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Synthesis of organosilicon polymers with cyclohexasilane fragments in the main chain

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Permethylated cyclolinear polysilanes and polyoxasilanes were synthesized by the reaction of 1,3- and 1,4-dichlorodecamethylcyclohexasilanes with metallic sodium (the Wurtz-type reaction) and *cis*-1,3-dihydroxydecamethylcyclohexasilane (heterofunctional polycondensation reaction). Thermal and thermooxidative stability, as well as spectroscopic properties of the polymers obtained and products of their thermal decomposition were studied.

Key words: dichlorodecamethylcyclohexasilane, *cis*-1,3-dihydroxydecamethylcyclohexasilane; cyclolinear polysilanes, polyoxasilanes.

Earlier, it has been reported on the synthesis of permethylated linear polyoxasilanes[1—7] and polysilane-siloxanes[1,2,8,9], as well as cyclolinear polysilane-siloxanes[10—12] and polycarbosilanes[13] containing linear or/and cyclic oligosilane fragments in their main chain. These polymers are of interest as ceramics-forming polymers (silicon-carbide and silicon-oxycarbide ceramics)[11,13,14] and polymeric photoinitiators of solidification of vinyl-containing organosilicon rubbers and compositions on their basis.[15—17] Permethylated polysilane-siloxanes, whose macromolecules consist of alternating cyclohexasilane and cyclohexasiloxane units linked *via* oxygen atom, can exist in mesomorphous state within a wide range of temperatures.[12]

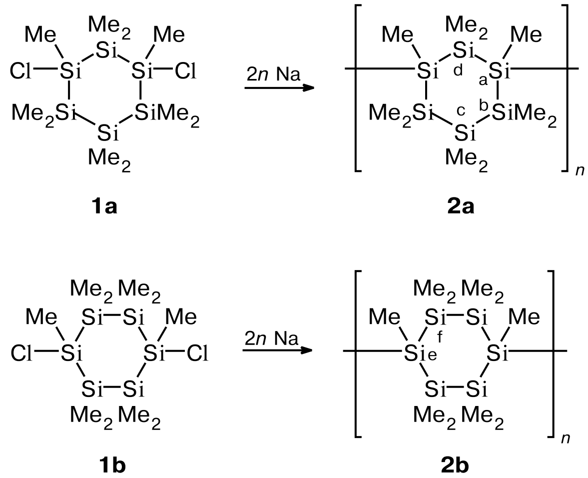
By now, there is virtually no reports in the literature on organosilicon polymer containing in the main chain cyclohexasilane units alone. It has been reported[18] only on the synthesis of poly(permethylcyclohexasilane), which contained approximately 10% of siloxane units.

The purpose of the present work is to synthesize organosilicon polymers of regular structure containing cyclohexasilane units in the polymeric chain, linked either directly to each other or through a heteroatom (oxygen), and to study their properties.

Results and Discussion

Synthesis of polycyclohexasilanes was carried out by the Wurtz-type reaction between 1,3-dichlorodecamethylcyclohexasilane (**1a**) or 1,4-dichlorodecamethylcyclohexasilane (**1b**) with metallic Na dispersed in boiling toluene (Scheme 1). Dichlorocyclosilanes **1a** and **1b** were used as mixtures of *cis*- and *trans*-isomers in the ratio ~1 : 1.

Scheme 1



The reaction of dichlorocyclosilane **1a** with metallic Na after reprecipitation gave a polymer **2a** as a white amorphous powder, which was soluble in aromatic and chlorinated hydrocarbons (Fig. 1). The yield and molecular-mass characteristics of polymer **2a** are given in Table 1.

Unlike dichlorocyclosilane **1a**, dichlorocyclosilane **1b** reacts with metallic Na to form considerable amount (28%) of an insoluble polymer. Polymer **2b** (see Table. 1) was obtained after separation of soluble polymeric fraction by reprecipitation with methanol, the former according to the X-ray diffraction data is partially crystalline. Diffraction pattern of polymer **2b** (Fig. 2) shows two reflections with the angle positions 10.8 and 12.5° and an amorphous halo at 20—30°. Diffraction pattern of insoluble fraction of polymer **2b** contains additional reflections with the angle positions 24.5 and 32.0°.

