S_{nf}1, 100	—	82	S_{nf}1, 100	—	19.3	2.91	30	1.0	s
28	S_{nf}2, 100	—	67	S_{nf}2, 100	—	50.2	2.82	46	2.0	s
29	F1, 100	—	60	F1, 100	—	18.5	2.01	38·	1.0	s
30	FS2, 100	—	56	FS2, 100	—	31.0	1.96	69	2.0	s
31	FF2, 100	—	68	FF2, 100	—	37.3	2.12	75	2.0	w
32	SF2, 100	—	78	SF2, 100	—	29.7	1.84	69	2.0	w

Table II. continued

No.	Feed		Yield	Composition[b]		$M_w{}^c$	M_w/M_n	Siloxane[d]	Silicon[e]	Appear-ance[f]
	M_1/wt%	M_2/wt%	%	M_1/wt%	M_2/wt%	$\times 10^4$		wt%	number	
33	B1, 100	—	36	B1, 100	—	83.0	1.78	46	1.0	s
34	B2, 100	—	60	B2, 100	—	56.4	2.68	61	2.0	w
35	B2, 93	St, 7	62	B2, 95	St, 5	49.2	1.86	58	1.8	w
36	B2, 85	St, 15	52	B2, 83	St, 17	52.2	1.81	51	1.3	s
37	MS3, 15	FA, 85	84	MS3, 16	FA, 84	—	—	13	0.5	w
38	M5, 100	—	89	M5, 100	—	24.2	2.87	70	5.0	o
39	M5, 90	St, 10	58	M5, 88	St, 12	12.5	1.55	62	3.0	o
40[f]	M5, 80	St, 20	56	M5, 80	St, 20	43.0	1.97	56	2.2	o
41	M5, 70	St, 30	58	M5, 70	St, 30	7.9	1.83	49	1.6	o
42	M5, 50	St, 50	52	M5, 50	St, 50	7.1	1.81	35	0.9	o
43	M5, 47	FA, 53	90	M5, 47	FA, 53	17.6	2.23	33	2.8	o
44	M5, 13	FA, 87	88	M5, 12	FA, 88	10.4	2.55	8	0.7	o
45	M60, 50	MMA, 50	60	M60, 42	MMA, 58	7.8	1.84	41	1.0	s
46	M60, 50	St, 50	57	M60, 55	St, 45	5.8	1.45	53	1.6	s
47	M120, 50	MMA, 50	60	M120, 42	MMA, 58	8.4	1.46	41	1.0	s
48	M120, 50	St, 50	62	M120, 53	St, 47	5.3	1.79	51	1.4	s

[a] Polymerizations were carried out at 60°C in THF with 0.1—0.2 mol% AIBN as an initiator.
[b] Determined by ^{1}H NMR.
[c] Determined by GPC correlated to standard polystyrene.
[d] Weight percent of oligosiloxane substituent in the polymer.
[e] Number of silicon atoms per monomer unit.
[f] s, solid; w, waxy; o, oily.

phenylmagnesium chloride and Mn macromer are made. In the syntheses, the overall yields of macromers Sn and Mn were not necessarily satisfactory.[2] Efforts were made to obtain high and reproducible yields, although the reported[2] synthetic routes were basically followed. Ultrasonic irradiation, which has been recently recognized effective to enhance especially heterogeneous reactions,[10-13] was used in the formation of p-vinylphenylmagnesium chloride, which is the precursor of the terminating agent SSiCl.[2] The yield increased from the reported 51% (at most)[2] to 76% (reproducible). Ultrasonic irradiation was also effective in obtaining expected functionality of ω-methacrylyl macromer Mn. The results are shown in Table I.

The order of introduction of siloxane side chain and vinyl group can be reversed if it is favorable. For instance, the monomers S1—S4 can be synthesized according to Scheme 5.

The cross-coupling reactions of p-oligoorganosiloxane substituted phenyl grignard reagents with vinyl chloride go rather nicely when the siloxane chain is short. However, the efficiency of the introduction of vinyl group[13] became low with increasing chain length. In the synthesis of S3, the compound was formed in 83% selectivity along with 13% uncoupled product 1-phenylheptamethyltrisiloxane. It was necessary to separate the products by careful column chromatography.

