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Configurations of cyclolinear polyphenylsilsesquioxanes as studied by ^{29}Si NMR spectroscopy

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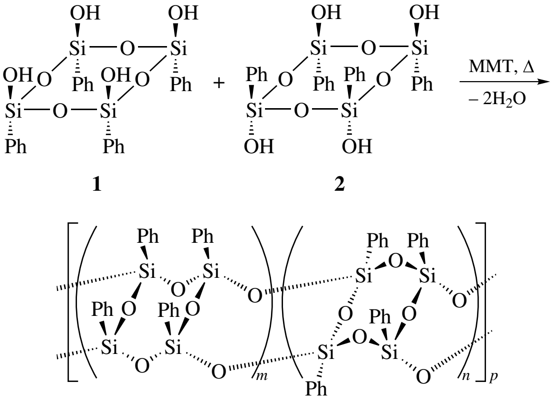
The polycondensation of the *cis* and *cis-trans-cis* stereoisomers of (tetrahydroxy)(tetraphenyl)cyclotetrasiloxane in different ratios in solution in the presence of montmorillonite affords polyphenylsilsesquioxanes with different unit conformations and cyclolinear siloxane framework configuration as confirmed by ^{29}Si NMR spectroscopy.

Recently, interest has quickened in cyclolinear (ladder) polyorganosilsesquioxanes synthesized by the polycondensation of 1,1,3,3-tetrahydroxy-1,3-diphenyldisiloxane, hydrolytic polycondensation, dehydrogenation, stepwise polycondensation and other reactions of tetrafunctional tetraorganocyclotetrasiloxanes isomers[1–7] in contrast to the use of the anionic polymerization of prepolymer (forpolymer) polyorganosilsesquioxanes.[8,9] The fact that polycondensation leads to a cyclolinear (CL) structure of the polyorganosilsesquioxane (POSSO) chain was established by ^{29}Si NMR and IR spectroscopy with the determination of the number of signals and their width in the ^{29}Si NMR spectrum for not only organosilsesquioxane groups ($RSiO_{1.5}$) but also R(OH)SiO groups or $OSiMe_3$ and $OR_2SiOSiR_2O$ terminal groups.[1–7,10] Earlier,[11,12] the ^{29}Si NMR studies of the configurations of cyclolinear poly[oxy(hexaorganocyclotetrasiloxane-2,8-diyl)s] and poly[oxy(decaorganocyclohexasiloxane-2,8-diyl)s] were reported. It was shown that the chemical shifts of organosilsesquioxane groups in the cyclosiloxane unit irrespective of the cycle size are most sensitive to changes in the configurations of the siloxane chain in contrast to diorganosiloxane fragments. In atactic CL polyorganosiloxanes (POSs), changes in the chemical shifts ($\Delta\delta$) of $RSiO_{1.5}$ groups span a range from 0.30 to 0.75 ppm for poly[oxy(hexaorganocyclotetrasiloxane-2,8-diyl)s] or from 0.06 to 0.13 ppm for poly[oxy(decaorganocyclohexasiloxane-2,8-diyl)s] depending on substituents with the width ($\Delta\delta_{1/2}$) of individual signals (for *trans-trans*, *trans-cis* and *cis-cis* joints in the chain) $0.015 \leqslant \Delta\delta_{1/2} \leqslant 0.025$ ppm. For *trans*- and *cis*-tactic CL organosiloxane copolymers (POSC), a singlet with $0.007 \leqslant \Delta\delta_{1/2} \leqslant 0.025$ ppm was observed for $RSiO_{1.5}$ group in this region.[13,14] A comparison of the values of $\Delta\delta$ and $\Delta\delta_{1/2}$ for $RSiO_{1.5}$ in CL POSC with corresponding data for CL POSSOs[1–3,6,7] shows that an increase in the equilibrium rigidity of the CL chain causes the $\Delta\delta$ and $\Delta\delta_{1/2}$ intervals to extend by one or two orders of magnitude in the ^{29}Si NMR spectrum in the region of $RSiO_{1.5}$ groups compared to single-stranded CL POS and POSC. Thus, ^{29}Si NMR spectroscopy enables both qualitative assessment and quantitative analysis of configurations of the siloxane main chain.