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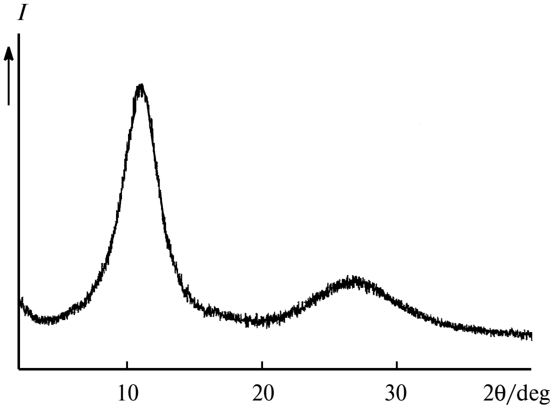

Fig. 1. Diffraction pattern of polymer **2a**.

The reaction of heterofunctional polycondensation of mixtures of *cis*- and *trans*-isomers 1,3-dichlorocyclosilane **1a** or 1,4-dichlorocyclosilane **1b** with *cis*-dihydroxydecamethylcyclohexasilane (**3**) in the presence of pyridine as an acceptor of HCl resulted in polymers **4a** and **4b**, respectively, containing in the main chain cyclohexasilane fragments linked *via* oxygen bridges (Scheme 2). Polymers **4a** and **4b** are viscous liquids, their yields and molecular-mass characteristics are given in Table 1. Not very high molecular weights of these polymers are apparently due to the low reactivity of functional groups in the cyclohexasilanes. It is known[19] that monochlorine derivative of cyclohexasilane is very stable to hydrolysis, while its monohydroxy derivative to condensation. In this case, homocondensation of hydroxycyclohexasilane at elevated temperatures occurs with the ring opening and formation of Si—H and Si—O—Si bonds. The IR spectra of polymers **4a** and **4b** have no absorption bands characteristic of a Si—H bond in the region 2060 cm^{-1}. This allows us to suggest that no ring opening occurs in dihydroxycyclohexasilane **3** during synthesis of these polymers.

It is known[9,20] that the nature of the HCl acceptor in the reaction of heterofunctional polycondensation affects yields and molecular weights of polymer. Molecular mass and yield of polymer **4a** were increased when 4-dimethylaminopyridine (DMAP), possessing high nucleophilicity, was added to pyridine (see Table. 1).

Scheme 2

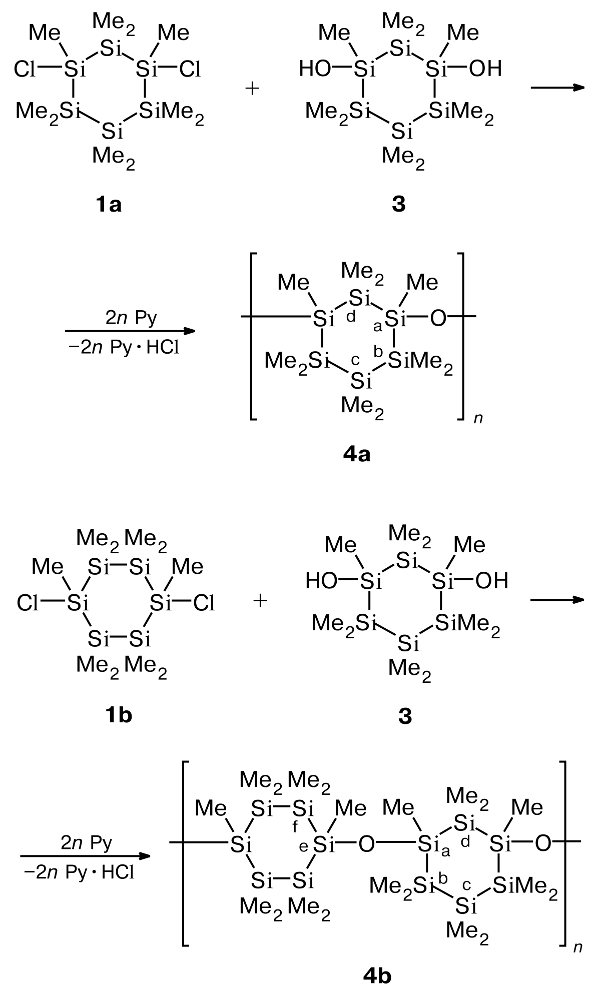

Table 1. Yields, molecular-mass characteristics, and intrinsic viscosity of polymers **2a,b** and **4a,b**

Polymer	Yield (%)	$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	M_w/M_n	[η] (dL g^{-1})
2a	71.1	7.0	3.3	2.1	0.033
2b	82.3	7.8	4.1	1.9	0.041
4a	57.3	2.5	1.9	1.3	0.022
4a*	73.2	2.9	2.1	1.4	0.025
4b	61.1	2.7	1.8	1.5	0.023

* The pyridine—DMAP mixture (10 : 1) was used as an acceptor of HCl.

