Syntheses of Poly[(tetraphenyl-*p*-silphenylenesiloxane)-*co*-(tetramethyl-*p*-silphenylenesiloxane)]s and the Physical Properties of Their Films

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ABSTRACT: In order to obtain a polysilarylenesiloxane having a high glass transition temperature (T_g), a high thermal degradation temperature (T_d), and a good solubility in common solvents to prepare a film, the copolycondensation of 1,4-bis(hydroxydiphenylsilyl)benzene with 1,4-bis(hydroxydimethylsilyl)benzene was studied. Their thermal properties were studied by using a differential scanning calorimetry and a thermogravimetry analysis. The physical properties of copolymer films were also investigated. All the copolymers exhibited the T_g's, and those increased with the increase of the molar ratio of the units based on 1,4-bis(hydroxydiphenylsilyl)benzene (**PS** units). The T_g of one of the copolymers, **CP-a**, reached to 127 °C. **CP-c** having a relatively high molecular weight showed the highest thermal stability in air, whose T_{d5} was 524 °C. Tough self-standing films were obtained from the copolymers by the casting method. These films had much lower gas permeability coefficients than that of polydimethylsiloxanes and low surface energy similarly to the silicon-containing polymers having a phenylene moiety. The gas permeability coefficients of the films decreased, and the densities and the tensile strength of films increased with the increase of the molar ratio of **PS** units. These results indicated that dense and tough films were obtained from these copolymers.
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KEY WORDS Polysilarylenesiloxane / Thermal Degradation Temperature / Copolymerization / Glass Transition Temperature / Gas Permeability /

Polysilarylenesiloxanes[1,2] and their copolymers[2–19] have been studied as high temperature elastomers whose degradation temperature (T_d) was greatly higher than that of polydimethylsiloxane (**PDMS**). Poly-(tetramethyl-*p*-silphenylenesiloxane) (poly**MS**) of a typical polysilarylenesiloxane was synthesized by Merker *et al.*[5] and their thermal properties were investigated. According to the literature,[3–5] poly**MS** shows a glass transition temperature (T_g) of −20 °C, a melting point (T_m) of 135 °C and a thermal degradation temperature (T_d) of 370–390 °C under helium flow. Poly**MS**/PDMS and poly**MS**/PDMS derivatives were synthesized and their thermal and physical properties were also reported.[2–19]

The common characteristics of these poly**MS**-containing polymers are their high T_d and the low T_g, which resulted from their flexible tetramethyldisiloxane units in the main chain. The mechanical strength of these polymers is not enough at high temperature to use as the heat-resistant materials such as a high-temperature coating and a low dielectric insulation material in semiconductor devices. Recently, Kawakami *et al.*,[20–22] reported the polymer derived from *cardo*-type 9,9′-bis[4-(dimethylsilyl)phenyl]-fluorene using a new method of the catalytic cross-dehydrocoupling polymerization, and that this polymer exhibited high T_g of 160 °C,[22] however, the physical properties were not reported. We reported that the fully aromatic polysilarylenesiloxanes, poly(tetraphenyl-*p*-silphenylenesiloxane) (poly**PS**) and poly-(tetraphenyl-*p,p′*-silbiphenylenesiloxane) (poly**BS**), showed no weight loss in air below 500 °C and had high melting temperatures of 323 °C and 391 °C, respectively.[23] Unfortunately, these polymers were obtained as insoluble powder, and could not be formed as a thin-film or a self-standing film. Therefore, the physical properties could not be investigated.

On the contrary, poly**MS** are soluble in common solvents such as chloroform, tetrahydrofuran and toluene, and can be formed as a tough self-standing film.[24] However, a copolycondensation of a bis(hydroxydiphenylsilyl)arylene and a bis(hydroxydimethylsilyl)arylene have never been studied.

