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A facile synthesis of hydro- and vinyl-functionalized di- and tetrasiloxanes and polyaddition via hydrosilylation

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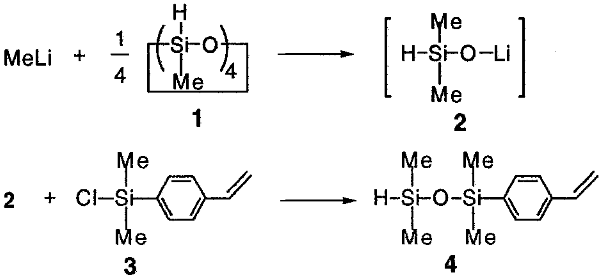
Summary

Hydro- and vinyl-bifunctionalized di- or tetrasiloxane were synthesized by degradative cleavage of functional cyclic siloxanes with methyllithium followed by quenching with a functional chlorosilane, or by ring-opening of hexamethylcyclotrisiloxane (D_3) by functional alkyllithium followed by quenching with a functional chlorosilane. These bifunctionalized siloxanes were used as monomers in polyaddition with transition metal catalysts.

Introduction

We recently reported a synthesis of functionalized disiloxanes via alkylative cleavage of cyclic trisiloxane; D_3, which opened a facile way for the preparation of mono- and bifunctionalized disiloxanes(1,2). Functionalized tetrasiloxane could be synthesized by controlling the molar ratio of the alkyllithium and D_3(3). These siloxanes possess potential utilities as monomers in a variety of polymerization reactions including addition polymerization and polyaddition(4).

Although the functional group of the disiloxane or tetrasiloxane was introduced by the reaction of the functionalized alkyllithium with D_3 in the previous report(1), it is sometimes difficult to prepare the functional organolithium reagent, such as (4-vinylphenyl)lithium. The reaction of an alkyllithium like methyllithium with cyclic siloxanes having a functional group, if possible, is an alternative way to such functionalized disiloxanes. Synthesis of bifunctionalized disiloxane using 1,3,5,7-tetaramethylcyclotetrasiloxane(D_4H, **1**), methyllithium, and quenching with an olefinic chlorosilane is represented in the Scheme 1.



Scheme 1. Synthesis of 1-hydro-3-functionalized disiloxane from **1**.

The bifunctional disiloxane or tetrasiloxane thus prepared will be used as potential monomers for polyaddition via transition metal catalyzed hydrosilylation(4).

Experimental

General

^1H NMR and ^{13}C-{^1H} NMR spectra were recorded on a Varian NMR spectrometer model Gemini 300 (300 MHz for ^1H, 75.4 MHz for ^{13}C). ^{29}Si NMR and ^1H-^1H COSY spectra

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were recorded on Varian Unity 400(79.5 MHz for ^{29}Si) and 500 (500 MHz for ^{1}H). Molecular weight of the polymers were estimated by a JASCO gel permeation chromatography (GPC) model 980 at 40 °C equipped with Shodex KF-800P(precolumn), KF-801(exclusion molecular weight, polystyrene *M*n = 1,500), and KF-804(exclusion molecular weight, polystyrene *M*n = 400,000) columns and JASCO 875-UV, 830-RI detectors using THF as an eluent (1 mL/min). The molecular weight was calibrated using standard polystyrenes.

Typical synthetic procedures are given.

1-Hydro-3-(4-vinylphenyl)-1,1,3,3-tetramethyldisiloxane

Methyllithium (50.4 mmol) was added to a solution of **1** (3.00 g, 12.5 mmol) in Et_2O under argon atmosphere at 0 °C. After stirring at room temperature for 1 day, dimethyl(4-vinylphenyl)chlorosilane (9.61 mL, 50.0 mmol) was added, and stirred overnight. The reaction was stopped by the addition of saturated aqueous NaCl solution. The organic phase was separated, dried over anhydrous $MgSO_4$. Concentration and distillation under reduced pressure gave 1-hydro-3-(4-vinylphenyl)-1,1,3,3-tetramethyldisiloxane (8.35 g, 71 %) as a colorless oil(5).

