

Synthesis of New Organic Crosslinking Reagents Containing SiH Bonds and Curing System Thereof

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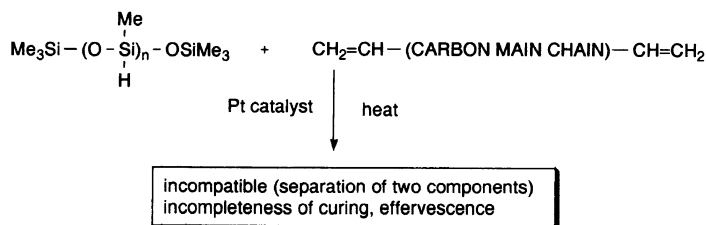
ABSTRACT: New organic crosslinking reagents **1** containing SiH bonds have been synthesized by platinum-catalyzed "Selective Hydrosilylation"(SHS) reaction of either 1,9-decadiene **2a** or diallyl ether of bisphenol A **2b** with 2,4,6,8-tetramethylcyclotetrasiloxane [$\text{CH}_3(\text{H})\text{SiO}$]₄ (**3**) (hereafter called hydrocyclotetrasiloxane) (eq 1). Identification of the new crosslinking reagents **1** was well performed by ¹H NMR. The cyclic structure of the starting hydrocyclotetrasiloxane **3** was retained in the product **1** after the SHS reaction, as evidenced by ¹³C NMR analysis. The storage stability of **1** was significantly influenced by the amount of Pt catalyst still remaining in it. It could get much better when a decreased amount of Pt catalyst was used for SHS reaction and benzothiazole was added. Curing system composed of **1a** and allyloxy end-blocked poly(propylene oxide) **4a** was examined. Curing ability of the system was found to be dependent on temperature, amount of the Pt catalyst employed, and the number of the SiH bond per molecule of **1a**. Rubbery materials could be obtained in a short period of time.

KEY WORDS Selective Hydrosilylation (SHS) / Pt-Catalyzed / Hydro-Cyclotetrasiloxane / NMR Analysis / C-O Bond Cleavage / Storage Stability / Curing System / Gel Time / Modulus / Gel Content

Hydrosilylation reaction has been widely employed for curing (crosslinking) of so-called addition-type polysiloxanes. Although this type of polysiloxanes has several excellent properties such as high curing rate at high temperature, good dimensional stability etc., application of this addition-type-curing tech-

nology to organic polymers or oligomers has been eventually limited (Scheme 1). One of the significant reasons is probably the poor compatibility of hydrogenpolysiloxanes with organic molecules, which leads to the serious problems.¹

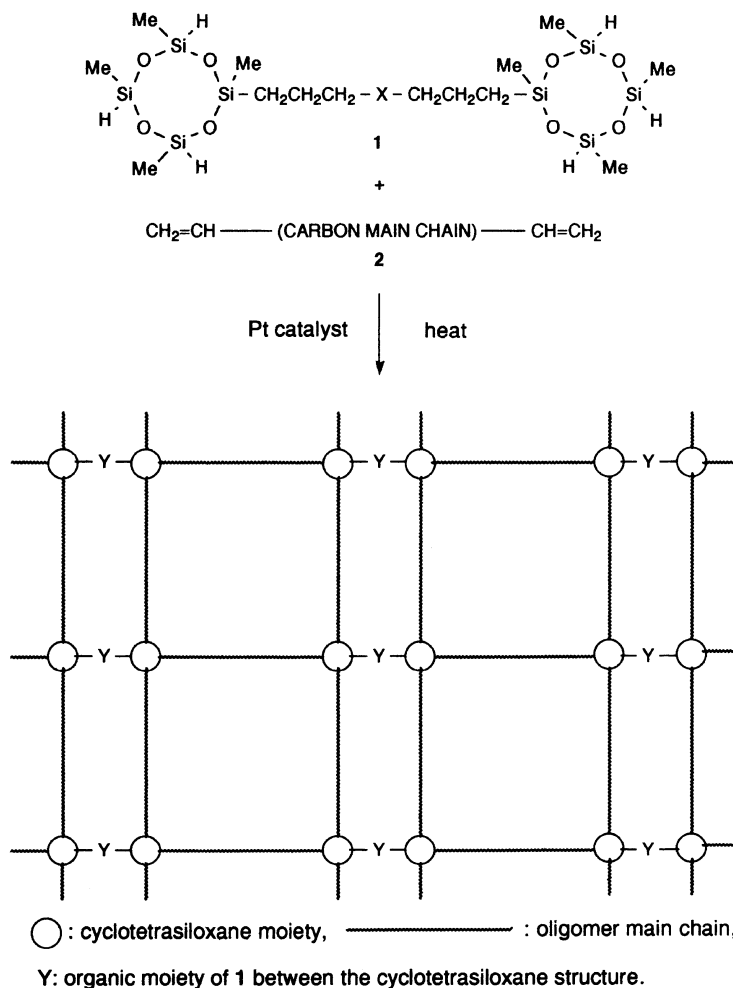
We have thus considered to prepare various



Scheme 1. Curing system composed of a hydrogenpolysiloxane and C-C unsaturated-bond-containing oligomer.

