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Synthesis of methylcyclotetra(hexa)siloxanes with different reactive groups at the same silicon atom

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Representatives of methylcyclotetra(hexa)siloxanes with two different reactive groups at the same silicon atom (CH_2=CH and Cl, H and Cl, CH_2=CH and OH) were synthesized for the first time by condensation of trichlorovinylsilane with dihydroxydimethylsilane, and by stepwise condensation of trichloro- and trichlorovinylsilane with 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane in the presence of amines (aniline, pyridine, and triethylamine). The condensation with 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane with a large excess of trichlorosilane, unlike the condensation with trichlorovinylsilane, occured intramolecularly to give monochlorotetramethylcyclotrisiloxane in a high yield and intermolecularly to give 1,1,7,7-tetrachloro-3,3,5,5-tetramethyl-1,7-dihydrotetrasiloxane. The structures of the synthesized compounds were confirmed by ^{1}H and ^{29}Si NMR spectroscopy, IR spectroscopy, and mass spectrometry.

Key words: difunctional cyclosiloxanes, cyclosiloxanes with reactive groups, condensation.

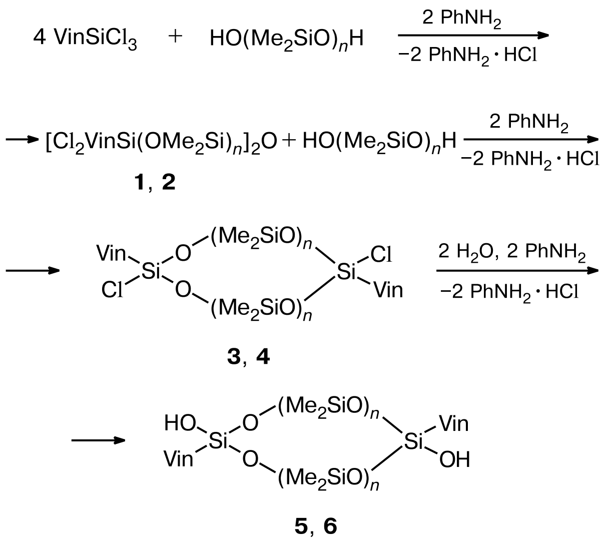
Previously, difunctional methylcyclosiloxanes ranging from cyclotetra- to cyclooctasiloxane have been synthesized[1,2] and converted into cyclolinear polymethylsiloxane homo- and copolymers[3,4] capable of self-assembly in the bulk to form a mesomorphic state and in Langmuir films.[3—5] Unique features of films of these polymers include the ability to form mono- and multimolecular layers at the water/air interface and existence in the free state.[6—8] In view of these unique properties of cyclolinear polymethylsiloxanes, we set ourselves the task to synthesize methylcyclotetra(hexa)siloxanes with different reactive groups and cyclolinear methylsiloxane polymers based on them, which can be used as the backbones to prepare liquid-crystalline polymers with mesogenic side groups.

The purpose of this study is to prepare methylcyclotetra(hexa)siloxanes with two different reactive groups (CH_2=CH and Cl, H and Cl, or CH_2=CH and OH) at the same silicon atom.

Results and Discussion

Methylcyclosiloxanes with different reactive groups at the same silicon atom were synthesized by condensation of trichlorovinylsilane with dimethylsilanediol or stepwise polycondensation with 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane (Scheme 1).

Scheme 1



Vin is CH_2=CH
n = 1 (**1**, **3**, **5**), 2 (**2**, **4**, **6**)

Previously, we showed that upon an increase in either the bulk or the length of substituents in either of the reactants, polycondensation of organotrichlorosilanes with α,ω-dihydroxypoly(diorganosiloxanes) gives not only α,α,ω,ω-tetrachloropoly(diorganosiloxanes) but also chloroorganocyclosiloxanes resulting from intramolecular cyclization.[3,9] Therefore, we first studied the effect of the stoichiometric ratio of the reactants on the yield of

