

Convenient Synthesis of New Si–H and Si–Vinyl Functionalized Stereospecific 8–, 12– and 24–Membered Cyclosiloxanes

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Two approaches to the selective synthesis of polyfunctional stereoregular cyclosiloxanes from polyhedral organometallasiloxanes are reported. The molecules of organometallasiloxanes possess sandwich or globular structure and contain one or two stereoregular organocyclosiloxanolate fragments coordinated to metal ions. According to the first approach organometallasiloxanes were prepared primarily and then were treated with chlorodimethylsilane or dimethylchlorovinylsilane. The second method is based on the initial transforming of organometallasiloxanes into cyclic polysiloxanols reacted afterwards with corresponding chlorosilanes. The synthesized functional stereoregular cyclosiloxanes are fully characterized by NMR- and IR-spectroscopy, HRMS, TGA, and DSC.

Keywords: Polyhedral organometallasiloxanes, stereoregular organocyclosiloxanes, NMR-, IR-spectroscopy, TGA, DSC.

Удобный метод синтеза новых Si–H и Si–Vinyl функциональных стереоспецифичных 8–, 12– и 24–членных циклосилоксанов

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В данной работе представлены два подхода селективного синтеза Si–H и Si–Vinyl функциональных стереоспецифичных 8-, 12- и 24-членных циклосилоксанов из полиэдрических органометаллосилоксанов. Молекулы таких органометаллосилоксанов имеют сэндвичевую или глобулярную структуру и содержат один или два стереорегулярных органоциклосилоксанолятных фрагмента, координированных ионами металлов. Согласно первому подходу, полученные первоначально органометаллосилоксаны обрабатываются хлордиметилсиланом или диметилвинилхлорсиланом. По второму методу вначале из полученных органометаллосилоксанов синтезируют циклические полисилоксаноли, которые затем вступают в реакцию с соответствующими хлорсиланами. Структура и состав всех полученных органоциклосилоксанов полностью подтверждены ЯМР-, ИК-спектроскопией, масс-спектрометрией и ДСК, ТГА.

Ключевые слова: Полиэдрические органометаллосилоксаны, стереорегулярные органоциклосилоксаны, ЯМР-, ИК-спектроскопия, ТГА, ДСК.

Introduction

Organocyclosiloxanes are basic members of the broad family of silicone materials mostly used as an intermediate or basic raw material in the production of silicone rubbers, gels, and resins.^[1,2] They are used in combination or alone in personal care products, and as carriers, lubricants, and solvents in a variety of commercial applications. Cyclic siloxanes also can be used as a core or frameworks in the synthesis of dendrimers,^[3,4] liquid-crystallines,^[5,6] multimetallic compounds,^[7] organic optoelectronic materials,^[8–11] ligands.^[12]

Interest to these compounds in the field of organosilicon chemistry is caused by exceptionally wide synthetic possibilities and investigations on the structure and properties of cyclic systems. The high reactivity of the cycle in various rearrangements and polymerizations offers unlimited possibilities for synthesis and investigation of macromolecules of polyorganosiloxanes.

The organocyclosiloxanes with a functional group or groups at silicon atom in a cycle are of special interest due to a possibility of their further modification.

Such type of cyclosiloxanes is generally prepared by the hydrolytic condensation of mixtures of organochlorosilanes or organoalkoxysilanes containing two and three reactive groups.^[13] Usually a mixture of various cyclic products with various size and stereoregularities is formed with a low yield of the target cyclosiloxanes.

Our group has developed an alternative to the traditional approaches used in siloxane chemistry for the synthesis of functional cyclic siloxanes. Earlier we have found a new method to selectively create stereoregular organocyclosiloxanes with cyclization degree equal to 4 and higher.^[14–23] We have elaborated a metal ion-directed self-assembly pathway to form selectively polyhedral organometallasiloxane molecules with well-defined regular configurations by means of hydrolytic condensation reaction of different trifunctional organoalkoxysilanes in the presence of alkaline and transition metals ions.

Depending on the metal ions used, the desired polyhedral molecules contain only one type of a stereoregular cyclosiloxanolate fragment coordinated to a metal ions matrix. According to this strategy the metal ions serve both as templating units and structural elements. The subsequent reaction of the organometallasiloxanes either with chlorotrimethylsilane or with dilute hydrochloric or acetic acids allowed us to remove the metal ions effectively and to obtain trimethylsiloxy-siloxane cycles and polysiloxanols.^[23–25] Later this method was used by other research groups too.^[26–28]

In this paper we have generalized data on such objects and describe the synthesis of new stereoregular 8-, 12- and 24-membered functional organocyclosiloxanes with Si-H and Si-Vin functional groups. The presence of functional groups allows utilizing these cycles in various reactions such as hydrosilylation, hydrothiolation, metathesis, Heck reactions and others. It seems of interest to use the unique cyclic systems as precursors for preparation of new polymeric materials and the supramolecular devices of the organo-inorganic nature.

Experimental

General Methods and Materials

All solvents were purified before use. Toluene was distilled from calcium hydride. Ethanol, *n*-butanol and hexane were distilled. Potassium hydroxide, sodium hydroxide and pyridine were purchased from Acros Organics. Methyltriethoxysilane, triethoxyvinylsilane, phenyltriethoxysilane, chlorodimethylsilane and chlorodimethylvinylsilane were purchased from Acros Organics and distilled before use. Infrared spectra were recorded on Bruker Equinox 55/S spectrometer (Germany). ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Bruker Avance II spectrometer (300 MHz; Germany) and a Bruker Avance™ 600 spectrometer (600 MHz; Germany). Chemical shifts are reported relative to chloroform ($\delta=7.25$ ppm) for ¹H NMR and chloroform ($\delta=77.00$ ppm) for ¹³C NMR. High-resolution mass spectra (HRMS) were measured using a Bruker micrOTOF II instrument with electrospray ionization (ESI) (Germany).

A DSC study was carried out on a Mettler-822e differential scanning calorimeter at a heating rate of (10 °C/min under an argon atmosphere. Thermogravimetric analysis (TGA) was performed by Derivatograph-C (MOM, Hungary) on samples with weight of about 20 mg at a heating rate of 5 °C/min in air. The temperature at which a weight loss of 1 % was detected was considered to be the decomposition onset temperature.

Synthesis

Potassium *cis*-tetramethylcyclotetrasiloxanolate (**2a**) and potassium *cis*-tetravinylcyclotetrasiloxanolate (**2b**) were synthesized by the method described earlier.^[21] Sodium *cis*-tetraphenylcyclotetrasiloxanolate (**2c**) was synthesized by the method described earlier.^[15,18]

General procedure for the synthesis of 3a,b. “Salt” **2** (0.01 mol) was slowly added to solution of chlorodimethylsilane (0.06 mol) and pyridine (0.06 mol) in toluene (50 mL). The mixture was stirred at room temperature for 6 h. The solid precipitate was filtered off and filtrate was washed with water. The organic layer was separated and dried (Na₂SO₄). The solvent was evaporated *in vacuo* to give compounds **3a,b** as colourless oil.

***cis*-Tetra[methyl(dimethylsiloxy)]cyclotetrasiloxane (3a).** The product was purified by distillation *in vacuo*. Yield 87 %. ¹H NMR (300 MHz, CDCl₃) δ_{H} ppm: 0.07 (s, 12H, SiCH₃), 0.22 (d, 24H, $J=2.7$ Hz, Si(CH₃)₂), 4.72 (m, 4H, SiH). ¹³C NMR (75 MHz, CDCl₃) δ_{C} ppm: –3.2, 0.5. ²⁹Si NMR (59 MHz, CDCl₃) δ_{Si} ppm: –65.35, –5.24. IR (CCl₄) ν cm^{–1}: 2966, 2135, 1269, 1254, 1124, 1078, 1053, 910. HRMS (ESI) m/z calcd. for C₁₂H₄₀NaO₈Si₈ [(M+Na)⁺]: 559.0770, found 559.0761. Elemental analysis calcd. (%) for C₁₂H₄₀O₈Si₈: C, 26.83; H, 7.51; Si, 41.83. Found: C, 27.17; H, 7.84; Si, 41.62.

***cis*-Tetra[vinyl(dimethylsiloxy)]cyclotetrasiloxane (3b).** Yield 84 %. ¹H NMR (400 MHz, CDCl₃) δ_{H} ppm: 0.24 (d, 24H, $J=2.8$ Hz, Si(CH₃)₂), 4.76 (spt, 4H, $J=2.8$ Hz, SiH), 5.84–6.01 (m, 12H, SiCH=CH₂). ¹³C NMR (75 MHz, CDCl₃) δ_{C} ppm: 0.5, 131.3, 135.2. ²⁹Si NMR (79 MHz, CDCl₃) δ_{Si} ppm: –79.66, –4.07. IR (CCl₄) ν cm^{–1}: 2959, 2137, 1409, 1254, 1114, 1067, 903, 772, 580. HRMS (ESI) m/z calcd. for C₁₆H₄₀NaO₈Si₈ [(M+Na)⁺]: 607.0770, found 607.0761. Elemental analysis calcd. (%) for C₁₆H₄₀O₈Si₈: C, 32.84; H, 6.89; Si, 38.40. Found: C, 32.84; H, 6.81; Si, 38.32.