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SiH-Containing Crosslinking Reagents



Scheme 2. Curing system composed of **1** and C–C unsaturated-bond containing oligomer.

aromatic protons). Signals at δ 3.30–3.50, 4.90–5.22, 5.9–6.0, 6.67–6.77, and 6.93–7.10 ppm are likely attributed to Claisen-rearrangement-type products² $-\text{C}_6\text{H}_3(o\text{-OH})\text{CH}_2\text{-CH}=\text{CH}_2$. IR (neat, cm^{-1}): 3070 (m, $\nu_{\text{C-H}}$), 3030 (m), 2960 (s), 2920 (s), 2860 (s, C–H), 1645 (m, $\nu_{\text{C=C}}$), 1620 (s), 1520 (s), 1290 (s), 1235 (s), 1180 (s), 1025 (s), 1000 (s), 920 (s), and 825 (s). *Elemental Anal.* Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2$: C, 81.78%; H, 7.84%. Found C, 81.96%; H, 7.96%.

SiH-containing Crosslinking Reagent 1a (Entry 1 in Table II)

A 100-ml 4-necked round-bottomed flask was equipped with a motor-driven stirrer, a 50-ml pressure-equalized dropping funnel, a reflux condenser, a 3-way stopcock, and a thermometer. In the flask were placed 12.03 g (50 mmol) of $[\text{CH}_3(\text{H})\text{SiO}]_4$ (**3**) and 20 ml of toluene. A toluene solution which was composed of 2.76 g (20 mmol) of 1,9-decadiene and 20 ml of 10-wt% chloroplatinic acid catalyst solution (3.9×10^{-3} mmol, 1×10^{-4} mol relative to 1 mol of C=C bonds) and 30 ml of

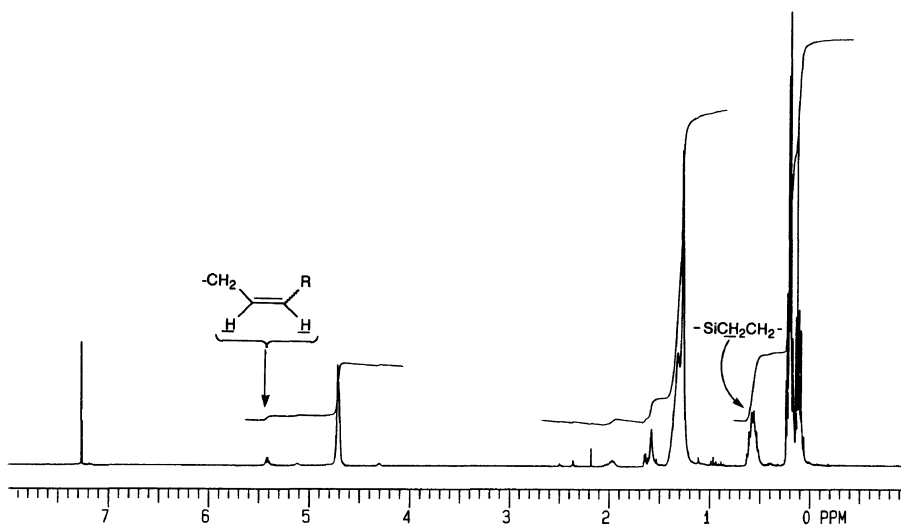


Figure 1. ^1H NMR of SiH-containing crosslinking reagent **1a**.

toluene was added to the flask at 50°C over 2 h. An IR spectrum revealed that the absorption at 1640 cm^{-1} due to $\text{C}=\text{C}$ stretching completely disappeared 1 h after completion of the addition. The toluene solution was washed with saturated NaCl aqueous solution ($100\text{ ml} \times 1$) and ion-exchanged water ($100\text{ ml} \times 1$) and then dried over sodium sulfate. Filtration and evaporation of the solution followed by pumping the residue at 80°C left 9.11 g of **1a** as a colorless clear liquid.

