Review

Control of Molecular Weight, Stereochemistry and Higher Order Structure of Siloxane-containing Polymers and Their Functional Design

Yusuke Kawakami*, Yuning Li, Yang Liu, Makoto Seino, Chitsakon Pakjamsai,
Motoi Oishi, Yeong Hee Cho, and Ichiro Imae

Graduate School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST) 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

Abstract: We describe the precision synthesis schemes of siloxane-containing polymers, i.e., the control of their molecular weight, stereoregularity, and higher-order structures. First, we found a new catalytic dehydrocoupling reaction of water with bis(dimethylsilyl)benzene to give poly(phenylene-disiloxane). Together with this reaction, we applied hetero-condensations to the synthesis of thermally stable poly(arylene-siloxane)s. The dehydrocoupling reaction was applied to the synthesis of syndiotactic poly(methylphenylsiloxane) and poly(silsesquioxane)s, which we also prepared by hydrolysis and deaminative condensation reactions. We discuss the tendency for loop formation to occur in the synthesis of poly(silsesquioxane) by hydrolysis, and provide comments on the design of functionality of the polymers produced. By taking advantage of the low energy barrier to rotation in the silicon-oxygen bond, we designed selective oxygen-permeable membrane materials and liquid crystalline materials. The low surface free energy of siloxane-containing systems allows surface modification of a blend film and the design of holographic grating materials.

Keywords: siloxane-containing polymers, precision synthesis.

Introduction

The importance of controlling the molecular weight, stereoregulality, and higher order structure of the polymers has become well-recognized as necessary for developing the most desirable properties of polymers. This is also true for silicon-containing polymers. Although silicon compounds are often used as protective or activating groups in organic and polymer syntheses,[1,2] the silicon moiety is not contained in the resulting products in many cases. If the silicon components remain in the products, new characteristic function will appear as silicon-containing polymers.

Silicon-containing polymers,[3] such as poly(siloxane),[4] poly(carbosilane),[5] and poly(silylene)[6] have practical importance in the applications for rubber, gas separation and pervaporation membrane, precursor of silicon carbide, photo- and electroactive polymers, but they have been insufficiently studied in relation to their chemical structure, such as molecular weight, stereoregularity, and higher order structure. If the reactions for the polymerizations of silicon compounds are controlled, the resulting polymers are expected

to exhibit unique properties reflecting the controlled structure of the polymers. In this review, application of dehydrocoupling reaction to the synthesis of poly(phenylene-disiloxane) is described first, and the application of the reaction together with hetero-coupling condensation reactions are described to synthesize variety of the controlled structure of siloxane-containing systems. Finally, functional designs of siloxane-containing polymers based on dynamic and surface active properties are described.

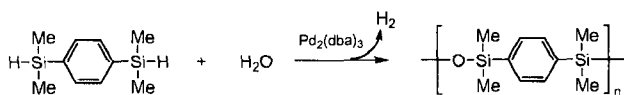## Polymers Containing Silphenylene Moiety *via* Catalytic Dehydrocoupling Polymerization

Silarylene-containing polymers, which exhibit a wide range of physical properties depending on their composition and structure, have received considerable academic and industrial interests over the past 40 years.[7] One of the prominent properties of silarylene-siloxane polymers is their excellent thermal stability. Most of the methods employed for the synthesis of silarylene-siloxane polymers up till now are the self-polycondensation of arylenedisilanols or the copolycondensation of arylenedisilanols with other bifunctional compounds.[8] However, the preparation of arylenedisilanols requires many tedious procedures, and no industrially fea-

sible synthetic pathway to the arylenedisilanols has yet been found. This obstacle still stands in the way to the commercialization of these useful polymers although they were first prepared in laboratory as early as in 1960s.

We found the construction of Si-O linkage by catalytic dehydrocoupling reaction of organosilanes with water or labile hydrogen containing compounds as shown in Scheme I.[9] It was found that the easily accessible 1,4-bis(dimethylsilyl) benzene (p-BSB) could react with water in the presence of a catalytic amount of transition metal (Pd, Pt, Rh, etc) compounds at room temperature to afford high molecular weight poly[(oxydimethylsilylene)(1,4-phenylene)(dimethylsilylene)] with evolution of H_2 as the only by-product. We extended the reaction to the polymerization of p-BSB with other labile-hydrogen-containing compounds, such as ammonia, disilanol, aliphatic and aromatic diols, and dicarboxylic acids to prepare a series of silphenylene-containing polymers, including polycarbosilazane, polycarbosiloxanes, poly(silyl ether)s, and poly(silyl ester)s. The Si-O (Si-O-Si or Si-O-C) and Si-N linkages could modify the chemical and physical properties of polymers and render some useful functionality, such as excellent low temperature properties (low T_gs), chemo- and biological degradability. $Pd_2(dba)_3$ is an excellent catalyst for the polymerization of p-BSB with water to give a high molecular weight polymer (M_n = 16,300) at room temperature in a short time (2 h), showing a high catalytic activity for both the hydrolysis of Si-H and the Si-O-Si bond formation steps. Several attempts made by other research groups to prepare polysilazanes by the dehydrocoupling reaction of organosilanes with ammonia or amines in the presence of $Ru_3(CO)_{12}$, $Rh_6(CO)_{16}$, or dimethyltitanocene (Cp_2TiMe_2) resulted in the formation of rather low molecular weight products (M_n < 3,000).[10] In our case, when an ammonia solution in 1,4-dioxane (0.5 M) was used to polymerize with p-BSB in the presence of $Pd_2(dba)_3$ at room temperature, a polymer with a relatively high molecular weight (M_n = 7,100) in 76.1% yield (confirmed by the size-exclusion chromatography (SEC) curve of the reaction mixture) was formed after reacting for 72 h.

have a potential application for controlled drug release systems. These polymers were only successfully approached by transsilylation reactions between α,ω-bis(trimethylsilyl) esters and α,ω-dichlorosilanes. The cross-dehydrocoupling polymerization of p-BSB with adipic acid could afford a poly (silyl ester) (M_n = 4,400) under a mild condition (50 °C, 20 h), demonstrating that this is an efficient alternative route to poly (silyl ester)s. An aromatic dicarboxylic acid, terephthalic acid, was also used to react with p-BSB under the same conditions.

Differential scanning calorimetry (DSC) analyses of polymers indicate that as the constitutional unit (X group) between silphenylenes was varied from -O- to $-O(CH_2)_2O-$ and $-O(CH_2)_3O-$, the glass transition temperature (T_g) decreased markedly from -19.1 to -38.0 and -43.7 °C, respectively. On the other hand, introducing $-OSi(Ph)_2O-$ and $-O(o-C_6H_4)O-$ groups increased the T_g to -3.3 and 2.7 °C, respectively, indicating that incorporating aromatic groups in both side chain or main chain increased the barrier of the longitudinal motion of the polymer chains. While polycarbosilazane with X = NH and poly(silyl ester) with X = -OCO $(CH_2)_4COO-$ showed similar or a little higher T_gs (-10.5 and -14.2 °C, respectively). In addition to a glass transition temperature, polymers from p-BSB with H_2O and NH_3 also exhibited a melting point T_m (123.5 and 92.5 °C) and a crystallization temperature T_c (34.0 and 37.6 °C). A well-developed spherulite texture was observed for polymer (X = -O-), and nematic schlieren structure for polymer (X = -NH-) (Figure 1).

The influence of the structure of X groups on the thermal stability of polymers was studied by thermogravimetric analysis (TGA) and the results were represented in Figure 2. Polymer having X=-O-, a well-known thermally stable polymer, showed an on-set decomposition temperature at 475 °C and a residue of 28.3% at 600 °C (at a heating rate of 5 °C min^{-1} in nitrogen). As the X groups were changed to -NH- and $-OSi(Ph)_2O-$, no obvious changes were observed in their on-set decomposition temperatures (T_d = 480 °C (X =-NH-) and 469 °C (X = $-OSi(Ph)_2O-$), respectively),

Scheme I

The $Pd_2(dba)_3$ was not a proper catalyst for the polymerization of p-BSB with aliphatic diols like ethylene glycol and 1,3-propanediol, and rather low molecular weight poly (silylether)s were obtained (M_n = 1,000~3,000). On the other hand, 10% Pd/C was an efficient catalyst to afford higher molecular weight (M_n = 9,400 and 12,400, respectively) at an elevated temperature (50 °C) in 3 h. Poly(silyl ester)s containing -Si-OCO- linkages, as a new class of degradable polymers with variable and predictable degradation behavior,
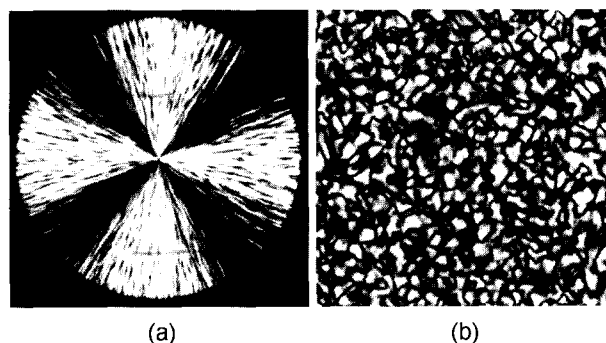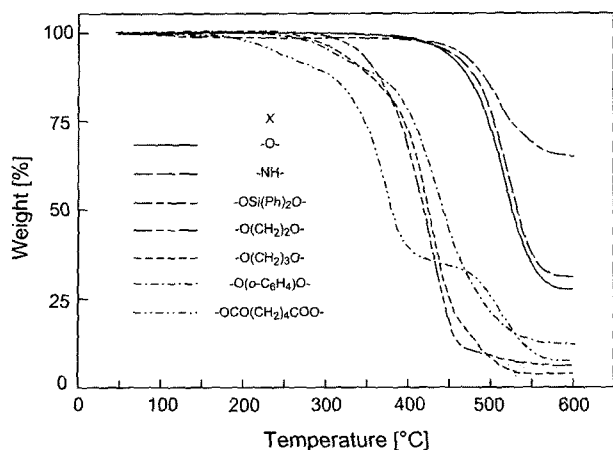
(a)   (b)

Figure 1. Crystalline textures of (a) the polymer from p-BSB with H_2O (X=-O-), and (b) the polymer from p-BSB with NH_3 (X=-NH-).

Figure 2. TGA curves of polymers at a heating rate of 5 °C min⁻¹ under nitrogen (50 mL min⁻¹).

while the residual weight of the latter polymer was remarkably increased (64.9%) comparing to that of the polymer having X =-O-. On the other hand, incorporating -O(CH₂)₂O-, -O(CH₂)₃O-, -O(o-C₆H₄)O-, and -OCO(CH₂)₄COO- groups into main chain greatly decreased the thermal stability of these polymers.