The results of the polymerizations are shown in Table II. Homopolymers are generally waxy or oily except for those containing less than two silicon atoms per monomer unit, and polySt4. Especially, those of methacrylate type polymers lacking in film forming properties. In order to improve the film forming property, copolymerizations with styrene, methyl methacrylate, or FA were carried

out, and the result are shown in the table. Some graft copolymers were also synthesized. The copolymer composition are very close to those in feed. These results indicate the reactivities of the oligosiloxane substituted styrenes or methacrylates, including macromers, are very close to that of styrene or methyl methacrylate itself, at least in copolymerization reactions. Similar results have been reported by other authors, too.[14–17] It is of interesting that regarding the reactivity of macromers, the methacrylate type macromer seems to have higher reactivity toward styrene than methyl methacrylate. The effects of polymerizable functional group[18] and solvent system[19] on the reactivity of macromers have been reported.

Although the difference in molecular weight must be considered, the copolymers of Sn monomers having more silicon atoms than two per monomer unit were waxy, and still lacked in self-supporting properties. The copolymers tend to be waxy or oily even with lower siloxane content compared with homopolymers. Graft copolymers of S94 which contain less than two silicon atoms per monomer unit were solid. Fluorine containing polymers (S_{nf}) were solid. The difference in appearance seems to be closely related to T_g of the polymers. The change of T_g is shown in Figure 2 and Table III along with that of poly(p-alkylstyrene)s.

T_g of polyS1 was found at 136°C. Such high T_g was also found with poly[p-(t-butyl)styrene] ($T_g = 130$°C) in which bulky t-butyl groups are attached to p-positions of polystyrene. The difference in T_g of these two polymers may be attributed not only to the difference in the size of the two substituents, but also to the difference in bonding nature of the substituents. In polyS1, the bulky trimethylsilyl groups are attached directly to aromatic rings. In such systems, a $d\pi$–$p\pi$ interaction between silicon atom and aromatic ring would partially restrict the rotation of trimethylsilyl group. Such rotationally restricted large substituents will
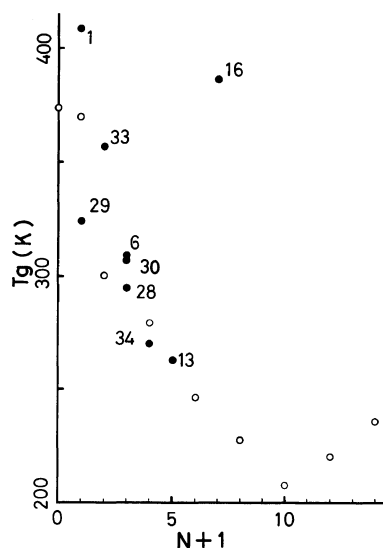

Figure 2. Change in glass transition temperature of poly(p-substituted styrene)s with the change of the length of side chain. ●, poly(p-oligosiloxanylstyrene); ○, poly(p-alkylstyrene); n, number of spacer atoms along the chain between trimethylsilyl (●) or methyl (○) and aromatic ring. Numbers in the figure are same with those in Table II. PolySt4 was plotted at the same N value with polyS4.

Table III. Glass transition temperatures of selected polymers

No	Sample	T_g °C
1	PolyS1	136
6	PolyS2	36
13	PolyS3	−10
16	PolySt4	114
33	PolyB1	85
34	PolyB2	−3
29	PolyF1	52
30	PolyFS2	34
28	PolyS$_{nf}$2	22
2	Copoly[S1—S5 (73—27)]	90
3	Copoly[S1—S5 (53—47)]	51
19	Copoly[S5—St (53—47)]	18
25	Copoly[S94—St(42—58)]	86
4	Copoly[S94—S1(30—70)]	101
5	Copoly[S94—S1(47—53)]	73

make the movement of polymer back bone more difficult compared with poly[p-(t-butyl)styrene] resulting in higher T_g of polyS1

than poly[p-(t-butyl)styrene]. Such speculation seems to be supported by the fact that polyB1, which has larger substituents than polyS1, shows much lower T_g (85°C) compared with polyS1. In polyB1, the bulky trimethylsilyl groups are not directly attached to aromatic rings, and thus lose the $d\pi$–$p\pi$ interaction. The free rotation of the substituents will reduce the resistance of the movement of polymer back bone, resulting in lower T_g. In case of polySt4 in which tetrasiloxane is attached to p-position of polystyrene as a compact branched form, the T_g (114°C) is much higher than that of polyS4 (< -30°C) in which tetrasiloxane is attached as a linear chain. The entropy change in glass transition will be larger for polyS4 than polySt4, resulting in lower T_g of polyS4. The silicon atom directly attached to the aromatic nuclei may also reduce the flexibility of the bulky tetrasiloxane substituents. Introduction of disiloxane chain at the para position of polystyrene lowered the T_g of back bone polymer (T_g 100°C) sharply and dramatically ($T_g = 36$°C). PolyB2 has even lower T_g (-3°C). Introduction of longer siloxane chain than trisiloxane lowered the T_gs too much; consequently, the polymers lack self-supporting properties.