General procedure for the synthesis of 4a,b. Similar to the synthesis of **3a,b** from “salt” **2** (0.01 mol), chlorodimethylvinylsilane (0.06 mol), pyridine (0.06 mol) and toluene (50 mL).

***cis*-Tetra[methyl(dimethylvinylsiloxy)]cyclotetrasiloxane (4a).** Yield: 82 %. ¹H NMR (300 MHz, CDCl₃) δ_{H} ppm: 0.05 (s, 12H, SiCH₃), 0.18 (s, 24H, Si(CH₃)₂), 5.71–6.20 (m, 12H, SiCH=CH₂). ¹³C NMR (75 MHz, CDCl₃) δ_{C} ppm: –2.8, 0.1, 131.9, 138.9. ²⁹Si NMR (59 MHz, CDCl₃) δ_{Si} ppm: –66.41, –2.54. IR (CCl₄) ν cm^{–1}: 2964, 3051, 1408, 1269, 1255, 1126, 1041, 957, 852. HRMS (ESI) m/z calcd. for C₂₀H₄₈NaO₈Si₈ [(M+Na)⁺]: 663.1396, found 663.1395. Elemental analysis calcd. (%) for C₂₀H₄₈O₈Si₈: C, 37.46; H, 7.54; Si, 35.04. Found: C, 37.27; H, 7.55; Si, 34.90.

cis-Tetra[vinyl(dimethylvinylsiloxy)]cyclotetrasiloxane (4b). Yield 91 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: 0.23 (s, 24H, $\text{Si}(\text{CH}_3)_2$), 5.79 (dd, 4H, $J_1=20.4$ Hz, $J_2=3.8$ Hz, Vin), 5.86–5.99 (m, 16H, Vin), 6.17 (dd, 4H, $J_1=20.5$ Hz, $J_2=14.9$ Hz, Vin). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: 0.2, 131.9, 132.1, 134.9, 138.7. ^{29}Si NMR (119 MHz, C_6D_6) δ_{Si} ppm: –80.50, –1.48. IR (CCl_4) ν cm^{-1} : 2960, 2599, 1600, 1408, 1255, 1116, 1061, 1008, 838, 789. HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{48}\text{NaO}_8\text{Si}_8$ $[(\text{M}+\text{Na})^+]$: 711.1396, found 711.1398. Elemental analysis calcd. (%) for $\text{C}_{24}\text{H}_{48}\text{O}_8\text{Si}_8$: C, 41.82; H, 7.02; Si, 32.60. Found: C, 41.72; H, 7.00; Si, 32.65.

cis-Tetraphenylcyclotetrasiloxanetetraol (5) was synthesized by the method described earlier.^[23]

cis-Tetra[phenyl(dimethylsiloxy)]cyclotetrasiloxane (3c). Similar to the synthesis of **3a,b** from compound **5** (4.4 mmol), chlorodimethylsilane (0.022 mol), pyridine (0.022 mol) and toluene (60 mL). Yield 76 %. ^1H NMR (600 MHz, C_6D_6) δ_{H} ppm: 0.38 (d, 24H, $J=2.9$ Hz, $\text{Si}(\text{CH}_3)_2$), 5.25 (spt, 4H, $J=2.8$ Hz, SiH), 6.99 (t, 8H, $J=7.4$ Hz, Ph), 7.06 (t, 4H, $J=7.4$ Hz, Ph), 7.65 (d, 8H, $J=6.7$ Hz, Ph). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: 0.6, 127.5, 130.0, 132.4, 133.9. ^{29}Si NMR (119 MHz, C_6D_6) δ_{Si} ppm: –77.65, –3.38. IR (CCl_4) ν cm^{-1} : 2963, 2135, 1258, 1135, 1120, 1067, 901, 698, 486. HRMS (ESI) m/z calcd. for $\text{C}_{32}\text{H}_{48}\text{NaO}_8\text{Si}_8$ $[(\text{M}+\text{Na})^+]$: 807.1396, found 807.1384. Elemental analysis calcd. (%) for $\text{C}_{32}\text{H}_{48}\text{O}_8\text{Si}_8$: C, 48.94; H, 6.16; Si, 28.61. Found: C, 49.18; H, 6.15; Si, 28.35.

cis-Tetra[phenyl(dimethylvinylsiloxy)]cyclotetrasiloxane (4c). Similar to the synthesis of **3a,b** from compound **5** (4.4 mmol), chlorodimethylvinylsilane (0.022 mol), pyridine (0.022 mol) and toluene (60 mL). Yield 82 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: 0.27 (s, 24H, $\text{Si}(\text{CH}_3)_2$), 5.81 (dd, 4H, $J_1=20.5$ Hz, $J_2=3.7$ Hz, Vin), 5.97 (dd, 4H, $J_1=14.9$ Hz, $J_2=3.7$ Hz, Vin), 6.20 (dd, 4H, $J_1=20.4$ Hz, $J_2=14.9$ Hz, Vin), 7.10 (t, 8H, $J=7.5$ Hz, Ph), 7.28 (t, 4H, $J=7.4$ Hz, Ph), 7.32 (d, 8H, $J=7.4$ Hz, Ph). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: 0.3, 127.3, 129.7, 132.3, 132.8, 134.0, 138.7. ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: –79.55, –1.06. IR (CCl_4) ν cm^{-1} : 2961, 1408, 1256, 1135, 1110, 1061, 837, 788, 698, 571, 488. HRMS (ESI) m/z calcd. for $\text{C}_{40}\text{H}_{56}\text{NaO}_8\text{Si}_8$ $[(\text{M}+\text{Na})^+]$: 911.2022, found 911.2028. Elemental analysis calcd. (%) for $\text{C}_{40}\text{H}_{56}\text{O}_8\text{Si}_8$: C, 54.01; H, 6.35; Si, 25.26. Found: C, 54.20; H, 6.64; Si, 25.03.

Nickel/sodium phenylsiloxane (6) and *cis-hexaphenylcyclohexasiloxanexaol (7)* were synthesized by the method described earlier.^[23]

cis-Hexa[phenyl(dimethylsiloxy)]cyclohexasiloxane (8). Similar to the synthesis of **3a,b** from compound **7** (4.4 mmol), chlorodimethylsilane (0.022 mol), pyridine (0.022 mol) and toluene (60 mL). Yield 76 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: 0.28 (d, 36H, $J=2.9$ Hz, $\text{Si}(\text{CH}_3)_2$), 5.25 (spt, 6H, $J=2.7$ Hz, SiH), 6.99 (t, 12H, $J=7.6$ Hz, Ph), 7.21–7.23 (m, 18H, Ph). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: 0.7, 127.3, 129.5, 132.9, 134.0. ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: –80.45, –4.42. IR (CCl_4) ν cm^{-1} : 2963, 2137, 1254, 1132, 1067, 905, 697, 573, 488. HRMS (ESI) m/z calcd. for $\text{C}_{48}\text{H}_{72}\text{KO}_{12}\text{Si}_{12}$ $[(\text{M}+\text{K})^+]$: 1215.1887, found 1215.1853. Elemental analysis calcd. (%) for $\text{C}_{48}\text{H}_{72}\text{O}_{12}\text{Si}_{12}$: C, 48.94; H, 6.16; Si, 28.61. Found: C, 49.18; H, 6.14; Si, 28.15.

cis-Hexa[phenyl(dimethylvinylsiloxy)]cyclohexasiloxane (9). Similar to the synthesis of **3a,b** from compound **7** (4.4 mmol), chlorodimethylvinylsilane (0.022 mol), pyridine (0.022 mol) and toluene (60 mL). Yield 70 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: 0.21 (s, 36H, $\text{Si}(\text{CH}_3)_2$), 5.74 (dd, 6H, $J_1=20.5$ Hz, $J_2=3.7$ Hz, Vin), 5.91 (dd, 6H, $J_1=14.9$ Hz, $J_2=3.7$ Hz, Vin), 6.15 (dd, 6H, $J_1=20.5$ Hz, $J_2=14.9$ Hz, Vin), 6.89 (t, 12H, $J=7.5$ Hz, Ph), 7.14 (d, 12H, $J=7.2$ Hz, Ph), 7.16 (t, 6H, $J=7.5$ Hz, Ph). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: 0.5, 127.1, 129.3, 132.1, 133.3, 134.2, 138.9. ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: –81.48, –1.73. IR (CCl_4) ν cm^{-1} : 2962, 1408, 1256, 1132, 1064, 837, 787, 698, 572, 487. HRMS (ESI) m/z calcd. for $\text{C}_{60}\text{H}_{88}\text{NO}_{12}\text{Si}_{12}$ $[(\text{M}+\text{NH}_4)^+]$: 1350.3532, found 1350.3515. Elemental analysis calcd. (%) for $\text{C}_{60}\text{H}_{84}\text{O}_{12}\text{Si}_{12}$: C, 54.01; H, 6.35; Si, 25.26. Found: C, 54.20; H, 6.64; Si, 25.03.