However, when application of these polymers is considered as highly temperature-resistant insulating materials in demand in computer chip fabrication technology, the materials require not only high thermal stability but also high mechanical strength and low crystallinity.

At first, copolymers from *p*- and *m*-BSB and water in various isomeric ratios were prepared (Scheme II).[11]

It was found that there is a tendency for the molecular weight of the polymer to become small as the feed ratio of *m*-BSB increased, because of the formation of cyclic oligomers.[12]

¹H NMR spectra of the polymers from *p*-BSB or *m*-BSB and water showed simple signals reflecting their regular structures, while those of the polymer from the mixture of *p*- and *m*-BSB with water showed splitting signals. To estimate the reactivity of each isomer, it is necessary to estimate the sequence regularity of the polymer. The split methyl proton signals seem to be overlapped, and it is difficult to estimate the definite sequence regularity of the polymer. Contrary to this, signals of aromatic protons split and can be reasonably considered to reflect the triad regularity of the monomer sequence in the polymer. The relative intensity of the signals changed linearly with the change of the feed ratio. By considering the amounts of monomers consumed
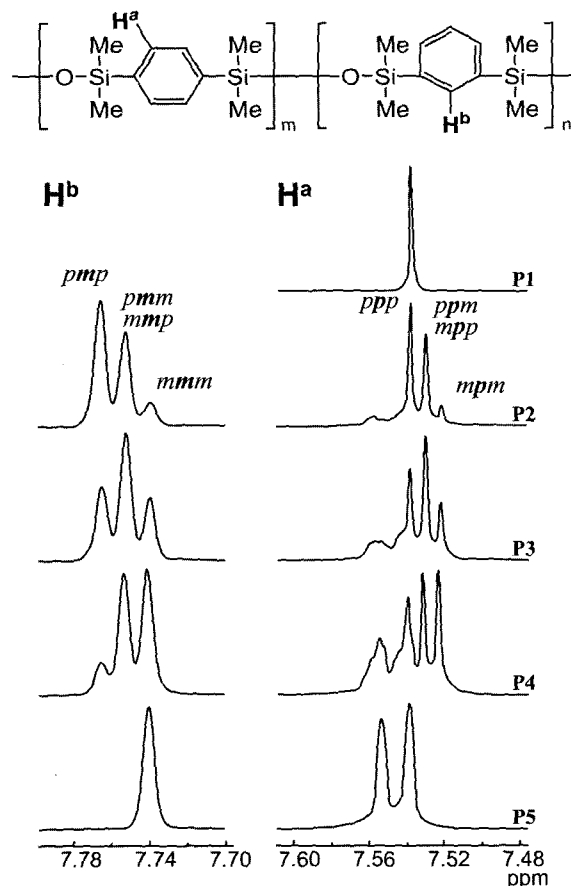
Figure 3. Influence of triad regularity on NMR spectra of polymers.

in oligomer formation, the real probability of the triad can be calculated from the polymer composition, which coincided well with the measured values. This result strongly supports the equal reactivity of *p*- and *m*-BSB in the dehydrocoupling reaction with water.

Thermal properties of these polymers were investigated by DSC and TGA. With the increase of *m*-BSB unit, the T_g decreased from -23 to -49 °C. Crystallinity observed in the polymer obtained from *p*-BSB and water was removed by incorporating a small amount of *m*-BSB unit. T_d was not changed so much by the difference of the isomeric chemical structure.

We also investigated the further modification of the polymer structure by the introduction of rigid aromatic moieties. Among them, the polymer obtained from the *cardo*-type 9,9'-bis[4-(dimethylsilyl)phenyl]fluorene with water (**PBSF**)
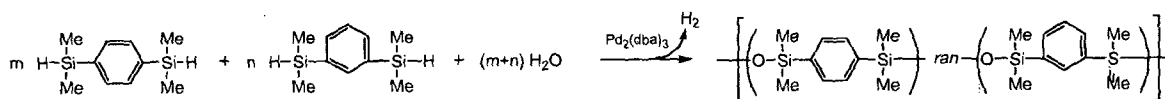
Scheme II

Table I. Dehydrocoupling Polymerization of Isomeric BSB[a]

| Isomer Ratio[b]		Yield [%][d]	M_n[e]	M_w/M_n[e]	T_g	T_c	T_m	T_d
Feed	Composition[c]							
100/0	100/0	87	34,800	1.66	-23	15,95	127	505
70/30	74/26	76	30,400	1.65	-33	-	-	505
50/50	57/43	72	26,800	1.66	-38	-	-	506
30/70	38/62	62	24,200	1.68	-44	-	-	505
0/100	0/100	50	16,800	1.72	-49	-	-	505

[a]reaction conditions: 10 mmol of isometric **BSB** and 10 mmol of water in 4 mL of THF; 25 μmol of metal; 3 h in room temperature. [b][p-**BSB**/m-**BSB**]. [c]estimated by ^{1}H NMR. [d]after 3 reprecipitations in methanol. [e]estimated by SEC with polystyrene standard.

showed the highest thermal stability, and it showed much superior thermal and mechanical properties to commonly used polyimide and epoxy resins.[13]

For further improvement of thermal properties of the polymer, some functional groups such as vinyl, hydride, hydroxy, and epoxy groups, instead of methyl group on silylene unit were introduced into the polymer structure.[14] Polycondensation of 1,4-bis(N,N-dimethylaminomethylvinyl-silyl)benzene (**VSB**) or 1,4-(N,N-dimethylaminomethylsilyl) benzene (**HSB**) with 1,4-bis(dimethylhydroxysilyl)benzene (**HOSB**) gave the alternating polymers (Scheme III). From the ^{1}H, ^{13}C, and ^{29}Si NMR data, these polymers have exactly alternating structures. When the oligomer having hydroxy groups on its terminal (**oHOSB**, M_n = 2,800, M_w/M_n = 1.03) which was prepared by the dehydrogenative coupling of p-**BSB** and water in the presence of palladium catalyst was used instead of **HOSB**, the polymer which has **BSB** unit as a main component and vinyl or hydride group in the rest of the units was also obtained.

Vinyl and hydride groups can be converted to hydroxy
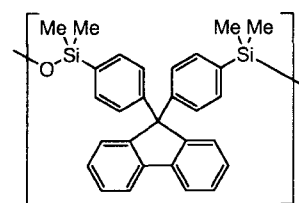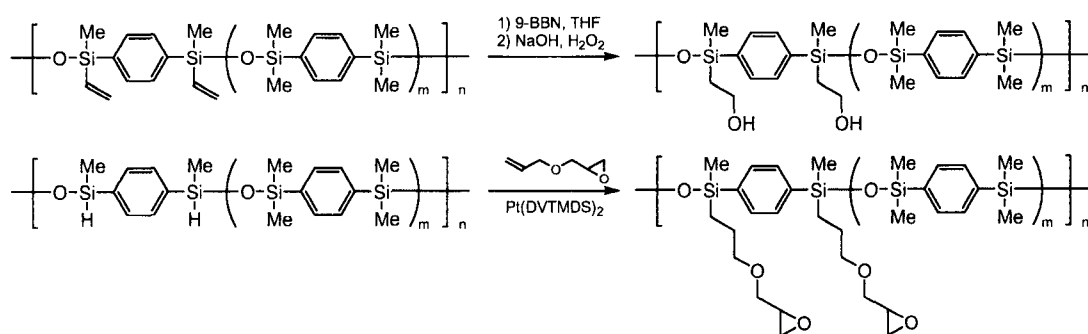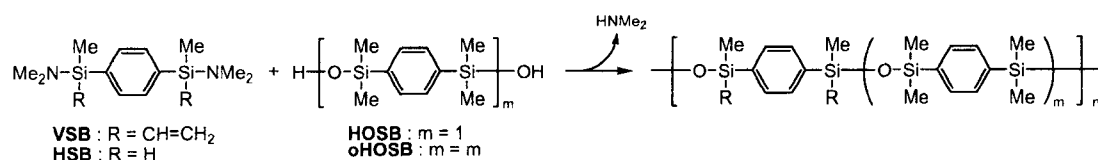
Figure 4. Silarylene-siloxane polymer having *cardo*-type arylene unit (**PBSF**).

and epoxy groups by the hydroboration using 9-BBN (9-bora-[3.3.1]-bicyclononane) and following oxidation reaction of vinyl group and hydrosilylation of hydride group with allyl glycidyl ether by platinum catalyst, respectively (Scheme IV).

Among them, it was found that the polymer prepared from **VSB** and **HOSB** showed the highest thermal stability ($T_{d,onset}$ = 498 °C, $T_{50\% weight}$ = >800 °C, residual weight at 800 °C = 67%). It suggests that the introduction of vinyl group

VSB : R = CH=CH₂
HSB : R = H

HOSB : m = 1
oHOSB : m = m

Scheme III

Scheme IV

Table II. Comparison of Thermal Properties of PBSF with Those of Conventional Resins

Polymers	T_g [°C]	Coefficient of Thermal Expansion [$\times 10^{-5}$/°C]
PBSF	161	9
Polyimide Resin	400	66
Epoxy Resin	150	6

improves the thermal properties of the polymer most efficiently. Further introduction of vinyl group into the polymer structure was also investigated (Scheme V). By changing the polymerization method, the vinyl content of the polymer was controlled from 25 to 100%. The glass-transition temperatures of these polymers are still not high (-50 to -30 °C), but their thermal degradation temperatures become much higher than the other polymers prepared previously. Among them, all-vinyl substituted polymer showed the highest thermal stability, and its residual weight at 1000 °C was 90%.