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linear compounds **1** and **2**. It was found that with a trichlorovinylsilane : 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane ratio equal to 2 : 1, the content of 1,1,7,7-tetrachloro-3,3,5,5-tetramethyl-1,7-divinyltetrasiloxane (**2**) in the reaction mixture is 77%, while 23% fall on 2-chloro-4,4,6,6-tetramethyl-2-vinylcyclotrisiloxane. The composition of the reaction products was monitored by GLC and GLC/MS. When the reactant ratio was increased to 3 : 1, the content of compound **2** increased to 95%. With a fourfold excess of trichlorovinylsilane, the content of 2-chloro-4,4,6,6-tetramethyl-2-vinylcyclotrisiloxane in the reaction mixture was <1%, while the isolated yield of siloxane **2** being 83%. Compound **1** was obtained in 71% yield at a trichlorovinylsilane : $Me_2Si(OH)_2$ ratio of 3 : 1.

In the condensation of compounds **1** and **2** with dihydroxydimethylsilane and 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane, the yields of 2,6-dichloro-4,4,8,8-tetramethyl-2,6-divinylcyclotetrasiloxane (**3**) and 2,8-dichloro-4,4,6,6,10,10,12,12-octamethyl-2,8-divinylcyclohexasiloxane (**4**) were 55 and 31%, respectively.

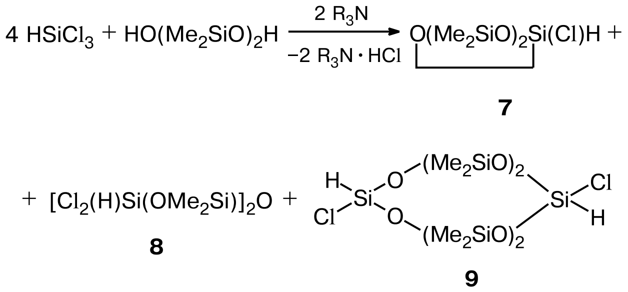
Compounds **1—4** were identified based on ^{1}H NMR, ^{29}Si NMR, and IR spectroscopy and elemental analysis. The ^{1}H NMR spectra of compounds **1** and **2** exhibit singlets for the Me-group protons with δ 0.36 and 0.24, respectively. Compounds **3** and **4** exist as *cis*- and *trans*-isomers, differing in the mutual positions of the Cl atoms. In the case of compound **3**, the spectrum contains two signals (δ 0.20 and 0.34) for the *cis*-isomer due to different spatial arrangements with respect to the cyclotetrasiloxane plane and a singlet (δ 0.27) for the Me_2SiO group in the *trans*-isomer with an intensity ratio of 2 : 1 relative to the two signals with δ 0.20 and 0.34. The ^{1}H NMR spectrum of compound **4** displays two signals (δ 0.14 and 0.21) for the *cis*-isomer and two singlets (δ 0.16 and 0.19) for the *trans*-isomer. The *cis* to *trans* ratios in compounds **3** and **4** are ~45 : 55. The signals were assigned based on the calculations performed earlier for dichloro(dihydroxy)methylcyclotetra(penta,hexa,hepta,octa)siloxanes.[10]

The ^{29}Si NMR spectrum of compound **3** exhibits two singlets for the Me_2SiO groups at δ −13.36 and −13.76 and two singlets corresponding to the $CH_2=CH(Cl)SiO$ groups at δ −58.06 and −58.20 for the *trans*- and *cis*-isomers, respectively. For compound **4**, two signals at δ −18.41 and −18.49 correspond to the Me_2SiO groups and two signals at δ −60.72 and −60.78 are due to the $CH_2=CH(Cl)SiO$ groups in the *trans*- and *cis*-isomer, respectively. The IR spectra of compounds **3** and **4** contain absorption bands at 791 ($SiMe_2$), 1075 (Si—O), 1255 (Me—Si), 1412 ($CH_2=CH—Si$), and 1600 cm^{-1} ($CH_2=CH$).

Hydrolysis of compounds **3** and **4** gave the corresponding dihydroxy derivatives **5** and **6**, which represent mixtures of *cis*- and *trans*-isomers, from which the *trans*-isomers were isolated. No inversion of conformation was observed for the isomers.