Copper/sodium methylsiloxane (10a),^[19] *copper/sodium vinylsiloxane (10b)*,^[14] and *copper/sodium phenylsiloxane (10c)*^[23] were synthesized by the methods described earlier.

General procedure for the synthesis of 11a,b. “Salt” **10** (6.3 mmol) was slowly added to solution of chlorodimethylsilane (0.15 mol) and pyridine (0.075 mol) in hexane (180 mL). The mixture was stirred at 50 °C for 6 h. The solid precipitate was filtered off and filtrate was washed with water. The organic layer was separated and dried (Na_2SO_4). The solvent was evaporated *in vacuo* to give compound **11a,b** as colourless solid.

Tris-cis-tris-trans-dodeca[(methyl)(dimethylsiloxy)]dodecasiloxane (11a). Yield 65 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: 0.11 (s, 12H, $\text{Si}(\text{CH}_3)_2$), 0.20–0.21 (m, 24H, $\text{Si}(\text{CH}_3)_2$), 4.73 (spt, 4H, $J=2.8$ Hz, SiH). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: –2.63, –2.60, 0.5. ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: –66.39, –66.14, –6.32, –6.28. IR (CCl_4) ν cm^{-1} : 2965, 2134, 1268, 1127, 1048, 909, 836, 794, 773. HRMS (ESI) m/z calcd. for $\text{C}_{36}\text{H}_{124}\text{NO}_{24}\text{Si}_{24}$ $[(\text{M}+\text{NH}_4)^+]$: 1626.2970, found 1626.2946. Elemental analysis calcd. (%) for $\text{C}_{36}\text{H}_{120}\text{O}_{24}\text{Si}_{24}$: C, 26.83; H, 7.51; Si, 41.83. Found: C, 26.80; H, 7.56; Si, 41.90.

Tris-cis-tris-trans-dodeca[(vinyl)(dimethylsiloxy)]dodecasiloxane (11b). Yield 60 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: 0.18 (d, 72H, $J=2.7$ Hz, $\text{Si}(\text{CH}_3)_2$), 4.72 (spt, 12H, $J=2.7$ Hz, SiH), 5.83–5.98 (m, 36H, Vin). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: 0.58, 0.60, 131.8, 132.0, 135.01, 135.14. ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: –80.96, –80.85, –5.34, –5.23. IR (CCl_4) ν cm^{-1} : 2960, 2136, 1409, 1254, 1131, 1059, 905, 772, 543, 436. HRMS (ESI) m/z calcd. for $\text{C}_{48}\text{H}_{124}\text{NO}_{24}\text{Si}_{24}$ $[(\text{M}+\text{NH}_4)^+]$: 1770.2970, found 1770.2986. Elemental analysis calcd. (%) for $\text{C}_{48}\text{H}_{120}\text{O}_{24}\text{Si}_{24}$: C, 32.84; H, 6.89; Si, 38.40. Found: C, 32.69; H, 6.64; Si, 38.30.

General procedure for the synthesis of 12a,b. Similar to the synthesis of **11a,b** from “salt” **10** (0.0063 mol), chlorodimethylvinylsilane (0.15 mol), pyridine (0.075 mol) and hexane (180 mL).

Tris-cis-tris-trans-dodeca[(methyl)(dimethylvinylsiloxy)]dodecasiloxane (12a). Yield 71 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: 0.08 (s, 36H, $\text{Si}(\text{CH}_3)_2$), 0.17 (s, 72H, $\text{Si}(\text{CH}_3)_2$), 5.73 (dd, 12H, $J_1=20.5$ Hz, $J_2=3.8$ Hz, Vin), 5.92 (dd, 12H, $J_1=14.9$ Hz, $J_2=3.7$ Hz, Vin), 6.13 (dd, 12H, $J_1=20.4$ Hz, $J_2=14.9$ Hz, Vin). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: –2.04, –1.98, 0.23, 0.24, 137.75, 139.11, 139.12. ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: –67.28, –67.01, –3.60, –3.55. IR (CCl_4) ν cm^{-1} : 2964, 1407, 1267, 1125, 1046, 840, 787. HRMS (ESI) m/z calcd. for $\text{C}_{60}\text{H}_{148}\text{NO}_{24}\text{Si}_{24}$ $[(\text{M}+\text{NH}_4)^+]$: 1938.4848, found 1938.4832. Elemental analysis calcd. (%) for $\text{C}_{60}\text{H}_{144}\text{O}_{24}\text{Si}_{24}$: C, 37.46; H, 7.54; Si, 35.04. Found: C, 37.30; H, 7.58; Si, 35.10.

Tris-cis-tris-trans-dodeca[(vinyl)(dimethylvinylsiloxy)]dodecasiloxane (12b). Yield 66 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: 0.15 (s, 72H, $\text{Si}(\text{CH}_3)_2$), 5.70 (dd, 12H, $J_1=20.4$ Hz, $J_2=3.9$ Hz, Vin), 5.84–5.95 (m, 48H, Vin), 6.11 (dd, 12H, $J_1=20.3$ Hz, $J_2=14.9$ Hz, Vin). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: 0.4, 131.8, 132.3, 132.5, 134.9, 135.1, 139.1. ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: –81.69, –2.72, –2.58. IR (CCl_4) ν cm^{-1} : 2959, 1409, 1253, 1128, 1058, 1007, 957, 839, 787. HRMS (ESI) m/z calcd. for $\text{C}_{72}\text{H}_{148}\text{NO}_{24}\text{Si}_{24}$ $[(\text{M}+\text{NH}_4)^+]$: 2082.4848, found 2082.4842. Elemental analysis calcd. (%) for $\text{C}_{72}\text{H}_{144}\text{O}_{24}\text{Si}_{24}$: C, 41.82; H, 7.02; Si, 32.60. Found: C, 41.78; H, 7.06; Si, 32.54.

Tris-cis-tris-trans-dodecaphenylcyclododecasiloxanedodecaol (13) was synthesized by the method described earlier.^[23]

Tris-cis-tris-trans-dodeca[(phenyl)(dimethylsiloxy)]dodecasiloxane (11c). Similar to the synthesis of **3a,b** from compound **13** (0.004 mol), chlorodimethylsilane (0.06 mol), pyridine (0.06 mol) and toluene (100 mL). Yield 71 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: –0.21 (d, 24H, $J=2.8$ Hz, $\text{Si}(\text{CH}_3)_2$), –0.20 (d, 24H, $J=2.8$ Hz, $\text{Si}(\text{CH}_3)_2$), –0.09 (d, 24H, $J=2.8$ Hz, $\text{Si}(\text{CH}_3)_2$), 4.44 (spt, 8H, $J=2.7$ Hz, SiH), 4.59 (spt, 4H, $J=2.7$ Hz, SiH), 7.13–7.16 (m, 24H, Ph), 7.27–7.32 (m, 12H, Ph), 7.37 (d, 8H, $J=7.2$ Hz, Ph), 7.47 (d, 16H, $J=7.2$ Hz, Ph). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: 0.14, 0.16, 0.4, 127.36, 127.39, 129.60, 129.62, 133.27, 133.30, 134.26, 134.29. ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: –79.52, –4.73, –3.95. IR (CCl_4) ν cm^{-1} : 2962, 2136, 1254, 1142, 1051, 904, 772, 698, 574, 487. HRMS (ESI) m/z calcd. for $\text{C}_{96}\text{H}_{144}\text{KO}_{24}\text{Si}_{24}$ $[(\text{M}+\text{K})^+]$: 2391.4142, found 2391.4145. Elemental analysis calcd. (%) for $\text{C}_{96}\text{H}_{144}\text{O}_{24}\text{Si}_{24}$: C, 48.94; H, 6.16; Si, 28.61. Found: C, 49.25; H, 6.27; Si, 28.15.

