Effects of the Structure of p-Oligodimethylsiloxanyl Substituents of Polystyrene on Glass Transition Temperature and Oxygen Permeability of the Polymer

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ABSTRACT: Polystyrenes with isomeric p-oligodimethylsiloxanyl substituents were synthesized in order to elucidate the roles of these substituents on their film forming properties and oxygen permeation behavior. Branched chain oligodimethylsiloxanyl substituents gave polymers with higher glass transition temperatures than did straight chain substituents. It was indicated from the permeation experiments that trimethylsiloxyl groups in p-oligodimethylsiloxanyl substituents played essential roles in permeation by increasing the diffusion coefficient. The roles of the substituents are further discussed based on the spin-relaxation behavior of the polymers in the solid state.

KEY WORDS   p-Oligodimethylsiloxanylstyrene / Membrane / Glass Transition Temperature / Oxygen Permeation / Diffusion / Spin-Relaxation /

It is generally admitted that the permeation of a gas through a homogeneous film at rubbery state is controlled by the diffusion and solubility coefficients of a gas in or through the film.

$$P = DS \qquad (1)$$

Where P, D, and S are the permeability, the diffusion and the solubility coefficient, respectively.

In our previous papers, we suggested that trimethylsiloxyl groups in p-substituents of poly(p-oligodimethylsiloxanylstyrene)s such as poly(p-pentamethyldisiloxanylstyrene) play essential roles to enhance the permeability of oxygen through increase in the diffusion coefficient.[1-7] We also suggested that the frequency factor principally contributed to the increase in the diffusion coefficient.[3]

In order to confirm further the importance of the role of trimethylsiloxyl groups in enhancing the diffusion coefficient in permeation, polystyrenes having various numbers of trimethylsiloxyl groups in isomeric p-substituents were synthesized and the oxygen permeation behavior through the polymer film was studied.

EXPERIMENTAL

General

Column chromatography was performed on silica gel using n-hexane as the eluent. ^{1}H-NMR spectra were recorded on a JEOL 60 MHz spectrometer in CCl_4, and the chemical shifts are given as δ values in ppm from TMS as an internal standard. Spin-relaxation behavior of the polymers in the solid state was studied on a BRUKER 90 MHz spectrometer model CXP-90 at 90.13 MHz at 30°C and 65°C for proton, and on a JEOL 270 MHz CP MAS spectrometer model PX-270 at 25°C for carbon. Spin-lattice relaxation times (T_1) were determined by 180°-t-90° pulse method. The

linewidth of a signal at half-height was esti-mated from the Fourier-transformed spec-trum. Glass transition temperatures (T_g) of polymers were estimated by a SEIKO instru-ments DSC, model DSC 100 at heating rate 100 K min^{-1}. Gas permeation behavior was estimated for supplied air by measuring the amount of gas permeated by gas chromatog-raphy, maintaining the upstream pressure at 1 atm and the downstream as zero at 25°C on a Yanaco gas permeability measuring system model GTR-20. The detailed method of the measurement and treatment of the data are reported in ref 1 and 3.

Synthesis of Monomers

New monomers in this study were synthe-sized according to Scheme 1.