The aim of this work was to study the influence of the structure of two stereoisomers of 2,4,6,8-tetrahydroxy-2,4,6,8-tetraphenylcyclotetrasiloxane $[PhSi(OH)O]_4$, namely, *cis*- (**1**) and *cis-trans-cis*- (**2**), at different ratios in the polycondensation in solution in the presence of montmorillonite (MMT) on the conformation of chain units and configuration chain of the CL polyphenylsilsesquioxane (PPSSO) by ^{29}Si NMR spectroscopy.

Compounds **1** and **2** were synthesized by the hydrolysis of phenyltrichlorosilane in accordance with a published procedure[15] with the subsequent fractional crystallization.[16] The crystal structure of **1** was confirmed by X-ray analysis.[17]



1 **2**

3 $m = 1, n = 3$
4, **5** $m = 1, n = 1$
6 $m = 3, n = 1$
7 $n = 0$
8 $m = 0$

Scheme 1

The polycondensation of **1** and **2** was carried out in toluene and anisole solutions at 110 and 130 °C at different **1**:**2** ratios (3:1, 1:1 and 1:3) to afford PPSSO. The completion of the reaction was monitored by ^{1}H NMR and IR spectroscopy until disappearance of the signal for OH groups in isomers **1** and **2** at δ 6.20–6.45 in the ^{1}H NMR spectrum and an absorption band at 3400–3700 cm^{-1} in the IR spectrum. The reaction conditions (Table 1) were analogous to those of the polycondensation of four stereoisomers of 2,4,6,8-tetrahydroxy-2,4,6,8-tetraphenylcyclotetrasiloxane.[18] The composition and structure chain of PPSSOs **3**–**6** were determined by GPC, IR, ^{1}H and ^{29}Si NMR spectroscopy.[†]

Changes in the molecular mass distribution of PPSSO **3**–**6** with different isomer ratios were estimated by GPC. Figure 1 shows that PPSSOs with higher molecular masses are formed at an **1**:**2** ratio of 1:3. PPSSO **6** with the lowest molecular mass was synthesized at an **1**:**2** ratio of 3:1. To prove the occurrence

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[†] ^{29}Si NMR spectra were recorded on AV-400 (monomers) and AV-600 (polymers) Bruker spectrometers. The IR spectra were recorded on a Specord M-82 spectrophotometer using KBr pellets and CCl_4 solution. The average molecular masses and the molecular mass distributions were determined by GPC using a Waters instrument with an M601 pump, an M-484 UV-VIS detector (λ = 260 nm), an M-410 refractometric detector for two U-Styragel linear columns and a Millenium data processing system using THF as solvent at a flow rate of 1 ml min^{-1} at 30 °C.

Table 1 Synthesis of PPSSOs **3**–**8** by polycondensation of isomers **1** and **2** at 110 °C.

PPSSO	**1**:**2** ratio	Solvent	*t*/min	MM of product
3	1:3	anisole	150	1700–50 000
4	1:1	anisole	150	1700–50 000
5	1:1	anisole	150	1300–16 000
6	3:1	anisole	150	1600–12 000
7	1:0	toluene	120	2000–25 000
8	0:1	anisole	150	1500–75 000

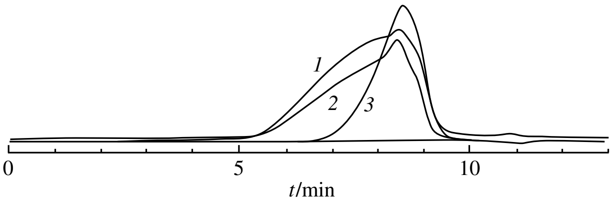

Figure 1 GPC traces of PPSSOs: (*1*) **3**, (*2*) **4** + **5** and (*3*) **6**.

of the copolycondensation of isomers **1** and **2** in 1:1 ratio, fractionation was carried out. At δ from –78.5 to –79.2, the ^{29}Si NMR spectrum exhibited two signals for both high-molecular-mass PPSSO **4** and low-molecular-mass fraction PPSSO **5**, which confirms identical composition for the entire range of molecular masses. Table 1 summarizes the characteristics of PPSSOs **3**–**6**.