Spectroscopic characteristics of polymers 2a,b and 4a,b. The structures of synthesized polymers were studied by

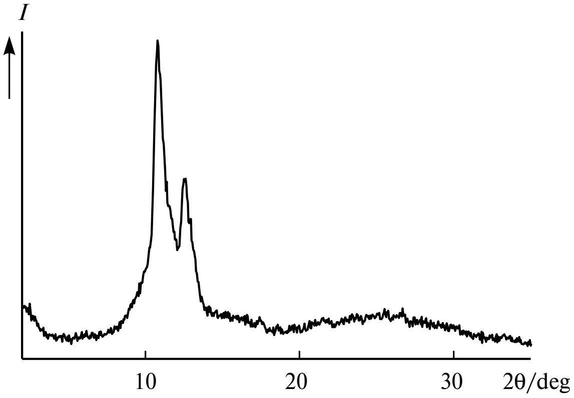

Fig. 2. Diffraction pattern of polymer **2b**.

spectroscopic methods (IR, UV, and ^{29}Si NMR spectroscopy). The UV spectra of all the polymers obtained have the absorption maxima (λ_{max}) of the silane ring in the region 250—260 nm, while the spectra of polymers **2a,b** have additional maxima in the region 310 nm due to the presence of the Si atoms bonding the rings (Table. 2). The IR spectra of polymers **4a,b** exhibit strong wide absorption bands in the region 1080—1070 cm^{-1} characteristic of the stretching vibrations of Si—O—Si bonds.

The ^{29}Si NMR spectra confirm that polymers of regular structure are formed, whose main chains consist of cyclohexasilane units linked to each other either directly (polymers **2a,b**), or through the oxygen bridges (polymers **4a,b**). Polymers **2a** and **2b**, whose cyclohexasilane fragments of the polymeric chain are bonded to each other at positions 1 and 3 (polymer **2a**) and 1 and 4 (polymer **2b**), have virtually the same chemical shifts for the Si$_a$ (polymer **2a**) and Si$_e$ atoms (polymer **2b**), which are about –62.5 ppm (see Table. 2). At the same time, the chemical shift for the Si$_a$ atom in polymer **2a** is somewhat different from the chemical shift for the analogous Si atom (about –67 ppm) in bis(undecamethylcyclohexasilan-1,3-yl),[21] which, essentially, is a dimeric unit of polycyclohexasilane. Introduction of the oxygen bridge between the cyclohexasilane fragments of the polymer (polymers **4a,b**) leads to a considerable change in the character of the spectrum: the signals for the Si$_a$ and Si$_e$ atoms are sharply downfield shifted (from δ –62.5 for polymers **2a,b** to δ ~7.5 for polymers **4a,b**). It should be noted that each Si atom in the cyclosilane fragment of the polymers gives two signals in the spectrum, since the starting dichlorocyclosilanes **1a,b** are, as it was indicated above, mixtures of *cis*-, *trans*-isomers.

Thermooxidative and thermal stabilities of polymers 2a,b and 4a. Thermooxidative and thermal stability of the polymers synthesized were studied by thermogravimetric analysis (TGA). Thermooxidative decomposition of polymers **2a,b** in air (Fig. 3, *a*) proceeds in two steps: in the temperature ranges 250—350 °C (I) and 350—550 °C (II). At higher temperatures (up to 1000 °C), the weight of the samples remains unchanged. The loss in weight of polymers **2a** and **2b** is virtually the same and considerably lower than that of high-molecular-weight polydimethylsilane (PDMS), whose intensive loss in weight begins already at 200 °C (see Fig. 3, *a*, curve *3*).