3-Chloroheptamethyltrisiloxane. Bis(trimeth-ylsiloxy)methylsilane (8.50 g, 38.2 mmol) was chlorinated with dry chlorine gas in hexane under dark at 0°C.[8] The product was isolated by distillation after removal of the solvent. 60% Yield. bp 39°C (7 mmHg). Chemical
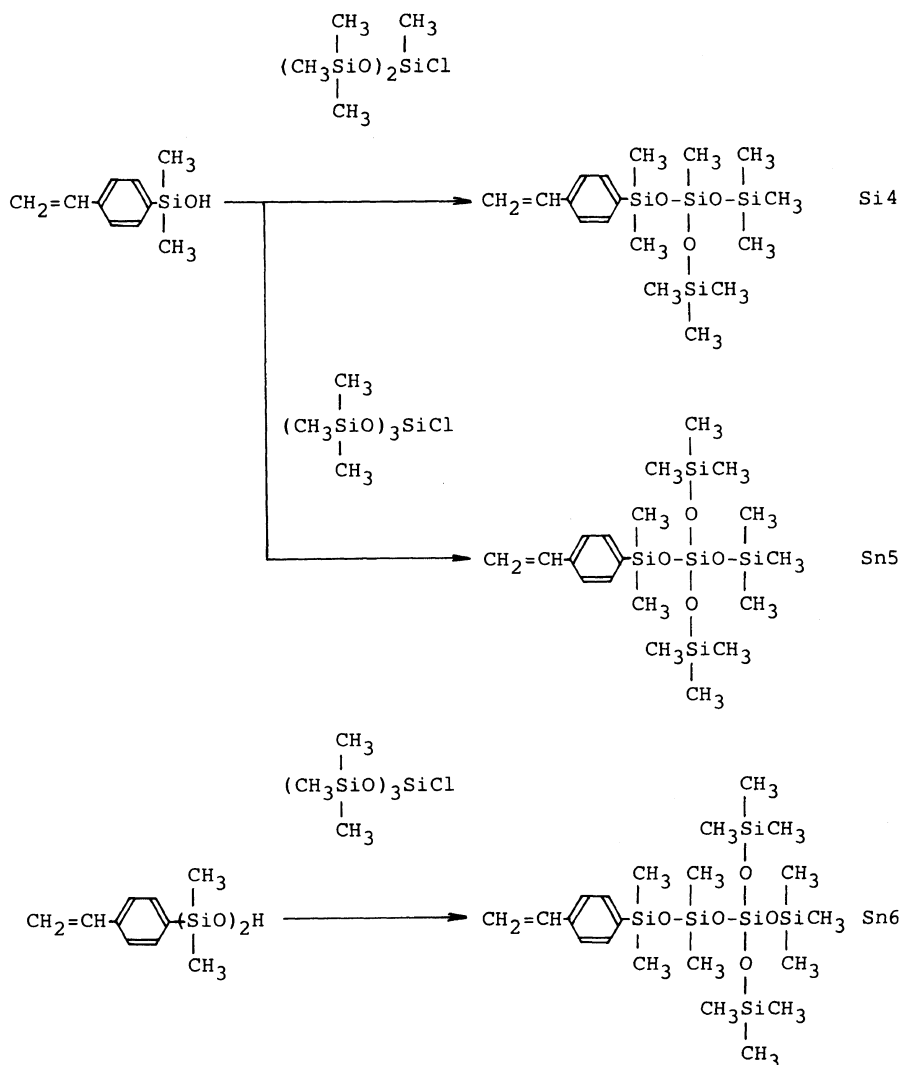

Scheme 1. Synthesis and structure of the new monomers.

shifts: 0.21 (s, 18H, OSiC$\underline{H}_3$), 0.41 (s, 3H, ClSiC$\underline{H}_3$).

p-(3-Trimethylsiloxyhexamethyltrisiloxan-1-yl)-styrene(Si4). *p*-Vinylphenyldimethylsilanol (1.37 g, 7.68 mmol)[6] was treated with 3-chloroheptamethyltrisiloxane (2.00 g, 7.78 mmol) in the presence of pyridine (0.67 g, 8.47 mmol) in diethyl ether (70 ml) at room temperature. The product was isolated on column chromatography. 83% Yield. Chemical shifts: 0.03 (s, 3H, C$\underline{H}_3$SiO), 0.10 (s, 18H, (C$\underline{H}_3$)$_3$Si), 0.36 (s, 6H, $\langle\underline{}\rangle$-Si(C$\underline{H}_3$)$_2$), 5.15 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 10.0$ Hz, $\underline{H}$), 5.64 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 18.0$ Hz, $\underline{H}$), 6.62 (q, 1H, $J_1 = 10.0$ Hz, $J_2 = 18.0$ Hz, =< $\overset{\underline{H}}{}$), 7.21 (d, 2H, $J = 8.0$ Hz, aromatic protons), 7.39 (d, 2H, $J = 8.0$ Hz, aromatic protons).