Unlike stepwise condensation of trichlorovinylsilane with 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane, the reaction of trichlorosilane with the latter under an excess of $HSiCl_3$ from 3.85 moles to 7.4 moles gives intra- and intermolecular condensation products (Scheme 2). Under comparable conditions where the yields of linear siloxanes **1** and **2** reach 71 and 83%, the yield of linear 1,1,7,7-tetrachloro-3,3,5,5-tetramethyltetrasiloxane **8** is 15—75% due to competing intramolecular cyclization giving rise to 2-chloro-4,4,6,6-tetramethylcyclotrisiloxane (**7**).

Scheme 2



Data on the effect of variation of the reaction conditions (see Scheme 2) on the yields of compounds **7** and **8** are presented in Table 1. By varying the concentrations of both components in the solution, the amine basicity, the reaction temperature, and the order of reactant addition, one can increase the yield of linear compound **8** (see Table 1).

Note that the composition of the reaction products (compounds **7** and **8**) markedly changes on passing to larger amounts of starting trichlorosilane and 1,3-di-

Table 1. Effect of the reaction conditions on the yields of compounds **7** and **8** (see Scheme 2)

Diol : $HSiCl_3$	C/mol L^{-1}		Amine	**7** : **8***
	$HSiCl_3$	Diol		
1 : 4.5	1.0	0.40	C_5H_5N	50 : 50
1 : 4.0	1.6	0.40	C_5H_5N	20 : 75
1 : 4.0	1.6	0.70	C_5H_5N	60 : 40
1 : 5.2	1.7	0.40	C_5H_5N	45 : 54
1 : 7.4	2.0	0.30	C_5H_5N	50 : 50
1 : 4.1	4.4	0.42	C_5H_5N	60 : 20
1 : 4.0	1.6	0.60	$PhNH_2$	81 : 19
1 : 4.0	6.0	0.30	$PhNH_2$	85 : 15
1 : 4.0	1.6	0.40	Et_3N	—**

* Ratio of the compounds in the reaction mixture.

** Compound **9** is the major product.

hydroxy-1,1,3,3-tetramethyldisiloxane. According to GLC data, during isolation of compounds **8** and **9**, the composition of the mixture changes due to disproportionation, which occurs with time at elevated temperature. The structures of isolated compounds **7**—**9** were confirmed by ^{1}H and ^{29}Si NMR and IR spectroscopy, mass spectrometry, and elemental analysis.

Thus, the first representatives of linear and cyclic methylsiloxanes with different reactive groups at the same silicon atom were synthesized. These methylcyclotetra(hexa)siloxanes can be used to prepare cyclolinear polymethylsiloxanes, which provides a route to comb-like liquid-crystalline polymers with mesogenic groups.

Experimental

^{1}H and ^{29}Si NMR spectra were recorded on a Bruker AMX-400 instrument at 20 °C in a $CDCl_3 + CCl_4$ or acetone-d$_6$ solution. IR spectra were measured on a Specord M-82 spectrometer in KBr pellets. Mass spectra were run on a Polyaris GC/MS instrument with sample injection through a gas liquid chromatograph. Chromatographic analysis was carried out on a LKhM-80 instrument (3 m × 3 mm column, SE-30 on Chromaton, helium as the carrier gas, supply flow rate 30 mL min^{-1}, evaporator temperature 270 °C, heat conductivity detector, programmed increase in the column temperature from 50 to 300 °C).

Dihydroxydimethylsilane was prepared by a known procedure.[11] Yield 79%, m.p. 99—100 °C (hexane).

1,3-Dihydroxy-1,1,3,3-tetramethyldisiloxane was synthesized as described previously.[12] Yield 41%, m.p. 68.0 °C (pentane).