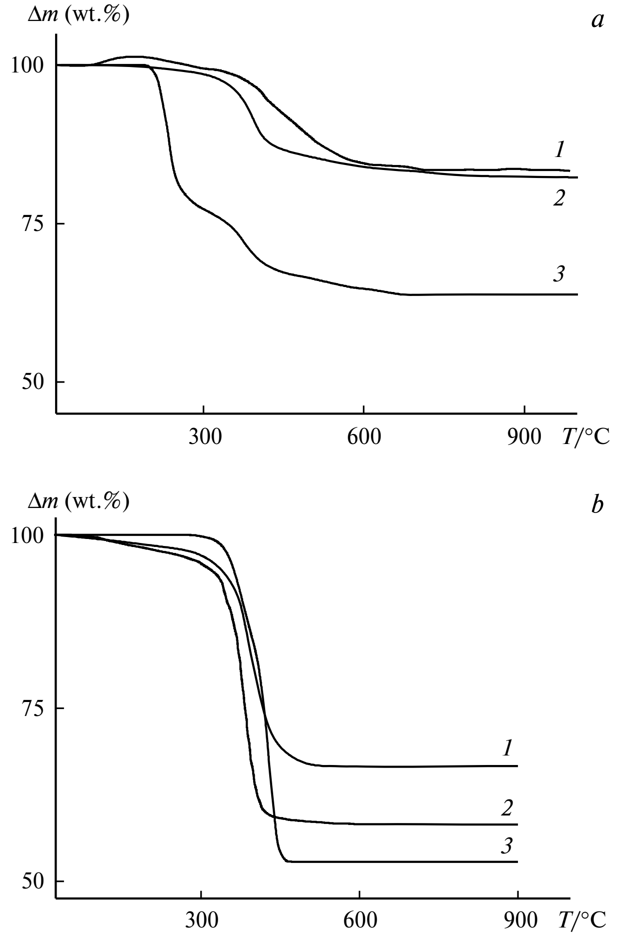

Fig. 3. TGA curves of the samples of polymers **2a** (*1*), **2b** (*2*), and PDMS (*3*) on heating in air (*a*) and in the argon atmosphere (*b*).

The TGA curves of polymers **2a,b** and PDMS (for comparison) in argon are given in Fig. 3, *b*. The main loss in weight of the polymers takes place in the temperature range 300—450 °C; at higher temperatures, the mass of the samples remains virtually unchanged. Note that thermolysis of polycyclosilanes **2a,b**, as well as their thermooxidative decomposition is characterized by lower loss in weight for these polymers than for PDMS.

Table 2. ^{29}Si NMR and UV spectra of polymers **2a,b** and **4a,b**

Polymer	^{29}Si NMR, δ,				UV, λ_{max}/nm
	Si$_a$	Si$_b$, Si$_c$, Si$_d$	Si$_e$	Si$_f$	
2a	–62.36, –62.57	–(38.43—39.05)	—	—	252, 313
2b	—	—	–62.51, –62.80	–38.23, –39.16	250, 310
4a	7.21, 7.34	–(42.53—45.58)	—	—	260
4b	7.23, 7.31	–(42.18—44.96)	7.72, 7.78	–41.86, –42.13	262

Comparison of the IR spectra (Fig. 4) of the starting polymer **2a** before and after heating in argon atmosphere at various temperatures allows one to draw a number of conclusions on chemical transformations occurring in the polymer during its thermolysis. The main loss in weight of polymer **2a** (see Fig 3, *b*), observed in the temperature range 300—450 °C, is accompanied by its crosslinking and transition to the insoluble state. This is apparently due to the elimination of the Me group from the Si atoms in the polymeric chain and rearrangement of the skeleton of the polymeric chain itself (the cyclohexasilane unit ring openings); this is indicated, from the one hand, by decreased intensities of the absorption bands for the C—H, Si—C bonds and Me group and, from the other hand, by appearance of absorption bands of stretching vibrations of the Si—H (at 2110 cm^{-1}) and Si—CH_2—Si bonds (in the region 1040—1080 and at 800 cm^{-1}) in the IR spectrum of polymer **2a** after its heating at 350 °C for 0.5 h. The formation of Si—H and Si—CH_2—Si bonds in the polymeric chain, obviously, is due to the Kumada rearrangement taking place at 350 °C.[22] After heating at 500 °C for 1 h, the IR spectrum exhibits further decrease in intensity of the absorption band of the Si—Me bond (at 1260 cm^{-1}) and increase in intensity of the absorption band of the Si—H and Si—CH_2—Si bonds, which indicates that even more deep rearrangement occurs. In addition, significant dehydrogenation of the polymer is observed: the intensity of the absorption band of the C—H bond (at 2950 and 2890 cm^{-1}) decreases. The process of dehydrogenation becomes even stronger after heating at 700 °C: the absorption bands of the C—H and Si—H bonds virtually disappear from the IR spectrum and formation of the structure of silicon carbide begins (broad absorption bands at 1050 and 780 cm^{-1}). Polymer **2a** upon heating at 900 °C for 1 h is transformed to the silicon carbide material: the IR spectrum (see Fig. 4) virtually has no absorption bands of the Me groups in the region of frequencies 2960 and 2900 cm^{-1}, while the absorption bands of the Si—CH_2—Si and Si—C bonds are present at 1070 and 800 cm^{-1}, respectively, at the same time, there is no absorption band of the Si—H bonds in the region of frequencies 2100 cm^{-1} of the spectrum.