In this paper, the syntheses of the copolymers, poly-[(tetraphenyl-*p*-silphenylenesiloxane)-*co*-(tetramethyl-*p*-silphenylenesiloxane)]s, (**CP** series) were investigated (Scheme). The chemical and the physical structure were studied by the ^{29}Si NMR spectra and X-ray

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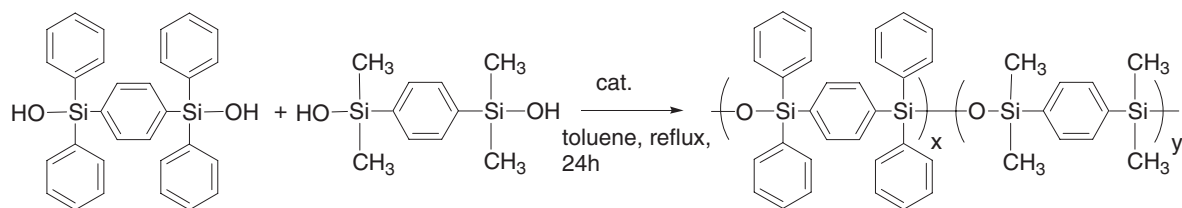
Scheme 1. Synthesis of copolymers.

diffraction (XRD) patterns. The thermal properties of the copolymers were investigated in detail by using a thermogravimetry analysis (TGA) and a differential scanning calorimetry (DSC). The physical properties of the copolymer films, that is, gas permeability, density, surface energy and mechanical strength were also investigated. From these results, the influence of the units based on 1,4-bis(hydroxydiphenylsilyl)benzene (**PS** units) on the thermal and physical properties of the copolymers and their films will be discussed.

EXPERIMENTAL

Materials

Toluene was distilled over sodium to remove a small amount of water. 1,4-bis(hydroxydiphenylsilyl)-benzene (**M1**) was synthesized according to our previous report.[23] 1,4-Bis(hydroxydimethylsilyl)benzene (**M2**) was purchased from Chisso Corp. and purified by recrystallization from a mixture solution of tetrahydrofuran (THF) and *n*-hexane before use. Tris(2,4-pentanedionato)chromium (III) was purchased from Dojindo Laboratories. Diiodomethane was purchased from Tokyo Chemical Industry Co., Ltd and used without any purification. Tetramethylguanidine di-2-ethylhexanoate was prepared by mixing tetamethyl-guanidine and 2-ethylhexanoic acid in 1:2 mol ratio for several days to use as a basic catalyst. Poly**PS**, oligo**PS** and poly**MS**'s were synthesized also according to our previous report.[23] Poly**MS**-1 and poly**MS**-2 were synthesized in refluxed benzene for 24 h and 63 h, respectively. Model compound was synthesized from 1,4-bis(chlorodimethylsilyl)benzene and triphenylsilanol in THF in the presence of pyridine.

Copolymerizations

Poly[(tetraphenyl-*p*-silphenylenesiloxane)-*co*-(tetra-methyl-*p*-silphenylenesiloxane)]s (**CP** series) were synthesized in refluxed toluene in the presence of the basic catalyst. A typical procedure for **CP-a** is as follows.

M1 (0.42 g, 0.88 mmol) and **M2** (0.020 g, 0.087 mmol) were refluxed for 24 h in toluene (5.0 mL) in the presence of a few drops of tetramethylguanidine di-2-ethylhexanoate as a catalyst using an azeotropic

trap to remove water. The reaction mixture after removing the precipitate was poured into an excess amount of methanol to obtain the polymer. Yield: 0.24 g (56%). ^{1}H NMR δ (ppm, THF-d_8, 400 MHz): 0.2–0.4 (12H, CH$_3$ × 4), 7.0–7.6 (182H, Ph). ^{29}Si NMR δ (ppm, CDCl$_3$, 79.5 MHz): 0.798 (-$\underline{Si}$(CH$_3$)$_2$-O-Si(Ph)$_2$-), −1.23 (-$\underline{Si}$(CH$_3$)$_2$-O-$\underline{Si}$(CH$_3$)$_2$-), −17.7 (-$\underline{Si}$-OH), −18.7 (-$\underline{Si}$(Ph)$_2$-O-$\underline{Si}$(Ph)$_2$-), −20.5 (-$\underline{Si}$(Ph)$_2$-O-Si(CH$_3$)$_2$-). IR, ν (cm^{-1}, KBr disk): 3069 (m), 3049 (m), 3000 (m), 1590 (w), 1429 (s), 1136 (s), 1117 (s), 1058 (s, br, Si-O-Si), 1027 (s), 1018 (s), 997 (s), 740 (m), 713 (s), 698 (s), 550 (s), 531 (s), 505 (s).