Similarly, when 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (7.78 g, 30.1 mmol) and dimethylchlorosilane (10 mL, 90 mmol) were used, 1-hydro-3-vinyl-1,1,3,3-tetramethyldisiloxane (3.32 g, 23 %) was obtained(6).

1-Hydro-3-allyl-1,1,3,3-tetramethyldisiloxane

A solution of D_3 (4.48 g, 13.3 mmol) in Et_2O was added to allyllithium prepared from *n*-butyllithium (40 mmol) and tetraallyltin (2.86 g, 10.0 mmol) in Et_2O(7). After stirring for 1 day, dimethylchlorosilane (2.25 mL, 40 mmol) was added, and stirred for further 1 hour. Lithium chloride was removed by filtration through celite, and the filtrate was concentrated. The crude product was purified by trap-to-trap distillation to give 1-hydro-3-allyl-1,1,3,3-tetramethyldisiloxane (3.11 g, 45 %) as a colorless oil(8).

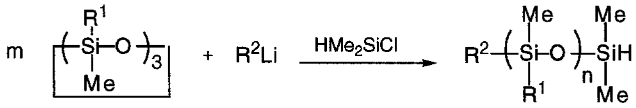
By the use of equimolar amounts of vinyllithium to D_3 followed by quenching with dimethylchlorosilane, 1-hydro-7-vinyl-1, 1, 3, 3, 5, 5, 7, 7-octamethyltetrasiloxane was successfully synthesized(73 %).

Results and discussion

Synthesis of 1-Hydro-3-(4-vinylphenyl)-1, 1, 3, 3-tetramethyldisiloxane

The reaction of **1** required 4 equivalent of methyllithium to bring about the complete cleavage of the siloxane linkage to give the disiloxanes. Olefinic chlorosilane, typically, **3** was used as the quenching agent to obtain **4**. Equimolar amounts of alkyllithium to D_3 was used to obtain the lithium 2,2,4,4,,6,6,6-heptamethyltrisiloxanlate which was transformed into 1-hydro-7-vinyl-functionalized tetrasiloxane on the treatment with chlorosilane. The results of the synthesis of the oligosiloxanes are summarized in Table 1.

Table 1. Synthesis of Bifunctionalized Oligosiloxanes.



Run	m	R^1	R^2	n	Yield (%) [a)]
1	1/3		Me	1	23
2	1/3	Me		1	45
3	1	Me		3	37

a) Isolated yield.

Regioselectivity in hydrosilylation reaction

Regiochemistry in hydrosilylation(9) is important if it is used as an elementary reaction of polyaddition reaction. Model reactions using styrene and 1-hydro-1,1,3,3,3-pentamethyldisiloxane with hexachloroplatinic acid(H_2PtCl_6•$6H_2O$) or tris(triphenylphosphine)rhodium chloride[$Rh(PPh_3)_3Cl$] as a catalyst were carried out. ^{1}H NMR spectrum of the product mixture catalyzed by $Rh(PPh_3)_3Cl$ is shown in Figure 1.