1,1,5,5-Tetrachloro-3,3-dimethyl-1,5-divinyltrisiloxane (1). Trichlorovinylsilane (51.3 g, 0.32 mol) in anhydrous Et_2O (70 mL) was placed into a four-necked flask prefilled with argon and equipped with a stirrer, reflux condenser, thermometer, and a dropping funnel. A solution of dihydroxydimethylsilane (9.8 g, 0.11 mol) and aniline (19.7 g, 0.21 mol) in anhydrous Et_2O (120 mL) was added from a dropping funnel with stirring at −5 to −10 °C over a period of 1 h. The $PhNH_2 \cdot HCl$ residue was filtered off, and Et_2O and unreacted $CH_2=CHSiCl_3$ were distilled off. Distillation of the reaction products gave 24.9 g (71%) of compound **1**, b.p. 210—215 °C. IR, ν/cm^{-1}: 780, 823 ($SiMe_2$); 847 (Si—Me); 1080 (SiOSi); 1265 (Si—Me); 1413 ($Si-CH=CH_2$); 1560, 1600 ($CH_2=CH$); 2974 (Me); 3056 ($CH=CH_2$). ^{1}H NMR, δ: 0.36 (s, 6 H, Me_2SiO); 6.12, 6.24 (dd, 3 H, $CH_2=CHSi(Cl)$, $J_{trans} = 15.5$ Hz, $J_{cis} = 6.6$ Hz, $J_{gem} = 2.9$ Hz).* ^{29}Si NMR, δ: −11.93 (s, Me_2SiO); −33.26 (s, $CH_2=CHSi(Cl)O$).

1,1,7,7-Tetrachloro-3,3,5,5-tetramethyl-1,7-divinyltetrasiloxane (2). Trichlorovinylsilane (44.78 g, 0.28 mol) in anhydrous Et_2O (200 mL) was placed into a four-necked flask prefilled with argon and equipped with a stirrer, a reflux condenser, a thermometer, and a dropping funnel. A solution of 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane (11.15 g, 0.07 mol) and aniline (12.9 g, 0.14 mol) in anhydrous Et_2O (200 mL) was added from a dropping funnel with stirring at 0 °C over a period of 3 h. The $PhNH_2 \cdot HCl$ precipitate was filtered off, and Et_2O and unreacted $CH_2=CHSiCl_3$ were distilled off. Distillation of the reaction products gave 23.25 g (83%) of compound **2**, b.p. 166—168 °C (30 Torr). Found (%): C, 22.78; H, 4.46; Si, 26.58. $C_8H_{18}Cl_4O_3Si_4$. Calculated (%): C, 23.08; H, 4.36; Si, 26.98. IR, ν/cm^{-1}: 790, 813 (Me_2Si); 847 (Si—Me); 1091 (SiOSi); 1266 (Me—Si); 1408 ($CH_2=CH-Si$); 1560, 1600 ($CH_2=CH$); 2964 (Me); 3066 ($CH_2=CH$). ^{1}H NMR, δ: 0.24 (s, 6 H, Me_2SiO); 6.10—6.24 (m, 3 H, $CH_2=CHSi(Cl)$, $J_{trans} = 15.7$ Hz, $J_{cis} = 6.2$ Hz, $J_{gem} = 2.1$ Hz). ^{29}Si NMR, δ: −15.85 (s, Me_2SiO); −34.17 (s, $CH_2=CHSi(Cl)O$).

2,6-Dichloro-4,4,8,8-tetramethyl-2,6-divinylcyclotetrasiloxane (3). ***A.*** Anhydrous Et_2O (60.0 mL) was placed in a four-necked flask prefilled with argon and equipped with a stirrer, a thermometer, and two dropping funnels. A solution of dihydroxydimethylsilane (20.0 g, 0.22 mol) and aniline (39.2 g, 0.42 mol) in anhydrous Et_2O (200 mL) and a solution of trichlorovinylsilane (34.0 g, 0.21 mol) in anhydrous Et_2O (200 mL) were added synchronously from two dropping funnels with stirring at −7 to −10 °C over a period of 1.5 h. Distillation of the reaction products gave 12.5 g (33%) of compound **3**, b.p. 70—72 °C (1 Torr). Found (%): C, 26.41; H, 4.99; Cl, 19.31; Si, 30.90. $C_8H_{18}Cl_2O_4Si_4$. Calculated (%): C, 26.58; H, 5.02; Cl, 19.62; Si, 31.08. IR, ν/cm^{-1}: 790, 813 ($SiMe_2$); 847 (Si—Me); 1091 (SiOSi); 1266 (Si—Me); 1408 ($Si-CH=CH_2$); 1560, 1600 ($CH_2=CH$); 2964 (Me). ^{1}H NMR, δ: 0.20, 0.27, 0.34 (all s, 1 : 2 : 1, 6 H, Me_2SiO); 5.97—6.15 (m, 3 H, $CH_2=CHSi(Cl)$, $J_{trans} = 18.0$ Hz, $J_{trans} = 12.4$ Hz, $J_{cis} = 8.2$ Hz, $J_{cis} = 6.4$ Hz, $J_{gem} = 3.6$ Hz).* ^{29}Si NMR, δ: −13.36 (s, Me_2SiO, *trans*-isomer); −13.76 (s, Me_2SiO, *cis*-isomer); −58.06 (s, $CH_2CHSi(Cl)O$, *trans*-isomer); −58.20 (s, $CH_2CHSi(Cl)O$, *cis*-isomer).

