Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2015, **25**, 229–231
Mendeleev Communications

Effect of stereoisomerism of (tetrahydroxy)(tetraphenyl)cyclotetrasiloxanes on the siloxane framework in polyphenylsilsesquioxanes obtained by polycondensation in the presence of layered-architecture compounds

Irina M. Petrova,[a] Alexey K. Buryak,[b] Alexander S. Peregudov,[a] Tatyana V. Strelkova,[a] Elena G. Kononova,[a] Ivan S. Bushmarinov[a] and Nataliya N. Makarova[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 135 5085; e-mail: nmakar@ineos.ac.ru*
[b] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation. Fax: +7 495 952 5308; e-mail: akburyak@mail.ru*

DOI: 10.1016/j.mencom.2015.05.025

Polycondensation of four stereoisomers of (tetrahydroxy)(tetraphenyl)cyclotetrasiloxane in solution in the presence of layered-architecture compounds afforded polyphenylsilsesquioxanes with different conformational and configurational structures of the siloxane framework, determined by IR, ^{29}Si NMR spectroscopy, powder X-ray diffraction and MALDI analysis.

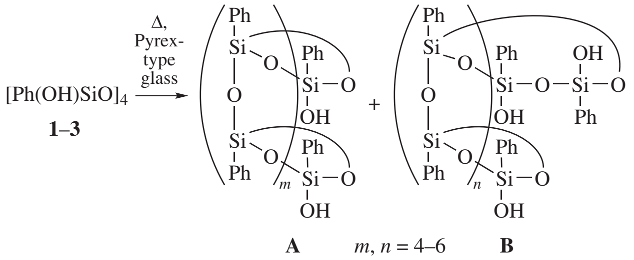
Organosilsesquioxane polymers[1–5] are of interest due to their unique physicochemical properties. Among them, there are cyclolinear organosiloxane polymers (so-called ladder polymers) synthesized by different methods using 1,1,3,3-tetrahydroxy-1,3-diphenyldisiloxane,[6] *cis*-tetrahydroxy(tetraphenyl)cyclotetrasiloxane or *cis*-tetrahydroxy(tetravinyl)cyclotetrasiloxane[7,8] or *cis-anti-cis*-tetrahydroxy(tetramethyl)cyclotetrasiloxane,[9] which possess a unique structure of the framework. Previous publications[10,11] reported that conformational changes in the siloxane framework of organosilsesquioxane polymers depended on organic substituents in the trifunctional silanes, products of partial hydrolysis of these silanes and the synthesis conditions. Studies on the hydrodynamic and electrooptical properties of polyorganosilsesquioxane solutions revealed differences in the α values in the Mark–Kuhn–Houwink equation and in the Kuhn segment depending on the organic substituent at Si atom and the structure of the prepolymer.[12–14] Polycondensation of hydroxy derivatives of cyclic and linear siloxanes afforded polyorganosilsesquioxanes with defect cyclolinear structures containing residual PhSi(OH)O groups and low molecular masses.[6–9]

Recently, the synthesis of stereoregular α,ω-dihydroxypoly(oxy-2,8-diorgano-4,4,6,6,10,10,12,12-octamethylcyclohexasiloxane-2,8-diyls) by polycondensation of *trans*-2,8-dihydroxy-2,4,4,6,6,8,10,10,12,12-decaorganocyclohexasiloxanes in the presence of layered-architecture compounds (LAC) was documented,[15,16] no cleavage of the siloxane bond in the cyclohexasiloxane moiety having occured up to 110 °C.

The aim of this work was to study influence of the structure of four stereoisomers of 2,4,6,8-tetrahydroxy-2,4,6,8-tetraphenylcyclotetrasiloxane on those of obtained polyphenylsilsesquioxane (PPSSO). Such PPSSO were prepared by polycondensation in solution in the presence of LAC. We compared the configurational properties in the siloxane framework of the PPSSO backbone with the conformational ones in the starting monomers by NMR, IR spectroscopy, X-ray diffraction and matrix activated laser desorption/ionization (MALDI) analysis.[†]

Four stereoisomers of 2,4,6,8-tetrahydroxy-2,4,6,8-tetraphenylcyclotetrasiloxane $[PhSi(OH)O]_4$, namely, all-*cis* **1**, *cis-cis-trans* **2**, *cis-trans-cis* **3** and all-*trans* **4**, were synthesized by hydrolysis of trichlorophenylsilane with subsequent fractional crystallization.[2,17] The crystal structures of two stereoisomers, **1** and **4**, were confirmed by X-ray diffraction analysis;[18] the lattice constants of **4** are the same as those published earlier.[19]

Polycondensation of compounds **1–4** in toluene and ditolylmethane at 110 °C in quartz or Pyrex-type glassware afforded PPSSO **5–7** (Scheme 1) and water that was subsequently removed using a Dean–Stark trap. The completion of the reaction was monitored by ^{1}H NMR and IR spectroscopy until disappearance of a signal in the region δ 6.20–6.45 in the ^{1}H NMR spectrum and an absorption band at 3400–3700 cm^{-1} in the IR spectrum.



