

Synthesis of dichloro derivatives of linear and cyclic permethyloligosilanes and cyclolinear permethylpolysilane-siloxanes and permethylpolyoxysilane based on them

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The reactions of dodecamethylcyclohexasilane with chlorides of I, II, IV–VI, and VIII Group metals were studied as a promising approach to the synthesis of functional oligosilanes. When cyclohexasilane reacts with metal chlorides without a solvent at elevated temperatures, the process is intensified and, in some cases, the selectivity of formation of chloro derivatives of linear and cyclic permethyloligosilanes increases. The cyclolinear permethylpolysilane-siloxanes were prepared by heterofunctional polycondensation of the resulting oligosilanes with bifunctional cyclic and linear permethyloligosiloxanes. Cyclolinear permethylpolyoxysilane was synthesized for the first time by the reaction of 1,3-dihydroxycyclohexasilane with 1,3-dichlorohexamethyltrisilane.

Key words: metal chlorides, α,ω -dichloropermethyloligosilanes, chloro derivatives of cyclohexasilane, 1,3-dihydroxydodecamethylcyclohexasilane; heterofunctional polycondensation, cyclolinear permethylpolysilane-siloxanes and permethylpolyoxysilane.

The synthesis and properties of polysiloxanes¹ $-(\text{SiR}_2\text{O})_n-$ and, in recent years, polysilanes^{2,3} $-(\text{SiR}_2)_n-$, which possess unusual chemical and physico-chemical properties, have been well studied. Polysilane-siloxanes of regular structure, which combine to a certain extent the properties of two classes of organosilicon compounds, polysiloxanes and polysilanes, have been much less studied. For example, the introduction of siloxane units into polysilanes results in a higher solubility and meltability.^{4,5} In addition, polysilane-siloxanes retain unusual spectral properties (absorption in the UV region, and the ability to undergo photochemical curing), peculiar in polysilanes. At particular ring size and symmetry and polymer chain tacticity, cyclolinear permethylpolysiloxanes⁶ can form a mesophase. In this connection, synthesis and investigation of properties of copolymers with the silane-siloxane structure is a topical scientific task.

To date, methods for the synthesis of linear permethylpolysilane-siloxanes of regular structure $-(\text{SiMe}_2)_k-\text{O}-(\text{SiMe}_2\text{O})_m-$ ($k = 2-4, 6; m = 0-3$) are known.^{4,5,7-12} Recently,¹³⁻¹⁵ we reported the synthesis of cyclolinear permethyloligosilane-siloxanes based on dichlorooligosilanes. However, a number of combinations of these structural elements remained inaccessible because of the absence of appropriate monomers, which, in turn, is due to the inadequate selectivity of the methods of their synthesis.

Bifunctional linear and cyclic permethyloligosilanes are convenient starting compounds for the preparation of various copolymers containing oligosilane fragments.

The method used most widely to prepare dihalo-substituted oligosilanes is the reaction of oligocyclosilanes $(\text{R}_2\text{Si})_n$ with various halogenating agents. Thus α,ω -dichloropermethyloligosilanes $\text{Cl}(\text{Me}_2\text{Si})_n\text{Cl}$ (**1a-d** with $n = 2-4$ and 6 , respectively) are prepared by treatment of dodecamethylcyclohexasilane $(\text{Me}_2\text{Si})_6$ (**2**) with chlorinating agents such as chlorine,^{16,17} thionyl chloride,¹⁸ phosphorus pentachloride,¹⁹ and gallium(III), tin(IV), and titanium(IV) chlorides.²⁰ Chloro derivatives of cyclohexasilane **2** with the general formula $\text{Cl}_m\text{Si}_6\text{Me}_{12-m}$ (**3a-c** with $m = 1-3$, respectively) are prepared by chlorodemethylation of cyclosilane **2** on treatment with dry HCl in the presence of catalytic amounts of AlCl_3 (chlorocyclosilane **3a**)²¹ or by the reaction of cyclosilane **2** with SbCl_5 (monochloro-, dichloro-, and trichlorocyclosilanes **3a-c**).^{20,22-25}

This study deals with the reaction of cyclohexasilane **2** with metal chlorides of various chemical natures and aims at increasing the selectivity of the preparation of the dichloro derivatives of linear and cyclic oligosilanes. The prepared functional oligomers were used to synthesize cyclolinear permethylpolyoxysilane and permethylpolysilane-siloxanes containing linear and/or cyclic oligosilane fragments in the polymer chain.