Poly(silsesquioxane)s

Dehydrogenative polycondensation reaction can be applied to the synthesis of poly(silsesquioxane), having the empirical formula $RSiO_{1.5}$ (R= Ph, Me, H etc) by using trifunctional $RSiH_3$ as a monomer.[15] Generally, poly(silsesquioxane) is prepared by hydrolysis and condensation of trichlorosilane or trialkoxysilane in the presence of acid or base as a catalyst.[16] The reaction usually gives high molecular weight products, but control of chemical structure of the formed polymer is not easy because of the occurrence of Si-O bond cleavage and recombination processes.
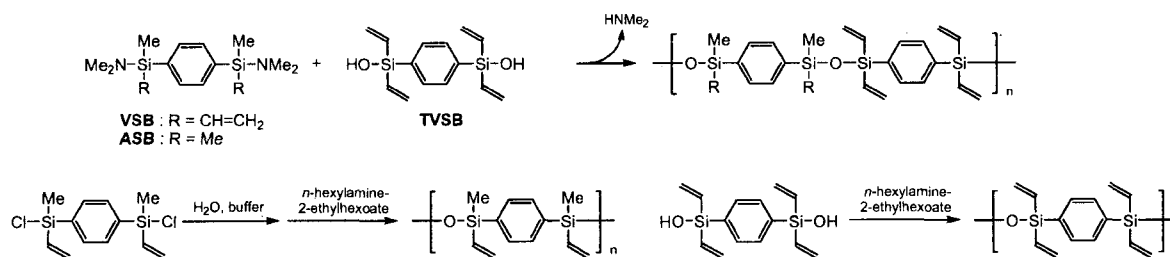
$Pd_2(dba)_3$, reported[9a] as an efficient catalyst for the dehydrocoupling polymerization, gave high molecular weight product with apparently broad and roughly bimodal distribution after 42 h (Figure 5(b), $M_w/M_n = 21,400/1,750$). The lower molecular weight fraction could be removed by reprecipitation into ethanol/hexane. The insoluble fraction was proved to be a high molecular weight polymer (Figure 5(b), $M_w/M_n = 62,200/25,400$). ^{1}H NMR spectrum of the polymer showed two broad signals at around 2.70~3.60, and 6.40~7.80 ppm, which are ascribed to hydroxyl and phenyl protons. ^{29}Si NMR spectrum exhibited main signals at -79.1~
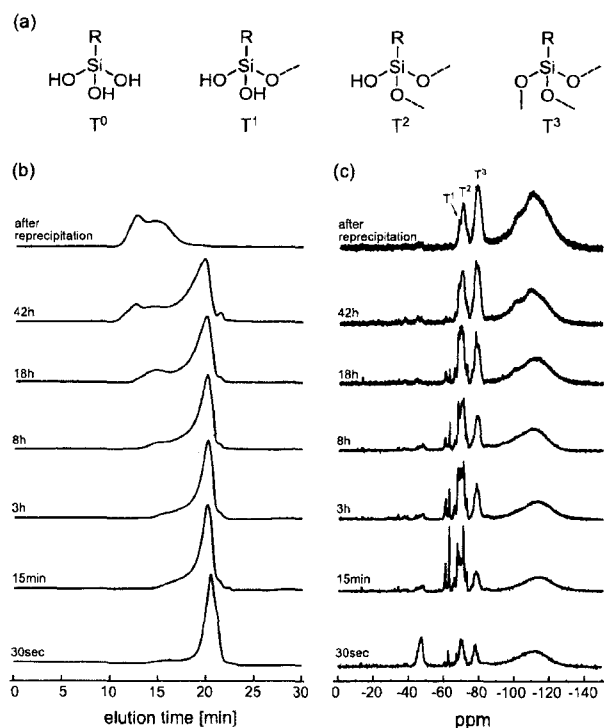
Figure 5. (a) Abbreviation of siloxane structure, (b) SEC, and (c) ^{29}Si NMR of the polymerization products.

70.45, and -67.97 ppm, which are assigned to $PhSi(O-)_3$ (T^3), $PhSi(O-)_2OH$ (T^2) and $PhSi(O-)(OH)_2$ (T^1) structure,[17] respectively (Figure 5(c)). The area ratio is roughly 60 : 31 : 9. The fact that the polymer is soluble in common organic solvent strongly suggests that the polymer has only small amounts of cross-linking even with about 60% of T^3 structure.

To obtain the insights of the polymerization at initial stage, the polymerization was stopped after 30 sec by capping the products with trimethylchlorosilane (Me_3SiCl). Some of the peaks in SEC chromatogram were separated and characterized. These are $PhSi(Me_3SiO)_3$, $PhSiH(Me_3SiO)_2$, $(Me_3SiO)_2PhSiOSiPhH(OSiMe_3)$, $\{(Me_3SiO)_2PhSi\}_2O$, and $\{(Me_3SiO)PhSiO\}_3$. These compounds should be formed from phenylsilanetriol $\{PhSi(OH)_3\}$ and phenylsilanediol $\{PhSiH(OH)_2\}$. It should be stressed that no phenylsilane ($PhSiH_3$), nor phenylsilanol ($PhSiH_2OH$) was detected in

Scheme V

the reaction system. This fact suggests that hydrolysis of SiH function with water by Pd catalyst is fast in the very early stage of the reaction, and that not only the first but also the second silane functions are more reactive than the third silane function toward hydrolysis. Dehydration reaction of {PhSi(OH)$_3$} is a relatively slower process compared with the reactions which consume SiH function.[9a] This inference is in accordance with hydrogen evolution from the system,[18] where a violent evolution of hydrogen corresponding to about 70% of calculated amounts occurred in the initial 10 sec, and almost quantitative amount of hydrogen was generated {16.5 mL (the calculated amount, 16.8 mL)} after 60 sec.

^{29}Si NMR analysis was carried out to detect the progress of the polymerization (Figure 5(c)). In ^{29}Si NMR after 15 min, basically five kinds of signals were observed at around -78.4, -70.5, -67.4; -65.9, -62.8; -60.7, and -47.5 ppm. The signal at -78.4 ppm is assigned to T^3, and that at -70.5 to T^2. The signals at -67.4; -65.9 ppm are assigned mainly as T^1 (may include the signal of SiOEt, since it was later found that the stabilizer ethanol in chloroform is reacting with the SiH function when the reaction system was diluted), respectively. Sharp signals at -62.8; -60.7 ppm are reasonably considered to originate from T^2 of low molecular weight products, for example, cyclic structure like cyclotrisiloxane. The multiplicity of the signals is considered to reflect stereochemical structures of the cyclic compounds. The signal at -47.5 ppm might be assigned to PhSi(O-)$_2$H (D^H), by referring the chemical shift of (Me$_3$SiO)$_2$PhSiH (-49.38 ppm) as in the case of the signal at 30 sec. In the signal after 30 sec, the major peaks are observed at -78.5, -70.2, and -47.4 ppm. It should be stressed that in the very early stage of the polymerization, the species present in the system are, T^3, T^2, and D^H and only small amounts of T^1 present. After 15 min, the signal of D^H almost disappeared, and instead, the signals of T^2 and T^1 (-70.5, -62.8; -60.7 and -67.4; -65.9 ppm) and T^3 (-78.4 ppm) became stronger. The signals at -62.8; -60.7 and -67.4; -65.9 ppm assignable to T^2 and T^1 decreased gradually with reaction time after taking maximum, and became weak after 42 h. Especially the change of T^2 assignable to low molecular weight products is notable. The signal of T^2 at -70.5 ppm became stronger and broader with reaction time, and that of T^3 also became stronger. After 42 h, the peak of T^3 became the strongest. The major structure of polymer is consisted of T^2 and T^3 structure.

The results of SEC and ^{29}Si NMR indicated that the basic reactions occurring in this polymerization are (1) fast hydrolysis of SiH functions of phenylsilane with water, and (2) cross-dehydrocoupling reaction between SiH and SiOH, followed by (3) slow condensation of SiOH functions. Intramolecular cyclization between SiH and SiOH functions are also occurring in the early stage of the polymerization. The reactions to give oligomers might be depicted as Scheme VI.

The solubility in organic solvent and the ratio of T^1, T^2

and T^3 strongly suggest non cross-linked structure of the polymer having cyclic moiety as shown in Scheme VI. Judging from the structures of initial oligomers, it will be reasonable to assume that the principal chemical structure of the polymer is poly{oxy(phenylhydroxysilylene)} with branched SiH(OH), Si(O-)OH or Si(OH)$_2$ functions. In the early stage of the polymerization, when higher concentration of SiH functions present compared to later stage of the polymerization, branching and cyclization should occur more frequently. Cyclization of D^H functions in the branches, or reaction of {Ph(OH)SiO}$_2$(PhHSiO) with T^1 or T^2 functions of the main chain or branches is quite plausible to reduce the amounts of D^H, T^1 or T^2 relatively to T^{3}structure, and result in 2:3 (T^1 + T^2) and T^3 ratio in the polymer. Cross-linking through the condensation of SiOH groups of T^2 units seems quite slow.

Interests have been given to the formation of cage shape poly(silsesquioxane), especially to octa-functional cubic octasilsesquioxane, octa functional pentacyclo[9.5.1.1^{3,9}. 1^{5,15}.1^{7,13}]octasiloxane, or S$_8$ derivatives, such as hydride

Hydrolysis of phenylsilane (PhSiH$_3$)

Cross-dehydrocoupling of 1, 2, 3, and 4

R$_1$-R$_5$ = H or OH

Plausible Structures in the Polymer[b]

Scheme VI. Plausible mechanism of dehydrogenative coupling polymerization between phenyislane and water. [a]Not isolated. [b]Concentration of SiH is very low.

functionalized **S₈-H**, or dimethylsilyloxy functionalized **S₈-OMe₂SiH** as a component to construct nano-structured composite systems.[19] Such **S₈** systems act not simply as constituents of nano-hybrid systems, but can function in advanced display technology as a support for amorphous and functional dye dispersant system, when the radial direction of attachment of functional groups is considered. To realize such a system, it is essential to establish a method to obtain aromatic-substituted cubic **S₈** systems.

There is a competition during the condensation process between "intermolecular condensation" to give randomly branched polymers, and ladder polymers,[20] and "intramolecular condensation" to give loop structure, which eventually forms cyclic polyhedral cage products.[21] Both types of condensation products were observed in the system,[22] and the products usually contain unreacted silanol groups depending on their structures. These unreacted silanols have a great influence on the reactivity, viscosity, and solubility of the polymer in subsequent processing step.

Recently, Wallace *et al.*[23] reported that high resolution matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF) could be applied to identify the products with loop structure formed by intramolecular condensation of silanols from *n*-propyl-, *n*-decyl-, and 3-methacryloxypropyltrimethoxysilane. It was pointed out that there is a significant substituent effect on intramolecular condensation. The benzene-soluble components in hydrolysis and condensation reactions of (4-substituted phenyl)trimethoxysilane was analyzed by MALDI-TOF MS.[24]

After 4 h refluxing, precipitates were formed in the systems of (4-dimethylamino-phenyl)-, phenyltrimethoxysilane and 4-trimethoxysilylbiphenyl. The oligo(silsesquioxane) was obtained from benzene solution as sticky white to pale yellow solid. (4-Methoxyphenyl)trimethoxysilane gave only benzene-soluble fraction after hydrolysis and condensation.