SiH content: $0.767\text{ mol}/100\text{ g}$. ^1H NMR (Figure 1): δ 0.05–0.15 (m, $-\text{CH}_2\text{SiCH}_3$),*¹ 0.15–0.25 (m, $-\text{Si}(\text{H})\text{CH}_3$),*¹ 0.45–0.67 (m, $-\text{CH}_2\text{Si}$), 1.14–1.44 (m, $-(\text{CH}_2)_n-$), and 4.63–4.78 ppm (m, $\text{Si}-\text{H}$ with a $^{29}\text{Si}-^1\text{H}$ satellite of $J = 242\text{ Hz}$). Signals at δ 0.85–1.12, 1.50–1.66 (includes the absorption of H_2O in CDCl_3), 1.90–2.08, and 5.30–5.45 ppm are likely attributed to the internal olefins formed by isomerization of 1,9-decadiene.³ IR (neat, cm^{-1}): 2970 (m), 2920 (s), 2850 (s), 2160 (s, $\nu_{\text{Si}-\text{H}}$), 1470 (m), 1410 (m), 1260 (s), 1070 (br s, $\text{Si}-\text{O}-\text{Si}$), 900 (s), 855 (s), and 765 (s).

The other **1a** (entries 2–4 in Table II) were

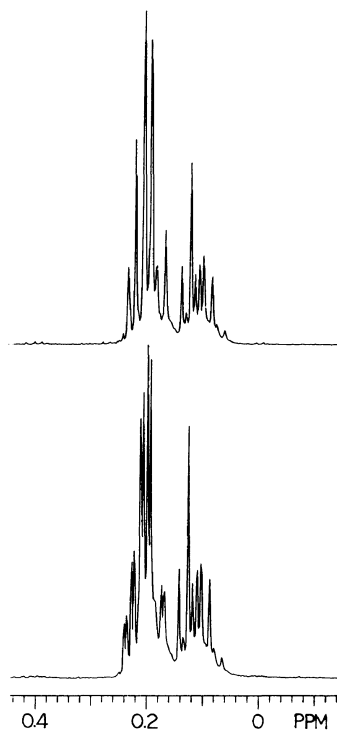


Figure 2. $\text{Si}-\text{CH}_3$ region of ^1H NMR of SiH-containing crosslinking reagent **1a**; irradiated at δ 4.7 ppm (upper), original (lower).

*¹ When the SiH signal of **1a** at 4.63–4.78 ppm was decoupled, the five signals in the lower part of $\text{Si}-\text{CH}_3$ region, each of which was a doublet as the result of the coupling with $\text{Si}-\text{H}$, turned to a singlet. Those in the higher part, on the other hand, did not change at all (Figure 2).

Table I. Conditions for synthesis of SiH-containing crosslinking reagents **1b—1d**

No.	Allyl-containing compound			PhMe	[CH ₃ (H)SiO] ₄		PhMe	Pt cat. eq rel. to allyl	Temp °C (h)	Yield g
	No.	g	mmol	ml	g	mmol	ml			
1b	2b	6.16	20	50	12.03	50	20	2 × 10 ⁻⁴	70 (1.5)+80 (2)	12.0
1c	2c	9.84	40	100	29.73	124	—	2 × 10 ⁻⁴	65~70 (1.7)	25.85
1d	2d	5.49	20	50	12.03	50	20	2 × 10 ⁻⁴	70 (1.5)	10.2

not submitted to the aqueous workup mentioned above and benzothiazole (30 equiv relative to Pt cat. used) was added to the reaction mixture before pumping.

The other SiH-containing crosslinking reagents **1b—1d** were synthesized similarly (Table I) to the procedure for **1a** except for using aqueous media at the work up.

1b; SiH content: 0.602 mol/100 g. ¹H NMR δ 0.10—0.31 (m, SiCH₃), 0.50—0.78 (m, —CH₂Si), 1.61 (s, —C(CH₃)₂—), 1.74—1.92 (m, —OCH₂CH₂CH₂Si), 3.78—3.97 (m, —OCH₂—CH₂CH₂Si), and 4.61—4.79 ppm (m, Si—H with ²⁹Si—¹H satellite of *J*=246 Hz), 6.94 (AA'BB'q, *J*=116 Hz, 10.4 Hz, aromatic protons). Signals around δ 2.5—2.7 and 6.6—7.0 ppm are likely attributed to the hydrosilylated products (C₆H₃(OH)CH₂CH₂CH₂Si—) of the Claisen-rearrangement-type precursors, which is a byproduct of **1a**. Signals around δ 1.7, 4.8—4.9, 5.3—5.4, 6.3—6.4 ppm are likely attributed to the internal olefins formed by isomerization of bisphenol A. IR (neat, cm⁻¹): 3030 (m), 2960 (s), 2920 (s), 2860 (s), 2160 (s, ν_{Si-H}), 1605 (m), 1505 (s), 1255 (s), and 1070 (br s, Si-O-Si).