Tris-cis-tris-trans-dodeca[(phenyl)(dimethylvinylsiloxy)]-dodecasiloxane (12c). Similar to the synthesis of **3a,b** from compound **13** (4 mmol), chlorodimethylvinylsilane (0.06 mol), pyridine (0.06 mol) and toluene (100 mL). Yield 75 %. ^1H NMR (600 MHz, CDCl_3) δ_{H} ppm: -0.26 (s, 24H, $\text{Si}(\text{CH}_3)_2$), -0.24 (s, 24H, $\text{Si}(\text{CH}_3)_2$), -0.05 (s, 24H, $\text{Si}(\text{CH}_3)_2$), 5.40 (dd, 8H, $J_1=20.0$ Hz, $J_2=4.4$ Hz, Vin), 5.57 (dd, 4H, $J_1=20.4$ Hz, $J_2=3.9$ Hz, Vin), 5.95 (dd, 4H, $J_1=20.4$ Hz, $J_2=14.8$ Hz, Vin), 5.63 – 5.77 (m, 20H, Vin), 7.08 – 7.13 (m, 24H, Ph), 7.25 (t, 4H, $J=7.3$ Hz, Ph), 7.30 (t, 8H, $J=7.6$ Hz, Ph), 7.33 (d, 8H, $J=7.8$ Hz, Ph), 7.44 (d, 16H, $J=7.3$ Hz, Ph). ^{13}C NMR (150 MHz, CDCl_3) δ_{C} ppm: -0.21 , -0.15 , 0.23 , 127.30 , 127.34 , 129.45 , 129.53 , 131.42 , 131.80 , 133.46 , 133.71 , 134.58 , 134.65 , 138.87 , 138.98 . ^{29}Si NMR (119 MHz, CDCl_3) δ_{Si} ppm: -81.02 , -80.98 , -2.65 , -1.76 . IR (CCl_4) ν cm^{-1} : 2962 , 1596 , 1432 , 1408 , 1257 , 1149 , 1055 , 836 , 787 , 735 , 698 , 487 . HRMS (ESI) m/z calcd. for $\text{C}_{120}\text{H}_{168}\text{KO}_4\text{Si}_{24}$ $[(\text{M}+\text{K})^+]$: 2703.6020 , found 2703.7588 . Elemental analysis calcd. (%) for $\text{C}_{120}\text{H}_{168}\text{O}_{24}\text{Si}_{24}$: C, 54.01; H, 6.35; Si, 25.26. Found: C, 53.84; H, 6.48; Si, 24.89.

Results and Discussion

Synthesis

For the synthesis of Si-H and Si-Vinyl functionalized stereoregular cyclosiloxanes the individual organometallasiloxanes prepared from the corresponding organoalkoxysilane were used. A general view of the molecular structures of sodium or potassium *cis*-tetraorganocyclotetrasiloxanolate (A), the polyhedral organonickelsodiumsiloxanolate (B) and organocoppersodiumsiloxanolate (C) and their schematic depiction are presented in Figure 1.

The desired functional organocyclosiloxanes were synthesized by two methods. According to the first one organometallasiloxanes were prepared primarily and then destructed by treatment with functional chlorosilanes. A disadvantage of this method is the use of a large amount of chlorosilanes because the coordination sphere of organometallasiloxanes contains solvents (alcohols, water) which also can react with

chlorosilanes. The second method also includes the synthesis of organometallasiloxane precursors which then converted into cyclic polysiloxanols by treatment with hydrochloric acid. Then the reaction of cyclic polysiloxanols with corresponding chlorosilanes gives the target compounds.

The synthesis of hydride and vinyl containing *cis*-tetramethylcyclotetrasiloxane and *cis*-tetravinylcyclotetrasiloxane as well as *tris-cis-tris-trans*-dodecamethylcyclododecasiloxane and *tris-cis-tris-trans*-dodecavinylcyclododecasiloxane was realized in two stages proceeding from $\text{MeSi}(\text{OEt})_3$ and $\text{ViSi}(\text{OEt})_3$. At the first stage potassium salt of the appropriate cyclotetrasiloxanolate anions **2a,b** were received by the technique described earlier (Scheme 1).^[21] The reaction of the salts **2a,b** with Me_2SiHCl or Me_2ViSiCl in a toluene solution gives the corresponding hydride **3a,b** and vinyl **4a,b** derivatives. The reaction was carried out at room temperature using pyridine as an acceptor of HCl. The target products were isolated by vacuum distillation with high yields.

The synthesis of *cis*-tetraphenylcyclotetrasiloxane containing Si-H or Si-Vin functional groups was carried out by the second method. At the first stage sodium salt of the phenylcyclotetrasiloxanolate anion **2c** was obtained from phenyltriethoxysilane **1c** (Scheme 2).^[15,18] By the treatment of the salt **2c** with aqueous hydrochloric acid in toluene/ethanol mixture *cis*-tetraphenylcyclotetrasiloxanetetraol **5** was obtained with a good yield. The reaction of **5** with Me_2SiHCl and Me_2ViSiCl in a toluene solution gives the corresponding hydride **3c** and vinyl **4c** derivatives.

The 12-membered functional organocyclosiloxanes **8** and **9** were obtained similar to 8-membered phenyl analogue from the corresponding nickel/sodium phenylsiloxane **6** according to Scheme 2.

The synthesis of 24-membered functional stereoregular organocyclosiloxanes **11a-c** possessing *tris-cis-tris-trans*-

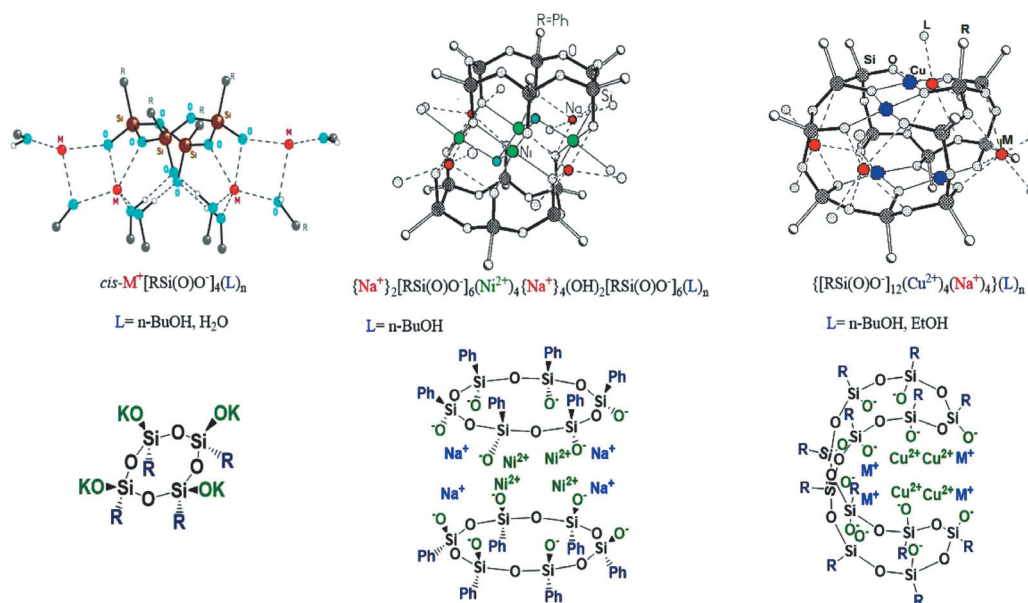
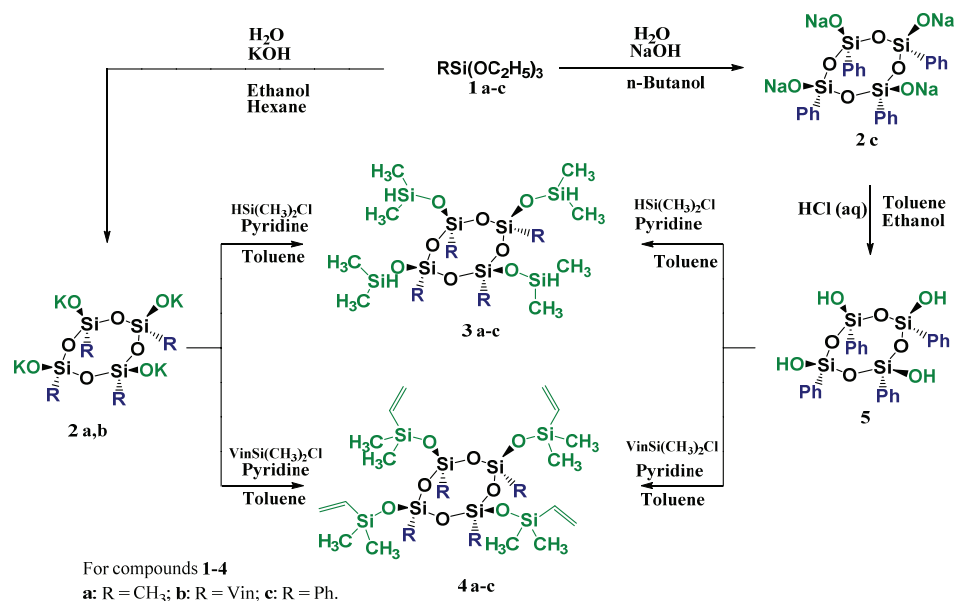
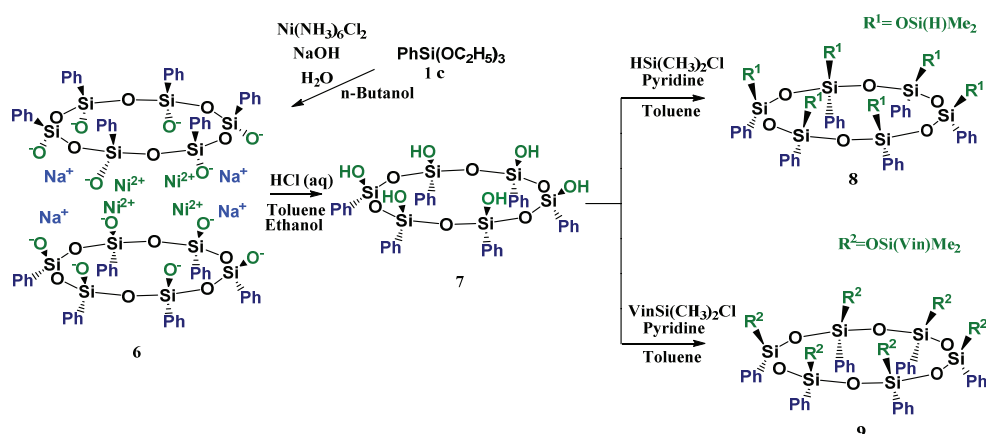