Scheme VII

SEC indicates that products of molecular weight higher than 1,500 but not higher than 3,000 (polystyrene) were mainly produced in the benzene-soluble fraction. By ^{29}Si NMR, it was found that all benzene-soluble oligo(silsesquioxane)s showed 2 principal peaks in the range of $\delta = -69 \sim -72$, and $-78 \sim -81$ ppm, assignable to well-known T² and T³ structure.[25] No T¹ signal was observed.

When hydrolysis of methoxy groups attached to silicon atoms occurs, formation and condensation of silanol functions will proceed. The structure and reactivity of the silanol groups of the initially formed oligo(silsesquioxane) will basically determine the structure of the products, and even-

tually the loop structure produced by condensation of silanol groups. If hydrolysis of the one methoxy group is slower than the other two methoxy groups, and than condensation between two silanol groups, linear or low branched structure will basically be formed as the initial products. SEC results showed that the condensation of initially formed oligo (silsesquioxane) proceeds to a stage of formation of oligo (silsesquioxane) with maximum 8 to 10 silicon atoms. The aromatic moiety might have functioned to differentiate the reactivity of three methoxy groups (two methoxy groups of higher and one with lower reactivity) in the hydrolysis process, and possibly to give linear like structure soluble in benzene among many possible condensed oligomeric intermediate.

In the discussion of the oligo(silsesquioxane) structure, the structure was simplified by representing by dot and line symbols. Dot indicates the silicon atom, and line siloxane bond. The dot connected to only 1 line indicates T¹ structure. Dot connected to 2 and 3 lines indicates T² and T³ structure, respectively.

The oligo(silsesquioxane)s consisting of 6, 7, 8, and n silicon atoms are abbreviated as **S₆**, **S₇**, **S₈**, and **Sₙ**. In the structure, T¹ and T² are the silanol groups which can further condense to form loop structure. In this paper, actual ring size will not be discussed, because it is difficult to identify the ring size by mass spectroscopy. Typical MALDI-TOF MS is shown in Figure 7.

The degree of condensation (*f*) was defined as the extent of intramolecular condensation of silanol groups as typically
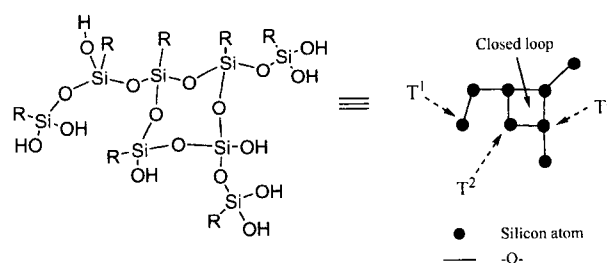

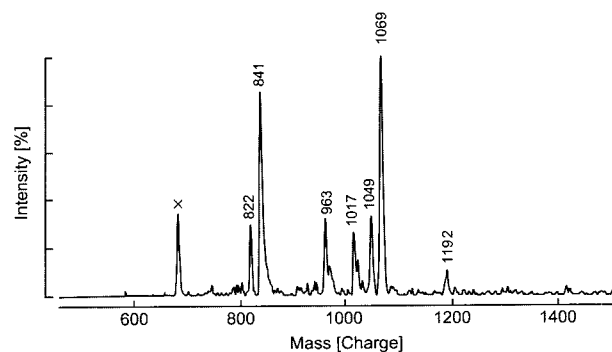**Figure 6.** Typical structure of oligo(silsesquioxane).

Figure 7. MALDI-TOF mass spectrum of soluble fraction in benzene.

shown, assuming the formation of 8-membered ring, in Figure 8 in the cases of 8 silicon atom-containing oligo(silsesquioxane)s.

In case of 8 silicon atom-containing system, 10 silanols can condense to form maximum 5 loops structure. Therefore, degree of condensation by the formation of one loop (f) is 0.20. We wanted to note that there are many possible structures of f from 0.00 to 1.00, depending on the initial linear or low branched-structure product formed. When the fifth loop is formed, the sixth loop is simultaneously formed too. In case of 7 silicon atom-containing system, 8 silanols can condense to form maximum 4 loops structure. Therefore, the degree of condensation by the formation of one loop (f) is 0.25.

Since one water molecule is lost on each condensation, the molecular weight is decreased by 18 on each cyclization, and the molecular weight of oligo(silsesquioxane) can be calculated by adding 18 (terminal OH and H).

$$M = n \times M_{unit} - 18t + 18 \tag{1}$$

where, M is the mass of the oligo(silsesquioxane) with n silicon atoms, M_{unit} is the mass of the unit fraction $[O_{0.5}(RSiOH)O_{0.5}]$, and t is the number of loops.

The signals of MS spectra can be classified into several groups based on the number of silicon atoms (n). The number of non-condensed OH in each compound in the group depends on the degree of condensation, namely the number of the loops (t). Hereafter, $S_n(OH)_x$ is defined as oligo(silsesquioxane) with n silicon atoms and x non-condensed OH groups. $S_n(OH)_{n+2}$ is converted to $S_n(OH)_n$, when one condensation occurs to form one loop (Figure 9).

Each peak in MS was assigned based on eq. (1), and the degree of condensation (f) was calculated as shown in Table III.

In benzene-soluble fraction, oligo(silsesquioxane)s containing 6 to 9 silicon atoms, with loops but incompletely cyclized to cage structure, were observed as the main products. With 4-dimethylamino substituent, S_8 and S_9 fractions were formed the most with small amounts of S_6 fraction, and the

amount of S_9 was the highest among the compounds studied. Contrary, S_9 was the least for [methoxy (10%)-, non (3%)- and phenyl (13%)-substituted]phenyltrimethoxysilane. This seemed to indicate that the intermolecular condensation of silanol groups in the hydrolyzate of (4-dimethylamino-phenyl) trimethoxysilane is faster than those with other substituents. Fractions containing 7 and 8 silicon atoms are the major fractions of the products, irrespective of the substituent. Definite trend in the relative rate of the intermolecular condensation could not be observed for the different substituents. Solubility of the compounds and steric effect might also have big influences on the reaction rate. 8 silicon atom-con-
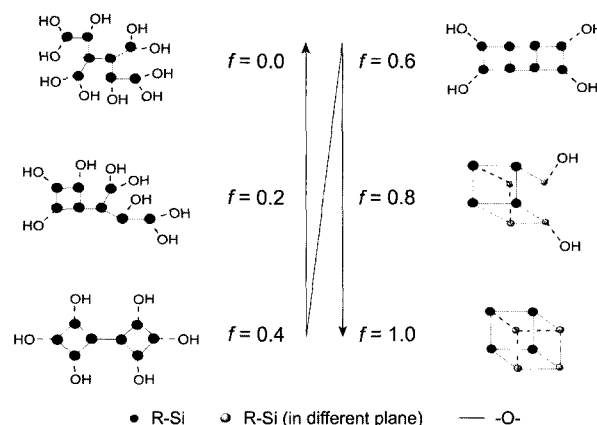

• R-Si   ○ R-Si (in different plane)   —— -O-

Figure 8. Degree of condensation of oligo(silsesquioxane) containing 8 silicon atoms.

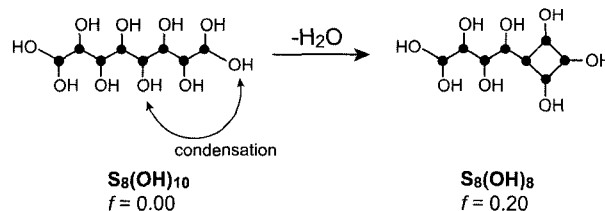**Figure 9.** Conversion from $S_8(OH)_{10}$ to $S_8(OH)_8$.

Table III. MS Peak and f Values for the Products from Phenyltrimethoxysilane

Structure	$M_{w\ cald.}$	$M_{w\ meas}$	Σf_{Hi}	f_{Hi}	f	$f \times f_{Hi}$	$f \times f_{Hi}/\Sigma(f \times f_{Hi})$
$S_6(OH)_8$	846	841	0.36	0.27	0.00	0.000	0.000
$S_6(OH)_6$	828	822		0.09	0.25	0.022	0.061
$S_7(OH)_7$	966	963	0.18	0.10	0.25	0.025	0.069
$S_7(OH)_3(OCH_3)_4$	1,022	1,017		0.08	0.25	0.020	0.055
$S_8(OH)_2$	1,050	1,049	0.42	0.10	0.80	0.192	0.529
$S_8(OH)_4$	1,068	1,069		0.32	0.60	0.080	0.220
$S_9(OH)_3$	1,188	1,192	0.03	0.03	0.80	0.024	0.066

S_n: oligosilsesquioxane with n silicon atoms. f_{Hi}: height of peak in mass spectrum of oligosilsesquioxane with same number of silicon atoms. $f \times f_{Hi}$: mole fraction of oligosilsesquioxane with same number of silicon atoms.

taining systems had $f = 0.6$ and 0.8. 9 silicon-containing systems had $f = 0.80$ and 1.00. The degree of condensation (extent of loop formation) was the highest for 9 silicon-containing systems. It is worth to note that there were not much oligomer fractions higher than S_{10} in hydrolysis with any kinds of 4-substituent of oligo(silsesquioxane)s. It was believed that the bulky aryl-substituent compared with alkyl substituent had the tendency to give low molecular weight products as the soluble products composed of mainly S_6 - S_9 fractions in weak hydrolysis system using methanolic benzyltrimethyl-ammonium hydroxide as a basic catalyst.

S_6 system had little tendency to form loops for any (4-substituted phenyl)trimethoxysilane (found 9% in only phenyl substituted system). The high mobility of the molecule might make the molecule difficult to bring two silanols function together. Only one loop in low silicon containing system ($n < 7$) might not be able to stabilize the system. The tendency became higher with the increase in silicon number of the oligo(silsesquioxane), namely S_7 (maximum $f = 0.50$), S_8 (maximum $f = 0.80$), and S_9 (maximum $f = 1.00$) formed loops in much higher concentration. Such loop structure might become stable when silicon number increased. This tendency was not much affected by the difference of 4-substituent of phenyl group.

If the major loop is assumed as 8-membered ring, the existence of $S_7(OH)_7$, $S_7(OH)_5$ and almost non-existence of $S_7(OH)_3$ and $S_7(OH)$ might indicate easy formation of the first 8-membered ring ($n = 4$) as the loop, but successive loop formations were difficult. The maximum f value of 0.5 for S_7 fraction might indicate the difficulty of the formation of 6-membered ring as the third loop. In S_8 system, $S_8(OH)_4$ and $S_8(OH)_2$ were principal products. Formation of fused two 8-membered loop with a sheet structure was probable. To make one more loop, the molecule should be bent. Apparently this process is not difficult, because similar amounts of $S_8(OH)_2$ with $S_8(OH)_4$ were formed. The maximum value of 0.8 for S_8 fraction might indicate that the loop formation to cage structure was difficult, because the remaining two silanols were not necessary located close to each other. Although the amounts of S_9 were smaller than S_6 - S_8, the tendency of forming the complete loop structure was the highest.