B. Anhydrous Et_2O (60.0 mL) was placed into a four-necked flask prefilled with argon and equipped with a stirrer, a thermometer, and two dropping funnels. A solution of dihydroxydimethylsilane (4.6 g, 0.05 mol) and aniline (9.7 g, 0.1 mol) in anhydrous Et_2O (125 mL) and a solution of compound **1** (17.35 g. 0.05 mol) in anhydrous Et_2O (125 mL) were added synchronously from two dropping funnels with stirring at −5 to −10 °C over a period of 1.5 h. After 24 h, the $PhNH_2 \cdot HCl$ precipitate was filtered off, and ether was distilled off. Distillation of the reaction products gave 8.5 g (24%) of compound **3**, b.p. 73—75 °C (1 Torr). Found (%): C, 26.46; H, 4.96; Cl, 19.24; Si, 31.30. $C_8H_{18}Cl_2O_4Si_4$. Calculated (%): C, 26.58; H, 5.02; Cl, 19.62; Si, 31.08. IR, ν/cm^{-1}: 790, 813 ($SiMe_2$); 847 (Si—Me); 1091 (SiOSi); 1266 (Si—Me); 1408 ($Si-CH=CH_2$); 1560, 1600 ($CH_2=CH$); 2964 (Me). ^{1}H NMR, δ: 0.20, 0.27, 0.34 (all s, 1 : 2 : 1, 6 H, Me_2SiO); 5.97—6.15 (m, 3 H, $CH_2=CHSi(Cl)$, $J_{trans} = 18.0$ Hz, $J_{trans} = 12.4$ Hz, $J_{cis} = 8.2$ Hz, $J_{cis} = 6.4$ Hz, $J_{gem} = 3.6$ Hz). ^{29}Si NMR, δ: −13.29 (s, Me_2SiO, *trans*-isomer); −13.69 (s, Me_2SiO, *cis*-isomer); −58.01 (s, $CH_2CHSi(Cl)O$, *trans*-isomer); −58.15 (s, $CH_2CHSi(Cl)O$, *cis*-isomer).

2,8-Dichloro-4,4,6,6,10,10,12,12-octamethyl-2,8-divinylcyclohexasiloxane (4). Anhydrous Et_2O (85.0 mL) was placed in

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* Here and in the ^{1}H NMR spectrum of compounds **2** and **6**, the constants for the $CH_2=CH$ groups were average for the two isomers.

* Here and in method *B* for the synthesis of compound **3**, the presence of two *trans*- and *cis*-constants for the $CH_2=CH$ groups is related to different averaging of the Si—O—Si angles in the cyclotetrasiloxane isomers.