Other copolymers were prepared by the similar method as the preparation of **CP-a** by changing the ratio of **M1** and **M2**.

Characterizations of Copolymers

^{1}H NMR and ^{29}Si NMR spectra of the copolymers were measured with Bruker BioSpin AVANCE DRX 400 Spectrometer at 400 MHz and 79.5 MHz, respectively. In the case of the ^{29}Si NMR measurements, the concentration of the polymer in deuterio chloroform solution was 0.1 g mL^{-1}, and 0.05 mol L^{-1} of tris(2,4-pentanedionato) chromium(III) was added to the polymer solution as a relaxation agent in order to obtain quantitative ^{29}Si spectra.[25] 1,000–37,000 scans were needed to obtain adequate signal/noise ratios for quantitation. IR spectra were recorded with PerkinElmer PARAGON FT-IR. Gel permeation chromatography (GPC) was carried out to determine the number-average and weight-average molecular weights with Tosoh HLC-802A instrument by using THF as an eluent, equipped with four columns of TSK gels, G5000H$_6$, G4000H$_6$, G3000H$_6$ and G2000H$_6$. Standard polystyrenes were used for calibration. X-Ray diffraction (XRD) patterns by the powder method were collected on a RIGAKU RINT 2000 Diffractometer using CuKα radiation. Samples were annealed for 1 h at 160 °C before measurements.

Thermal Analyses

TGA was performed by using a Shimadzu DTG 60A at a heating rate of 10 °C min^{-1} with an air flow rate of 50 mL min^{-1} in order to investigate the thermal degradation behavior. DSC was conducted by using a

SII DSC6200 at a heating rate of $10\,°C\,min^{-1}$ with nitrogen flow rate of $50\,mL\,min^{-1}$ in order to determine T_g and/or T_m.

Preparation of Copolymer Films

Toluene solutions containing 3 wt. % of the copolymer were cast on polytetrafluoroethylene sheets put at level, and the solvent was evaporated for a few days. The thicknesses of films were in the range of 100–$300\,\mu m$. The films were dried *in vacuo* for 16 h before measuring each physical property.

Gas Permeability Coefficients Measurements

Gas permeation measurement was conducted according to the vacuum method using a Tsukuba Rika Seiki, K-315N-01 at 30 °C. A pressure on the permeation side was monitored with a BARATRON® Pressure Transducer. The permeability coefficient, P (Barrer), was calculated from a slope of time-pressure curve at a steady state. The diffusion coefficient, D $(cm^2\,s^{-1})$, was calculated from a film thickness, l (cm), and a time lag, θ (sec), according to the following equation, $D = l^2/6\theta$. The solubility coefficient, S $[cm^3\ (s.t.p.)\,cm^{-3}\,cmHg^{-1}]$, was also calculated by the equation, $S = P/D$.

Stress-Strain Measurements

The film samples were cut into rectangular strips of length 50 mm and width 5 mm. Load-elongation curves obtained on a Shimadzu EZTest. The gauge length was 30 mm and the crosshead speed was $5\,mm\,min^{-1}$.

Contact Angle Measurements

Measurement of static contact angle was performed with KYOWA INTERFACE SCIENCE Co., Ltd, Contact Angle Meter CA-D. Static contact angle was determined by the 4–5 µL sessile drop method at 20 ± 3 °C using water distilled twice and diiodomethane. Each contact angle value was the mean of ten independent measurements. The film samples were annealed at 160 °C for 1 h before measurements.

Film Density Measurements

The density of each copolymer film was calculated from a precise weight and a precise volume of the product of a film area and a thickness, which was measured with a precision digital micrometer.