Results and Discussion

Reactions of cyclohexasilane **2** with metal chlorides.

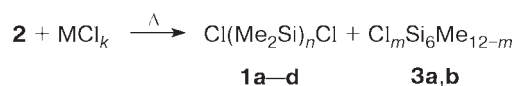
Previously,²⁰ it was shown that the reaction of cyclohexasilane **2** with SnCl₄ in CH₂Cl₂ gives not only dichlorohexasilane **1d** (*n* = 6) as the major product but also its lower homologs **1a–c** (*n* = 2–4, respectively) formed upon cleavage of the Si–Si bond in **1d**. Later,⁷ it was found that the reaction of cyclohexasilane **2** with SnCl₄ is accompanied by not only Si–Si bond cleavage in cyclohexasilane **2** and dichlorohexasilane **1d** but also by cleavage of the Si–Me bonds in the initial cyclohexasilane **2** to give its monochloro (**3a**) and dichloro (**3b**) derivatives.

Cyclohexasilane **2** reacts with TiCl₄ in CH₂Cl₂ in a similar way, *i.e.*, with Si–Si and Si–Me bond cleavage in cyclohexasilane **2** to give dichlorooligosilanes **1a–d** and monochlorocyclohexasilane **3a**.^{7,20} The reaction of cyclohexasilane **2** with tin and titanium chlorides in CH₂Cl₂ proceeds slowly with a relatively low degree of conversion of the initial cyclic compound. Thus²⁰ in the case of SnCl₄, the degree of conversion of cyclohexasilane **2** after 24 h was 33%, while in the case of TiCl₄, this value reached 51% after 70 h. It was also shown²⁰ that in the absence of a solvent, the degree of conversion of cyclohexasilane **2** in the reaction with SnCl₄ at 170 °C was 100% after 4 h, linear dichlorooligosilanes **1a–d** being formed as the only products.

In this respect, we studied the reaction of several nontransition and transition (HgCl₂, SnCl₄, SbCl₅, CuCl₂,

FeCl₃, TiCl₄, ZrCl₄, MoCl₅, WCl₆) metal chlorides with cyclohexasilane **2** in the absence of a solvent at elevated temperatures. Under these conditions (Scheme 1, Table 1), cyclohexasilane **2** reacts with the above metal chlorides with cleavage of its Si–Si and Si–Me bonds to give linear and cyclic chloro-substituted permethyloligosilanes.

Scheme 1



n = 2 (**1a**), 3 (**1b**), 4 (**1c**), 6 (**1d**);
m = 1 (**3a**), 2 (**3b**), 3 (**3c**);
m > 3 (**3d**)

It should be noted that tin and mercury chlorides react with cyclohexasilane **2** mainly with cleavage of the Si–Si bond giving predominantly linear dichlorooligosilanes **1a–d** (the content of chloro-substituted cyclohexasilanes **3a–c** in the products did not exceed 7.5%), the degree of conversion of cyclohexasilane **2** being rather high (80–100%). In the reactions of the rest of metal chlorides studied with cyclohexasilane **2**, the intensity of cleavage of the Si–Me bonds in the initial ring increases, which results in markedly higher proportions of chloro-substituted cyclohexasilanes in the products. Indeed, ZrCl₅ and WCl₆ react with cyclohexasilane **2** with the predominant formation of chloro-

Table 1. Conditions and products of the reaction of cyclohexasilane **2** with metal chlorides MCl_{*k*}