a four-necked flask prefilled with argon and equipped with a stirrer, a thermometer, and two dropping funnels. A solution of 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane (10.0 g, 0.06 mol) and aniline (11.2 g, 0.12 mol) in anhydrous Et_2O (85 mL) and a solution of compound **2** (20.0 g, 0.048 mol) in anhydrous Et_2O (85 mL) were added synchronously from two dropping funnels with stirring at –7 to –10 °C over a period of 1.5 h. Distillation of the reaction products gave 7.61 g (31%) of compound **4**, b.p. 97—98 °C (1 Torr). Found (%): C, 28.24; H, 5.91; Cl, 13.32; Si, 32.96. $C_{12}H_{30}Cl_2O_6Si_6$. Calculated (%): C, 28.27; H, 5.93; Cl, 13.91; Si, 33.06. IR, ν/cm^{-1}: 790, 813 ($SiMe_2$); 847 (Si—Me); 1091 (SiOSi); 1266 (Si—Me); 1408 (Si—CH=CH_2); 1560, 1600 (CH_2=CH); 2964 (Me); 3066 (CH=CH_2). ^{1}H NMR, δ: 0.14, 0.21 (both s, 12 H, Me_2SiO, *cis*-isomer); 0.16, 0.19 (both s, 12 H, Me_2SiO, *trans*-isomer); 5.97—6.15 (m, 3 H, CH_2=CHSi(Cl), J_{trans} = 16.5 Hz, J_{cis} = 7.6 Hz, J_{gem} = 2.4 Hz).* ^{29}Si NMR, δ: –18.41, –18.49 (both s, Me_2SiO); –60.72, –60.78 (both s, CH_2=CHSi(Cl)O).

2,6-Dihydroxy-4,4,8,8-tetramethyl-2,6-divinylcyclotetrasiloxane (5). Water (0.11 mL, 0.006 mol) and $PhNH_2$ (0.60 g, 0.006 mol) in dry Et_2O (5 mL) were placed in a three-necked flask equipped with a magnetic stirrer, a reflux condenser, a dropping funnel, and a thermometer. Compound **3** (1.1 g, 0.003 mol) in dry Et_2O (3 mL) was added from the dropping funnel with stirring at –1 °C over a period of 15 min. The $PhNH_2 \cdot HCl$ precipitate was filtered off, the ether fraction was repeatedly washed with water, and ether was distilled off to give 0.92 g (93%) of the reaction products, whose recrystallization from ether (0.2 mL) and heptane (10 mL) gave 0.8 g (81%) of partially crystallized compound **5**. Found (%): C, 29.44; H, 6.13; Si, 34.41. $C_8H_{20}O_6Si_4$. Calculated (%): C, 29.60; H, 6.17; Si, 34.62. IR, ν/cm^{-1}: 808, 857 ($SiMe_2$); 908 (Si—Me); 1054 (SiOSi); 1266 (Si—Me); 1408 (Si—CH=CH_2); 1560, 1600 (CH_2=CH); 2964 (Me); 3056 (CH=CH_2); 3260 (Si—OH). ^{1}H NMR, δ: 0.09, 0.15 (both s, 6 H, Me_2SiO, *cis*-isomer); 0.12 (s, 6 H, Me_2SiO, *trans*-isomer); 5.95 (s, 1 H, HOSi); 6.56—7.30 (m, 3 H, $C\underline{H}_2C\underline{H}Si(OH)$, J_{trans} = 14.4 Hz, J_{cis} = 8.3 Hz, J_{gem} = 1.4 Hz). ^{29}Si NMR, δ: –18.26 (s, Me_2SiO, *cis*-isomer); –18.41 (s, Me_2SiO, *trans*-isomer); –70.27 (s, CH_2CHSi(HO)O, *cis*-isomer); –70.37 (s, CH_2CHSi(HO)O, *trans*-isomer).