RESULTS AND DISCUSSION

Chemical Structure of Copolymers

The conditions and the results of the copolycondensation of **M1** and **M2** are listed in Table I. The molar ratio of **M1** to **M2** in feed was changed from 9/91 to

Table I. Characterizations of copolymers

| Polymer	Composition (molar ratio)		Yield (%)	$M_n\ 10^{-4\,d}$	$M_w/M_n{}^d$
	Feed x/y	Observed[b] x/y			
oligoPS	100/0	100/0	51[c]	0.10	1.0
CP-a[a]	91/9	86/14	56[c]	6.1	1.5
CP-b[a]	75/25	75/25	65	3.7	1.5
CP-c	50/50	45/55	60	14	1.8
CP-d	25/75	24/76	85	29	1.6
CP-e	9/91	8/92	81	11	1.5
polyMS-1	0/100	0/100	80	4.5	1.5
polyMS-2	0/100	0/100	80	21	1.7

[a]These copolymers contained the low molecular weight products. [b]Determined by ^{29}Si NMR. [c]Soluble parts of polymers. [d]M_n and M_w are the number-average molecular weight and weight-average molecular weight, respectively.
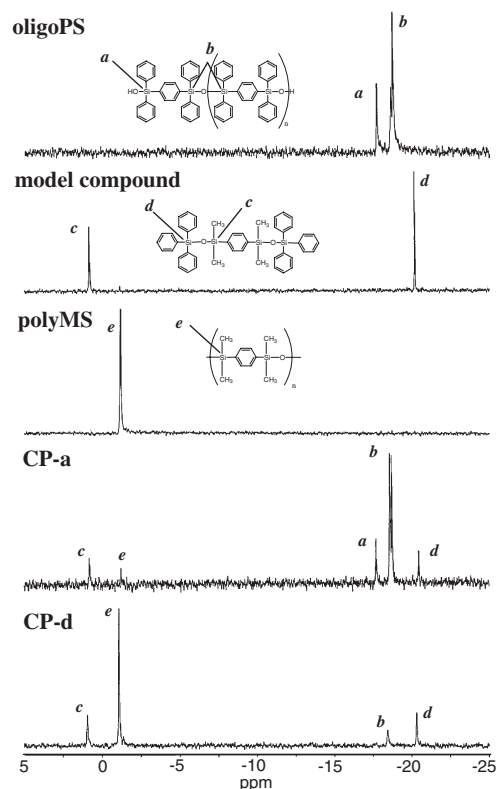

Figure 1. ^{29}Si NMR spectra of copolymers.

91/9. The soluble polymers were obtained in all the compositions except for **CP-a**. For **CP-a**, a small amount of precipitate was formed in the reaction mixture. Figure 1 shows the ^{29}Si NMR spectra of the copolymers and the related materials. The quantitative capability of ^{29}Si spectra was confirmed by the accordance of the integrated peak intensities of the peaks *c* and *d* in the model compound. In the spectra of **CP-c**, **d** and **e** (**CP-c** and **e** are not shown), four peaks were observed at -20, -18, $-1.2--1.1$ and 0.8–1.0 ppm. These peaks were assigned by the comparison with those of the oligo**PS**, the model com-

Table II. Molar ratios of siloxane units

Polymer	CH₃–Si(CH₃)–O–Si(CH₃)–CH₃		CH₃–Si(CH₃)–O–Si(Ph)–Ph		Ph–Si(Ph)–O–Si(Ph)–Ph	
	Calc.[a]	Obs.	Calc.[a]	Obs.	Calc.[a]	Obs.
CP-c	0.30	0.36	0.50	0.37	0.20	0.27
CP-d	0.57	0.61	0.37	0.31	0.06	0.08
CP-e	0.84	0.84	0.15	0.16	0.006	0.004

[a]Molar ratio of the ideal random copolymers.