1c; SiH content: 0.649 mol/100 g. ¹H NMR: δ 0.05—0.38 (m, SiCH₃), 0.50—0.80 (m, —CH₂Si), 1.71—1.98 (m, —CO₂CH₂CH₂CH₂—Si), 4.18—4.46 (m, —CO₂CH₂CH₂CH₂Si), 4.60—4.94 (m, Si—H), 7.43—7.64, 8.10—8.44, and 8.60—8.80 ppm (m, aromatic protons). Signals at δ 0.38—0.54 (m, —SiCH₂CH₂CH₃), 0.80—1.04 (m, —SiCH₂CH₂CH₃), and 1.26—

1.55 (m, —SiCH₂CH₂CH₃) ppm are likely attributed to [CH₃(H)SiO]_n[CH₃(CH₃CH₂—CH₂)SiO]_{4-n}. IR (neat, cm⁻¹): 3055 (w), 2945 (s), 2905 (m), 2875 (m), 2150 (s, ν_{Si-H}), 1780 (s, ν_{C=O}), 1605 (m), 1436 (m), 1407 (m), 1385 (m), 1300 (s), 1259 (s), 1235 (s), and 1168 (br s).

1d; SiH content: 0.442 mol/100 g. ¹H NMR δ 0.05—0.31 (m, SiCH₃), 0.50—0.72 (m, —CH₂Si), 1.65—1.86 (m, —OCH₂CH₂CH₂Si), 3.68—3.80 (m, —OCO₂CH₂CH₂OCH₂CH₂O—CO₂—), 4.02—4.18 (t, *J*=7 Hz, SiCH₂CH₂—CH₂OCO₂—), 4.22—4.37 (m, —OCO₂CH₂—CH₂OCH₂CH₂OCO₂—), and 4.59—4.80 (m, Si—H with ²⁹Si—¹H satellite of *J*=243 Hz). Signals at δ 0.31—0.43 (m, —SiCH₂CH₂CH₃), 0.96 (t, *J*=7 Hz, —SiCH₂CH₂CH₃), 1.30—1.55 (m, —SiCH₂CH₂CH₃) are likely attributed to [CH₃(H)SiO]_n[CH₃(CH₃CH₂CH₂)SiO]_{4-n}.

IR (neat, cm⁻¹): 2950 (m), 2915 (m), 2880 (m), 2165 (s, ν_{Si-H}), 1750 (s, ν_{C=O}), 1458 (m), 1402 (m), 1360 (m), 1260 (s), 1071 (br s, ν_{Si-O-Si}), 902 (s), 885 (s), 860 (s), and 770 (s).

Determination of SiH Content

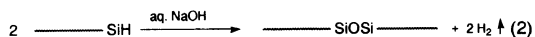
A case of the reagent **1b** is taken as an example here.

(1) Alkaline hydrolysis method^{1a}

SiH-containing crosslinking reagent **1b** (0.492 g) was exactly weighed and dissolved in 10 ml of peroxide-free THF (distilled from Na/Ph₂CO just before use^{*2}). The THF solution was submitted to alkaline hydrolysis with 5 ml of 0.5 N NaOH aqueous solution at room temperature. The evolution of hydrogen gas

*2 Unpurified THF should not be used because the peroxide in it consumes SiH.

was finished within 2–3 min after completion of the addition of the NaOH solution. The gas evolved (72.2 ml) was collected by means of a gas buret. According to eq 2, the SiH content (*S*) is given as follows:



S (mol/100 g) = $100PV/WRT = [100 \times (762/760) \times 0.0722]/(0.492 \times 0.082 \times 290) = 0.619$ *P*, atmospheric pressure at measurement (atm); *V*, gas volume captured (l); *W*, sample weight (g); *R*, gas constant 0.082 (l atm mol⁻¹ K⁻¹), *T*, temperature at measurement (K).

(2) Internal standard method by ¹H NMR

The same SiH-containing crosslinking reagent **1b** (0.446 g) above and dimethyl maleate (0.270 g, *M_w* = 144.13) were dissolved in CDCl₃ homogeneously and submitted to 300 MHz ¹H NMR measurement. From the integral intensities of SiH (32.0 mm at 4.6–4.8 ppm) and CH₃O₂CHC=CHCO₂CH₃ (43.1 mm at 6.25 ppm), the SiH content (*S*) is given as follows: S (mol/100 g) = $[(0.270 \times 2)/144.13] \times (32.0/43.1) \times (100/0.446) = 0.624$

Measurement of Gel Time⁴

Certain amounts of SiH-containing crosslinking reagent **1a**, allyloxy end-blocked poly(propylene oxide) **4a** (SiH/allyl molar ratio = 1), and chloroplatinic acid catalyst solution were well mixed at room temperature. About 0.1 g of the mixture was placed on a hot plate whose temperature had been already controlled a certain value. The sample was then mixed with a tooth pick. The time when the sample turned to an elastomer was determined as an end point. The interval between the time when a sample was put on the plate and the end point was defined as the gel time.