Thermooxidative decomposition of polymer **4a**, whose main chain consists of cyclohexasilane fragments linked *via* oxygen bridges, in air takes place also in two steps (Fig. 5, curve *1*): in the temperature ranges 250—350 °C (I) and 350—600 °C (II). At higher temperatures (up to 1000 °C), the weight of the sample does not change. The TGA curve of polymer **4a** in argon is shown in Fig. 5, curve *2*. The main loss in weight of the polymer occurs in the temperature range 300—450 °C, at higher temperatures, the loss in weight virtually is not observed. Note that thermolysis of polyoxacyclosilane **4a**, as well as its thermooxidative decomposition are characterized by lower loss in weight for this polymer than that for the linear PDMS, but somewhat higher than for polycyclosilanes **2a,b** (*cf.* Fig. 3 and 5).

Structural changes in polymer **4a** during its thermolysis were tracked using IR spectroscopy. Heating the polymer at 350 °C in the argon atmosphere for 1 h is accompanied (as in the case of polymers **2a,b**) by decomposition of the polymer, its crosslinking, and rearrangement of the polymeric chain skeleton. If compare the IR spectra of the starting polymer and the sample of polymer **4a** subjected to heating, one can observe a decrease in intensity of the absorption band of the Me group and appearance of the absorption band of the Si—H (at 2100 cm^{-1}) and Si—CH_2—Si bonds (in the region 1040—1080 and at 800 cm^{-1}), that is due to the Kumada rearrangement (Fig. 6). Note that the vibration band of the Si—CH_2—Si bonds overlaps with the vibration bands of the Si—O—Si and Si—Me bonds, which is indicated by their significant broadening as compared to the spectrum of the starting polymer. Heating at 500 °C leads to the formation of silicon-carbidoxide structure: the IR spectrum exhibits broad-

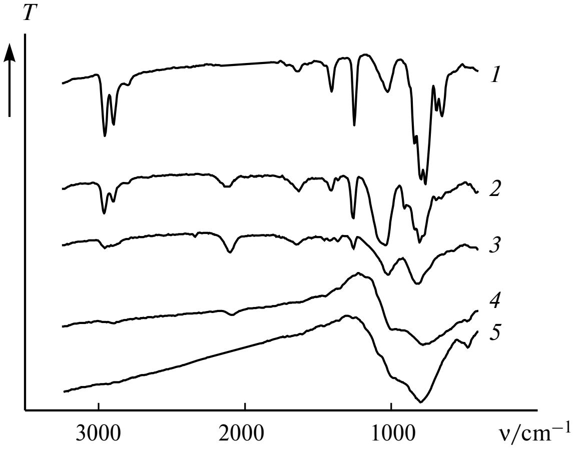

Fig. 4. IR spectra of polymer **2a** before (*1*) and after heating at 350 (*2*), 500 (*3*), 700 (*4*), and 900 °C (*5*).