pound and the poly**MS**. As a result, the peaks *c* and *d* were assigned to the diphenyldimethyldisiloxane units. The peak *b* and *d* were assigned to the tetraphenyldisiloxane units and tetramethyldisiloxane units, respectively. In the case of **CP-a** and **b** (**CP-b** are not shown), another peak was also observed at −17.7 ppm which arose from the silanol in the chain end similarly to that of oligo**PS**. This result showed that the chain ends of these polymers were **PS** units. However, its peak intensity was larger than the value predicted by their molecular weights. This discrepancy was caused by the low molecular weight products contained in these copolymers, and the split of peak *b* was also due to these products. On the other hand, peak *a* was not observed in the spectra of **CP-c**, **d** and **e**. The low molecular weight products were not detected in their GPC charts. Therefore, the chemical structures of **CP-c**, **d** and **e** were investigated in detail. The compositions of these copolymers determined by the ratio of the peak intensities of the diphenylsilyl group (the peaks *b* and *d*) against the dimethylsilyl group (the peaks *c* and *e*) are also shown in Table I. All of the compositions of these copolymers almost coincided with the feed ratios of the monomers. Table II shows the ratios of the three kinds of siloxane units of these copolymers determined by ^{29}Si NMR spectra. Here, the average intensities of the peaks *c* and *d* were used for the calculation in the case of the diphenyldimethyldisiloxane units. The observed unit ratios of **CP-e** almost accorded with those of the calculated values of the ideal random copolymers. However, the ratios of the tetramethyldisiloxane units and the tetraphenyldisiloxane units of **CP-c** and **d** were slightly larger than those of the calculated values. Especially, in the case of **CP-c**, the difference between the observed value and the calculated value of each siloxane unit was the largest. These results showed that these copolymers had slightly block character rather than the ideal random copolymers. Considering the yield and the molecular weight decreased with the increase of **PS** units as shown in Table I, the block character would be caused by the lower rate of polymerization of **M1** than that of **M2**.
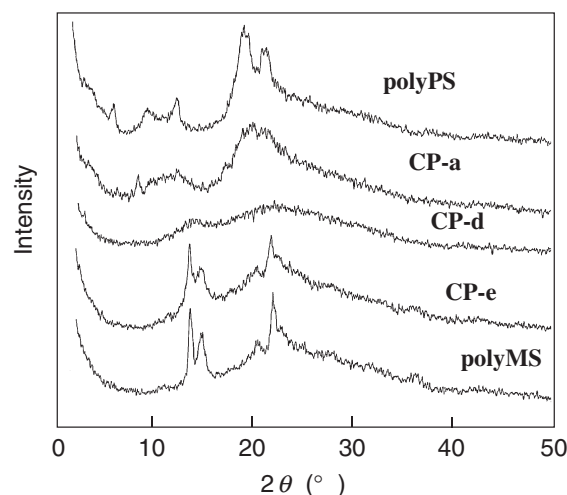
Figure 2. XRD patterns of copolymers.

Physical Structure of Copolymers

The XRD patterns of **CP** series are shown in Figure 2. Poly**PS** and poly**MS** were crystalline polymers as reported in the literature.[23,26] In the chart of **CP-a**, the diffraction peaks were observed at $2\theta = 8.6°$, $12.6°$, $20°$ and $21°$, and these peaks coincided with those of poly**PS**. In the chart of **CP-e**, the sharp peaks were observed at $2\theta = 14°$, $15°$ and $22°$, and these peaks agreed with those of poly**MS**. Therefore, **CP-a** and **CP-e** would contain the crystalline region arising from the **PS** units and the **MS** units, respectively. In the charts of **CP-b**, **c** and **d** (**CP-b** and **c** are not shown), only two broad halos were observed at $2\theta = 14°$ and $21°$. From these results, these polymers were amorphous polymers.