Entry	MCl _{<i>k</i>}	2 : MCl _{<i>k</i>}	<i>T</i> /°C	<i>t</i> /h	Composition of the reaction mixture (%) ^a								Yield ^b 1 (%)	Conver- sion of 2 (%)
					1a	1b	1c	1d	2	3a	3b	3c		
1	HgCl ₂	1 : 2	210	2	33.1	45.0	13.8	2.3	2.0	0.8	1.2	1.8	86.9	98.2
2	SnCl ₄	1 : 1	175	0.5	7.5	11.3	9.6	46.1	18.1	3.9	1.6	1.9	86.5	82.6
3	SnCl ₄	1 : 1	175	1	9.0	14.8	11.3	44.3	14.2	3.4	1.4	1.6	87.2	86.5
4	SnCl ₄	1 : 1	175	2	13.5	19.1	13.5	40.2	10.9	0.9	1.5	0.4	89.5	89.8
5	SnCl ₄	1 : 2	175	1	29.9	34.7	25.8	1.5	0.6	1.8	0.8	4.9	78.9	99.5
6	SnCl ₄	1 : 2	175	2	41.5	37.0	18.7	—	—	0.8	0.4	1.6	86.9	100
7	SbCl ₅ ^c	1 : 1	25	2	—	—	—	0.5	2.8	5.4	89.3	2.0	0.5	97.2
8	SbCl ₅	1 : 2	25	0.002	43.4	11.4	10.8	3.1	—	4.5	6.8	19.3 ^d	66.3	100
9	CuCl ₂	1 : 1	180	1	5.8	9.6	4.6	16.1	44.3	2.1	11.2	6.3	53.8	60.2
10	CrCl ₃	1 : 2	210	2	0.1	0.3	0.4	2.6	89.7	0.2	6.7	—	33.0	10.3
11	FeCl ₃	1 : 1	180	2	1.4	3.6	2.3	5.7	84.3	0.3	2.4	—	53.5	19.6
12	TiCl ₄	1 : 1	175	3	8.0	9.2	9.3	28.4	21.2	2.2	16.4	5.3	55.5	81.3
13	ZrCl ₄	1 : 1	200	2	1.9	1.9	2.2	23.4	25.7	6.4	16.2	19.0 ^e	27.3	80.2
14	MoCl ₅	1 : 1	185	3	10.9	6.3	4.4	17.8	27.4	14.0	10.1	9.1	40.2	78.2
15	WCl ₆	1 : 1	205	1	17.8	9.4	5.9	6.7	6.9	7.5	4.6	11.8 ^f	34.6	94.3

^a Unidentified by-products were neglected.

^b Total yield of oligomers **1a–d** from all reaction products (including unidentified ones) and in relation to the reacted cyclohexasilane **2** (according to GLC).

^c The reaction was carried out in CCl₄.

^d The reaction mixture contains 0.7% polychloro-substituted cyclohexasilanes **3d**.

^e The reaction mixture contains 3.3% polychloro-substituted cyclohexasilanes **3d**.

^f The reaction mixture contains 29.4% polychloro-substituted cyclohexasilanes **3d**.

substituted cyclosilanes **3a–c**; polychlorinated cyclosilanes $\text{Cl}_m\text{Si}_6\text{Me}_{12-m}$ (**3d**, $m > 3$) are also formed. For example, CrCl_3 and FeCl_3 proved to be the poorest chlorinating agents for cyclosilane **2**; the degree of conversion of **2** was $\leq 20\%$; however, even in those cases where the conversion of cyclosilane **2** in the reactions with metal chlorides was rather high, the yield of linear dichloro-oligosilanes **1a–d** did not exceed 55%.