Optically Active Polysiloxanes

Control of stereoregularity and optical activity of polymers
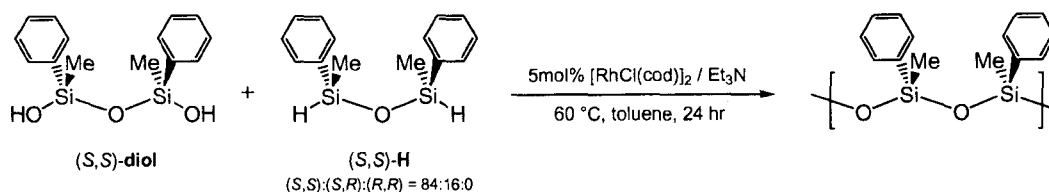
has been a challenging theme in the field of polymer synthesis. Configurationally optically active polymers are interesting as well as conformationally optically active polymers.[26] We reported the synthesis of isotactic poly[(methylphenylsilylene) trimethylene] having asymmetric silicon centers by the polyaddition of optically active (*S*)-allylmethylphenylsilane.[27] However, the optical activity itself is lost in the polymer since the asymmetric centers of the resulting polymer are pseudo-asymmetric. One of the practical methods to obtain configurationally optically active polymers is to prepare polymers containing optically active stereorepeating unit of the type A-X*-B (X*, optically active center; A≠B). Based on this concept, we obtained optically active and isotactic poly[oxy-(*S*)-(1-naphthylphenylsilylene)ethylene(dimethyl-silylene)] by polyaddition reaction of (1*S*)-1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane, which is the first example of stereoregular and optically active silicon-containing polymer.[28] This polymer was also obtained by ring-opening polymerization.[29] In these cases, X*, A, and B are Si*, O, and CH_2, respectively.

Polysiloxane is a class of important hydrophobic silicon-containing polymer. Poly(dimethylsiloxane)s have been widely used as silicone oil, silicone rubber, main chain for liquid crystalline polymers,[30] and polymer support for metallocene catalyst,[31] as well as other useful materials[32] by taking advantage of their highly flexible structure and high thermal stability. In spite of the existence of pseudo-asymmetric silicon centers in unsymmetrically substituted poly (siloxane)s, their stereoregularity and optical activity are relatively unexplored compared with hydrocarbon polymer systems. If stereorgularity and optical activity are induced in polysiloxanes, the resulting polymers are expected to exhibit unique properties different from those of ordinary polysiloxanes without controlled stereochemistry.

Meanwhile, we recently reported the synthesis of optically active (*S,S*)-1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediol ((*S,S*)-**diol**).[33] This (*S,S*)-diol is considered suitable as the constitutional units of stereoregular and optically active polysiloxanes.

Rh-catalyzed cross-dehydrocoupling polymerization of optically pure (*S,S*)-**diol** with (*S,S*)-1,3-dihydro-1,3-dimethyl-1,3-diphenyl-1,3-disiloxane ((*S,S*)-**H**) [(S,S):(S,R):(R,R) = 84:16:0] was carried out (Scheme VIII).[34] Diastereomer mixture of *meso/dl*-**diol** and *meso/dl*-**H** was also polymerized to prepare atactic PMPS. The stereoregularity of the

Scheme VIII. Synthesis of PMPS rich in syndiotacticity.
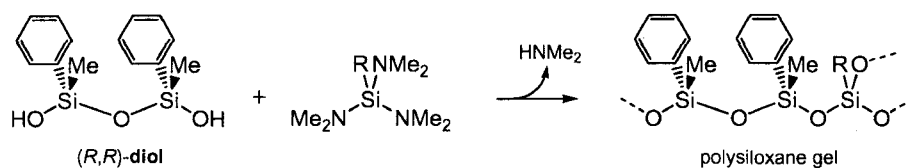
Scheme IX. Synthesis of optically active polysiloxane gel.

resulting PMPS was characterized by means of ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR of methyl protons of atactic PMPS showed three singlet peaks at 0.04, 0.09, and 0.14 ppm arisen from triad tacticity. From the ratio of these peaks, singlet peak at 0.09 ppm was assigned to the hetero-tactic triad signal (*H*). However, it is not clear which peak (0.04 and 0.14 ppm) should be assigned to the syndiotactic (*S*) or isotactic (*I*) triad signal. Methyl carbon peaks (*I*=-0.47, *H*=-0.38, *S*=-0.29 ppm) and meta-carbon peaks (*I*=127.53, *H*=127.49, *S*=127.43 ppm), in particular, *ipso*-carbon peaks (*I*=137.1, *H*=136.9, *S*=136.7 ppm) showed definite splitting patterns based on the triad tacticity (Figure 10). The triad tacticity of PMPS prepared from optically pure (*S,S*)-diol and (*S,S*)-H [(S,S):(S,R):(R,R) = 84:16:0] was estimated as *S:H:I* = 60:32:8. Some apparent decrease in syndiotacticity may be due to the racemization during the polymerization.

Chiral materials with chirality induced by asymmetric silicon atoms in the main chain was not reported. If optical activity is induced, the resulting poly(silsesquioxane) is expected to find new potential applications as enantiorecognitive separating membrane or chiral column packing materials.

The conceptual reaction path of *racemic*-diol with methyltris(dimethylamino)silane is shown in Scheme IX.[35] It was found that the concentration over 3 mol/L of **diol** is necessary for obtaining insoluble product. The GPC trace and ^{29}Si NMR analysis indicated that, in the early stage of the polymerization, cyclization by self-condensation of **diol** and oligomerization occurred. The first and second amino group of methyltris(dimethylamino)silane seems to have higher reactivity than that of the third amino group. In the later part of the polymerization, branching occurred by the reaction of

the remaining third amino group with silanol function to form hyperbranched structure, followed by the gradual cross-linking to give insoluble product.

To obtain optically active polysiloxane gel, the polycondensation of optically active (*R,R*)-diol with methyltris(dimethylamino)silane was carried out under similar reaction condition with *racemic*-diol. Optical activity was evaluated for the polycondensation products before the gelation occurred. The polycondensation reaction gave the poly(silsesqioxane) with molecular weight (*M_n*) 15,000 (purified by repeated reprecipitaion into MeOH) by GPC (exclusion limit $M_n = 4.0 \times 10^5$), when the reaction was stopped after 2 h. This polymer showed optical activity ($[\alpha]_D^{27} = -1.77$ ($c = 1.25$, $CHCl_3$)), which is considered to be induced by the asymmetric silicon atoms of (*R,R*)-diol unit in the polymer structure. The poly(silsesquioxane)s prepared from *racemic*-diol and *meso*-diol for comparison, did not show any optical activity. These results strongly support that polysiloxane gel prepared from (*R,R*)-diol has asymmetric silicon atoms in siloxane network, and is optically active. The gel prepared from (*R,R*)-diol is considerd to have potential applications as enantiorecognitive separating membrane or chiral column packing materials.

Segmental Mobility and Functionality of Oligosiloxane-substituted Polymers

Oxygen Permeable Membrane Materials. In the permeation of a gas through a condensed film, the gas molecules permeate through the dynamic gaps between polymer chains, less than 1-2 nm in size, determined by micro-Brownian motion and interaction with permeating molecules. The permeation of gases is treated by Fick's and Henry's laws.[36]
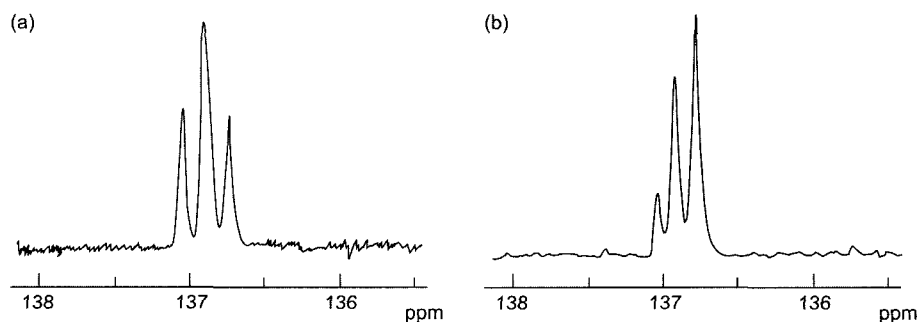
Figure 10. ^{13}C NMR spectra of *ipso*-carbon of phenyl group of PMPS: (a) atactic and (b) rich in syndiotacticity.

$$P = D \times S \qquad (2)$$

Poly(dimethylsiloxane) (PDMS) has the highest permeability coefficient given by large diffusion coefficient among industrial membrane materials, since it is composed of very flexible SiO linkages and has large free volume. However, it also has the lowest O_2/N_2 permeation selectivity value for membrane polymers, *i.e.*, $\alpha = P_{O_2}/P_{N_2} = 2$. Moreover, it has only insufficient self-supporting characteristics. Polymers consisting of dimethylsiloxane side chains, which contribute to permeation, and a main chain component with high glass transition temperature (T_g), which lends high permeation selectivity and gives film-forming properties, should demonstrate well-balanced permeation properties. Properties of the polymers with polystyrene as a main chain and oligo-dimethylsiloxane as side chains (Figure 11) are listed in Table IV.

The polymers show only one T_g, and the absolute T_g value is lowered significantly by the introduction of the siloxane linkages. **PS***n***5** showed the highest permeability coefficient maintaining reasonable selectivity and self-supporting property.

It can be seen from the table that the permeability coefficient is mainly controlled by the diffusion coefficient. Thus, permeation behavior of a gas through polymeric membrane must be closely related to the nature and relaxation behavior of the polymer segments in bulk which control the diffusibility of the permeating gas.

Spin-lattice relaxation time, T_1 of the silicon atom directly attached to phenyl ring (**Si¹**) in these polymers as shown in Figure 12, reflects the rotational motion along the Si-C bond. Accordingly, the value is considered a standard of the mobility of the side chain. Each silicon atom in side chain of these polymers gives not only different chemical shifts but independent T_1 as typically shown for **PS***i***3** in Figure 13. Thus, T_1 of **Si¹** must have strong correlation with the mobil-

ity of the side chain as a whole. However, since the thermal relaxation process varies among polymers with different T_gs, it is sometimes meaningless to directly compare T_1 of polymers with different T_gs.