Scheme 1

Polycondensations of compounds **1–3** are completed in nearly the same time. Stereoisomer **4** is the least active under these conditions. The molecular masses of PPSSO **5–7** determined by GPC are 1500.

The polycondensation of stereoisomer **1** gives product **5**. In chemical ionization mass spectrum of product **5** there are two groups of peaks: the fist one is the peaks of masses 1309, 1567, 1825 corresponding to cage-like compounds of structure **A**, where m = 4–6 (Scheme 1), the second one is characterized by masses 1447, 1705 and 1963, which are a homologous series of compounds of structure **B** with n = 4–6. The ratio of intensities of sum of peaks of structures **A** and **B** is 3:1.

The polycondensation of isomer **2** results in product **6**. Its mass spectrum contains peaks of abovementioned masses but intensities of peaks assigned to structures **A** and **B** ($m = n = 4$) are higher than those of product **5** under the general increase in the content of compounds of structure **B** (**A**:**B** = 2:1). The polycondensation of stereoisomer **3** gives product **7** whose mass

[†] For experimental and characterization details, see Online Supplementary Materials.

Table 1 Homocondensation of stereoisomeric cyclotetrasiloxanes **1–4** in the presence of LAC.[a]

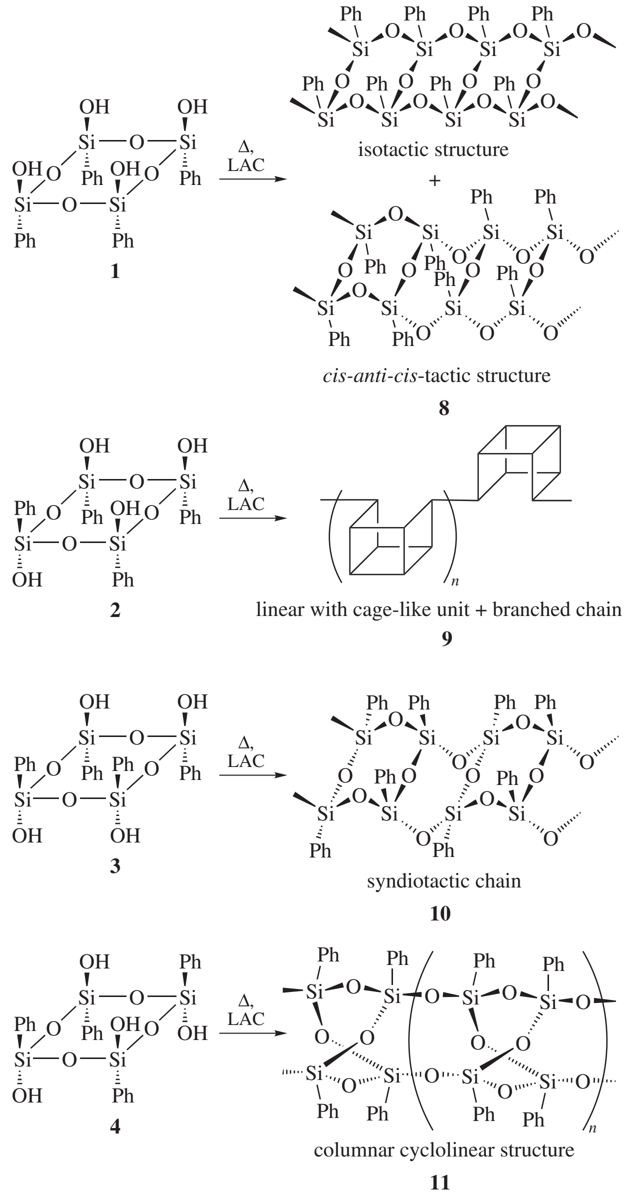
Entry	Starting monomer	LAC	Solvent	T/°C	Reaction time/h	Product	Yield (%)	M_w	Presence of OH groups in the product: ^{1}H NMR	Presence of OH groups in the product: IR
1	**1**	MMT	toluene	110	4	**8**	100	2000–25000	–	–
2	**1**	coal	anisole	150	4	**8′**	100	1400–4000	–	–
3	**2**	MMT	toluene	110	3	**9**	100	2000–75000	–	–
4	**3**	MMT	toluene	110	1.5	**10**	100	2000–15000	–	–
5	**4**	MMT	toluene	110	15	**11**	5[b]	–	Yes	Yes
6	**4**	MMT	anisole	110	13	**11**	60	2000–75000	Yes	Yes
7	**4**	coal	anisole	150	10	**11′**	100	1200–25000	–	–
8	**4**	MMT	ditolylmethane	200	4	**11″**	100	–	–	–