Tris(trimethylsiloxy)silane. To trichlorosilane (3.11 g, 23.0 mmol) in diethyl ether (10 ml) was added dropwise lithium trimethylsilanolate (7.17 g, 74.6 mmol) in tetrahydrofuran (50 ml) at dry ice temperature. The reaction mixture was allowed to warm to room temperature and further reacted for 20 h at the temperature. The product was isolated by distillation. 67% Yield. bp 55°C (11 mmHg). Chemical shifts: 0.10 (s, 27H, C$\underline{H}_3$), 4.20 (s, 1H, Si$\underline{H}$).

Tris(trimethylsiloxy)chlorosilane. Tris(trime-thylsiloxy)silane (3.00 g, 9.06 mmol) was chlorinated with dry chlorine gas.[8] 69% Yield. bp 50°C (3 mmHg). Chemical shift: 0.16 (s, 27H, C$\underline{H}_3$).

p-[3,3-Bis(trimethylsiloxy)pentamethyltrisiloxan-1-yl]styrene (*Sn5*). Tris(trimethylsiloxy)chlorosilane (3.57 g, 10.8 mmol) was reacted with *p*-vinylphenyldimethylsilanol (1.94 g, 10.9 mmol) in the presence of pyridine (0.98 g, 12.0 mmol) as a base at room temperature in diethyl ether (70 ml). The product was isolated on column chromatography. 67% Yield. Chemical shifts: 0.09 (s, 27H, (C$\underline{H}_3$)$_3$Si), 0.35 (s, 6H, $\langle\underline{}\rangle$-Si(C$\underline{H}_3$)$_2$), 5.19 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 10.0$ Hz, $\underline{H}$), 5.67 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 18.0$ Hz, $\underline{H}$), 6.66 (q, 1H, $J_1 =$

10.0 Hz, $J_2 = 18.0$ Hz, =< $\overset{\underline{H}}{}$), 7.25 (d, 2H, $J = 8.0$ Hz, aromtic protons), 7.45 (d, 2H, $J = 8.0$ Hz, aromatic protons).

p-(3-Chlorotectramethyldisiloxan-1-yl)styrene. 1,3-Dichlorotetramethyldisiloxane (25 g, 123 mmol) was selectively mono arylated by adding drop-wise *p*-vinylphenylmagnesium chloride prepared from *p*-chlorostyrene (8.5 g, 61.3 mmol) and magnesium (3.0 g, 120 mmol). 49.6% Yield. bp 86—88 (0.4 mmHg). Chemical shifts: 0.45 (s, 12H, C$\underline{H}_3$), 5.23 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 10.0$ Hz, $\underline{H}$), 5.72 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 18.0$ Hz, $\underline{H}$), 6.68 (q, 1H, $J_1 = 10.0$ Hz, $J_2 = 18.0$ Hz, =< $\overset{\underline{H}}{}$), 7.31 (d, 2H, $J = 8.0$ Hz, aromatic protons), 7.48 (d, 2H, $J = 8.0$ Hz, aromatic protons).

p-[5,5-Bis(trimethylsiloxy)heptamethyltetrasiloxan-1-yl]styrene (*Sn6*). *p*-(3-Chlorotetramethyldisiloxan-1-yl)styrene (2 g, 7.38 mmol) was hydrolyzed to silanol similarly to the synthesis of *p*-vinylphenyldimethylsilanol. The silanol was isolated by extraction with ether and evaporation of the solvent after drying with magnesium sulfate, and immediately reacted with tris(trimethylsiloxy)chlorosilane (2.81 g, 8.49 mmol) in the presence of pyridine (0.74 g, 9.35 mmol). The product was isolated on column chromatography. 36.7% Yield. Chemical shifts: 0.07 (s, 6H, OSi(C$\underline{H}_3$)$_2$), 0.10 (s, 27H, OSi(C$\underline{H}_3$)$_3$, 0.34 (s, 6H, $\langle\underline{}\rangle$-Si(C$\underline{H}_3$)$_2$), 5.18 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 10.0$ Hz, $\underline{H}$), 5.66 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 18.0$ Hz, $\underline{H}$), 6.67 (q, 1H, $J_1 = 10.0$ Hz, $J_2 = 18.0$ Hz, =< $\overset{\underline{H}}{}$), 7.24 (d, 2H, $J = 8.0$ Hz, aromatic protons), 7.45 (d, 2H, $J = 8.0$ Hz, aromatic protons).