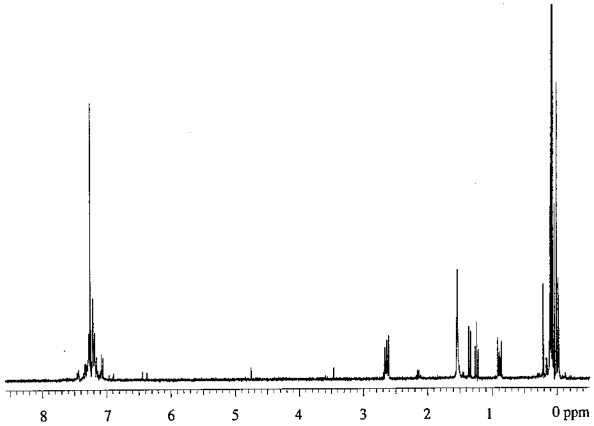
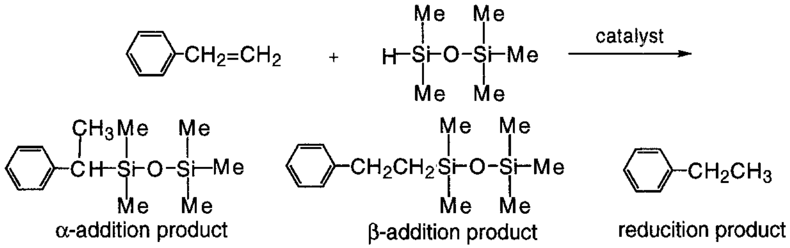


Figure 1. 300MHz ^{1}H NMR spectrum of the reaction mixture of model reaction.

By the help of ^{1}H-^{1}H COSY spectrum, the signals at 0.90 and 2.66 ppm are assigned to methylene protons of the β-addition product attached to silicon atom and phenyl ring, respectively. The signals at 1.36 and 2.20 ppm are assigned to methyl and methine protons of α-addition product. A pair of triplet at 1.26 ppm and quartet at 2.66 ppm which is buried in the big methylene signal of β-addition product are assigned to ethyl protons of reduction product, ethylbenzene.



Scheme 2. Reaction of styrene with 1-hydro-1,1,3,3,3-pentamethyldisiloxane.

Table 2. Selectivity in Model Reactions.

Run	Cat. (mol%)	Solv.	Temp (°C)	Time (h)[a]	Ratio (α/β/EB)[b]
1	$Rh(PPh_3)_3Cl$ (0.1)	bulk	50	18	22/55/23
2	$[Rh(COD)Cl]_2$ (0.1)	Tol.	50	24	19/54/27
3	$H_2PtCl_6 \cdot 6H_2O$ (1.0)	bulk	r.t.	2	25/62/13
4	$H_2PtCl_6 \cdot 6H_2O$ (0.1)	bulk	r.t.	4	29/71/0
5	PtDVTMDS (2.0)	bulk	r.t.	0.1	24/63/13
6	PtDVTMDS (0.1)	bulk	r.t.	0.1	28/72/0
7	cis-$PtCl_2(PhCN)_2$ (1.0)	Tol.	50	14	26/71/3
8	cis-$PtCl_2(PhCN)_2$ (0.1)	Tol.	50	1	22/78/0
9	$Co_2(CO)_8$ (1.0)	bulk	50	8	1/86/13
10	$Co_2(CO)_8$ (0.5)	bulk	50	18	0/91/9

a) Pentamethyldisiloxane was completely consumed.

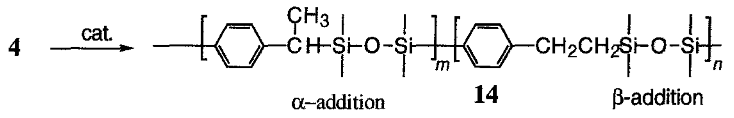
b) Determined by ^{1}H NMR.

The ratio of the product was estimated by the integral ratio of these signals. Results of hydrosilylation using several transition metal catalysts are summarized in Table 2.

Platinum catalyst such as $H_2PtCl_6 \cdot 6H_2O$ and PtDVTMDS(10) (DVTMDS: 1,3-divinyl-1,1,3,3-tetramethyldisiloxane) showed high reactivity in hydrosilylation reaction. Higher reaction temperature was required for rhodium catalyst. In the reaction, the catalysts generally gave two regioisomers(α-addition product/β-addition product). Ethylbenzene was not detected when small amounts (< 0.1 mol%) of platinum catalyst was used. Ethylbenzene was formed with rhodium catalyst or even with platinum catalyst of higher concentration(2.0% or higher). Cobalt catalyst showed high β-selectivity, however, considerable amounts of ethylbenzene was formed. In addition, higher reaction temperature was required.