2,8-Dihydroxy-4,4,6,6,10,10,12,12-octamethyl-2,8-divinylcyclohexasiloxane (6). Water (0.50 mL, 0.028 mol) and $PhNH_2$ (2.60 g, 0.028 mol) in dry Et_2O (65 mL) were placed into a three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel. Compound **4** (7.10 g, 0.014 mol) in dry Et_2O (30 mL) was added from the dropping funnel with stirring at –10 °C over a period of 1.5 h. The $PhNH_2 \cdot HCl$ precipitate was filtered off, and ether was distilled off. Distillation of the reaction products gave 6.0 g (44%) of compound **6**, b.p. 105—107 °C ($1 \cdot 10^{-2}$ Torr). Found (%): C, 30.44; H, 6.63; Si, 35.41. $C_{12}H_{32}O_8Si_6$. Calculated (%): C, 30.47; H, 6.82; Si, 35.64. IR, ν/cm^{-1}: 808, 847 ($SiMe_2$); 898 (Si—Me); 1074 (SiOSi); 1266 (Si—Me); 1408 (Si—H=CH_2); 1560, 1600 (CH_2=CH); 2964 (Me); 3056 (CH=CH_2); 3242 (Si—OH). ^{1}H NMR, δ: 0.10, 0.11 (both s, 12 H, Me_2SiO, *trans*-isomer); 0.13 (s, 12 H, Me_2SiO, *cis*-isomer); 5.58 (s, 1 H, HOSi); 5.88—6.02 (m, 3 H, $C\underline{H}_2=C\underline{H}Si(OH)$). ^{29}Si NMR, δ: –21.05 (s, Me_2SiO, *cis*-isomer); –21.30 (s, Me_2SiO, *trans*-isomer); –71.65 (s, CH_2CHSi(HO)O, *cis*-isomer); –71.85 (s, CH_2CHSi(HO)O, *trans*-isomer). Two fractional recrystallizations of compound **6** (5.1 g) from heptane (3 mL) gave crystals (3.1 g) of the *trans*-isomer of compound **6**, m.p. 78—80 °C. ^{1}H NMR, δ: 0.10, 0.13 (both s, 6 H, Me_2SiO); 5.59 (s, 1 H, HOSi); 5.88—6.02 (m, 3 H, $C\underline{H}_2=C\underline{H}Si(OH)$, J_{trans} = 15.1 Hz, J_{cis} = 8.0 Hz, J_{gem} = 1.1 Hz). ^{29}Si NMR, δ: –21.30 (s, Me_2SiO); –71.92 (s, CH_2=CHSi(HO)O).

1,1,7,7-Tetrachloro-3,3,5,5-tetramethyl-1,7-dihydrotetrasiloxane (8). Trichlorosilane (14.4 g, 0.10 mol) in dry toluene (70 mL) was placed into a three-necked flask equipped with a thermometer, a reflux condenser, a dropping funnel, and a magnetic stirrer. 1,3-Dihydroxy-1,1,3,3-tetramethyldisiloxane (4.45 g, 0.026 mol) and C_5H_5N (4.3 g, 0.054 mol) in dry toluene (70 mL) were added from the dropping funnel at 0 °C over a period of 1 h. The mixture was stirred for 30 min at 20 °C. The $C_5H_5N \cdot HCl$ precipitate was filtered off in an argon flow, and unreacted $HSiCl_3$ and toluene were distilled off (1—2 Torr). Distillation of the reaction products gave 2.0 g (33%) of compound **7** and 2.5 g (26%) of compound **8**. Compound 7. B.p. 72 °C (1 Torr). ^{1}H NMR, δ: 0.22, 0.25 (both d, 12 H, Me_2SiO, *J* = 6.0 Hz); 5.07, 5.08 (both d, 1 H, HSiClO). MS (EI, 70 eV), *m/z*: 213 $[M - Me]^+$, 199 $[M - C_2H_5]^+$, 163 $[M - HCl]^+$, 93 $[Me_2SiCl]^+$, 73 $[Me_3Si]^+$. Compound 8. B.p. 90 °C (1 Torr). Found (%): C, 13.44; H, 3.63; Si, 30.41. $C_4H_{14}Cl_4O_3Si_4$. Calculated (%): C, 13.20; H, 3.86; Si, 30.84. ^{1}H NMR, δ: 0.30 (s, 6 H, Me_2SiO); 5.71 (s, 1 H, $H(Cl_2)SiO$). MS (EI, 70 eV), *m/z*: 347 $[M - Me]^+$, 333 $[M - C_2H_5]^+$, 297 $[M - HCl]^+$, 93 $[Me_2SiCl]^+$, 73 $[Me_3Si]^+$.