Figure 1. A general view of the molecular structures of sodium *cis*-tetraorganocyclotetrasiloxanolate (A), the polyhedral organonickelsodiumsiloxanolate (B) and organocoppersodiumsiloxanolate (C) and their schematic depiction. The organic substituents and alkyl chains of *n*-butanol or ethanol molecules are omitted for clarity.



Scheme 1. The synthesis of SiH and SiVin functionalized stereospecific 8-membered cyclosiloxanes **3a-c** and **4a-c**.



Scheme 2. The synthesis of SiH and SiVin functionalized stereospecific 12-membered cyclosiloxanes **8** and **9**.

configuration was carried out by various ways depending on the substituent at the silicon atom in a cycle. Thus, compounds **11a,b** and **12a,b** were obtained by the first method and compounds **11c** and **12c** were obtained by the second method from the corresponding metallasiloxanes according to Schemes 3, 4.

NMR Investigations

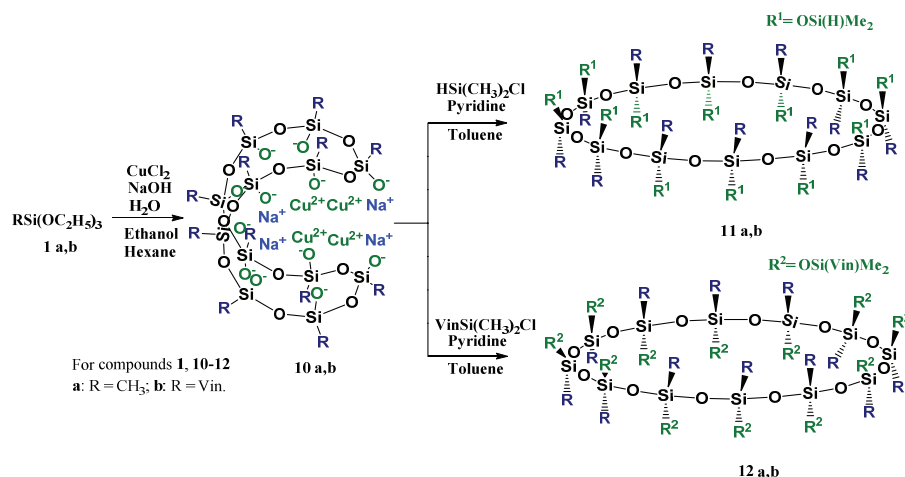
The ¹H NMR spectra in CDCl₃ of the compounds **3a,b** showed signals of SiH group at 4.72 ppm for **3a** and at 4.76 ppm as a septet with *J*=2.8 Hz for **3b**. The ²⁹Si NMR spectra of **3a,b** exhibited two resonance peaks for each compound (−65.35 ppm, −5.24 ppm for **3a** and −79.66 ppm, −4.07 ppm for **3b**). In the ²⁹Si NMR spectra of compounds **4a,b** resonance peaks are located at −66.41 ppm and −2.54 ppm for **4a** and at −80.50 ppm and −1.48 ppm for **4b**.

In the ¹H NMR spectrum (in C₆D₆) of the compound **3c** the signal of SiH group is shifted to lower field (a septet

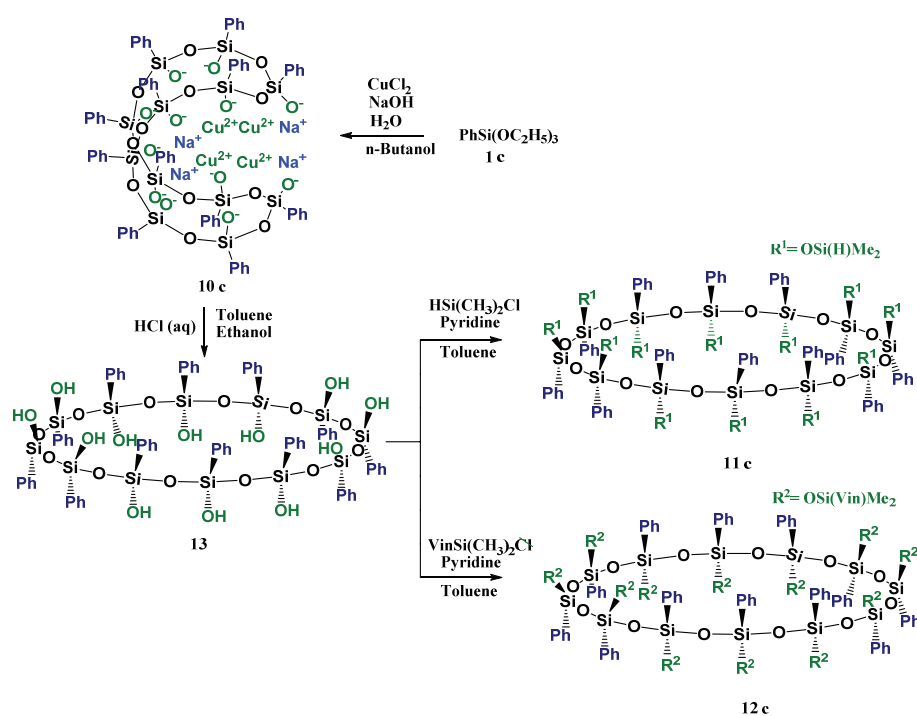
with *J*=2.8 Hz at 5.25 ppm) in comparison with compounds **3a,b** (Figure 2). The ²⁹Si NMR spectrum of **3c** exhibited two resonance peaks at −77.65 and −3.38 ppm (Figure 3).

Chemical shift of the SiH group (a septet with *J*=2.7 Hz at 5.25 ppm) in the ¹H NMR spectrum of the compound **8** is located in the same field as for the compound **3c**. In the ²⁹Si NMR spectrum of the compound **8** resonance peaks are shifted to lower field in comparison with compounds **3a-c** and located at −80.45 ppm and −4.42 ppm (Figures 4, 5).

²⁹Si NMR spectra of 24-membered cycles with tris-*cis*-tris-*trans*-configuration (the compounds **11a-c**, **12a-c**) show a difference with ²⁹Si NMR spectra of 8-membered and 12-membered cycles possessing *cis*-configuration. The spectra of the compounds with *cis*-configuration show the only one set of the signals for each structural fragment: ²⁹Si that are related to structural fragments OSi(Me)₂R' (range from −1 to −5 ppm) and O₃SiR (range from −65 to −81 ppm). In ¹H and ¹³C NMR spectra indicator nuclei of R and R' radicals and SiH(Me)₂ groups are magnetically equiva-



Scheme 3. The synthesis of SiH and SiVin functionalized stereospecific 24-membered cyclosiloxanes **11a,b** and **12a,b**.



Scheme 4. The synthesis of SiH and SiVin functionalized stereospecific 24-membered cyclosiloxanes **11c** and **12c**.

lent in the *cis*-cycles (8-membered and 12-membered) (Figures 6, 7).