[a] Stroked numbers of products relate to the polycondensation in different solvents. [b] Conversion of **4** → **11**.

spectrum exhibits peaks corresponding to structures **A** and **B** of analogous composition. The ^{29}Si NMR spectra of products **5–7** manifest broad signals in two ranges (–67.8 to –70.0 and –76.0 to –80.0 ppm) for fragments Ph(OH)SiO and $PhSiO_{1.5}$, respectively. Downfield multiplet in the spectrum of product **6** appears with an additional narrow singlet at –67.90 ppm, which agrees with mass spectrum data given above. The main compounds in products **5–7** are isomers of bis[(hydroxy)(phenyl)siloxy](decaphenyl)decasilsesquioxane.

Polycondensations of stereoisomers **1–4** in 30% solutions of toluene, cyclohexanone, anisole and ditolylmethane in the presence of 30 wt% of LAC including montmorillonite (MMT) and absorbent carbon in the temperature range 110–200 °C gave completely soluble PPSSO **8–11** (Table 1). When concentration of monomers was raised to 60%, insoluble products were formed. Homocondensation of compounds **1–4** was monitored by ^{1}H NMR and IR spectroscopy. Apparently, LAC create prerequisites for the formation of the siloxane framework in PPSSO with both different configurations of the chain unit (structures **8** and **10**) and different architectures of the PPSSO unit (structures **9** and **11**) (Scheme 2). Hypothetical PPSSO structures (see Scheme 1) allows one to propose that different-type tacticity of the cyclolinear backbone as well as defect formation in double-stranded chain are not impossible for the four PPSSO studied. One should also take into account that the higher the equilibrium rigidity of the PPSSO chain the more probable the defect formation (cleavage of the Si–O bond) in a chain. The structures of the chain unit of PPSSO obtained were compared based on their ^{29}Si NMR and IR spectra, as well as data of MALDI analysis and powder X-ray diffraction.

The IR spectra of reaction products **8–11** (Figure S1, Online Supplementary Materials) except for **10** exhibit a single absorption band at 1129–1133 cm^{-1} with a shoulder at 1030–1080 cm^{-1} and a width $\Delta\nu_{1/2}$ of 250–200 cm^{-1} in the region of asymmetrical stretching vibrations ν_{as} of the Si–O–Si bond. Products **10** are characterized by two bands at 1075–1080 and 1131–1133 cm^{-1} with comparable intensities in the spectral range from 1000 to 1150 cm^{-1}. The IR spectrum of reprecipitated product **11** in the range 1000–1200 cm^{-1} showed a single absorption band at 1133 cm^{-1} with a smallest width of $\Delta\nu_{1/2} \approx 100$ cm^{-1}. In this region of the IR spectrum, cage-like organosilsesquioxanes are characterized by an absorption band at 1130 cm^{-1} (ref. 20) in contrast to cyclolinear ladder polymers characterized by two absorption bands at 1040 and 1130 cm^{-1}.[4,21] In addition, the intensity of the absorption band at 1040 cm^{-1} increases with increasing molecular mass and approaches the intensity of the band at 1130 cm^{-1}. The IR spectra of all products **8–11** exhibit no Si–OH absorption band at 940 cm^{-1} and the OH band at 3300–3600 cm^{-1}. Product **11** can possess a columnar cyclolinear structure with two siloxane chains linked by cyclotetrasiloxane rather than bridge oxygen. This model is characterized by a larger number of $PhSiO_{1.5}$ groups that inherit the cyclotetrasiloxane conformation with the defect cage-like structure. It follows from the IR data that only homocondensation of stereoisomer **3** leads to a cyclolinear PPSSO structure (appearance of two absorption bands at 1075 and 1132 cm^{-1}).