The results of polyaddition of **4** catalyzed by platinum and cobalt catalysts in bulk condition are represented in Table 3.

Table 3. Polyaddition of Monomer **4**.



Run	Cat. (mol%)	Temp. (°C)	Time (h)[a]	*Mn*[b]	*Mw*/*Mn*	Ratio (α/β)[c]
1	PtDVTMDS (0.1)	r.t.	0.5	5600	1.3	28/72
2	*cis*-$Pt(PhCN)_2Cl_2$ (0.5)	50	1	2200	1.4	24/76
3	$Co_2(CO)_8$ (0.5)	50	3	1600	1.6	0/100

a) Reaction time when monomer was completely consumed.
b) Correlated by standard polystyrene.
c) Determined by ^1H NMR.

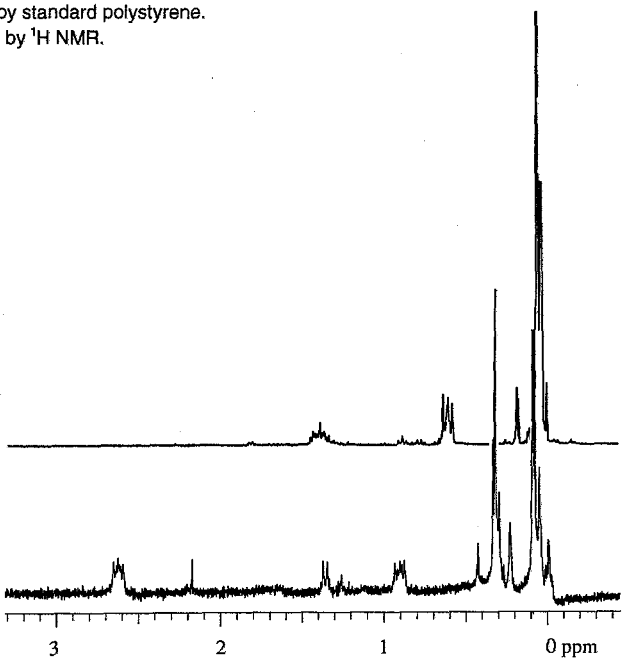
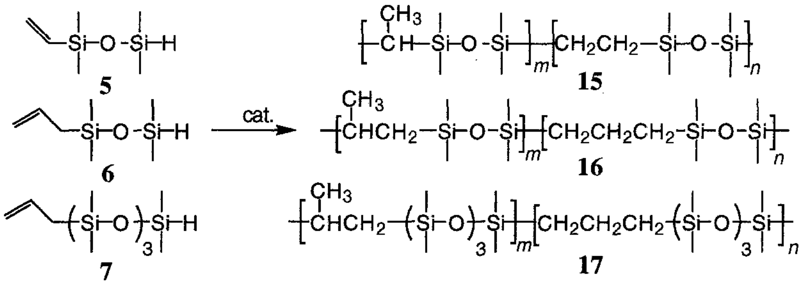


Figure 2. 300MHz ^1H NMR spectra of polymer **14**(lower) and **17**(upper).

Figure 2 shows ^{1}H NMR spectrum in 0~3 ppm region of the polymer **14** and **17**. Regioselectivity in the polyaddition to give polymer **14** estimated by the integral ratio of the signals at 1.36 and 0.90 ppm (α:β=3:7) is quite similar to that in the model reaction. With PtDVTMDS catalyst, polymer of *M*n = 5600 (*M*w / *M*n = 1.3) was obtained in 0.5h, however, further increase in the molecular weight was not observed. Cobaltoctacarbonyl catalyst gave only low molecular weight (*M*n = 1600) product. About 10% of styrene function of **4** was reduced to ethylbenzene group during the reaction evidenced by ^{1}H NMR. Formation of Si-Si bond was also evidenced by ^{29}Si NMR(around -20 ppm).