2,8-Dichloro-4,4,6,6,10,10,12,12-octamethyl-2,8-dihydrocyclohexasiloxane (9). Dry Et_2O (5 mL) was placed in a four-necked flask equipped with a thermometer, a reflux condenser, and two dropping funnels. Compound **8** (1.69 g, $4.6 \cdot 10^{-3}$ mol) in dry Et_2O (12 mL) and a solution containing 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane (0.77 g, $4.6 \cdot 10^{-3}$ mol) and C_5H_5N (0.75 g, $9.5 \cdot 10^{-3}$ mol) in dry Et_2O (10 mL) were added synchronously from two dropping funnels at –5 °C over a period of 80 min. The mixture was stirred for 30 min at 20 °C, the $C_5H_5N \cdot HCl$ precipitate was filtered off in an argon flow, and the unreacted $HSiCl_3$ and Et_2O were distilled off. Distillation of the remaining reaction products gave 0.72 g (34%) of compound **9**, b.p. 97—100 °C (10 Torr). Found (%): C, 20.81; H, 5.67; Cl, 15.11; Si, 37.21. $C_8H_{26}Cl_2O_6Si_6$. Calculated (%): C, 20.99; H, 5.72; Cl, 15.49; Si, 36.83. IR, ν/cm^{-1}: 760, 861 ($SiMe_2$); 1070 (Si—O); 1242 (Si—Me); 2140 (Si—H); 2955 (Me). ^{1}H NMR, δ: 0.15 (br.s, 12 H, Me_2SiO, *trans*-isomer); 0.19 (br.s, 12 H, Me_2SiO, *cis*-isomer); 4.32, 4.37 (both s, 1 H, HSi(Cl)O). MS (EI, 70 eV), *m/z*: 441 $[M - Me]^+$.

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References

1. N. N. Makarova, I. M. Petrova, Yu. K. Godovskii, and B. D. Lavrukhin, *Dokl. Akad. Nauk SSSR*, 1983, **269**, 1368 [*Dokl. Chem.*, 1983 (Engl. Transl.)].

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* Here and in the ^{1}H NMR spectrum of compound **5**, the constants for the CH_2=CH groups were average for four isomers.

2. N. N. Makarova and B. D. Lavrukhin, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1986, 652 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 596 (Engl. Transl.)].
3. N. N. Makarova, Yu. K. Godovskii, and B. D. Lavrukhin, *Vysokomolekulyar. Soedin., Ser. A*, 1995, **37**, 375 [*Polym. Sci., Ser. A*, 1995, **37** (Engl. Transl.)].
4. N. N. Makarova and Yu. K. Godovsky, *Prog. Polym. Sci.*, 1997, **22**, 1001.
5. S. I. Belousov, A. I. Buzin, and Yu. K. Godovskii, *Vysokomolekulyar. Soedin., Ser. B*, 1999, **41**, 1687 [*Polym. Sci., Ser. B*, 1999, **41**, 303 (Engl. Transl.)].
6. A. I. Buzin, Yu. K. Godovsky, N. N. Makarova, J. Fang, X. Wang, and C. M. Knobler, *J. Phys. Chem.*, 1999, **103B**, 11372.
7. T. R. Jensen, K. Kjaer, G. Brezesinski, J. Ruiz-Garcia, H. Mohwald, N. N. Makarova, and Yu. K. Godovsky, *Macromolecules*, 2003, **36**, 7236.
8. Yu. K. Godovsky, G. Brezesinski, J. Ruiz-Garcia, H. Mohwald, T. R. Jensen, K. Kjaer, and N. N. Makarova, *Macromolecules*, 2004, **37**, 4872.
9. N. N. Makarova. B. D. Lavrukhin, G. N. Turkel´taub, N. N. Kuz´min, I. M. Petrova, and E. V. Matukhina, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1989, 1351 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1234 (Engl. Transl.)].
10. B. D. Lavrukhin, N. N. Makarova, and A. A. Zhdanov, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1986, 559 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 508 (Engl. Transl.)].
11. T. Takiquchi, *J. Am. Chem. Soc.*, 1959, **81**, 2359.
12. G. J. Harris, *J. Chem. Soc.*, 1961, **12**, 5978.

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