Previously, it was shown²⁰ that the reaction of SbCl_5 with cyclosilane **2** in the presence of a solvent (CH_2Cl_2 , CHCl_3 , CCl_4) proceeds selectively with cleavage of only Si–Me bonds in the initial cyclosilane **2**, the Si–Si bonds remaining intact. When reproducing the procedure, we obtained almost analogous results (see Table 1, entry 7), namely, the content of the linear dichlorooligosilane **1d** in the reaction mixture was only 0.5%. Dichloro-substituted cyclosilane **3b** was formed as the major reaction product; as shown previously,^{22–24} this product was a mixture of structural isomers, namely, 1,3-dichlorocyclosilane (**3b'**) and 1,4-dichlorocyclosilane (**3b''**) (in $\sim 1 : 1$ ratio), which are, in turn, mixtures of *cis*- and *trans*-isomers (see Experimental, ²⁹Si NMR spectra of cyclosilanes **3b'** and **3b''**). A very reactive chlorinating agent for cyclosilane **2** is SbCl_5 . Treatment of cyclosilane **2** with SbCl_5 in a 1 : 2 ratio at $\sim 20^\circ\text{C}$ without a solvent bring about a vigorous exothermal reaction with 100% conversion of cyclosilane **2** over a period of several seconds; this gives not only chloro-substituted cyclosilanes **3a–d** but also linear α,ω -dichlorooligosilanes **1a–d** (the ratio of linear to cyclic chloro-substituted oligosilanes was $\sim 2 : 1$). Thus, unlike the reaction in solutions, not only Si–Me but also Si–Si bonds of cyclosilane **2** are cleaved in the solvent-free reaction.

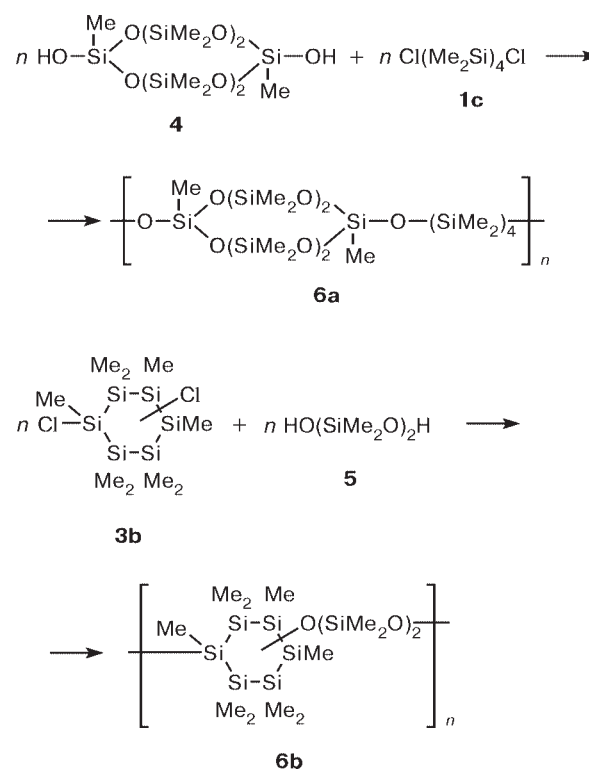
The influence of the reaction conditions on the conversion of cyclosilane **2**, on the yield and composition of the reaction products, and on the ratio between them was studied in relation to the reaction of **2** with SnCl_4 . An increase in the reaction time (*cf.* entries 2–4, 5, and 6 in Table 1) results in a higher yield of linear dichloro-oligosilanes **1a–d** and a lower content of chloro-substituted cyclosilanes **3a–c** in the reaction products. In addition, the content of short-chain linear oligomers **1a** and **1b** increases and the content of dichlorotetrasilane **1c** and dichlorohexasilane **1d** decreases. Evidently, this is due to an increase in the intensity of Si–Si bond cleavage in oligomers **1c** and **1d** following an increase in the reaction time. For equal reaction times, transition from 1 : 1 ratio of cyclosilane **2** to SnCl_4 to 1 : 2 ratio (*cf.* entries 3 with 5 and 4 with 6 in Table 1), allows one to attain virtually 100% conversion of cyclosilane **2** with simultaneous sharp decrease (to 0–1.5%) in the content of dichlorohexasilane **1d** in the reaction products. In addition, the content of short-chain oligomers **1a** and **1b** increases 2–3-fold.