²⁹Si NMR spectra of compounds **11a-c** and **12a-c** show two sets of the two signals ²⁹Si nuclei. A pair of signals in strong fields corresponds to a macrocycle fragment O₃SiR and characterizes by the values of chemical shifts from –66 to –81 ppm depending on the substituents. Another couple of signals is located in weaker fields (from –2 to –6 ppm) and applies to OSi(Me)₂R' fragment. The ratio of the intensities of the two signals in each pair is the same and equals to 2:1. The structure of macrocycles with tris-*cis*-tris-*trans*-configuration contains eight structural fragments –O–Si(R)(OSiR'Me₂)–O– in which one of the bridging oxygen atoms is connected to bridging silicon atom with *trans*-locations

of Si(R)(OSiR'Me₂)-substituent, and another oxygen atom is connected to bridged silicon atom with *cis*-locations of the same substituent. The macrocycle structure also has four structural fragments –O–Si(R)(OSiR'Me₂)–O–, where terminal oxygen atoms are connected with Si(R)(OSiR'Me₂)-fragments (both with *cis*-position). This leads to the fact that corresponding indicator ²⁹Si nuclei both in the macrocycle and in the substituents and also ¹H and ¹³C nuclei exhibit magnetic non-equivalence. NMR spectra of these compounds show two sets of signals.

Furthermore, a silicon atom in the aforementioned eight structural fragments with different spatial orientation Si(R)(OSiR'Me₂)-substituents is asymmetric that leads to the appearance of diastereotopic protons and ¹³C nuclei

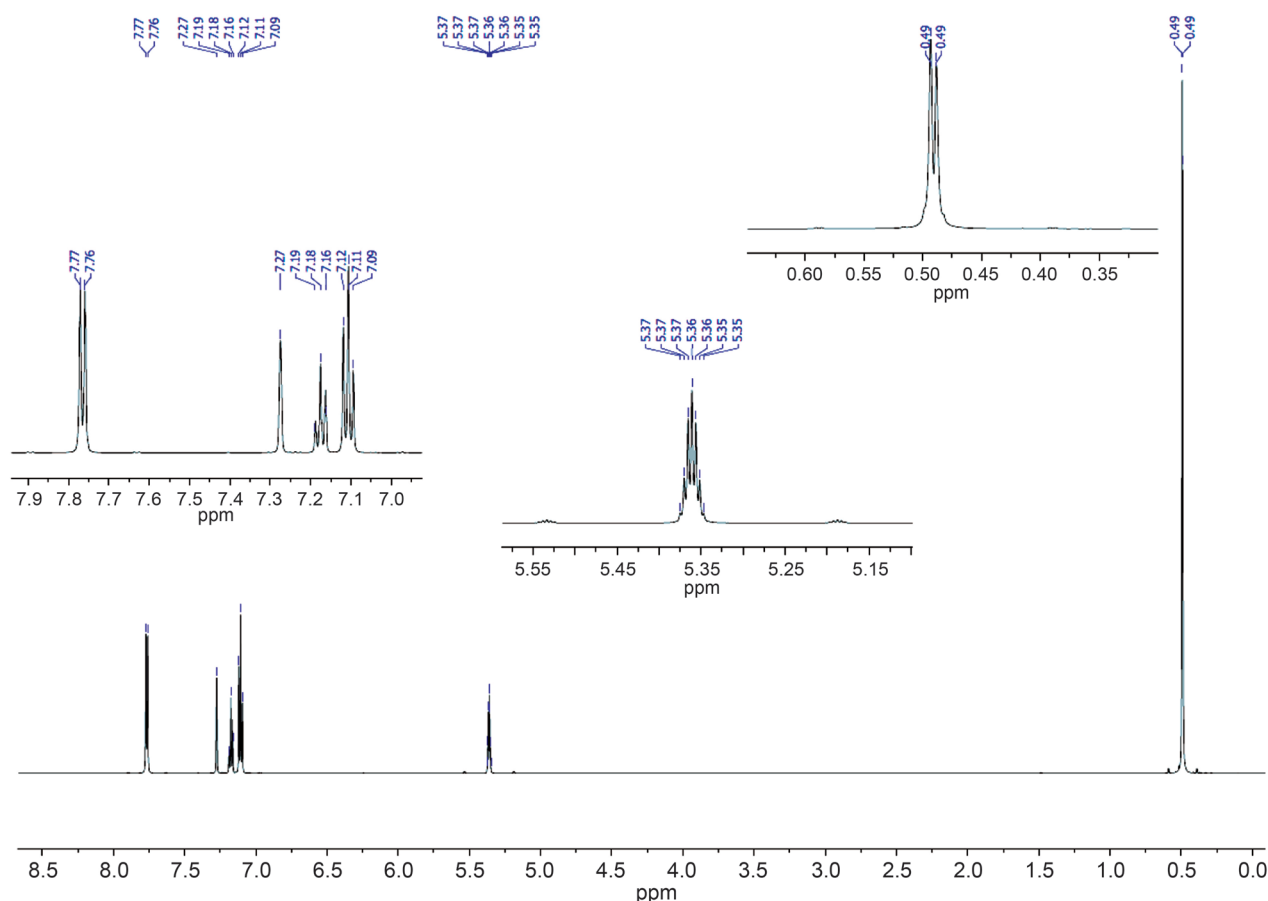


Figure 2. ^1H NMR spectrum of compound **3c** in C_6D_6 .

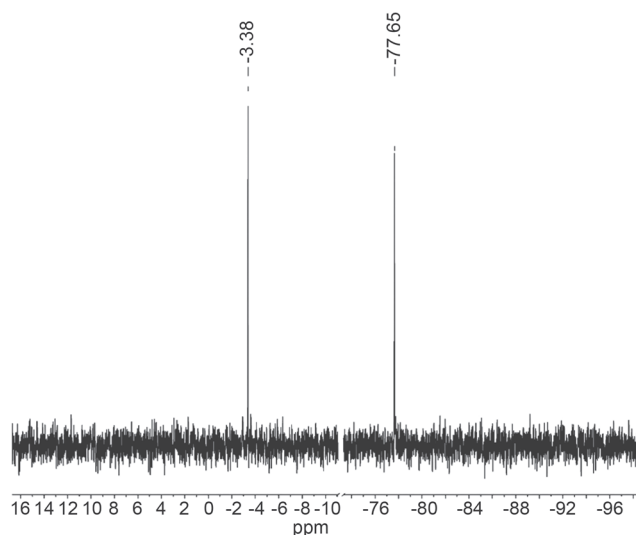


Figure 3. ^{29}Si NMR spectrum of compound **3c** in C_6D_6 .

connected with silicon atoms in the ^1H and ^{13}C spectra. A silicon atom in four structural fragments with the same spatial environment is not asymmetric. As a result three signals with the same intensity are observed in the ^1H and ^{13}C NMR spectra of methyl groups and two of them are diastereotopic. Membership of these signals precisely of this

type of methyl groups in the NMR spectra was determined from 2D spectra HMQC.

Thus, the following regularities in changing of shielding ^{29}Si nuclei depending on a cycle size for structures with the same substituents are observing. In the transition from 8-membered to 24-membered ring the shielding ^{29}Si nuclei for both types of fragments – O_3SiR and $\text{OSi}(\text{Me})_2\text{R}'$ is increasing. The corresponding changes of the chemical shifts are roughly the same for both types of ^{29}Si nuclei and are approximately 1 ppm. Moreover, these changes weakly depend on the nature of R and R'. A somewhat larger (about 2 ppm) change of chemical shift was noted for **3c** and **11c**. An increase of the shielding ^{29}Si nuclei with increasing of the size of cycle apparently is not associated with a large approaching of geometry silicon atom of O_3SiR fragment to sp^3 hybridized state in the 12-membered cycle compared with the 4-membered since a similar change take place for ^{29}Si nuclei of $\text{OSi}(\text{Me})_2\text{R}'$ fragment that is located outside the cycle. Probably that changing of shielding occurs due to some variation of influencing electronic and anisotropic effects of neighboring substituents. Interesting to note that transfer from 4-membered cycles to 6-membered cycles (the compounds **3c** – **8** and **4c** – **9**) leads to noticeable (2–2.8 ppm) increasing of shielding ^{29}Si nuclei in the cycle and to a weaker (0.6–1.0 ppm) shielding external ^{29}Si nuclei. Thus, transition from 6-membered to