Scheme 2

A comparison of the ^{29}Si NMR spectra (Figure S2, Online Supplementary Materials) of compounds **8–11** for $(PhSiO_{1.5})_n$ in the region from δ –74.50 to –81.00 reveals different number of signals and their intensities. For compounds **8** and **10**, the δ region –67 to –71 ppm contains less intensive signals compared to the region –74 to –81 ppm. In addition, changes in the downfield multiplet in the spectra of products **8–11** are more pronounced than those in the upfield multiplet at δ from –75 to –81. In the δ region from –67 to –71 a very weak, 'implicit', multiplet for **8**, a singlet for **9** and up to six lines for **11**[1] are observed. As to the upfield signals there are two most clearly seen ones at δ –76.32 ($\Delta\delta_{1/2}$ = 0.6 ppm) and δ –78.32 ($\Delta\delta_{1/2}$ = = 1 ppm) for PPSSO **8** and an unresolved signal with $\Delta\delta_{1/2} \approx 2$ ppm for PPSSO **9–11**. A comparison of the $\Delta\nu_{1/2}$ values for **8** with corresponding data for a PPSSO obtained by polycondensation of 1,1,3,3-tetrahydroxy-1,3-diphenyldisiloxane in acetonitrile by a known procedure,[6] with self-organization on a solid surface ($\Delta\delta_{1/2}$ = 2.5 ppm, $\Delta\delta_{1/2}$ = 3.1 ppm, respectively) and for a low-molecular-mass PPSSO[22] ($\Delta\delta_{1/2}$ = 4–5 ppm) suggests that changes in the chemical shifts in the ^{29}Si NMR spectra in the δ region from –74.50 to –81.00 characterize (i) configurational differences between the chain units of the cyclolinear structure of PPSSO and (ii) conformational differences between the starting isomers. The appearance of two or more signals in this region indicate the formation of different types of configuration sequences of chain units in the cyclolinear chain. Most probably, a cyclolinear double-stranded chain with alternation of the all-*cis* and *cis-anti-cis* conformational sequences is formed. In the case of stereoisomer **3**, not only the tail-to-head, but also the tail-to-tail sequence is allowed, which leads to a larger number of nonequivalent positions of Si atoms in the cyclolinear chain. Analysis of ^{29}Si NMR data for products **8–11** demonstrates that compound **8** is characterized by the smallest $\Delta\delta_{1/2}$ value (full width at half-height) in the δ region from –74.50 to –81.00, which testifies to a lesser number of configurations and conformations of chain units in the cyclolinear structure.

The MALDI mass spectra of compounds **8–10** exhibit no peaks of the starting monomers. This is consistent with the ^{1}H NMR spectra that show no chemical shifts of OH groups in the region δ 5.40. As to PPSSO **11**, its mass spectrum manifests a peak with a mass of 552 and the ^{1}H and ^{29}Si NMR spectra demonstrate the chemical shift of isomer **4**. Peaks with masses of 1083 and 1067 in the mass spectra of compounds **8–11** are indicative of the formation of dimers with one and two Si–O–Si bonds between two rings, respectively. The formation of different-structure dimers leads to an increase in the number of nonequivalent Si atoms in the Si–OH group to at least four. The mass spectra of PPSSO **8**, **10** and **11** in the mass range 3200–1800 show peaks of oilgomeric compounds with a successive mass difference of 120 and 138. Summation of the two numbers gives a value of 258, the mass of a hypothetical structure $Ph_2Si_2O_3$. Product masses in the spectrum of **9** differ from those of **8**, **10** and **11** in the whole mass range, which may be due to the defect cage-like structure or to a branched structure of the polymer containing these fragments.

Powder X-ray diffraction revealed inter-chain distances in products **8** and **11** being 12.20 and 12.35 Å, respectively. These values agree with the published data for a low- and high-molecular-mass PPSSO obtained by polycondensation[6] and anionic polymerization.[23,24] However, this method is inappropriate to detect conformational or configurational differences between chain units of the cyclolinear PPSSO **8–11**.

In summary, polycondensation of isomers **1–4** in the presence of layered-architecture compounds offers prospects for targeted synthesis of cyclolinear PPSSO with different configurational and conformational structures of chain units.

The authors are grateful to Dr. N. S. Ikonnikov for registration of APCI MS spectra. This work was supported by the Russian Foundation for Basic Research (grant no. 13-03-00541).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.05.025.