Thus, variation of conditions of the reaction between cyclosilane **2** and SnCl_4 makes it possible to control to a

certain extent the length of the oligomer chain in the resulting α,ω -dichlorooligosilanes **1**.

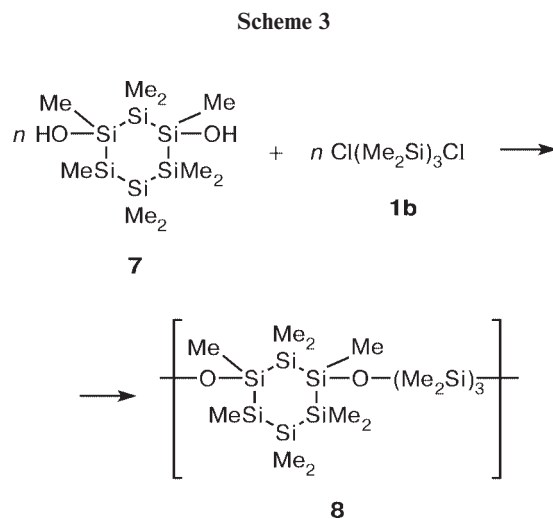
Synthesis of cyclolinear polysilane-siloxanes and polyoxysilane. Based on synthesized oligosilanes, studies on the preparation of new polymers and copolymers containing oligosilane structural fragments were continued. New cyclolinear permethylpolysilane-siloxanes were prepared by heterofunctional polycondensation of linear **1c** and cyclic **3b** dichlorooligosilanes with cyclic **4** and linear **5** dihydroxyoligosiloxanes, respectively (Scheme 2). Dichloro-substituted cyclosilane **3b** was used as a mixture of structural and spatial isomers (dichlorocyclosilanes **3b'** and **3b''** in $\sim 1 : 1$ ratio, see Experimental), and dihydroxycyclosiloxane **4**, as a mixture of *cis*- and *trans*-isomers ($\sim 2 : 3$).

Scheme 2



The reactions were carried out in the presence of Py as an HCl acceptor. The yield of copolymers **6a,b** was 80–94%. The molecular masses of copolymers **6a** and **6b** estimated from viscometry data were ~ 6000 and ~ 11000 , respectively. Heterofunctional polycondensation of 1,3-dihydroxydecamethylcyclohexasilane (**7**), prepared by hydrolysis of a mixture of dichlorocyclosilane isomers **3b'** and **3b''** using modification of a reported method,²⁴ with 1,3-dichlorotrisilane **1b** by a similar procedure gave cyclolinear permethylpolyoxysilane (**8**), whose backbone consisted of cyclic and linear silane fragments linked by

oxygen bridges, the product yield being 74% (Scheme 3). The weight average molecular mass M_w of copolymer **8** was 4670; polydispersity $M_w/M_n = 1.48$.



Copolymers **6a,b** and **8** are thick colorless liquids readily soluble in conventional organic solvents. The synthesized copolymers were characterized by IR, UV, and NMR spectroscopy. The ^{29}Si NMR spectra (see Experimental) confirm the formation of regular copolymers with the backbone consisting of alternating cyclic and linear fragments. The IR spectra of copolymers **6a,b** and **8** exhibit absorption bands in the region of ν 1070 and 1040–1025 cm^{-1} , typical of the Si–O–Si bond. Owing to the presence of oligosilane fragments in the polymer chain, copolymers **6a,b** and **8** retain the ability to absorb in the UV region inherent in compounds with a purely silane structure. Indeed, the UV spectrum of copolymer **6a** exhibits an absorption band at about 235 nm, whose position virtually coincides with that for the initial dichlorotetrasilane **1c** (234 nm). The UV absorption of copolymer **6b** is due to the presence of cyclosilane fragments in the polymer chain (two absorption bands in the region of 256 and 273 nm). The UV spectrum of copolymer **8** exhibits one absorption band at about 280 nm, typical of the cyclohexasilane unit present in the copolymer, while the absorption band corresponding to the linear oligosilane fragment in the polymer structure is missing. A similar pattern (the presence of absorption bands due to cyclic fragments and the absence of bands for the linear fragments) was observed in the UV spectra of cycloliner compounds with the purely silane structure, α,ω -bis(cyclopentasilanyl)oligodimethylsilanes.²⁶