Polymerization

Polymerizations were carried out typically using 0.05 mol% AIBN as the initiator in THF for 20—300 h at 60°C. Polymers were isolated by precipitating into methanol and purified by reprecipitation.

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Preparation of Film

Polymer films were prepared by casting a 5% polymer solution in tetrahydrofuran on a clean glass surface and evaporating the solvent off. The formed films were detached from the glass surface by immersing in water. The films for gas permeation measurement were conditioned at 40°C for 24 h.

RESULTS AND DISCUSSION

Monomers can be synthesized without any special difficulty. The abbreviations of the name and the structure of other monomers used in this study are shown in Figure 1. The results of the polymerization are shown in Table I.

p-Oligodimethylsiloxanylstyrene monomers showed reactivity as styrene monomer in polymerization and copolymerization. Copolymers having almost the same composition with feed were obtained. The appearance of the polymers seems to depend on the content and structure of the siloxane side chains in the polymer. The more siloxane components in the polymer tend to lose self-supporting film forming ability (No. 1, 2, 7: 3—8 in Table I) tolerable for gas permeation measurement. A branched structure of a side chain is better than a straight chain structure in maintaining self-support of the polymers (No. 3, 9).

Appearance and self-support seem strongly to depend not only on the molecular weight of the polymer but also on glass transition temperature as shown in Table II.

Introduction of flexible siloxane linkages in side chains will reduce the friction between polymer backbones in their motion and result in lower glass transition temperatures of the polymers with linear oligosiloxanyl side chains. Not only the number of siloxane linkages (No. 1, 2, 7: 9, 10: 12, 13, 15) but also the type of linkage, namely branching has significant effects on the glass transition temperature of the polymer. Branchig in the substituent makes the glass transition temper-
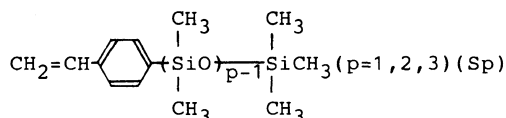
$p = 1$: *p*-Trimethylsilylstyrene (S1)
$p = 2$: *p*-Pentamethyldisiloxanylstyrene (S2)
$p = 3$: *p*-Heptamethyltrisiloxan-1-ylstyrene (S3)
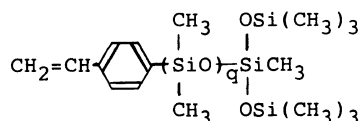
$q = 0$: *p*-Heptamethyltrisiloxan-3-ylstyrene (Si3)
$q = 1$: *p*-(3-Trimethylsiloxyhexamethyltrisiloxan-1-yl)styrene (Si4)
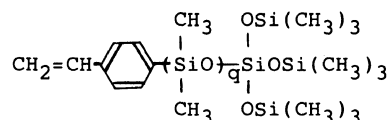
$q = 0$: *p*-Tris(trimethylsiloxy)silylstyrene (St4)
$q = 1$: *p*-[3,3-Bis(trimethylsiloxy)pentamethyltrisiloxan-1-yl]styrene (Sn5)
$q = 2$: *p*-[5,5-Bis(trimethylsiloxy)heptamethyltetrasiloxan-1-yl]styrene (Sn6)

Figure 1. The structure and the abbreviation of the names of monomers in this study.