Preparation of Poly(propylene oxide) Cured Sheet and Its Tensile Test

A composition of 115 g (allyl content = 25.2 mmol, 0.0219 mol/100 g) of allyloxy end-blocked poly(propylene oxide) **4a**, 3.155 g (SiH content = 25.2 mmol, 0.0798 mol/100 g) of SiH-containing crosslinking reagent **1a**, 1.18 g of 2,2'-methylene-bis(4-methyl-6-tert-butylphenol)^{*3}, and 65.3 μl (1.25 × 10⁻³ mmol, 5 × 10⁻⁵ mol relative to 1 mol of allyl) of 1 wt% chloroplatinic acid catalyst solution was well mixed. The mixture was then poured in the aluminum-made mold (70 × 60 × 5 mm), whose bottom and side area were covered with a Teflon sheet fitted with a both-sided adhesive tape (13 g × 8 pieces). Debubbling was carried out at room temperature under reduced pressure. The composition was cured at 80°C^{*4} for a certain period of time to give a rubber-like homogeneous sample with 2.5–3.0 mm thickness. From this cured sheet-like sample, several pieces of 2(1/3) type dumbbell were taken according to JIS K7113 and submitted to tensile test at the rate of 200 mm/min (*n* = 3).

Gel Content of Cured Poly(propylene oxide) 1a/4a

About 0.1–0.5 g of the cured sample wrapped in a stainless net was employed for evaluation. The sample weights both before and after acetone extraction (48 h at room temperature and drying at 80°C for 2 h) gave the gel content.

RESULTS AND DISCUSSION

SiH-containing organic crosslinking reagents **1** were synthesized by “Selective Hydrosilylation” (SHS) reaction of C–C unsaturated bonds (especially allyl substituents) of a low molecular-weight organic compound **2** with hydrocycloctetrasiloxane [CH₃(H)SiO]₄ (**3**) (eq 1).

^{*3} Nocrac NS-6 from Ohuchi Shinko Kagaku was used as a hindered phenol antioxidant for poly(propylene oxide) to prevent oxidative pyrolysis.

^{*4} A circulation-type oven from Tabai (HPS-212 model) was used.

By the SHS reaction we mean a reaction pattern in which only one of the four SiH bonds in each molecule of **3** "selectively" can enter into the hydrosilylation reaction and the rest of the SiH bonds remain unchanged in the products (see eq 1).

We have chosen hydrocycloctetrasiloxane $[\text{CH}_3(\text{H})\text{SiO}]_4$ (**3**) for the SiH moiety in the crosslinking reagents **1** because

(1) The SiH bonds in **3** are reactive enough toward hydrosilylation reaction; each of the Si holds two electron-withdrawing siloxy group.⁵

(2) Hydrocycloctetrasiloxane **3** is volatile enough to be removed from the mixture after SHS reaction (bp 69–70°C/100 Torr).

In order to make the SHS reaction proceed predominantly, we kept the amount of hydrocycloctetrasiloxane **3** in large excess over the allyl substituents of an allyl-containing compound **2** throughout the reaction; hence, a toluene solution of an allyl-containing compound **2** and chloroplatinic acid catalyst in EtOH/1,2-dimethoxyethane was added slowly to a toluene solution of hydrocycloctetrasiloxane **3**. The SHS reaction could be monitored by IR spectrometry. In every case the absorption around 1640–1650 cm^{-1} due to C=C stretching almost disappeared within a few hours after completion of the addition. Although the viscosity of the resulting product **1** apparently became larger than that of the starting allyl-containing compound **2**, **1** was obtained without gelation under appropriate conditions. The fact may indicate that the SHS reaction proceeded to a large extent.

Effects of Allyl-substituent Structures of 2 on the SHS Reaction

For an allyl-containing compound **2**, any of allyl alkylene, allyl ether-, allyl ester-, and allyl carbonate-containing compound has been employed (compounds **2a–2d**).