The IR spectra of PPSSOs **3**–**6** (Figure 2) exhibit no Si–OH and OH absorption bands at 940–980 and 3300–3600 cm^{-1}, respectively, due to a high conversion of isomers **1** and **2** in the course of polycondensation. In the region of asymmetric stretching vibrations ν_{as}(Si–O–Si), the IR spectra of PPSSOs **3**–**6** contain one absorption band at 1133 cm^{-1}. A shoulder at ~1068 cm^{-1} appears only in the spectra of **3** and **4**. It is broadened as the contour changes, as compared with that for PPSSO **5**. A comparison of the IR spectra of PPSSOs **3**, **4** and **8** shows that the PPSSO synthesized from starting isomer **2** or from mixtures of isomers **1** and **2** containing 50–75% of **2** manifest an increase in the area under the shoulder at 1068 cm^{-1} compared to the main peak at 1133 cm^{-1}, which seems to be a consequence of changes in the conformation of chain units and in the configuration sequences of the CL chain. The IR spectra of cage-like organosilsesquioxanes in this region exhibit a single absorption band at 1130 cm^{-1} (ref. 19) unlike CL ladder polymers characterized by two bands at 1040 and 1130 cm^{-1}.[20,21] An increase in the molecular mass was accompanied by an increase in the absorption band intensity at 1040–1070 cm^{-1}, which approaches the intensity of a band at 1130 cm^{-1}. The polycondensation of isomer **2** results in PPSSO **8**, which is characterized by two absorption bands at 1075 and 1132 cm^{-1}. This agrees with published data[20,21] and confirms the formation of configuration sequences typical of CL ladder structures.

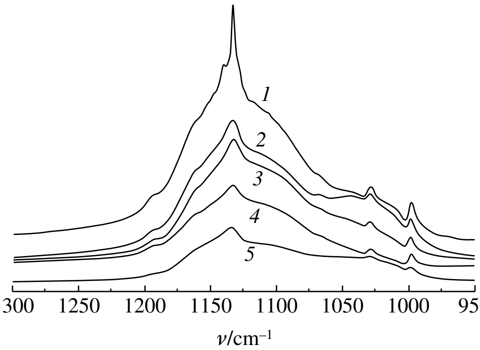

Figure 2 IR spectra of PPSSOs: (*1*) **3**, (*2*) **4**, (*3*) **5**, (*4*) **6** and (*5*) **8**.

The ^{1}H NMR spectra of PPSSOs **3**–**6** show no signals with δ 4.0 to 6.5 ppm due to the OH group proton at the Si atom, which were observed in the spectra of starting isomers **1** and **2**. The ^{29}Si NMR spectra of PPSSOs **3**–**6** (Figure 3) exhibit two groups of signals at δ –68.0 to –71.0 and at δ –77.0 to –81.0, the former signals being ten times less intense than the latter. None of the samples gave a well-resolved signal at δ –68.0 to –71.0. The ^{29}Si NMR spectra of compounds **3**–**6** at δ –77.0 to –81.0 are characterized by variable number of signals, their intensities and half-widths. For PPSSOs **3** and **4** three much weaker downfield signals are observed at δ –76.03 to –78.24, as compared to those of PPSSO **5**. The most intense upfield signal at δ –79.10 to –79.50 in the spectra of PPSSOs **3**, **4** should be assigned to the silicon atoms of isomer **2**.

As the concentration of isomer **1** was raised to 75% (PPSSO **6**), the intensity of the upfield signal at δ –79.10 to –79.50 decreased, while that of the signal at δ –78.30 to –78.80 increased. Thus, a variation in the ratio of starting isomers **1** and **2** in PPSSOs **3**–**6** changed the intensities of two ^{29}Si NMR signals for $(\mathrm{PhSiO}_{1.5})_n$ groups in the region of δ –78.20 to –79.50. Two or three downfield signals at δ –77.0 to –81.0 have different intensities depending on the **1**:**2** ratio and molecular masses of PPSSOs **4** and **5**, and they should be assigned to the first, second and third silicon atoms bonded to the terminal [PhSi(OH)O] group. This assignment is based on a comparison between chemical shifts in the ^{29}Si NMR spectra of organosiloxane oligomers with linear (**9**, unpublished results) and CL POS chain structure (**10**)[22] with different terminal groups (see Table 2).