Table I. Polymerization of *p*-oligodimethylsiloxanylstyrene

| No. | Feed | | | Yield | Composition | GPC[b] | | | Film formation |
	M1	M2 , wt%		%	M2, wt%[a]	$\bar{M}_w{}^b$	$\bar{M}_n{}^b$	$\dfrac{\bar{M}_w}{\bar{M}_n}$	
1	S1	—		96	0	21.7	10.3	2.11	Good
2	S2	St	0	90	0	23.8	8.6	2.78	Good
3			20.0	65	21	43.2	18.8	2.30	Good
4			40.0	57	40	46.5	21.5	2.16	Good
5			60.0	59	60	37.1	17.0	2.18	Good
6			80.0	53	80	40.3	20.1	2.00	Good
7	S3	St	0	71	0	78.1	36.5	2.14	Too soft
8			21.5	66	24	53.3	27.6	1.93	Too soft
9	Si3	—		74	0	52.5	20.2	2.50	Good
10	Si4	St	0	66	0	26.8	15.5	1.73	Too soft
11			20.0	62	19	23.5	14.4	1.64	Soft
12	St4	—		67	0	14.0	4.3	3.30	Brittle
13	Sn5	St	0	91	0	81.0	42.1	1.92	Brittle
14			20.0	54	19	22.5	13.0	1.73	Good
15	Sn6	St	0	86	0	15.4	10.9	1.41	Too soft
16			20.0	43	21	54.7	28.7	1.91	Soft

[a] Determined by ^{1}H NMR.
[b] Estimated correlating to standard polystyrene. $\bar{M}_w$ and $\bar{M}_n$ are given in $\times 10^{-4}$.

Table II. Glass transition temperature of polymers

No.	Polymer		T_g/K
1	PolyS1		409
2	PolyS2		309
3	Poly(S2-*co*-St)	(80—20)	314
4		(60—40)	333
5		(40—60)	349
6		(20—80)	362
7	PolyS3		263
9	PolySi3		325
10	PolySi4		264
11	Poly(Si4-*co*-St) (80—20)		284
12	PolySt4		387
13	PolySn5		314
14	Poly(Sn5-*co*-St) (80—20)		323
15	PolySn6		256
16	Poly(Sn6-*co*-St) (80—20)		289

ature of the polymer higher by increasing the friction between polymer back bones compared with the linear side chains (No. 7, 9: 10, 12).

It is reported that the collapse temperature of signals in NMR in the solid state roughly correlates to the glass transition temperature of the polymer.[9] In order to discuss the glass transition temperature of polymers, it will be essential to study the relaxation behavior of polymers in detail.

Only one glass transition temperature was found for each of the copolymers of styrene (M_2) with S2, Si4, Sn5, and Sn6 (M_1) (No. 3—6, 11, 14, 16) which indicates that no phase-separation is occurring in these copolymers.

Oxygen permeation behavior of the polymers is shown in Table III.

The permeability coefficients of poly(*p*-oligodimethylsiloxanylstyrene)s increased with the number of trimethylsiloxyl groups in the substituent (No. 2, 9, 13). The permeability coefficients of polySi3 and Sn5, which have two and three trimethylsiloxyl groups are 71 and 110 ($\times 10^{-10}$ cm^3 (STP)·cm·cm^{-2}· s^{-1}·cmHg^{-1}), respectively. The values are about 1.8 and 2.8 times higher compared with that of polyS2. The higher permeability coefficients of these polymers seem to be brought about through increase in the dif-

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Table III. Oxygen permeation behavior through membrane of the polymers

No.	Polymer	$P_{O_2}{}^a$	P_{O_2}/P_{N_2}	$D_{O_2}{}^b$	$D_{N_2}{}^b$	$S_{O_2}{}^c$	$S_{N_2}{}^c$
1	PolyS1	14	3.4	—	—	—	—
2	PolyS2	40	3.0	18.0	11	2.2	1.3
3	Poly(S2-co-St)	20	3.4	7.2	5.0	2.7	1.2
4		12	3.4	4.5	3.2	2.7	1.1
5		3.9	3.7	1.9	1.0	2.0	1.0
6		2.6	4.4	1.3	0.57	2.0	1.1
9	PolySi3	71	2.8	32	24	2.3	1.1
11	Poly(Si4-co-St)	36	2.8	16	11	2.1	1.1
13	PolySn5	110	2.6	49	40	2.2	1.1
14	Poly(Sn5-co-St)	50	2.8	21	15	2.4	1.1
16	Poly(Sn6-co-St)	64	2.8	27	23	2.4	1.0
17	PolySt	1.2	5.5	0.56	0.2	2.2	1.1

[a] In $10^{-10} \, cm^3$ (STP)$\cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$ unit.
[b] In $10^{-7} \, cm^2 \, s^{-1}$ unit.
[c] In $10^{-3} \, cm^3$ (STP)$\cdot cm^{-3} \cdot cmHg^{-1}$ unit.

fusion coefficient by increase in the numbers of flexible trimethylsiloxyl groups in these polymers. Change in the solubility coefficient was small. This trend is consistent with the discussion in the previous papers[3–7] on polymers having p-substituents containing siloxane linkages.