The glass transition temperature T_g of copolymer **8** was -100 °C, which is close to the calculated* T_g value

* The T_g value for copolymer **8** was calculated by Prof. A. A. Askadskii by the atomic constants method.²⁷

equal to -97 °C. This low T_g value of copolymer **8** is, apparently, due to the presence of oxygen bridges between cyclic and linear silane fragments in the copolymer backbone.

Thus, new cycloliner permethylpolysilane-siloxanes and permethylpolyoxsilane of a regular structure were synthesized by heterofunctional polycondensation.

Experimental

GLC analysis was carried out on a LKhM-8MD chromatograph (a 0.3×100 cm stainless-steel column, 5% SE-30 on Chromaton N-AW-DMCS; katharometer as the detector, temperature programming from 30 to 300 °C, heating rate 12 K min^{-1} ; helium as the carrier gas).

^{29}Si NMR spectra were recorded on Bruker WP-200 SY (39.76 MHz) and Bruker WP-400 SY (79.46 MHz) spectrometers using Me_4Si as the internal standard. IR and UV spectra were recorded in thin films using Specord M-82 and Specord M-40 spectrophotometers, respectively.

The intrinsic viscosity $[\eta]$ of polysilane-siloxanes **6a,b** was determined in toluene at 25 °C using a Ubbelohde viscometer with suspended level. The molecular masses of copolymers **6a,b** were roughly estimated using coefficients of the Mark–Kuhn–Houwink equation for cycloliner polysiloxanes reported previously.²⁸

The molecular-mass characteristics of copolymer **8** were determined by gel chromatography on a Bruker LC21 liquid chromatograph (refractometer as the detector, columns with the polystyrene-divinylbenzene gel, toluene as the eluent, calibration against the polystyrene standard).

Cyclosilane **2** was prepared by catalytic depolymerization of polydimethylsilane by a procedure described previously.⁷ Mono- and trichloro-substituted cyclosilanes **3a,c** were identified by comparison with reference samples synthesized by known procedures.^{21,25} 1,3-Dihydroxycyclosilane **7** was prepared by a modification of a published procedure.²⁴ Dihydroxycyclosiloxane **4** (a mixture of *cis*- and *trans*-isomers in $\sim 2 : 3$ ratio) was synthesized by a known procedure.²⁹ Dihydroxydisiloxane **5** was prepared by a known procedure.³⁰ Immediately prior to the use, TiCl_4 , SnCl_4 , and SbCl_5 were distilled in an N_2 flow, while the other metal chlorides were used as received. Ether and benzene were dried by refluxing followed by distillation over sodium metal in the presence of benzophenone in an N_2 flow; CCl_4 and MeCN were dried by distillation over P_2O_5 in an N_2 flow. Pyridine was distilled over NaOH granules. All the reactions were carried out in an atmosphere of dry argon or nitrogen.

Reaction of cyclosilane 2 with SnCl_4 (typical procedure) (Table 1, entry 3). Cyclosilane **2** (34.9 g, 0.1 mol) was placed in an ampoule equipped with a branch for reactant introduction and a Teflon stopcock, SnCl_4 (26.1 g, 0.1 mol) was added, and the ampoule was placed in an oil bath pre-heated to 175 °C. The reaction mixture was kept at this temperature with intense stirring for 1 h. The ampoule was cooled and 50 mL of anhydrous CCl_4 was added. The SnCl_2 precipitate was filtered off and washed with anhydrous CCl_4 (2×10 mL). The solvent was evaporated and the residue was analyzed by GLC (see Table 1). Fractionation of the residue gave 5.6 g (10.0% relative to the reacted cyclosilane **2**) of dichlorodisilane **1a**, b.p. 148–148.5 °C, ^{29}Si NMR (CCl_4), δ : 17.21; 8.1 g (16.5%) of dichlorotrisilane