As for the reactivity of the allyl substituents, **2a** seemed to be most easily subjected to the SHS reaction. Reaction of **2a** with $[\text{CH}_3(\text{H})\text{SiO}]_4$ (**3**) at 70°C caused an increase of the reaction temperature up to 80°C and the reaction mixture finally turned to a gel after completion of the addition of a toluene solution of **2a** and Pt catalyst when 1×10^{-4} mol (relative to 1 mol of allyl groups) of Pt catalyst was used. But the reaction at 50°C avoided the gelation. For the other three compounds **2b**, **2c**, and **2d**, reaction at 65–75°C proceeded smoothly without a distinctive generation of heat. Because these compounds have an electron-withdrawing group such as phenoxy, acyloxy, or carbonate attached to the allyl group, the coordination ability of allyl substituents to the Pt catalyst center seemed to get weaker than that of electron-donating allyl alkylene and consequently the hydrosilylation reaction seems to proceed under controlled conditions.⁶

Analysis by NMR

An introduction of the hydrocycloctetrasiloxane **3** unit at the both ends of the molecule **2** was confirmed by appearance of the characteristic absorptions of $-\text{SiCH}_2\text{CH}_2\text{CH}_2-$ around 0.4–0.7 ppm for all the SiH-containing crosslinking reagents **1**. Reagents **1a** and **1b** were synthesized with small amount of side reactions and fully identified while preparation of **1c** and **1d** were accompanied by a considerable amount of side reactions such as the allylic C–O bond cleavage⁷ (see EXPERIMENTAL).

Analysis by NMR

For a fear that the hydrocycloctetrasiloxane moiety in the crosslinking reagents **1** might be ring-opened as with the case of polysiloxane preparation,⁸ ¹³C NMR analysis of the Si–CH₃ region was performed (Figure 3). It was revealed that the main signals of crosslinking reagent **1a** due to $-\text{Si}(\text{H})\text{CH}_3$ were around 0–1 ppm and the peaks probably due to $-\text{CH}_2\text{SiCH}_3$ were around –1 ppm. This result combined with a comparison of spectra of both the hydrocycloctetrasiloxane $[\text{CH}_3(\text{H})\text{SiO}]_4$ (**3**) and a linear hydrooligosiloxane $(\text{CH}_3)_3\text{SiO}-[\text{CH}_3(\text{H})\text{SiO}]_n\text{Si}(\text{CH}_3)_3$ ($n=3-5$) probably supports the retention of the cyclic structure

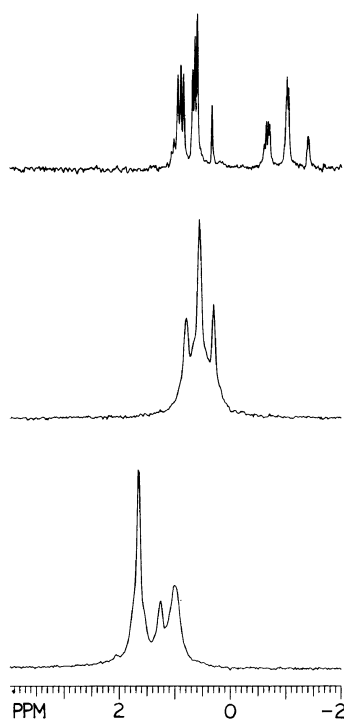


Figure 3. Si-CH₃ region of ¹³C NMR of **1a** and hydrogenpolysiloxanes. top, **1a**; center, [CH₃(H)SiO]₄; bottom, (CH₃)₃SiO[CH₃(H)SiO]_nSi(CH₃)₃ (*n* = 3–5).

derived from hydrocyclo-tetrasiloxane **3** after the SHS reaction.⁹

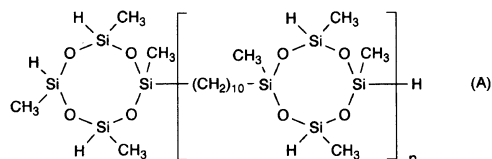
Relationship between Reaction Conditions and SiH Contents

Table II shows reaction conditions for the synthesis of crosslinking reagent **1a**, which is not almost accompanied by side reactions.

Although the SHS reaction did not proceed completely, the more amount of the hydrocyclo-tetrasiloxane **3** apparently made the SHS reaction more favored. When 10-fold excess of **3** (10 mol of **3** relative to 1 mol of 1,9-decadiene **2a**) was employed (entry 4), the SiH content (0.958 mol/100 g) obtained was close to that of the 100%-SHS-reaction product (0.969 mol/100 g).

Even if the SiH/olefin ratio was the same, the less amount of the Pt catalyst system gave the better selectivity of the SHS reaction (entry

1 vs. 3). Probably the fewer reaction sites in the reaction system may suppress the undesirable further hydrosilylation reaction, which leads to the higher homologues (**A**) as shown below (*n* = 2, 3, 4, ...).