The permeability coefficients of poly(S2-co-St)s increased with the decreasing concentration of St in the copolymers (No. 2—6, 17), a fact which implies the importance of disiloxane linkages in permeation. Since copolymers of S2, Si4, Sn5, and Sn6 (M_1) with styrene (M_2) showed only one T_g, it is not unreasonable to discuss the permeability of these copolymers, comparing with the results on homopolymers. The permeability coefficient of the copolymer containing 80 wt% S2 and 20 wt% styrene decreased to 20 ($\times 10^{-10} \, cm^3$ (STP)$\cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$ from 40 in the same unit which is the permeability coefficient of the homopolymer polyS2 (No. 2). The value is about 50% that of the homopolymer. The permeability coefficient of polySn5 is 110 in the same unit which is about 2.8 times that of homopolymer polyS2. The values are 36, 50, and 64, respectively, for the copolymers of p-oligodimethylsiloxanylstyrene with styrene containing 80% Si4, Sn5, and Sn6 (No. 11, 14,
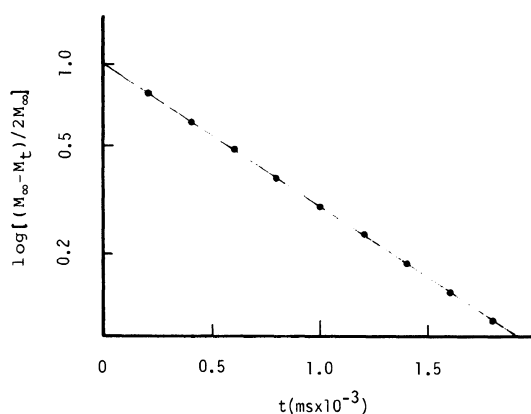

Figure 2. A typical decay of the magnetization of polySn5 at 30°C as a function of time in T_1 determination.

16). The value of the copolymer of Sn5 with St is about half that of the homopolymer. Although the P_{O_2} of pure polySi4 and polySn6 could not be estimated, it will be reasonable to presume that polySi4 and polySn6 have higher P_{O_2} compared with polyS2 because the permeability coefficients of the copolymers of Si4 and Sn6 with St have higher P_{O_2} than that of S2 with the same composition. The higher permeability coefficient seems to be brought about by the existence of more trimethylsiloxyl groups in these polymers compared with

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polyS2. The change in the solubility coefficient was small. The diffusion coefficients increased with the number of trimethylsiloxyl groups.

This is further supported by the results of the spin-relaxation study of the polymers in the solid state. The change in magnetization in $180°$-t-$90°$ pulse sequence in solid state ^{1}H NMR of polySn5 is shown in Figure 2.

$$\log[(M_\infty - M_t)/2M_\infty] = -t/2.303T_1 \qquad (2)$$

where M_∞ and M_t are equilibrium magnetization and magnetization at time t, respectively at a given static magnetic field.

All methyl protons in the side chain obeyed a single exponential decay, and from the slope, single spin-lattice relaxation time T_1 was determined. This is an important fact indicating that the spin-lattice relaxation of each methyl proton is averaged by the spin diffusion and that the relaxation of these polymers is mainly controlled by the relaxation of methyl groups in the side chains.

Only one T_1 was observed for each *p*-oligodimethylsiloxanyl substituted polystyrene. Thus, the relaxation of these polymers is also controlled by the relaxation of side chains. The results of relaxation behavior are shown in Table IV.