1b, b.p. 84–85 °C (10 Torr), ^{29}Si NMR (CCl_4), δ : 24.98 (SiMe_2Cl), –43.71 (SiMe_2); and 5.7 g (12.7%) of dichlorotetrasilane **1c**, b.p. 111–113 °C (5 Torr), ^{29}Si NMR (CCl_4), δ : 26.26 (SiMe_2Cl), –42.68 (SiMe_2). After evaporation of lower dichloro-oligosilanes **1a–c**, the initial cyclosilane **2** and chloro-substituted cyclosilanes **3a** and **3b** were removed by sublimation. Distillation of the residue gave 20.8 g (49.5%) of dichlorohexasilane **1d**, b.p. 166–167 °C (1 Torr), m.p. 45–46 °C. ^{29}Si NMR (CCl_4), δ : 26.35 (SiMe_2Cl); –40.90 (Si_bMe_2); –39.65 (Si_cMe_2).

Entries *1*, *2*, *4–6*, and *8–15* were carried out in a similar way (entry *8*, without heating) (see Table 1) except that the residue after removal of CCl_4 was not fractionated but was analyzed by GLC.

Reaction of cyclosilane **2** with SbCl_5 (Table 1, entry 7).

A solution of SbCl_5 (11.8 g, 39.4 mmol) in 30 mL of anhydrous CCl_4 was added dropwise to a solution of cyclosilane **2** (10.0 g, 28.7 mmol) in 55 mL of anhydrous CCl_4 cooled to 0 °C. The reaction mixture was vigorously stirred for 2 h at ~20 °C, the course of the reaction being monitored by GLC. The precipitate was filtered off and washed with anhydrous hexane (2 × 10 mL). The solvents were removed on a rotary evaporator and the initial cyclosilane **2** and the reaction products (chloro-substituted cyclosilanes **3a–c**) were extracted from the residue with anhydrous hexane (3 × 10 mL). Acetonitrile (6 mL) was added to the resulting solution for deactivation of antimony compounds and the hexane solution of the reaction products was separated using a separating funnel. Hexane was removed on a rotary evaporator. The initial cyclosilane **2** and monochloro-substituted cyclosilane **3a** were removed from the crystalline residue by sublimation (80 °C, 1 Torr). The residue after sublimation was recrystallized from anhydrous pentane to give 6.7 g (60%) of a mixture of 1,3- (**3b'**) and 1,4-dichlorocyclosilane (**3b''**) isomers (–1 : 1). ^{29}Si NMR (CCl_4 : CDCl_3 (1 : 1)), δ : **3b'** (*cis*-, *trans*-isomers): 15.42, 14.90 (SiMeCl), –37.05, –37.62 ($\text{ClSiSiMe}_2\text{SiCl}$), –38.94, –39.36 ($\text{Me}_2\text{SiSiMe}_2\text{SiCl}$), –42.48, –44.59 ($\text{Me}_2\text{SiSiMe}_2\text{SiMe}_2$); **3b''** (*cis*-, *trans*-isomers): 15.60, 15.13 (SiMeCl), –39.66, –39.92 (SiMe_2).

Synthesis of polysilane-siloxanes **6a,b** and polyoxysilane **8**.