The dependence of T_1 on temperature is shown in Figures 14 and 15. T_1 of **Si¹** showed a tendency to decrease sharply with the elevation of the temperature for these polymers with disiloxane linkage and having T_g at a little higher temperature than room temperature. T_1 of **Si²** also decreased with increasing temperature, but the change was not so sharp. Decrease in T_1 can be taken to mean higher mobility of the side chains in this temperature region. T_1 of **Si³** of **PS3** (see Figure 12) even increased with increasing temperature. This silicon atom has apparently high enough mobility even at -60 °C, and relaxation of this silicon atom by the contact
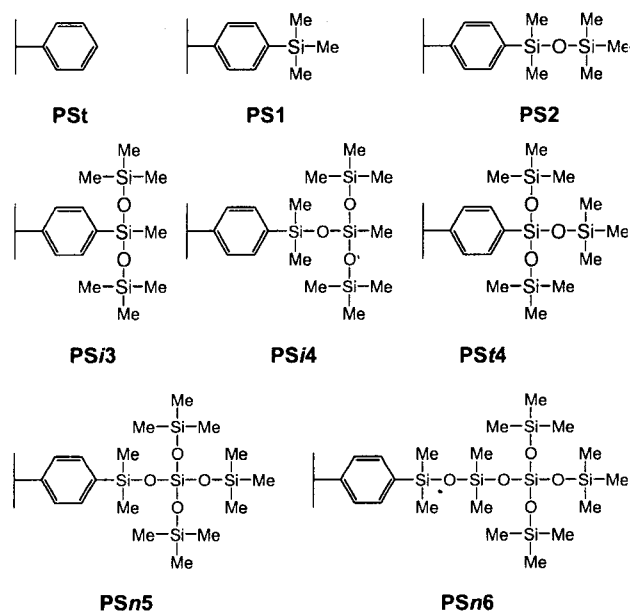

Figure 11. Structure of poly(p-oligodimethylsiloxanylstyrene)s.

Table IV. Properties of Poly(p-oligodimethylsiloxanylstyrene)s

Polymer	T_g[°C]	Δv[°C]	$P_{O_2}{}^b$	α	$D_{O_2}{}^c$	$S_{O_2}{}^d$
PSt	373	31.25	1	5.5	1	2.2
PS1	409	13.23	14	3.4	-	-
PS2	309	9.97	40	3.0	18	2.2
PS*i*3	325	8.27	71	2.8	32	2.3
PS*i*4	364	2.33	74	2.8	35	2.1
PS*t*4	387	5.52	-	-	-	-
PS*n*5	314	5.21	110	2.6	49	2.2
PS*n*6	256	2.76	141	2.6	64	2.2

$^a\Delta v$: half-amplitude width of the CH_3 signal in solid state ^{1}H NMR (90 MHz).
$^b 10^{-10}$cm^3(STP) · cm/(cm^2 · sec · cmHg). $^c 10^{-7}$cm^2/sec. $^d 10^{-3}$cm^3(STP)/ (cm^3 · cmHg).
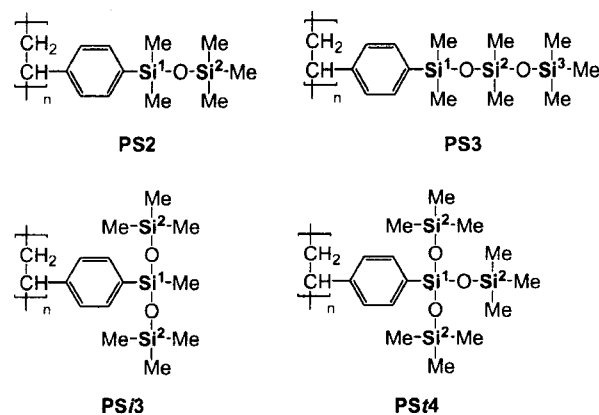
Figure 12. Si¹, Si², and Si³ in poly(p-oligodimethylsiloxanylsty-rene)s.
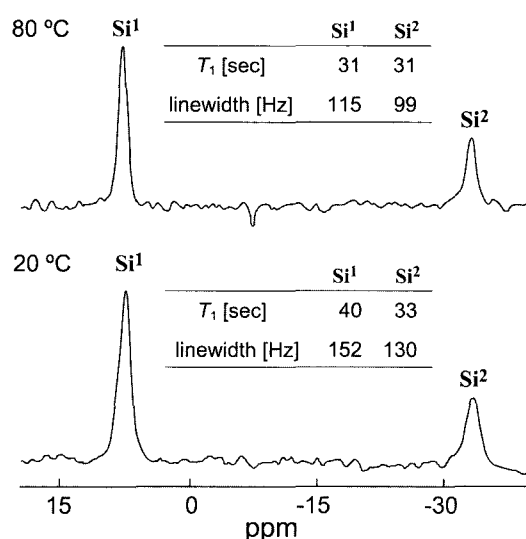
Figure 13. Change of T_1 of Si^1 and Si^2 of **PSi3** estimated by 79.6MHz ^{29}Si solid state NMR.
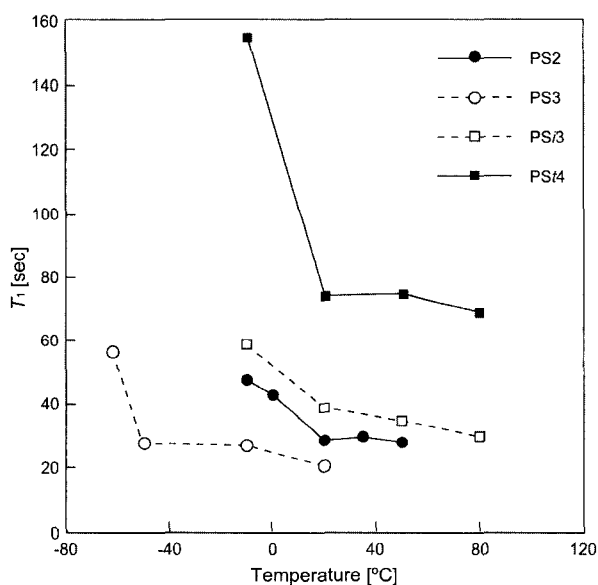

Figure 14. Change of T_1 of Si^1 of poly(p-oligodimethylsiloxanyl-styrene)s with temperature.
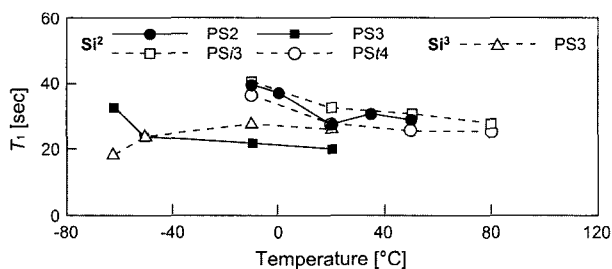

Figure 15. Change of T_1 of Si^2 and Si^3 of poly(p-oligodimethylsi-loxanylstyrene)s with temperature.

with lattice becomes inefficient by raising the temperature because the thermal motion of trimethylsilyl group connected through Si-O-Si-O (two siloxane linkages) becomes too fast. It can be said that silicon atom apart from main chain has higher mobility compared with that close to main chain.

Side-Chain Liquid Crystalline Polymers. We reported liquid crystalline polydiene with a siloxane linkage in the spacer.[37] The polydiene with cyanobiphenyl as a mesogenic group linked through the siloxane linkage (Figure 16) shows a well-organized smectic phase. The reason for the formation of the well-developed smectic structure of these polymers is considered not only because of the polar tail group, but also because of the flexibility of the polydiene main chain, and the very mobile disiloxane unit in the spacer which also spaces the mesogenic groups apart from each other along the polymer main chain, compared with ordinary vinyl polymers. The transition temperatures of the polymers range from room temperature to around 115°C. This might be an advantage when certain applications are considered. The benzoate mesogen gave a nematic phase.

Polysiloxane Macromonomers and Graft Copolymers

Macromonomers. Living polymerization created the idea of Macromer® (proposed by R. Milkovich, generic term is macromonomer) for synthesizing a graft copolymer of well-controlled structure.[38] A polymerizable group is usually introduced into a macromolecule of well-controlled molecular weight by initiating or terminating the living polymerization of a monomer with a compound having the polymerizable functional group. We reported the synthesis of PDMS macromonomers.[39]

In order to obtain a graft copolymer of well-controlled structure, control of the copolymerization reaction of a macromonomer with a comonomer is crucial. Caution must be given to the fact that macromonomer is a polymeric compound. In dilute solution, the concentration of the polymeri-
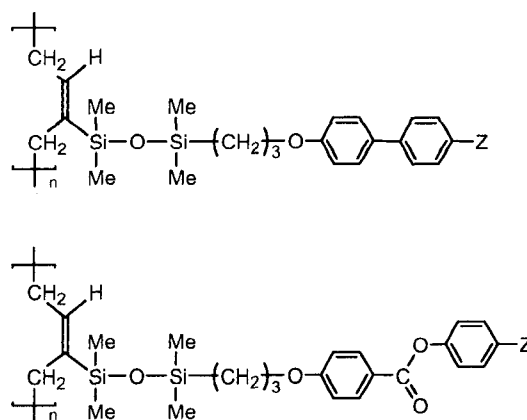

Figure 16. Polybutadienes having mesogens linked through a disiloxane spacer.

Fig. 8과 9는 실제 제작한 래치의 작동과 시계 방향과 반시계 방향에 대한 충격 실험을 나타내고 있다.

1차 실험을 통해 충격에 대한 락킹 기능은 잘 수행되지만 작동시에 액추에이터가 빠져나오지 못하고 래치에 걸리는 경우가 가끔 발생하였다. 이러한 작동시 발생하는 불안 요인은 액추에이터에 연결되어 있는 PCB 케이블의 탄성력과 피봇의 마찰로 인한 오차 등에 의해 실제 요구되는 스프링 상수 값과 수식
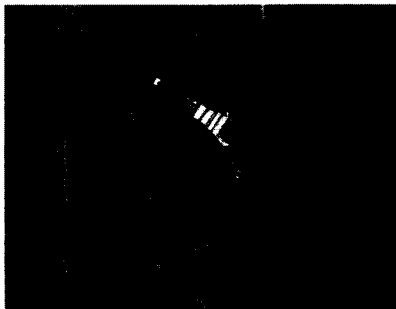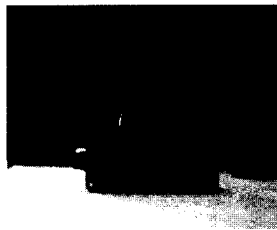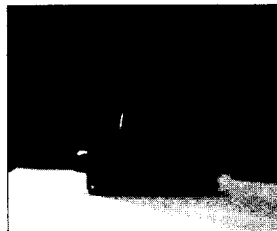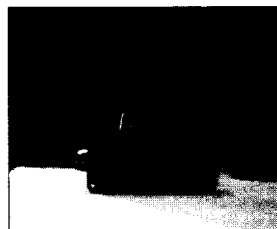

Fig. 7 Photograph of 1 inch micro optical disk drive

(a) Non-operation

(b) Counter clockwise rotation for operation

(c) Actuator loading using time gap

Fig. 8 Operating test

에 의해 계산된 스프링 상수 값과는 약간의 차이를 보이기 때문이다. 따라서 작동시 발생하는 불안 요인을 제거하고 래치 기능을 잘 수행할 수 있는 최적 조건을 맞추기 위해 스프링의 길이를 미세하게 조절할 수 있는 장치부를 주었다. 이 조절부를 통해 장치에 대한 최적 조건을 맞추어줌으로써 작동과 충격에 대해 좋은 성능을 보임을 알 수 있었다. 따라서 1차 실험을 통해 래치 성능을 확인하였고, 2차 실험을 통해 휴대용 장치로써 요구되는 정량적 충격 실험을 수행하였다.