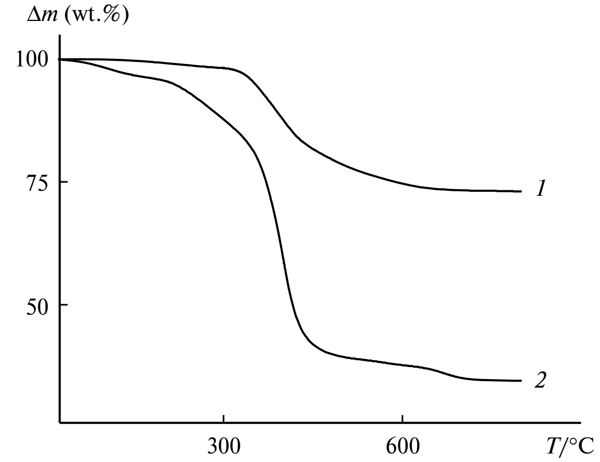

Fig. 5. TGA curves of the sample of polymer **4a** on heating in air (*1*) and in the argon atmosphere (*2*).

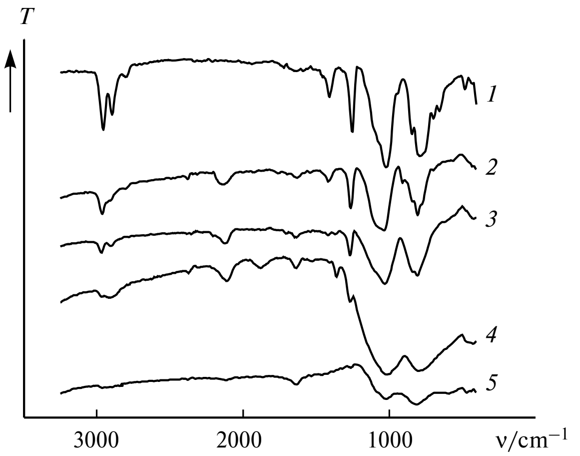

Fig. 6. IR spectra of polymer **4a** before (*1*) and after heating at 350 (*2*), 500 (*3*), 700 (*4*), and 900 °C (*5*).

ening of the absorption band of the Si—CH$_2$—Si and Si—C bonds and further decrease in intensity of the absorption band of the C—H (at 2960 and 2900 cm^{-1}) and Si—Me bonds (at 1250 cm^{-1}). Heating at 700 °C for 1 h is characterized by about 60% loss in weight and further formation of silicon-carbidoxide structure (broad absorption bands in the regions 1000 and 800 cm^{-1}). Subsequent heating at 900 °C is accompanied by the complete dehydrogenation of the polymer (absorption bands of the C—H and Si—H bonds disappear from the IR spectrum) and final formation of silicon-carbidoxide structure.

In conclusion, organosilicon polymers of regular structure, whose main chains consist of cyclohexasilane fragments linked to each other either directly, or through the oxygen bridges, have been obtained in the present work. The polymers synthesized are of interest as pre-ceramic polymers for the preparation of Si—C- and Si—O—C ceramic materials.

Experimental

^{29}Si NMR spectra were recorded on a Bruker WP-400 SY spectrometer (79.46 MHz) in CDCl$_3$ with Me$_4$Si as an internal standard. IR spectra in the region 400—3700 cm^{-1} were recorded on a Specord M-82 spectrophotometer in KBr pellets, UV spectra of samples of polymers (without solvent) in the region 200—335 nm were recorded on a Specord M-40 spectrophotometer.

Molecular-mass characteristics of polymers **2a,b** and **4a,b** were determined by gel-chromatography on a Bruker LC21 liquid chromatograph (with refractometer as a detector, a column filled with the polystyrene—divinylbenzene gel, toluene as an eluent, and graduation by the polystyrene standard). Intrinsic viscosities [η] of copolymers **2a,b** and **4a,b** were determined in toluene at 25 °C using Ubbelohde viscosimeter with a hanging level.

X-ray diffraction studies were performed on a DRON-3M diffractometer in the transmission mode (CuKα-irradiation, Ni-filter).

Thermal tests of polymers **2a,b** and **4a** were carried out on a Derivatograph-C instrument (MOM, Hungary) in air and in the argon atmosphere in the range of 20—1000 °C (at the rate of elevation 5 °C min^{-1}, the weight of samples was ~20 mg).

Dichlorocyclohexasilanes **1a,b** were synthesized according to the known procedure.[23] Dihydroxycyclohexasilane (**3**)[24] and polydimethylsilane[25] were obtained according to the procedures described earlier. Diethyl ether, benzene, and toluene were dried by reflux in the flow of argon over metallic Na in the presence of benzophenone with subsequent distillation. Trimethylchlorosilane was distilled in the flow of argon just before use. Pyridine (Merk) and 4-dimethylaminopyridine (Aldrich) were used as purchased. All the reactions were carried out in the atmosphere of dry argon.