The data in Table 2 show that, for organosiloxane oligomers, the chemical shifts of ^{29}Si NMR signals for the first, second, *etc.*, silicon atom relative to the terminal Si atom undergo a shift

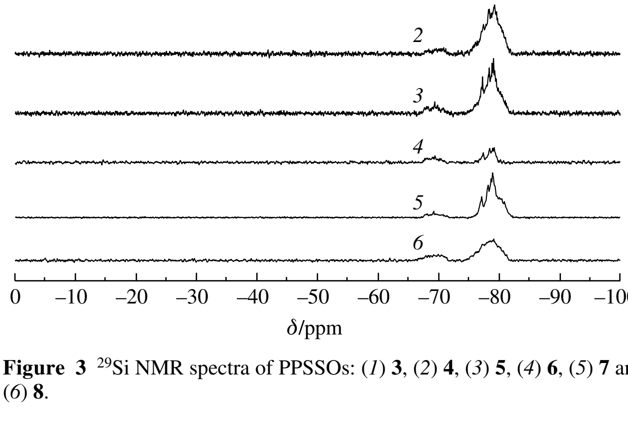

Figure 3 ^{29}Si NMR spectra of PPSSOs: (*1*) **3**, (*2*) **4**, (*3*) **5**, (*4*) **6**, (*5*) **7** and (*6*) **8**.

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cis-*Tetrahydroxy(tetraphenyl)cyclotetrasiloxane* **1**: mp 178–180 °C. ^{29}Si NMR (acetone-d_6) δ: –69.79 (s).

cis-trans-cis-*Tetrahydroxy(tetraphenyl)cyclotetrasiloxane* **2**: mp 219–221 °C. ^{29}Si NMR (acetone-d_6) δ: –69.95 (s).

Synthesis of CL polyphenylsilsesquioxanes **3**–**8**. Isomers **1** (0.072 g, 0.13 mmol) and **2** (0.072 g) were dissolved in anisole (0.48 ml) and MMT (0.043 g) was added. The mixture was heated at 130 °C for 3 min and then at 110 °C for 2.5 h. The polycondensation was monitored by IR and ^{1}H NMR spectroscopy. Water from the reaction mixture was removed into a Dean–Stark trap. MMT was filtered off, and the solvent was removed *in vacuo* until a constant weight. PPSSO (0.12 g) was obtained in 89% yield, flow point above 290 °C. The PPSSO was dissolved in C_6H_6 (0.25 ml); the subsequent addition of MeOH (0.20 ml) led to precipitation of PPSSO **4**, which was washed with MeOH (0.50 ml) and dried to constant weight. Yield, 0.055 g (46%), M = 1700–50000. After removing the solvents PPSSO **5** assembled (0.054 g, 45.0.%); M = 1300–16000.

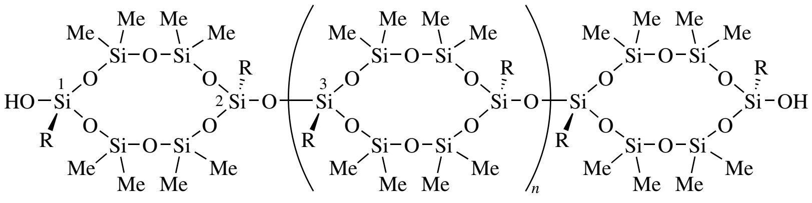
PPSSO **4**. IR (ν/cm^{-1}): 497 (ν_s SiO), 697, 739 (Ph), 998, 1029 (Ph), 1133 (ν_{as} SiO), 1431 (Si–Ph), 1492 (Ph), 1595(Ph). ^{1}H NMR (C_6D_6) δ: 6.70–7.10 (m, 5H, Ph). ^{29}Si NMR ($CDCl_3$) δ: –78.24 (s), –79.12 (s).