The difference between polysiloxane and polymethylene side chains lies in that the latter can crystallize when the chain length becomes longer than about 10 methylene units and the T_g goes up with increasing methylene units of more than 10.

The T_gs of polyS2, S3, B2, FS2, $S_{nf}2$ and the copolymers 2, 3, 19 in Table III were found between those of copolymer component homopolymers and they were much lower than that of polystyrene itself, a fact which suggests homogeneous distribution of the short siloxane chains. Although the T_gs of the graft copolymers (No. 2,3,19 in Table III) were also found between those of back bone and branch components, the decrease in T_g was much smaller than that of polymers with short siloxane chains, which suggests an incomplete
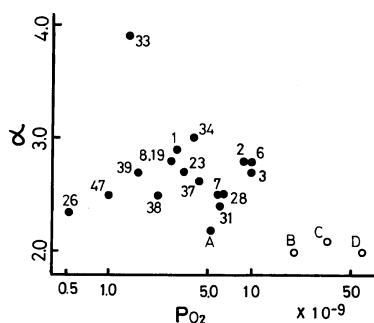

Figure 3. Oxygen permeation behavior of the polymer films. P_{O_2} in cm^3 (STP)·cm^{-1} cm^{-2}·s^{-1}·$cmHg^{-1}$. Numbers in the figure are the same as those in Table II. A, polyFA; B, copoly(bisphenol A carbonate-b-dimethylsiloxane);[6] C, p-Hydroxyphenol cross-linked PDMS;[7] D, PDMS.

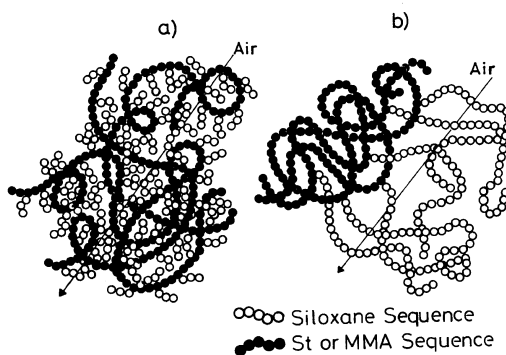
Figure 4. Imaginative gas permeation scheme through shortbranched(non phase-separated) and long-branched or block(phase-separated) polymer films. a) shortbranched; b) long-branched.

phase separated structure of these graft copolymers. A more detailed study is necessary to clarify the miscibility of the back bone and branch components.

The results of oxygen permeation determined by the gas chromatographic method are shown in Figure 3. The polymers generally showed permeation constants in the order of 10^{-9} cm^3 cm^{-1} s^{-1} cm^{-2} $cmHg^{-1}$, and selectivity of 2.5. Among them, polyS2 and polyB1 showed $P_{O_2} = 5.0 \times 10^{-9}$, 1.4×10^{-9} and $\alpha = 2.8$, 3.9, respectively. The selectivities are much higher than the commercialized block or cross-linked polymers. Longer siloxane side chain branched copolymers containing similar

amounts of siloxane units with homopolymers showed lower selectivity. Although a detailed discussion will be made in a future article, the selectivity in permeation through polyS2 at 5°C (lower than the T_g of the polymer) was 3.2. The selectivity was even higher at lower temperature. Accordingly, the difference in selectivity in permeation between polyS2 and long polysiloxane branched graft copolymers is not considered to be because of the difference in state of the polymer, but, at present, it is considered to be because of the effect of the micro phase separation. The phenomena described above suggest the following speculation as an imaginative effects of polymer back bone on permeation as shown in Figure 4. In the long branched polymers, the siloxane chains are basically phase-separated from the back bone components, and gases permeate through the phase-separated PDMS domain, accordingly, the P_{O_2} and α are quite similar to those of PDMS itself. In the short siloxane branched comb polymers, the short siloxane branches are distributed, presumably, homogeneously, as suggested by the decrease in T_gs, in the polymer back bone component. By this effects, the P_{O_2} is lowered a little compared with that of PDMS, but the increase in the selectivity in permeation compensates the decrease in permeation constant of such polymers as meterial for oxygen permeable membrane. In the blend systems, such an effect of a hard polymer back bone on permeation cannot be anticipated.

Although it is necessary to carry out more detailed studies to obtain insight on permeation phenomena, homogeneous distribution of short soft components in a hard back bone component which not only works as mechanically supporting component but also exerts selectivity in permeation, seems desirable in designing an oxygen permeable membrane.

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