Poly(decamethylcyclohexasilane-1,3-diyl) (2a). A solution of dichlorocyclosilane **1a** (1.2 g, 3.1 mmol) in anhydrous toluene (5 mL) was added dropwise to a dispersion of metallic Na (0.2 g, 0.0087 g-at) in boiling anhydrous toluene (10 mL) with vigorous stirring. The reaction mixture was stirred for 2.5 h. A precipitate was filtered off and washed with toluene, the filtrate was concentrated *in vacuo* to 5 mL. The polymer was isolated by precipitation with a three-fold excess of MeOH and dried in a vacuum oven at 60 °C until the weight was constant to obtain polymer **2a** (0.7 g) as a white powder. Found (%): C, 37.89; H, 9.68; Si, 52.44. C$_{10}$H$_{30}$Si$_6$. Calculated (%): C, 37.67; H, 9.48; Si, 52.85.

Poly(decamethylcyclohexasilane-1,4-diyl) (2b) was obtained similarly from metallic Na (0.15 g, 0.0063 g-at) in anhydrous toluene (7 mL) and dichlorocyclosilane **1b** (0.9 g, 2.32 mmol) in anhydrous toluene (4 mL) as a white powder (0.6 g). Found (%): C, 38.05; H, 9.77; Si, 52.18. C$_{10}$H$_{30}$Si$_6$. Calculated (%): C, 37.67; H, 9.48; Si, 52.85.

Poly[oxa(decamethylcyclohexasilan-1,3-diyl)] (4a). ***A.*** A solution of dihydroxycyclosilane **3** (0.904 g, 2.57 mmol) and pyridine (0.406 g, 5.14 mmol) in anhydrous diethyl ether (5 mL) was added dropwise to a solution of dichlorocyclosilane **1a** (0.997 g, 2.57 mmol) in anhydrous diethyl ether (5 mL) with vigorous stirring. The reaction mixture was stirred at room temperature for 10 h, followed by addition of anhydrous benzene (7 mL) and reflux with stirring for 24 h. A precipitate of Py • HCl was filtered off, the filtrate was washed with DI water to neutral, dried with Na$_2$SO$_4$. To block terminal hydroxy groups of the polymer, Me$_3$SiCl (0.15 mL) and pyridine (0.1 mL) were added to the filtrate, and the mixture was stirred for 1 h. A precipitate was filtered off, the filtrate was concentrated *in vacuo* to 4 mL. The polymer was isolated by precipitation with a three-fold excess of MeOH and dried in a vacuum oven at 60 °C until the weight was constant to obtain polymer **4a** (0.99 g) as a viscous liquid. Found (%): C, 36.15; H, 9.17; Si, 50.08. C$_{10}$H$_{30}$OSi$_6$. Calculated (%): C, 35.87; H, 9.03; Si, 50.32.

B. Polymer **4a** (0.68 g) was obtained similarly as a white solid from dichlorocyclosilane **1a** (0.485 g, 1.38 mmol) in anhydrous diethyl ether (5 mL) and a mixture of dihydroxycyclosilane **3** (0.535 g, 1.38 mmol), pyridine (0.204 g, 2.76 mmol), and DMAP (0.032 g, 0.276 mmol) in anhydrous diethyl ether (5 mL). Found (%): C, 36.21; H, 9.12; Si, 50.18. C$_{10}$H$_{30}$OSi$_6$. Calculated (%): C, 35.87; H, 9.03; Si, 50.32.

Poly[(decamethylcyclohexasilane-1,3-diyl)oxa(decamethylcyclohexasilane-1,4-diyl)] (4b) was synthesized similarly (0.88 g, method *A*) as a viscous liquid from dichlorocyclosilane **1b** (0.832 g, 2.15 mmol) in anhydrous diethyl ether (5 mL) and a mixture of dihydroxycyclosilane **3** (0.756 g, 2.15 mmol) and pyridine (0.340 g, 4.30 mmol) in anhydrous diethyl ether (5 mL). Found (%):

C, 36.14; H, 9.13; Si, 50.22. $C_{20}H_{60}O_2Si_{12}$. Calculated (%): C, 35.87; H, 9.03; Si, 50.32.

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