Storage Stability of SiH-Containing Crosslinking Reagents **1**

Table III shows the qualitative stabilities of the crosslinking reagents **1a**–**1d** when 2×10^{-4} eq (1×10^{-4} eq for **1a**) of the Pt catalyst relative to C=C bond of **2** was employed.

Although the cause of the instability of **1** has not been clear, Pt-related mechanism may work on the basis of the fact that the more amount of the Pt catalyst was used in the synthesis, the easier viscosity increase and gelation of **1** occurred.

It has been well known that the SiH bond which is oxidatively added on a coordinatively unsaturated group VIII metal (Pt, Pd, and Rh, etc.) is considerably activated and thus easily subject to nucleophilic substitution reactions.¹⁰ It is no surprise that the similar reaction may occur in case of the SiH-containing crosslinking reagent **1**. Contaminated water and silanol, although they are generally considered as a weak nucleophile, probably can attack the activated Si–H bond to produce SiOH and SiOSi linkages, respectively with liberation of the poor leaving group of the hydride, which may be prompted by the presence of proton derived from H₂PtCl₆ · 6H₂O solution (Figure 4).

As a whole, molecular increase of **1** seems to take place *via* eq 3 and finally to lead gelation.

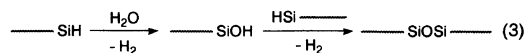


Table II. Relationship between reaction conditions for samples of crosslinking reagent **1a** and their SiH contents

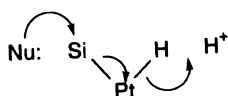
Entry no.	1,9-Decadiene		PhMe	[CH ₃ (H)SiO] ₄		PhMe	SiH/C=C molar ratio	Amount ^a of H ₂ PtCl ₆	Addition conditions		SiH ^b content mol/100 g	n ^c
	g	mmol	ml	g	mmol	ml			°C	h		
1	2.76	20	30	12.3	50	20	2.5	1 × 10 ⁻⁴	50	2	0.767	2.38
2	27.6	200	30	96.2	400	90	2.0	2 × 10 ⁻⁶	70	0.5	0.776 ^d	2.25
3	11.04	80	10	48.1	200	50	2.5	2 × 10 ⁻⁶	70	1	0.899	1.31
4	10	72.5	10	174	725	30	10	4 × 10 ⁻⁶	70	2	0.958	1.04

^a Relative to 1 mol of C=C bonds.^b Obtained from the hydrogen gas evolved by alkaline hydrolysis.^c *n* indicates the *n* in formula (A) calculated based on the SiH content. For example, when the SiH content is 0.767 mol/100 g, (6 + 2*n*)/[(240.5 + 138.3)*n* + 240.5 × 2 + 138.3] = 0.767/100. We can get *n* = 1.38.^d The SiH content was 0.775 mol/100 g after 3-month storage at room temperature.**Table III.** Storage stability of **1** at room temperature

Compound no.	Qualitative stability
1a	Gelation within a few hours. After being washed with water, it held liquid more than 1 week.
1b	Held liquid more than 1 week. (Viscosity increase but no gelation).
1c	Gelation on the surface within 1 week.
1d	Gelation between 3–7 days.

Table IV. Gel time of curing system **1a/4a**: effects of the amount of catalyst and cure temperature^a

Amount of Pt cat. ^b	Temperature/°C					
	60	70	80	90	100	120
1 × 10 ⁻⁴	11'39"	6'09"	3'30"	1'50"	1'01"	0'23"
5 × 10 ⁻⁵	—	>20'	12'35"	10'10"	5'08"	3'05"

^a Conditions, SiH/allyl = 1.^b Relative to 1 mol of allyl.**Figure 4.** Reaction of a nucleophile with the activated Si-H bond.

Interestingly, an extremely large amount of H₂O deactivated or eliminated the Pt catalyst for hydrocarbon-type reagent **1a** while carbonyl- and ether-moiety-containing reagent **1d** was not stabilized by water treatment.