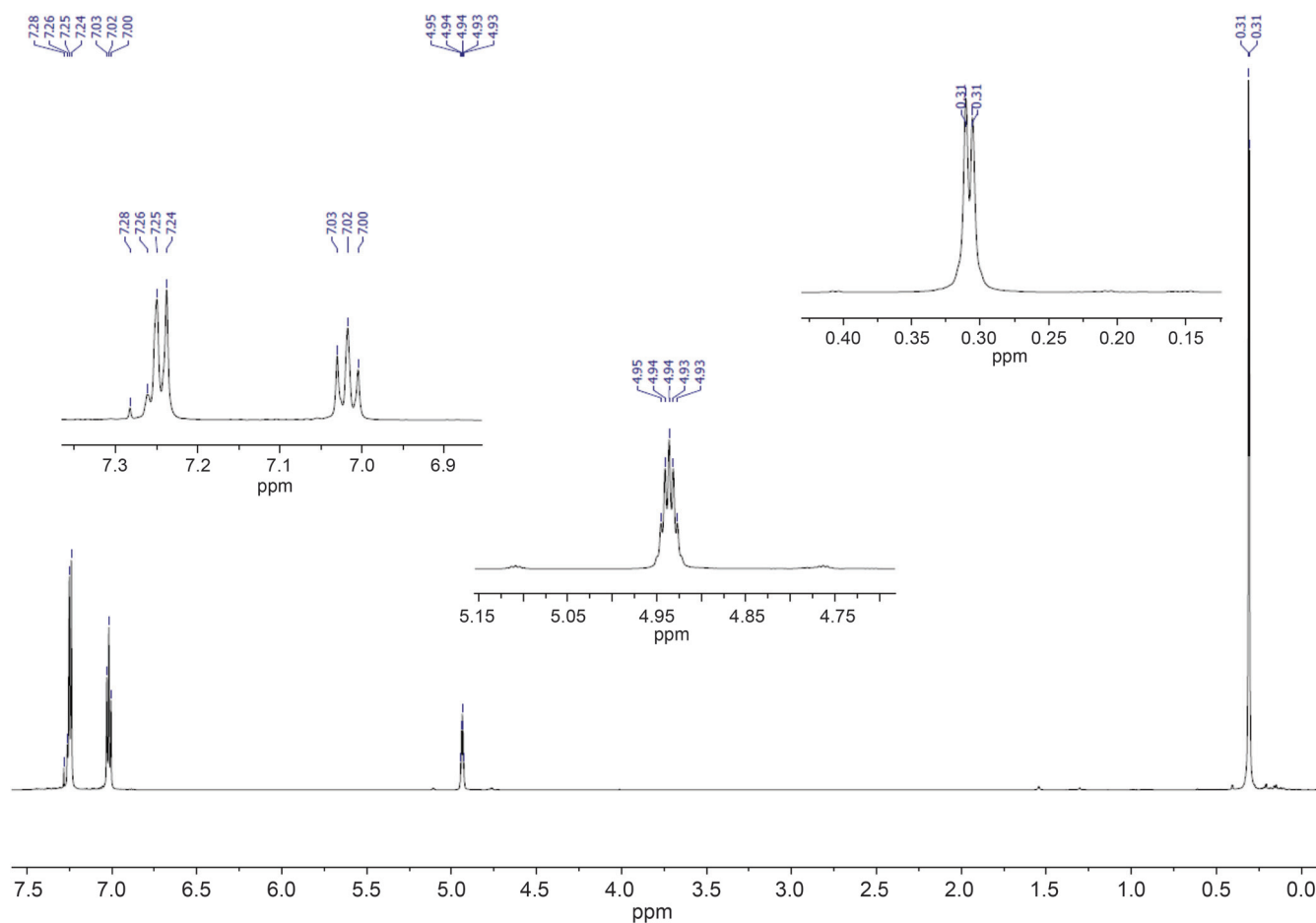


Figure 4. ^1H NMR spectrum of compound **8** in CDCl_3 .

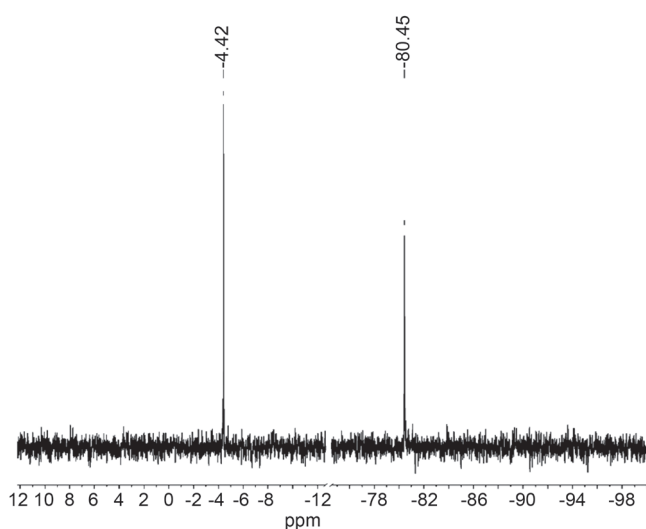


Figure 5. ^{29}Si NMR spectrum of compound **8** in CDCl_3 .

12-membered cycles weakly changes the shielding of ^{29}Si nuclei of both types.

As well as transition from 12-membered cycle to 24-membered one weakly changes the shielding of ^{29}Si nuclei of both types.

Thermogravimetric Analysis and DSC

Some thermal characteristics of synthesized stereoregular cyclosiloxanes are investigated and presented in Table 1. As it can be seen from the table data the values of glass transition temperature and decomposition temperature depend mainly on the nature of a substituent attached at silicon atom in a cycle. For Me and Vi substituted cyclosiloxanes glass transition temperature (T_g) increases with increasing of a cyclosiloxane ring size, whereas for Ph substituted cyclosiloxanes T_g decreases with increasing size of a cyclosiloxane ring. The onset decomposition temperature (T_d) depends on the ring size of cyclosiloxanes (Table 1, Figures 8–10). Destruction temperature onset for compounds **3a**, **3b** and **4a** is so small due to evaporation of the substances under heating up in the inert atmosphere in this case. The cyclosiloxanes with phenyl substituents at silicon atom in a cycle exhibit complex thermal behavior – two solid ordered phases at lower temperature exhibiting properties of a crystal and one at higher temperature exhibiting properties of a mesophase. A detailed examination of mesophase behavior and mesophase structure of phenyl containing cyclosiloxanes is a subject of our further study.

It has to be noted that changeover of one Me group in trimethylsiloxy group by Vi or H influences dramatically on thermal properties of cyclosiloxanes containing Me and Vi

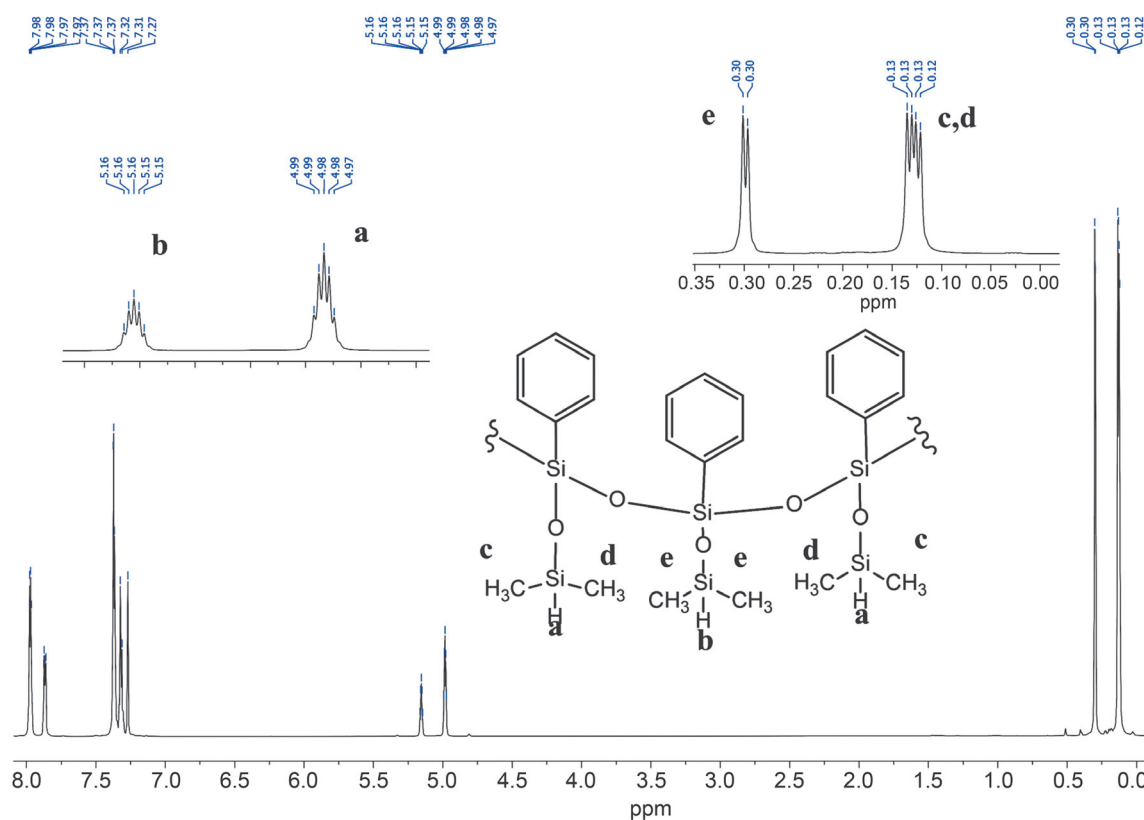


Figure 6. ^1H NMR spectrum of compound **11c** in CDCl_3 .