*Thermal Properties of Copolymers*

T_g, T_m and the enthalpy change (ΔH_m) of **CP** series are listed in Table III. All the copolymers of **CP** series showed T_g's. The increase of T_g was proportional to **PS** unit ratio. Oligo**PS** was prepared by pouring the soluble part of the reaction mixture which was obtained during the preparation of poly**PS**. As reported by our previous paper,[23] poly**PS** was a highly crystalline polymer and exhibited no T_g below 400 °C. On the other hand, oligo**PS** showed the T_g at 126 °C. The different thermal property of oligo**PS** from that of poly**PS** would be due to its low molecular weight. The T_g of 127 °C for **CP-a** was the similar value to that of the oligo**PS**, which was relatively high among the known polysilarylenesiloxanes.[2,6] On the other hand, T_m's of **CP-a** and **CP-e** were observed, which supported the results of the XRD measurements. In the case of **CP-e**, the endothermic peak was observed on only the first heating scan. Considering the sample kept at room temperature for several hours after heating process showed clearly an endothermic peak, **CP-**

Table III. Thermal properties of copolymers

Polymer	T_m^a (°C)	ΔH_m^a (J g^{-1})	T_g^a (°C)	T_{d5}^c (°C)	Weight residues^d (%) Calc.^{e}	Obs.
polyPS	323	−1.59	—	539	26.3	27.3
oligoPS	313	−6.39	126	418	26.3	22.4
CP-a	317	−1.02	127	464	28.4	25.1
CP-b	—	—	96	470	30.4	28.6
CP-c	—	—	62	524	37.4	34.3
CP-d	—	—	22	513	44.6	43.2
CP-e	123^b	−5.42^b	−3.8	519	52.4	41.8
polyMS-1	136	−30.2	—	411	57.4	32.4
polyMS-2	132	−23.2	—	516	57.4	35.0

^{a}The melting point, the enthalpy change at T_m and the glass transition temperature determined by DSC on the second heating scan. ^{b}The melting point and the enthalpy change at T_m determined by DSC on the first heating scan. ^{c}The 5% weight loss temperature estimated from TG curve. ^{d}Weight residues at 700 °C. ^{e}These values were calculated assuming that all of Si in the polymers were converted to SiO$_2$.
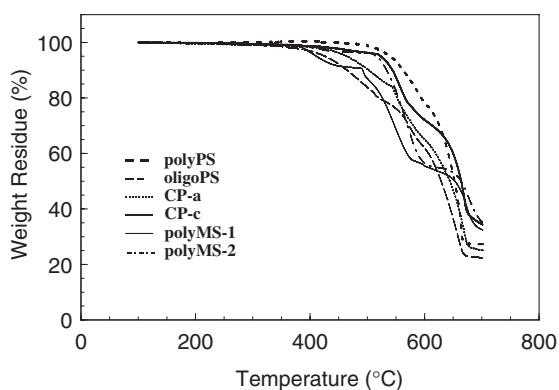
Figure 3. TGA curves of copolymers.

e would be at a supercooling state on the second heating scan.

The TG curves of poly**PS**, oligo**PS**, **CP-a**, **CP-c** and poly**MS**'s are shown in Figure 3. Oligo**PS**, **CP-a**, **CP-b** (not shown) and poly**MS**-1 rapidly decomposed at about 400 °C. The low thermal stability of these polymers would be caused by the thermal decomposition of the silanols in the chain ends because the molecular weights of these polymers were lower than those of other polymers as shown in Table I. From these results, the molecular weight of the polymers played an important role in the thermal degradation temperature. In the TG curve of **CP-c**, the weight loss of the second step was smaller and the weight residue above 600 °C was larger than that of poly**MS**-2. Therefore, the introduction of **PS** units was effective to improve the thermal stability of the copolymers. The T_{d5}'s and the weight residues of the copolymers estimated according to the TGA measurements are

listed in Table III. **CP-c**, which had relatively high molecular weight and high **PS** unit ratio, showed the highest thermal stability in air, and the T_{d5} of this copolymer was 524 °C. It was revealed that the copolycondensation of **M1** and **M2** were effective to obtain a polysilarylenesiloxane which was soluble in common solvents and showed high thermal stability in air and relatively high T_g. Further, the weight residue of **CP-d**, whose molecular weight was relatively high, coincided with the theoretical value, whereas, those of **CP-a** and **b** were smaller than the theoretical values. It would be caused by the elimination of the volatile organosilicon compound, such as a triphenyl silanol, from the chain-end as described in our previous report.[27] It was shown that the molecular weight of the copolymers also affected on the weight residues. On the other hand, the weight residues of **CP-e** and poly**MS**'s were much smaller than the theoretical values. This difference showed that the amount of the volatile organosilicon compound generated from **MS** units larger than those from **PS** units. The same tendency was shown in the literature.[16]