4.2 낙하 충격 실험

2차 실험에서는 충격 실험을 수행하였으며, Fig. 10은 충격 실험을 위한 실험 장치를 나타내고 있다.

2차 실험에서는 정량적인 충격 실험을 하기 위하여 실험 기준을 정하여 높이와 각도에 따른 실험을 수행하였다. 그리고 충격이 가해졌을 때, 드라이브의 작동을 보기 위해서 1초당 1024 프레임을 촬영할 수 있는 CCD 고속 카메라를 이용하여 촬영하였다.

실험은 시계 방향과 반시계 방향에 대해 수행되었으며, 신뢰성을 확보하기 위해 각각 높이에 대해 20회 반복 실험을 하였다. 또한, 휴대용이라는 특성을 고려하여 사람의 어깨 높이 정도인 1 m를 기준으로

(a) Clockwise   (b) Counter clockwise
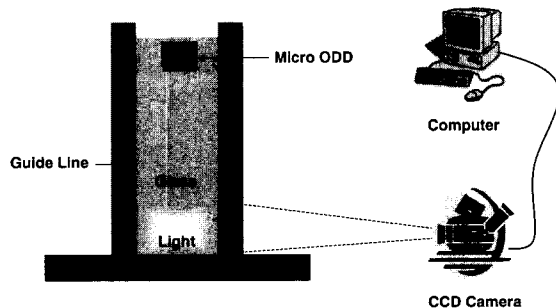
Fig. 9 Shock test

Fig. 10 Experimental set up

Diffraction Efficiency [%] $= I_d/I_t \times 100$ (3)

By Kogelnik's coupled wave theory,[46] maximum diffraction efficiency for the unslanted transmission hologram is given:[47]

$$\eta = \sin^2 \xi \qquad (4)$$

$$\xi = n \cdot \pi \cdot \Delta n \cdot T / [\lambda(n^2 - \sin^2\theta)^{1/2}] \qquad (5)$$

where η, n, θ, T, and λ are the maximum diffraction efficiency, average refractive index of the recording media, an angle within the recording medium between the probe radiation and a line perpendicular to the plane of the medium, the film thickness, and the recording wavelength, respectively. Δn is the modulation of refractive index, which is very important to determine the diffractive efficiency. In our experiment, T, θ, λ were fixed and n is varied by chemical structure of recording materials. Therefore, diffraction efficiency was mainly controlled by n and Δn.

Generally, η values become large when refractive index contrast of photopolymerizable solution and liquid crystal is large if there is no chemical affinity between the polymer and liquid crystal. When the chemical affinity is large or rigidity of the cross-linked system is high to resist phase separation, the η values will be small due to poor phase separation during the grating formation, even if their refractive index contrast was large. Therefore, it can be expected that a further enhancement of η can be achieved by molecular design of photopolymerizable monomer or oligomer having high refractive index contrast and low chemical affinity leading to good phase separation by enhancing Δn. The refractive index and diffractive efficiency of starting and recorded materials used in this study were summarized in Table V.

Table V also shows the diffraction efficiency according to the chemical structures of bis(cyclohexene oxide). Diffraction efficiency increased in the order of **EPCX-C4** < **EPCX-C1** < **EPCX-Si2**, with the order of refractive index contrast **EPCX-Si2** < **EPCX-C4** < **EPCX-C1**. **EPCX-C1** has larger refractive index contrast than **EPCX-C4**, thus has larger diffraction efficiency than **EPCX-C4**.

In case of **EPCX-Si2**, diffraction efficiency was pronouncedly higher than those of **EPCX-C1** and **EPCX-C4**, although its refractive index contrast was the smallest among them. This can be considered that flexible and incompatible siloxane materials have strongly influenced the phase separation of LC from the irradiated areas. The more coalescence of LC droplets was induced by the flexible chain of **EPCX-Si2** resulting in good phase separation and effective grating formation.

Holographic gratings with clearly phase-separated morphologies of periodic polymer rich layers (bright region) and LC rich layers (dark region) could be observed by SEM shown in Figure 19. The grating spacings of all ROP system (Figure 19(b), (c), and (d)) increased due to improved volume shrinkage than the case where only acrylate system (Figure 19(a)) was used. Especially, as shown in Figure 19(c) and (d), grating spacings of **EPCX-C1** and **EPCX-Si2** with cyclohexene oxide function were larger than those of **Glcd-Si1** (Figure 19(b)) with glycidyl ether function. Steric requirement of more bulky cyclohexene oxide function seems to have caused less volume shrinkage than glycidyl ether function.

Compared with **EPCX-C1**, **EPCX-Si2** with siloxane component had more clear phase separation of liquid crystal as shown in Figure 19(c) and (d). LC drop sizes are also much larger for **EPCX-Si2**. This is because of the incompatibility with LC and flexibility of siloxane component. This can also be discussed from the viewpoint of polymeri-

Table V. Refractive Index and Diffraction Efficiency of Starting and Recorded Materials

Momomer	Structure	Refractive Index (n^{20})	Refractive Index Contrast with LC	Diffraction Efficiency [%]
DPAc*	$H_2C=HCCOOCH_2-\overset{CH_2OCOCH=CH_2}{\underset{CH_2OCOCH=CH_2}{C}}-CH_2-O-CH_2-\overset{CH_2OCOCH=CH_2}{\underset{CH_2OCOCH=CH_2}{C}}-CH_2OR$ (R = H or COCH=CH₂)	1.4900	0.1282	45
Glcd-Si1	▷—CH₂-O-(CH₂)₃-Si(OMe)₃-OMe (OMe)	1.4290	0.0572	76
EPCX-C1	(cyclohexene)—C(=O)-O-CH₂—(cyclohexene oxide)	1.4980	0.1262	71
EPCX-C4	(cyclohexene)—CH₂-O-C(=O)-(CH₂)₄-C(=O)-O-CH₂—(cyclohexene oxide)	1.4930	0.1212	68
EPCX-Si2	(cyclohexene)—(CH₂)₂-Si(Me)₂-O-Si(Me)₂-(CH₂)₂—(cyclohexene oxide)	~1.435	0.0632	77

*mixture of dipentaerythritol pentaacrylate and dipentaerythritol hexaacrylate.

x 10 K   x 40 K
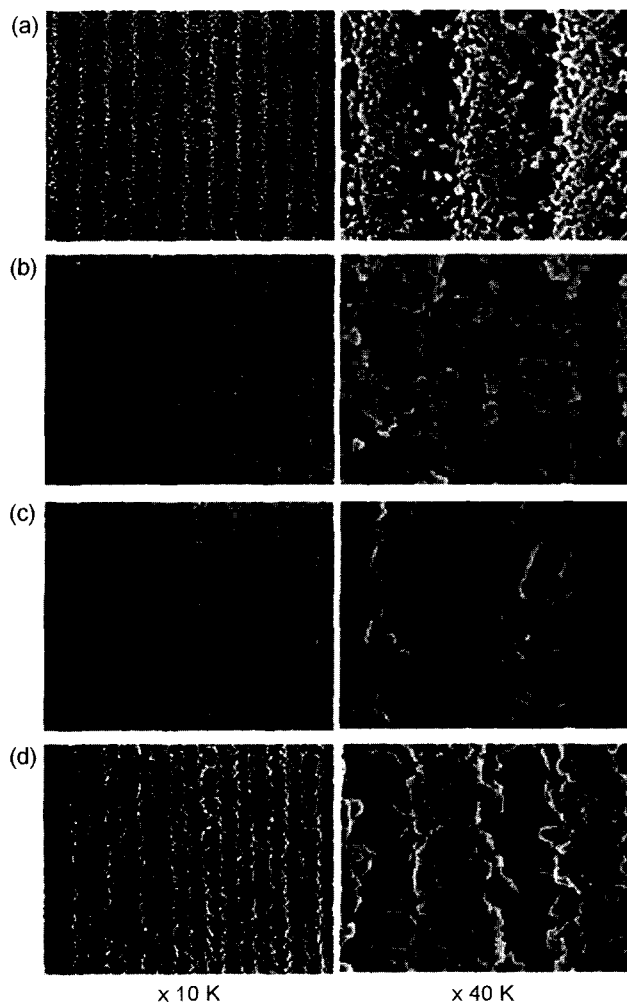
Figure 19. SEM images of holographic gratings prepared from (a) **DPAc**, (b) **Glcd-Si1**, (c) **EPCX-C1**, and (d) **EPCX-Si2**.

zation rate. J.V. Crivello et al. reported that **EPCX-Si2** is much more reactive than **EPCX-C1** in photoinitiated cationic polymerization despite of the apparent closely related structures.[48] Generally, in holographic PDLC systems, there is an optimum polymerization rate to obtain good phase separation. It can be expected that higher reactivity will form cross-linking fast, and cause more clear phase separation by pushing out LC fast from the polymerized system.

When **Glcd-Si1** is compared with **EPCX-Si2** with silicon component although their silicon number is different, the phase separation shown in Figure 19(b) and (d) is quite different. The reason seems similar to the discussion already made.

References

(1) T. W. Greene and P. G. M. Wuts, Protective Group in Organic Synthesis, 3rd ed., John Wiley & Sons, New York, 1999.

(2) H. R. Kricheldorf (Ed.), Silicon in Polymer Synthesis, Springer, Berlin 1996.

(3) R. G. Jones, W. Ando, and J. Chojnowski (Eds.), Silicon-Containing Polymers -The Science and Technology of Their Synthesis and Applications-, Kluwer Academic Publishers, Dordrecht, 2000.