References

1 J. F. Brown, *J. Polym. Sci., Part C*, 1963, **1**, 63.
2 J. F. Brown, *J. Am. Chem. Soc.*, 1965, **87**, 4317.
3 R. H. Baney, M. Iton, A. Sakakibara and T. Suzuki, *Chem. Rev*., 1995, **95**, 1409.
4 Y. Abe and T. Gunji, *Prog. Polym. Sci.*, 2004, **29**, 149.
5 V. N. Tsvetkov, *Zhestkotsepnye polimernye molekuly (Rigid-Chain Polymer Molecules)*, Nauka, Leningrad, 1986 (in Russian).
6 Z.-X. Zhang, J. Hao, P. Xie, X. Zhang, C. C. Han and R. Zhang, *Chem. Mater*., 2008, **20**, 1322.
7 M. Nowacka, A. Kowalewska, A. Tracz, T. Makowski, P. Sowinski, M. Florczak and B. Wiktorska, *Book of Abstracts of the 9th International Workshop on Silicon-Based Polymers*, Moscow, 2013, p. 75.
8 M. Nowacka, A. Kowalewska, A. Tracz and T. Makowski, *Book of Abstracts of the 9th International Workshop on Silicon-Based Polymers*, Moscow, 2013, p. 74.
9 H. S. Lee, S.-S. Choi, K.-Y. Baek, S. M. Hang, E. C. Lee, J.-C. Lee and S. S. Hang, *Eur. Polym. J.*, 2012, **48**, 1073.
10 K. A. Andrianov and N. N. Makarova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1969, **18**, 559 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 625).
11 K. A. Andrianov and N. N. Makarova, *Vysokomol. Soedin.*, 1970, **A12**, 663) (in Russian).
12 K. A. Andrianov, I. I. Tverdokhlebova, V. N. Emelyanov, T. A. Larina and A. Yu. Rabkina, *Vysokomol. Soedin.*, 1972, **A14**, 2246 (in Russian).
13 K. A. Andrianov, I. I. Tverdokhlebova, S.-S. A. Pavlova, I. I. Mamaeva, A. Yu. Rabkina and T. A. Larina, *Vysokomol. Soedin.*, 1977, **B19**, 406 (in Russian).
14 K. A. Andrianov, I. I. Tverdokhlebova, N. N. Makarova, I. I. Mamaeva. A. K. Chekalov, V. M. Men'shov and S.-S. A. Pavlova, *Vysokomol. Soedin.*, 1978, **A20**, 377 (in Russian).
15 N. N. Makarova and A. V. Tal'drik, *RF Patent 2447094*, 2012.
16 A. V. Tal'drik, *PhD Thesis*, Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 2013, p. 69 (in Russian).
17 N. N. Makarova, I. M. Petrova, P. V. Petrovskii, A. V. Kaznacheev, L. M. Volkova, M. A. Shcherbina, N. P. Bessonova, S. N. Chvalun and Yu. K. Godovskii, *Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1983 (*Izv. Akad. Nauk, Ser. Khim.*, 2004, 1902).
18 A. O. Dmitrienko, I. M. Petrova, N. N. Makarova and I. S. Bushmarinov, *CrystEngComm*., 2015, in press.
19 R. Ito, Y. Kakihana and Y. Kawakami, *Chem. Lett.*, 2009, **38**, 364.
20 J. F. Brown, L. H. Vogt and P. J. Prescott, *J. Am. Chem. Soc*., 1964, **86**, 1120.
21 S. A. Pavlova, V. I. Pakhomov and I. I. Tverdokhlebova, *Vysokomol. Soedin.*, 1964, **6**, 1275 (in Russian).
22 S. Yamomoto, N. Yasuda, A. Ueyama, H. Adachi and M. Ishikawa, *Macromolecules*, 2004, **37**, 2775.
23 J. F. Brown, H. Vogt, A. Katchman, J. W. Enstance, K. M. Kiser and K. W. Krantz, *J. Am. Chem. Soc*., 1960, **82**, 6194.
24 K. A. Andrianov, G. L. Slonimskii, D. Ya. Tsvankin, V. S. Papkov, V. Yu. Levin, Yu. P. Kvachev, M. N. Ilyina and N. N. Makarova, *Vysokomol. Soedin.*, 1974, **B16**, 208 (in Russian).

Received: 25th September 2014; Com. 14/4471