Adding 30 equiv of benzothiazole to the Pt catalyst used in the synthesis made the storage stability excellent enough for various evaluations. For instance, the SiH content of crosslinking reagent **1a** after 3-month storage

at room temperature was 0.775 mol/100 g and it was the same as the original value (0.776 mol/100 g, Table II). Benzothiazole and the compounds of that kind have been reported to deactivated the reactivity of the Pt catalyst by coordinating to it and occupying its coordination site.¹¹

Furthermore, addition of benzothiazole was found not to almost lower the curing ability (> 100°C) of the SiH-addition system probably because benzothiazole reversibly coordinates to the Pt and dissociate at higher temperature.^{1b}

Curing Abilities of the System Composed of SiH-Containing Crosslinking Reagent 1a and Allyloxy End-Blocked Poly(propylene oxide) 4a

Curing ability of the system was qualitatively

Table V. Relationship between gel time and the number of the SiH bonds per molecule of **1a** in the series of curing system **1a/4a**

Entry No.	SiH content of 1a mol/100 g	Gel time ^a		<i>n</i> in formula (A)	<i>M_n</i> ^b	Number of SiH ^c
		80°C	100°C			
1	0.782	1'23"	0'36"	2.16	1050	8.3
2	0.803	1'27"	0'43"	1.97	990	7.9
3	0.850	1'51"	0'51"	1.59	850	7.2
4	0.939	2'04"	0'54"	1.11	660	6.2

5	1.66 ^a	3'18"	1'20"	0	300	5
6	1.66 ^c	4'23"	1'56"	0	240	4

^a Pt cat. = 1×10^{-4} mol relative to 1 mol of allyl. SiH/allyl = 1.

^b Calculated from the formula (A) and the value of *n* (ref. 13).

^c Average number of the SiH bond per molecule.

^d [CH₃(H)SiO]₅ was employed.

^e [CH₃(H)SiO]₄ was employed.

Table VI. Properties of poly(propylene oxide) curing system **1a/4a**^a

Cure time min	Modulus/kg cm ⁻²				Elongation EB/%	Gel content %
	M50	M100	M150	TB		
13	1.4	2.3	3.0	6.8	380	84
14.5	1.5	2.4	3.2	6.5	360	85
16	1.8	2.9	3.8	7.0	320	86
17.5	2.0	3.1	4.1	7.0	300	88
19	2.8	4.4	5.7	7.5	220	91
30	3.3	5.2	6.9	6.5	150	94
90	3.5	5.5	7.2	7.2	150	94
180	3.8	6.0	7.9	8.0	160	94

^a Curing conditions: 80°C, SiH/allyl = 1, Pt = 5×10^{-5} mol relative to 1 mol of allyl. M50 means the tensile modulus at 50% elongation. The others do similarly. TB, tensile strength at break; EB, elongation at break.

examined by gel time (Table IV).

It was observed that the curing rate was largely dependent on both temperature and the amount of the Pt catalyst used. A fast curing behavior at higher temperature seems worthwhile from the point of productivity. These phenomena are similar to the case of so-called addition-type silicone rubber and can be regarded as an example of successful combination of an organic oligomer and SiH-addition-type curing.

Curing rate was, to our surprise, also very dependent on the number of the Si-H bond per molecule of **1** (Table V).¹²

The SiH-containing crosslinking reagent **1a** is, in a more exact sense, a mixture of the homologues shown as formula (A) and the degree of polymerization *n* can be calculated from the SiH content. Probably we can interpret the structure dependence of the gel time as follows: the more number of the SiH bond in one molecule of the SiH component, the easier and faster the oligomer molecules of **4a** can increase the molecular weight and get well crosslinked. This fact consequently led to observation of the shorter gel time.

The results obtained above implies that the lowest homologue of the formula (A) (*n* = 1),

which is the 100%-SHS-reaction product, is not the best choice to obtain a good curing ability.

Mechanical Properties and Gel Content of the Curing System 1a/4a

In accordance with the fast curing behavior of gel time experiment, the curing substances had already had rubbery properties when the gel content was 84% (Table VI).

For a shorter-cure-time sample, oligomer molecules that were not involved in the crosslinking reaction seemed to function as a plasticizer which might give the cured substances lower-modulus and higher-elongation properties. After the gel content reached a constant value (94%), the modulus was still increased. Even in a rubbery stage, the hydrosilylation reaction proceeded and thus the increase of the crosslinking density seemed to cause a raise of the modulus. In other words, the modulus can distinguish between smaller differences of the degree of crosslink of the rubbery materials than gel content does.

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REFERENCES AND NOTES

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- The results in Table V seem inconsistent with those in Table IV. But the different Pt solution was employed for each of the two cases. Recently it has been revealed that the older Pt solution gives shorter gel time. This activation behavior of the Pt species in an alcoholic solution is now under investigation by means of ^{195}Pt NMR spectrometry.
- Although **1a** actually contains the olefin-isomerized components, we ignored them at the calculation of molecular weight of **1a** because the amount of the normally-hydrosilylated components (δ 0.5–0.7 ppm) is much larger than that of the olefin-isomerized components (δ 5.4 ppm) (see Figure 1).