A mixture of dihydroxycyclosiloxane **4** (0.7 g, 1.56 mmol) and Py (0.24 g, 3.12 mmol) in 5 mL of anhydrous ether was added dropwise to a solution of dichlorotetrasilane (0.47 g, 1.56 mmol) **1c** in 1 mL of anhydrous ether with intense stirring. The reaction mixture was stirred for 8 h at ~25 °C, 2.5 mL of anhydrous benzene was added, and the mixture was brought to boiling and stirred for 20 h. Anhydrous benzene (15 mL) was added and the Py · HCl precipitate was filtered off and washed with anhydrous benzene (2 × 5 mL). The benzene solution was washed with water to a neutral reaction and dried with Na_2SO_4 . The polymer was precipitated by adding a threefold excess of MeOH and dried in a vacuum chamber (60 °C) to a constant weight to give 1.0 g (94.3%) of polysilane-siloxane **6a**, $[\eta] = 0.05 \text{ dl g}^{-1}$, molecular mass ~6000. Found (%): C, 31.47; H, 7.97; Si, 40.98. $\text{C}_{18}\text{H}_{54}\text{O}_8\text{Si}_{10}$. Calculated (%): C, 31.86; H, 7.96; Si, 41.40. UV, $\lambda_{\text{max}}/\text{nm}$: 235. IR (KBr), ν/cm^{-1} : 2958, 2913, 2879 (C–H); 1260, 853, 802, 762 (Si–Me); 1075, 1040 (SiOSi). ^{29}Si NMR (CCl_4 : CDCl_3 (1 : 1)), δ : 9.41, 8.73 ($(-\text{O})_2\text{SiOSiSi}$), –21.61, –22.10, –22.35, –22.78 (OSiOSiO), –47.67, –48.79 ($\text{OSi(Si)}_2\text{SiO}$), –64.65, –65.75 ($(-\text{O})_2\text{SiOSiSi}$).

The reaction of isomer mixture of dichlorocyclosilanes **3b'** and **3b''** (4.22 g, 10.87 mmol), dihydroxydisiloxane **5** (1.80 g, 10.87 mmol), and Py (1.72 g, 21.74 mmol) by a procedure simi-

lar to the previous one gave 4.19 g (80%) of polysilane-siloxane **6b**. Fractional precipitation gave the fraction (1.85 g) of copolymer **6b**, $[\eta] = 0.08 \text{ dl g}^{-1}$, molecular mass ~11000. Found (%): C, 34.47; H, 8.27; Si, 46.08. $\text{C}_{14}\text{H}_{42}\text{O}_3\text{Si}_8$. Calculated (%): C, 34.85; H, 8.71; Si, 46.47. UV, $\lambda_{\text{max}}/\text{nm}$: 256, 273. IR (KBr), ν/cm^{-1} : 2953, 2885 (C–H); 1261, 841, 802, 764 (Si–Me); 1074, 1025 (SiOSi). ^{29}Si NMR (CDCl_3), δ : 5.52, 5.04, ((Si) $_2$ SiO), 5.42, 4.96 (OSiSiSiO), –20.59, –21.07, –21.22, –21.39 (OSiOSiO), –43.12, –44.16 (OSi(Si) $_2$ SiO), –43.28, –43.35, –44.62, –44.75 (OSiSiSi, OSiSiSiO), –47.03, –47.54 (OSiSiSiSiSiO).

The reaction of dihydroxycyclosilane **7** (1.18 g, 3.35 mmol), dichlorotrisilane **1b** (0.82 g, 3.35 mmol), and Py (0.53 g, 6.70 mmol) carried out similarly to the synthesis of copolymer **6a** gave 1.30 g (74.3%) of polyoxysilane **8**. Reprecipitation gave a fraction (0.73 g) with $[\eta] = 0.10 \text{ dl g}^{-1}$, $M_w = 4670$, $M_n = 3160$. Found (%): C, 36.21; H, 9.05; Si, 47.85. $\text{C}_{16}\text{H}_{48}\text{O}_2\text{Si}_9$. Calculated (%): C, 36.58; H, 9.21; Si, 48.12. UV, $\lambda_{\text{max}}/\text{nm}$: 280. IR (KBr), ν/cm^{-1} : 2953, 2891 (C–H); 1249, 836, 802, 768 (Si–Me); 1028 (SiOSi). ^{29}Si NMR (CDCl_3), δ : 8.80 ((Si) $_5$ SiOSi); 6.98 ((Si) $_5$ SiOSiSiSiO); –42.79 (O(Si)SiSiSi(Si)O); –43.50 (OSiSiSiSiSiO); –48.00 (OSiSiSiSiSiO); –53.04 ((Si) $_5$ SiOSiSiSiO).

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