PPSSOs **3** and **6** were synthesized analogously.

$R^XMe_2Si(OMe_2Si)_nR^X$

9

R^X = Cl, $OSiMe_3$



10

R = Me, Ph

n = 3–5

Table 2 Chemical shifts in ^{29}Si NMR spectra of compounds **3**–**10**.

PPSSO	R^X	Si^1	Si^2	Si^3	Si^4	Reference
3		–76.62[a]	–77.46	–78.35	–79.56	
4		–76.03[a]	–77.37	–78.24	–79.07	
5		–77.25[a]	–78.34	–78.81	–79.05	
6		–77.53[a]	–78.42	–78.89	–79.12	
7		–77.07[a]	–78.15	–78.64	–78.88	18
8		–75.37[a]	–76.15	–77.19	–79.10	18
9	Cl Me_3SiO	3.36 7.13	–19.20 –21.55	–21.47 –22.18	–21.87 –22.02	
10 (R = Me)	HO	–54.86	–66.41	–67.54 –67.58		22
10 (R = Ph)	HO	–70.06	–81.15	–81.44 –81.49		22

[a] First Si in $(PhSiO_{1.5})$ unit by R(OH)SiO terminal group.

towards the upfield region irrespective of the structure of the main chain. The separation between signals, $\Delta\delta$, successively decreases with distance from the terminal Si atom. Note that the values of $\Delta\delta_{1/2}$ for the PPSSOs **7**, **8** synthesized from the pure starting isomers **1**, **2** and PPSSOs **3**–**6** synthesized from their mixtures are 2–3 ppm, being two orders of magnitude larger than those for stereoregular CL poly[oxy(hexaorganocyclotetrasiloxane-2,8-diyl)s] and poly[oxy(decaorganocyclohexasiloxane-2,8-diyl)s].[11,12] A comparison of the ^{29}Si NMR spectra (Figure 3) provides an additional confirmation of the correct assignment of downfield signals for PPSSO in the region of δ –77.0 to –81.0. Two signals observed in this region for high-molecular-mass PPSSO **4** are weaker than those observed for low-molecular-mass PPSSO **5**. The molecular mass of PPSSO **8** is higher than that of PPSSO **7**, but the downfield signals for the former are also much weaker than those for the latter. Therefore, irrespective of the starting compounds (pure isomers or their mixture) used for the synthesis of PPSSO, the ^{29}Si NMR spectra of polycondensation products exhibit not only the main broadened downfield singlet but also at least two signals for the silicon atoms successively bonded to the terminal Si atom through PhSi(OH)O groups. The ^{29}Si NMR spectra of CL ladder polymethylsilsesquioxane synthesized by dehydrocondensation of $[MeSi(H)O]_4$, the hydrolytic polycondensation of $[MeSi(X)O]_4$ (X = OEt, NCO),[3] and the polymerization of *cis-trans-cis*-tetrahydroxy(tetramethyl)cyclotetrasiloxane in the presence of K_2CO_3,[2] show a broadened singlet and at least two downfield signals of different intensities at δ –65.0 to –67.0. A comparison of the above results with published data[2,3] indicates that, irrespective of the structure of the starting isomer and substituents at the silicon atom, the ^{29}Si NMR spectra of CL POSSO (formed upon dehydrocondensation or polycondensation) in the region typical of $(RSiO_{1.5})_n$ polymers display not only the main broadened singlet in the downfield region but also signals whose intensities abruptly decreased with the molecular mass.

Thus, the polycondensation of *cis* and *cis-trans-cis* stereoisomers of (tetrahydroxy)(tetraphenyl)cyclotetrasiloxane **1** and **2** taken in different ratios in solution in the presence of MMT yields polyphenylsilsesquioxanes. The ^{29}Si NMR spectra of polycondensation products [in the region of $(PhSiO_{1.5})_n$ fragments] exhibit a broadened singlet with two maxima corresponding to the conformations of starting isomers **1** and **2** with the conservation of CL PPSSO configuration sequences for each isomer with increasing its concentration in the starting mixture.

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