Physical Properties of Copolymer Films

The films were prepared from the toluene solution of each copolymer by the casting method on the polytetrafluoroethylene sheets. The films of **CP-a** and **b** became brittle and fragile, whereas the tough films of **CP-c**, **d**, **e** and poly**MS** could be obtained with their thickness in the range of 100–300 μm. The difference of the film forming properties would be mainly caused by the different molecular weights as listed in Table I. Unfortunately, the copolymers, which have the same composition as **CP-a** and **b** high molecular weights suitable for the film preparation, could not be obtained by the copolymerizations. As a result, the physical properties of **CP-c**, **d**, and **e** films were investigated.

Permeation measurements of hydrogen, oxygen, nitrogen gasses for the **CP-c**, **d**, **e** and poly**MS** films were conducted at 30 °C. Unfortunately, the measurements for **CP-e** and poly**MS** films were not successfully managed because the no negligible pressure changes of a permeate side arising from a gas leak. Then, the evaluation for the poly**MS** film was referred to our previous paper.[24] Permeability coefficient, P, diffusion coefficient, D, and solubility coefficient, S, calculated from the obtained pressure curve are summarized in Table IV, together with values for a PDMS and a polystyrene, PSt, referred to the literature.[28,29] PDMS, which has been well known as a material for an oxygen-enriching membrane, indicates relatively high S_{O2} compared with S_{N2}. **CP-c**, **e** and poly**MS** indicated distinctly low values of permeation parameters against all gasses compared with those of a PDMS, in spite of these contained the same structure

Table IV. Gas permeation behavior of copolymer films

Code	density	P_{H2}	P_{O2}	P_{N2}	D_{H2}	D_{O2}	D_{N2}	S_{H2}	S_{O2}	S_{N2}
	g/cm^3		(Barrer)^c			(10^{-7} cm^2 s^{-1})			(10^{-4} cm^3 (s.t.p.) cm^{-3} cmHg^{-1})	
CP-c	1.0	28	4.5	1.1	176	4.4	2.5	1.6	10	4.4
CP-d	0.92	37	6.1	1.7	585	7.6	7.6	0.63	8.0	2.2
polyMS	0.71	—	8.8^d	2.8^d	—	—	—	—	—	—
PDMS^a	—	890	800	400	1400	340	340	6.6	24	12
PSt^b	1.0–1.1	23	2.6	0.79	436	1.1	—	0.53	24	—

^{a}Ref 28. ^{b}Ref 29. ^{c}1.0×10^{-10} [cm^3 (s.t.p.) cm cm^{-2} s^{-1} cmHg^{-1}]. ^{d}Ref 24.

Table V. Physical properties of copolymer films

Polymer	Contact angle (°)		Surface Energy (mN/m)	Tensile strength	Young's modulus	Maximum strain
	H$_2$O	DIM^a	γ^b	(MPa)	(MPa)	(%)
CP-c	103	62.2	27.4	12.5	4.5	10.8
CP-d	101	68.9	22.9	7.6	2.8	27.4
CP-e	105	66.4	24.9	6.0 (0.005)^c	1.3 (—)^{c,d}	5.1 (263)^c

^{a}Diiodomethane. ^{b}Calculated by the Owens-Wendt equation. ^{c}The data of the film cooled to r.t. after raising to 200 °C for 5 min. ^{d}Young's modulus was too small to be estimated.