Except for that of polySi3, T_1s are longer at higher temperature. This is characteristic for glassy polymers below and near T_g.[9] At higher temperature, polymer segments including side

chains become more mobile and lose thermal contact with the lattice (shorter correlation time) resulting in slower relaxation, namely, a longer relaxation time. Since all polymers have different glass transition temperatures, a comparison of T_1s of different polymers at the same temperature does not have significant meaning. However, limited discussion might be made on polymers of similar structure. The relatively long spin-lattice relaxation time T_1 compared with spin-spin relaxation time T_2 reflects a very local mode of motion of the side chain like rotation of methyl group. T_1 of polyS1 (695 ms) is shorter than that of polyS2 (892 ms) at 30°C. This is also shown in ^{13}C NMR spectra. Similarly to ^{1}H NMR, only one T_1 was observed for methyl groups of polyS2 also in ^{13}C NMR. The T_1 of polyS2 (3.90 s) is longer than that of polyS1 (3.28 s). These facts might imply that the rotational motion of pentamethyldisiloxanyl groups in polyS2 is faster than that of trimethylsilyl groups in polyS1.

Discussion about the local motion of a side chain as a whole, which may much more closely be related to the gas permeability and glass transition temperature of the polymer, can be made more adequately by consideration of the linewidth of the methyl signal at half-height which is reciprocally proportional to T_2^*, the measured spin-spin relaxation time.

$$\Delta v = 1/\pi T_2^* \qquad (3)$$

T_2^* reflects slow segmental motion of 4—6 bonds. The linewidth at half-height seems to well reflect the structural features of the siloxane side chain and its bulkiness. By introduction of siloxane linkage (polyS1 polyS2), the linewidth at half-height became narrow. This suggests the higher mobility of the pentamethyldisiloxanyl side chains than the trimethylsilyl side chains. PolyS3, which has trisiloxane linkages, shows T_g at 263 K and has the narrowest linewidth at half-height (2.15 kHz) almost comparable to that of rubbery polybutadiene (0.72 kHz).

Table IV. Relaxation characteristics of polymers

No.	Polymer	Δv(kHz)	T_1/ms	
		303/K	303/K	338/K
17	PolySt	31.35	—	—
1	PolyS1	13.23	695	916
2	PolyS2	9.97	892	890
7	PolyS3	2.15	602	678
9	PolySi3	8.27	1131	1026
10	PolySi4	2.33	643	661
12	PolySt4	5.52	896	1011
13	PolySn5	5.21	837	934
15	PolySn6	2.76	733	866

In polyS3, polySi4, and polySn5 series, the linewidth at half-height becomes wider in this order, which reflects the slower motion of the side chains by the introduction of bulkier substituents at the 3-position of the trisiloxane linkage [CH_3; $CH_3 \rightarrow CH_3$; $OSi(CH_3)_3 \rightarrow OSi(CH_3)_3$; $OSi(CH_3)_3$]. High T_g (314 K) of plySn5 may have made the measured linewidth of the polymer wider at 30°C than expected.

In polySt4, polySn5, and polySn6 series, the bulky tris(trimethylsiloxy)silyl groups are linked to backbone phenyl groups with or without spacers. In polySn6, tris(trimethyl-siloxy)silyl group is attached to the phenyl group with tetramethyldisiloxane spacer. While in polySt4 and polySn5, the tris(tri-methylsiloxy)silyl groups are directly attach-ed to the phenyl groups, or with dimethyl-siloxane spacers. The order of the narrowness of the linewidth at half-height reflects the mobility of side chains of these polymers. The side chains of polySn6, namely 5,5-bis-(trimethylsiloxy)heptamethyltetrasiloxanyl groups are the most mobile. Tris(trimethyl-siloxy)silyl groups of polySt4 are the least mobile, and 3,3-bis(trimethylsiloxy)penta-methyltrisiloxanyl side chains of polySn5 are intermediate. The faster motion can be considered to be given by the existence of the siloxane linkage. This discussion does not conflict with the change in T_g of the poly-mers.

The faster motion of the side chain results in a higher diffusion coefficient of a gas in per-meation. As reported earlier,[3] free volume is also an important factor to control perme-ability. The roles of trimethylsiloxyl groups in the side chains are considered to give large free volume and good mobility to the side chains. Correlation might be found between the per-meability coefficient, and T_2^* and free volume of the polymer. Further detailed research is needed.

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