The results of the polyaddition of the functionalized disiloxane and tetrasiloxane **5**, **6** or **7** are shown in Table 4.

Table 4. Polyaddition of Monomers **5**, **6** and **7**.



Run	Monomer	Cat. (mol%)	Temp. (°C)	Time (h)[a]	*Mn*[b]	*Mw*/*Mn*	Ratio (α/β)[c]
1	**5**	PtDVTMDS (0.1)	r.t.	1	5400	1.5	38/62
2		*cis*-Pt(PhCN)$_2$Cl$_2$ (0.5)	50	1	4700	1.5	37/63
3	**6**	PtDVTMDS (0.1)	r.t.	1	2800	1.3	0/100
4		*cis*-Pt(PhCN)$_2$Cl$_2$ (0.5)	50	1	2800	1.3	0/100
5	**7**	PtDVTMDS (0.1)	r.t.	1	5200	1.5	0/100
6		*cis*-Pt(PhCN)$_2$Cl$_2$ (0.5)	50	1	4400	1.4	0/100

a) Reaction time when monomer was completely consumed.
b) Correlated by standard polystyrene.
c) Determined by ^{13}C NMR.

Regioisomeric ratio of polymer **15** was estimated from the ratio of the signals at 0.91(methyl of α-addition) and 1.01(methylene of β-addition)ppm by ^{1}H NMR spectrum. In ^{1}H NMR spectrum of the polymers **16** and **17**(shown in Figure 2-upper), only two methylene signals were observed at 1.40(SiCH$_2$C*H*$_2$CH$_2$Si and 0.60(SiC*H*$_2$) ppm, and ^{13}C NMR spectra showed only three(1.0, 17.2, 23.0 ppm) and four(0.2, 1.2, 17.1, 22.0 ppm) kinds of signal for **16** and **17**, respectively. If α-addition occurred, five signals must be observed. These facts strongly indicate the addition in β-mode, and are consistent with the reported facts in the hydrosilylation reaction of vinyl and allyl functions by platinum compounds(9-13).

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5. IR (neat) 2960, 2123, 1389, 1254, 1059, 909 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.22 (d, *J* = 2.8 Hz, 6H), 0.37 (s, 6H), 4.79 (heptet, *J* = 2.7 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 5.82 (d, *J* = 17.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz), 6.78 (dd, *J* = 8.0, 17.6 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H); ^{13}C-{^{1}H} NMR (CDCl$_3$) δ 0.53, 0.83, 30.3, 114.3, 125.5, 133.2, 136.8, 138.4.
6. IR (neat) 2961, 2124, 1596, 1407, 1254, 1062, 910 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.16 (s, 6H), 0.18 (d, *J* = 2.8 Hz, 6H), 4.70 (heptet, *J* = 2.8 Hz, 1H), 5.74 (dd, *J* = 20.0, 4.2 Hz, 1H), 5.95 (dd, *J* = 14.8, 4.1 Hz, 1H), 6.13 (dd, *J* = 14.8, 20.0 Hz, 1H); ^{13}C-{^{1}H} NMR (CDCl$_3$) δ 0.08, 0.83, 131.8, 139.1.
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8. IR (neat) 3080, 2961, 2917, 2124, 1632, 1420, 1254, 1159, 1065, 908, 835, 767 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 0.10 (s, 6H), 0.17 (d, *J* = 2.8 Hz, 6H), 1.57 (d, J = 9.1 Hz, 2H,), 4.69 (hextet, *J* = 2.8 Hz, 1H), 4.88 (dd, J = 9.1, 16.8 Hz, 2H), 5.72-5.87 (m, 1H); ^{13}C-{^{1}H} NMR (CDCl$_3$) δ 0.44, 0.83, 26.1, 113.4, 134.2.
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