of dimethylsiloxane unit to a PDMS. The gas permeabilities of all gasses through the copolymer films decreased with an increase of **PS** unit ratio. These results would relate to their chemical structure and the mobility of their polymer chains. The T_g's of PDMS and polyMS were -120 °C and -20 °C, respectively.[2] Those of **CP-c** and **d** were higher than these values and increased with the increase of the **PS** unit ratio as shown in Table III. Therefore, the mobility of their polymer chain was lower than that of PDMS and polyMS. On the other hand, the densities of the films of **CP-c**, **d** and polyMS are also presented in Table IV. The densities increased with an increase of **PS** unit ratio. These results showed that the copolymer films were denser compared with PDMS or polyMS films. The high densities of these copolymers were attributed to the replacement of the methyl side groups by the phenyl groups. Therefore, these copolymers showed lower gas permeabilities than those of PDMS and polyMS. On the other hand, it was found that the gas permeation behavior of PSt was similar to that of **CP-c** and **d**. The density of **CP-c** was 1.0, and approximately coincided with that of PSt. The **PS** unit introduced into the structure of polyMS would behave as the same as the side-chain phenyl group of PSt.

The static contact angles on copolymer films against water and diiodomethane and their surface energy calculated by the Owens-Wendt equation[30] are summarized in Table V. The influence of pendant groups on the surface energy of silicon-containing polymers is not completely understood, however, it has been known that the surface energy is relatively high when the pendant group is bulky group such as a phenyl.[31] The surface energy of each copolymer

was slightly larger than that of a PDMS (22.8 mN/ m)[30] and the similar values to that of silicon-containing polymers having phenylene moiety such as a dimethylsiloxane-methylphenylsiloxane copolymer (50:50 mol %, 24.7 mN/m),[32] a poly(phenylmethyl-siloxane) (33.2 mN/m)[31] and a dimethylsiloxane-diphenylsiloxane copolymer (4.4:95.6 mol %, 24.0 mN/m).[32] Therefore, it was suggested that the surface energy of the copolymers did not change largely by the introduction of **PS** units and these copolymers had a low surface energy similar to the silicon-containing polymers that were applied to the practical uses.

The mechanical properties of the copolymer films are also shown in Table V. The tensile strength and Young's modulus increased with the increase of **PS** unit. These characteristics would be attributed to the stiffness of **PS** unit, which related to the results of the gas permeability and density measurements. The maximum strain of **CP-d** film was the largest among these copolymers. **CP-d** was an amorphous polymer and its T_g was 22 °C. It was considered that the mobility of the polymer chain was relatively high. On the contrary, the maximum strain of **CP-e** film was small which would be due to that **CP-e** was a crystalline polymer. However, the mechanical property of **CP-e** film drastically changed after raising 200 °C for 5 min. The maximum strain of the film was over 250%, and its tensile strength was about 1/1,000 of the film before heating. Considering the results of the DSC measurements, the **CP-e** film was an amorphous polymer immediately after cooling to the room temperature from the molten state. Therefore, it was shown that the crystalline region of the films exerted much influence on their mechanical properties.

CONCLUSIONS

The soluble and high molecular weight copolymers of M_n over 10^5 were obtained when the molar ratio of 1,4-bis(hydroxydiphenylsilyl)benzene in feed was less than 50%. According to the ^{29}Si NMR spectra of the copolymers, these copolymers had the slightly block character.

All the copolymers exhibited T_g's, those increased with the increase of **PS** unit ratio. The T_g of **CP-a** reached to 127 °C and it was relatively high among the known polysilarylenesiloxanes. From the results of the TGA measurements, the molecular weights of the copolymers played an important role in their thermal decomposition as well as the molar ratios of **PS** units. The T_{d5} of **CP-c** was 524 °C, which was nearly equal to that of the fully aromatic polysilaryleneoxanes. Tough self-standing films were obtained from the copolymers (**CP-c**, **d** and **e**) having relatively high molecular weights by the casting method. The gas permeability coefficients decreased and the density of films increased with the increase of the molar ratio of **PS** units. In addition, the tensile strength of the copolymers increased and the surface energy of the copolymers did not increase largely by the introduction of **PS** units. Consequently, it was revealed that the copolycondensation of a bis(hydroxydiphenylsilyl)arylene with a bis(hydroxydimethylsilyl)arylene was effective to obtain a polysilarylenesiloxane having relatively high T_g, high T_d in air, and the dense and tough films could be prepared from these copolymers owing to their good solubility.

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