(4) A. L. Smith, The Analytical Chemistry of Silicones, Wiley Interscience, New York, 1991.

(5) (a) S. Yajima, J. Hayashi, and M. Omori, Chem. Lett., 4, 931 (1975); (b) S. Yajima, K. Okamura, and J. Hayashi, Chem. Lett., 4, 1209 (1975).

(6) R. D. Miller and J. Michl, Chem. Rev., 89, 1360 (1989).

(7) P. R. Dvornic and R. W. Lenz, High Temperature Siloxane Elastomers, Hüthig & Wepf, Basel, 1990.

(8) (a) R. L. Merker and M. J. Scott, J. Polym. Sci., Part A, 2, 15 (1964); (b) R. L. Merker, M. J. Scott, and G. G. Haberland, J. Polym. Sci., Part A, 2, 31 (1964).

(9) (a) Y. Li, Y. Kawakami, Macromolecules, 32, 3540 (1999); (b) Y. Li, Y. Kawakami, Macromolecules, 32, 6871 (1999); (c) Y. Li, Y. Kawakami, Macromolecules, 32, 8768 (1999); (d) Y. Li, M. Seino, and Y. Kawakami, Macromolecules, 33, 5311 (2000); (e); (f); (g) Y. Liu, I. Imae, and Y. Kawakami, Sci. Tech. Adv. Mater., 4, 27 (2003).

(10) (a) Y. D. Blum and R. M. Laine, Organometallics, 5, 2081 (1986); (b) Y. D. Blum, K. B. Schwartz, and R. M. Laine, J. Mater. Sci., 24, 1707 (1989); (c) J. L. He, H. Q. Liu, J. F. Harrod, and R. Hynes, Organometallics, 13, 336 (1994).

(11) T. Kawakita, H.-S. Oh, J.-Y. Moon, Y. Liu, I. Imae, and Y. Kawakami, Polym. Int., 50, 1346 (2001).

(12) R. Zhang, J. E. Mark, and A. R. Rinhas, Macromolecules, 33, 3508 (2000).

(13) J.-Y. Moon, T. Miura, I. Imae, D.-W. Park, and Y. Kawakami, Silicon Chemistry, 1, 139 (2002).

(14) (a) Y. Liu, I. Imae, A. Makishima, and Y. Kawakami, Sci. Tech. Adv. Mater., 4, 27 (2003); (b) Y. Liu, I. Imae, and Y. Kawakami, Polym. Int., in press (2004).

(15) M. Seino, I. Imae, and Y. Kawakami, Polym. J., 35, 197 (2003).

(16) (a) R. H. Baney, M. Itoh, A. Sakakibara, and T. Suzuki, Chem. Rev., 95, 1409 (1995); (b) D. A. Loy and K. J. Shea, Chem. Rev., 95, 1431 (1995).

(17) (a) G. Engelhardt, M. Maegi, and E. Lippmaa, J. Organomet. Chem., 54, 115 (1973); (b) L. Guizhi, S. Lianghe, and Y. Meiling, Chin. J. Polym. Sci., 14, 41 (1996); (c) K. J. Shea, D. A. Loy, and O. Webster, J. Am. Chem. Soc., 114, 6700 (1992).

(18) Reaction condition: 0.25 mmol of phenylsilane, 0.375 mmol of water, and 1 μmol of $Pd_2(dba)_3$ in 50 μL of THF.

(19) R. O. R. Costa, W. L. Vasconcelos, R. Tamaki, and R. M. Laine, Macromolecules, 34, 5398 (2001).

(20) J. F. Brown, Jr., L. H. Vogt, Jr., A. Katchman, J. W. Eustance, and K. M. Kiser, J. Am. Chem. Soc., 82, 6194 (1960).

(21) (a) A. J. Barry, W. H. Daudt, J. J. Domicone, and J. W. Gilkey, J. Am. Chem. Soc., 77, 4248 (1955); (b) L. Matejka, O. Dukh, D. Hlavata, B. Meissner, and J. Brus, Macromolecules, 4, 6904 (2001).

(22) (a) J. F. Brown, Jr., L. H. Vogt, Jr., and P. I. Prescott, J. Am. Chem. Soc., 86, 1120 (1964); (b) J. F. Brown, Jr., J. Am. Chem. Soc., 87, 4317 (1965).

(23) W. E. Wallance, C. M. Guttman, and J. M. Antonucci, *Polymer*, **41**, 2219 (2000).

(24) C. Pakjamsai and Y. Kawakami, *Polym. J.*, in press (2004).

(25) K. Itoh (Ed.), *Silicone Handbook* (in Japanese), Nikkan Kogyo Shimbunsha, Tokyo, 1990.

(26) (a) Y. Ito, T. Miyake, T. Ohara, and M. Suginome, *Macromolecules*, **31**, 1697 (1998); (b) T. Nakao, Y. Satoh, and Y. Okamoto, *Polym. J.*, **30**, 635 (1998); (c) P. C. Innis, I. D. Norris, L. A. P. Kane-Magurie, and G. G. Wallace, *Macromolecules*, **31**, 6521 (1998); (d) H. Tang, M. Baba, I. Imae, and Y. Kawakami, *Polym. J.*, **31**, 313 (1999); (e) D. Y. Sogah and S. Zheng, *Polym. Prepr.*, **40**, 540 (1999).

(27) (a) Y. Kawakami, K. Takeyama, K. Komuro, and O. Ooi, *Macromolecules*, **31**, 551 (1998); (b) Y. Kawakami, T. Takahashi, Y. Yada, and I. Imae, *Polym. J.*, **31**, 1001 (1998).

(28) Y. Li, Y. Kawakami, *Macromolecules*, **31**, 5592 (1998).

(29) Y. Li, Y. Kawakami, *Macromolecules*, **32**, 548 (1999).

(30) (a) H. Finkelman, H. Ringsdof, and J. H. Wendorf, *Makromol. Chem.*, **179**, 273 (1978); (b) H. Finkelman, M. Happ, M. Portugal, and H. Ringsdof, *Makromol. Chem.*, **179**, 2541 (1978); (c) H. Finkelman and G. Rehage, *Makromol. Chem. Rapid Commun.*, **1**, 31 (1980).

(31) (a) K. Soga, T. Arai, H. T. Ban, and T. Uozumi, *Macromol. Chem. Rapid Commun.*, **16**, 905 (1995); (b) T. Arai, H. T. Ban, T. Uozumi, and K. Soga, *Macromol. Chem. Phys.*, **192**, 229 (1997); (c) T. Arai, H. T. Ban, T. Uozumi, and K. Soga, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 421 (1998).

(32) (a) S. S. Abed-Ali, B. J. Brisdon, and R. England, *J. Chem. Soc. Chem. Commun.*, 1565 (1987); (b) S. K. Duplock, J. G. Matison, A. G. Swincer, and R. F. O. Warren, *J. Inorg. Organomet. Polym.*, **1**, 361 (1991); (c) S. Getz and H. A. Schneider, *Makromol. Chem.*, **194**, 233 (1993); (d) G. B. Zhou, J. M. Khan, M. Ishrant, and J. Smid, *Macromolecules*, **26**, 2202 (1993).

(33) M. Oishi and Y. Kawakami, *Org. Lett.*, **1**, 549 (1999).

(34) M. Oishi, J.-Y. Moon, W. Janvikul, and Y. Kawakami, *Polym. Int.*, **50**, 135 (2001).

(35) (a) M. Oishi and Y. Kawakami, *Macromolecules*, **33**, 1960 (2000); (b) M. Seino, M. Oishi, I. Imae, and Y. Kawakami, *Polym. J.*, **34**, 43 (2002).

(36) (a) S.-T. H. Kammermeyer, *Membranes in Separation Process*, John Wiley & Sons, New York, 1975; (b) S. A. Stern and P. Meares (Ed.), *Membrane Separation Processes*, Elsevier, New York, 1976; (c) R. M. Barrer, *Trans. Farad. Soc.*, **35**, 628, 644 (1939).

(37) (a) Y. Kawakami, Y. Ito, and K. Toida, *Macromolecules*, **26**, 1177 (1993); (b) Y. Kawakami and K. Toida, *Macromolecules*, **28**, 816 (1995); (c) Y. Kawakami, M. Ichitani, H. Kunisada, and Y. Yuki, *Polym. J.*, **28**, 513 (1996).

(38) G. O. Schulz and R. Milkovich, *J. Appl. Polym. Sci.*, **27**, 4773 (1982).

(39) (a) Y. Kawakami, Y. Miki, T. Tsuda, R. A. N. Murthy, and Y. Yamashita, *Polym. J.*, **14**, 913 (1982); (b) Y. Kawakami, K. Ajima, M. Nomura, T. Hishida, and A. Mori, *Polym. J.*, **29**, 95 (1997).

(40) (a) Y. Tsukahara, K. Tsutsumi, Y. Yamashita, and S. Shimada, *Macromolecules*, **22**, 2869 (1989); (b) Y. Tsukahara, K. Tsutsumi, Y. Yamashita, and S. Shimada, *Macromolecules*, **23**, 5201 (1990).

(41) (a) Y. Kawakami, R. A. N. Murthy, and Y. Yamashita, *Polym. Bull.*, **10**, 368 (1983); (b) Y. Kawakami, R. A. N. Murthy, and Y. Yamashita, *Makromol. Chem.*, **185**, 9 (1984); (c) Y. Kawakami, T. Aoki, and Y. Yamashita, *Macromolecules*, **18**, 580 (1985).

(42) Y. H. Cho, M. He, B. K. Kim, and Y. Kawakami, *Sci. Tech. Adv. Mater.*, in press (2004).

(43) R. T. Pogue, R. L. Sutherland, M. G. Schmitt, L. V. Natarajan, S. A. Siwecki, V. P. Tondiglia, and T. J. Bunning, *Appl. Spectr.*, **54**, 12 (2000).

(44) M. S. Park, Y. H. Cho, B. K. Kim, and J. S. Jang, *Curr. Appl. Phys.*, **2**, 249 (2002).

(45) Y. Ohe, M. Kume, Y. Demachi, T. Taguchi, and K. Ichimura, *Polym. Adv. Technol.*, **10**, 544 (1999).

(46) K. Kogelnik, *Bell. Syst. Tech. J.*, **48**, 2909 (1969).

(47) (a) Y. Ohe, H. Ito, N. Watanabe, and K. Ichimura, *J. Appl. Polym. Sci.*, **77**, 2189 (2000); (b) R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia, and T. J. Bunning, *Chem. Mater.*, **5**, 1533 (1993).

(48) J. V. Crivello and J. L. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 479 (1990).