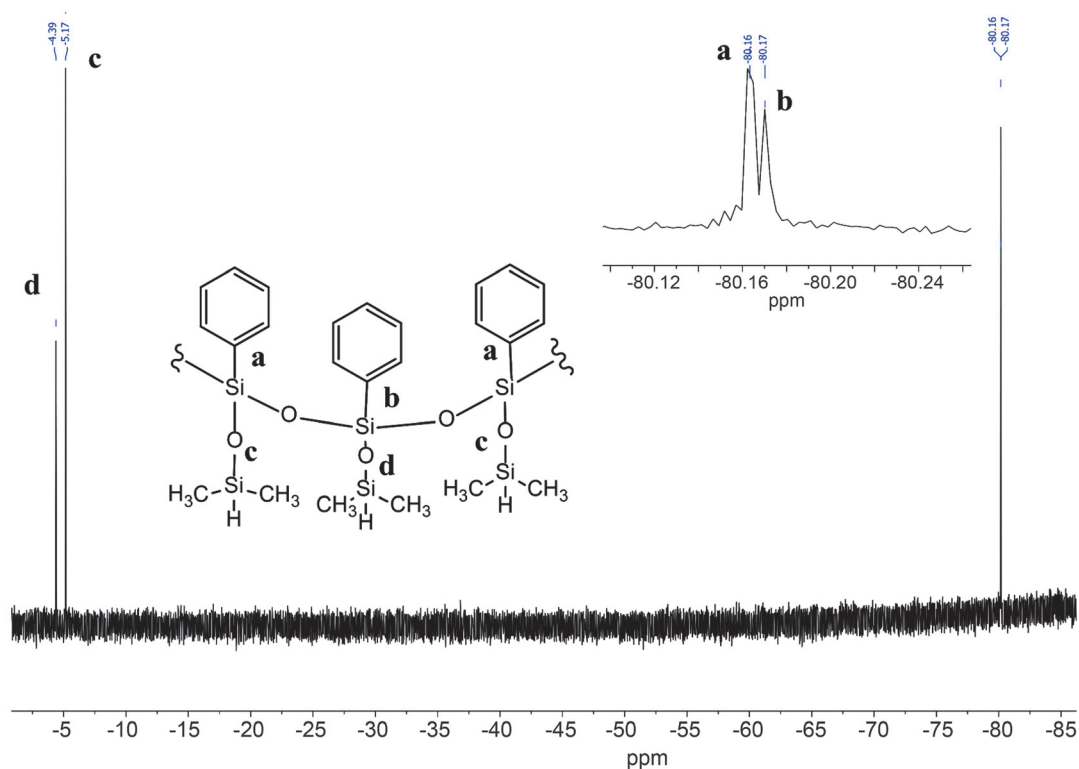
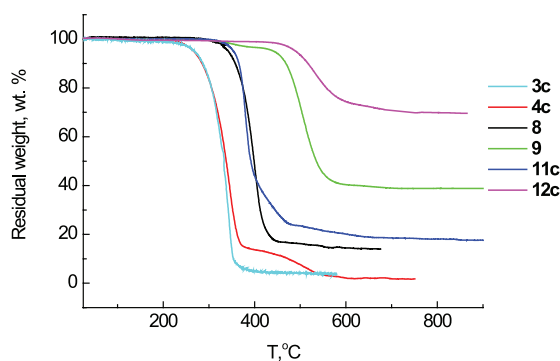
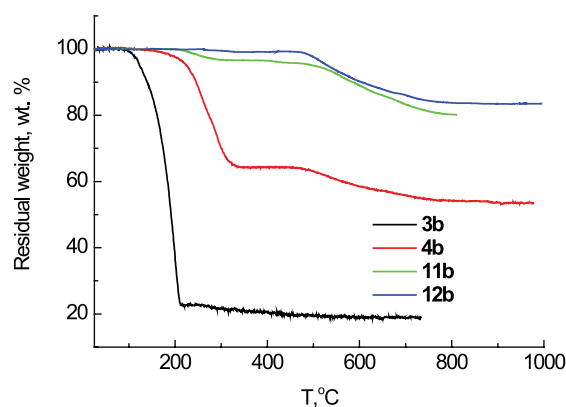
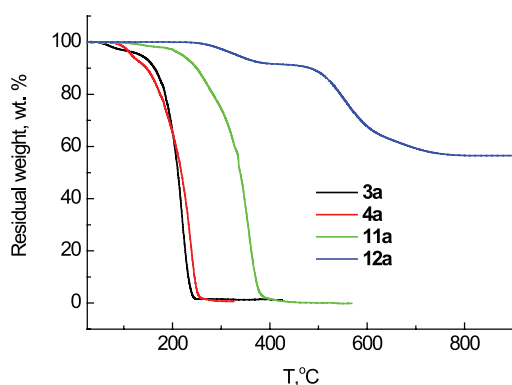


Figure 7. ^{29}Si NMR spectrum of compound **11c** in CDCl_3 .

Table 1. Thermal characteristics of synthesized compounds.

Compound	Formula	MW	T _g , °C	T _d ^{5%} , °C
3a	<i>cis</i> -[MeSi(O)OSi(Me) ₂ (H)] ₄	537.13	–139	140
3b	<i>cis</i> -[ViSi(O)OSi(Me) ₂ (H)] ₄	585.17	–145	124
3c	<i>cis</i> -[PhSi(O)OSi(Me) ₂ (H)] ₄	785.40	–	270
4a	<i>cis</i> -[MeSi(O)OSi(Me) ₂ (Vi)] ₄	641.27	–132	115
4b	<i>cis</i> -[ViSi(O)OSi(Me) ₂ (Vi)] ₄	689.32	–138	226
4c	<i>cis</i> -[PhSi(O)OSi(Me) ₂ (Vi)] ₄	889.55	–87	266
8	<i>cis</i> -[PhSi(O)OSi(Me) ₂ (H)] ₆	1178.10	–80	342
9	<i>cis</i> -[PhSi(O)OSi(Me) ₂ (Vi)] ₆	1334.33	–70	441
11a	<i>tris-cis-tris-trans</i> -[MeSi(O)OSi(Me) ₂ (H)] ₁₂	1611.39	–139	211
11b	<i>tris-cis-tris-trans</i> -[ViSi(O)OSi(Me) ₂ (H)] ₁₂	1755.51	–141	226
11c	<i>tris-cis-tris-trans</i> -[PhSi(O)OSi(Me) ₂ (H)] ₁₂	2356.20	–73	353
12a	<i>tris-cis-tris-trans</i> -[MeSi(O)OSi(Me) ₂ (Vi)] ₁₂	1923.81	–120	483
12b	<i>tris-cis-tris-trans</i> -[ViSi(O)OSi(Me) ₂ (Vi)] ₁₂	2067.96	–124	530
12c	<i>tris-cis-tris-trans</i> -[PhSi(O)OSi(Me) ₂ (Vi)] ₁₂	2668.65	–125	493

**Figure 8.** TGA curves of compounds **3a**, **4a**, **11a** and **12a**.**Figure 10.** TGA curves of compounds **3c**, **4c**, **8**, **9**, **11c** and **12c**.**Figure 9.** TGA curves of compounds **3b**, **4b**, **11b** and **12b**.

groups at Si atom in a cycle. In the case of *cis*-methyl- and vinylcyclotetrasiloxanes we observe cold crystallization depression of the substances, whereas in the case of Me- and Vi-cyclododecasiloxanes we observe glass transition temperature increase.^[20,21]

Conclusions

In this article we report an unique experimental approach to produce polyfunctional cyclosiloxanes. Using the metal template effect for the synthesis of individual organometallasiloxanes in a preliminary step, stereoregularly formed siloxane cycles are subsequently released under controlled conditions by the reaction with dimethyl(vinyl)- or dimethyl(hydride)-chlorosilanes. In each case these reactions give only one cyclosiloxane selectively and with high yields. The obtained Si-H and Si-Vinyl functionalized stereospecific cyclosiloxanes with mol. mass from 537 to 2668 and functionality from 4 to 12 are fully characterized by NMR-, IR- spectroscopy, IRMS and TGA and DCS. Such discrete molecules can be regarded as predetermined building blocks for the preparation of well-defined discrete supramolecular architectures. Investigations on the potential applications of these cyclosiloxanes for the synthesis of new compounds and new polymeric materials are currently under way in our laboratory.

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