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

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Experimental

^{29}Si NMR spectra were recorded on Bruker AV-400 and AV-600 spectrometers in C_6D_6 solutions at 20 ^{o}C. IR spectra were recorded on a Specord M-82 spectrophotometer using KBr pellets and in CCl_4 solution.

The average molecular masses and the molecular mass distributions were determined by GPC using a Waters instrument comprising 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.

The atmospheric pressure chemical ionization (APCI) mass spectra were measured on the Finnigan LCQ Advantage tandem dynamic mass-spectrometer equipped by octapole ion trap mass analyzer operated in positive ion mode with the Surveyor MS pump and the nitrogen generator Schmidlin-Lab. Nitrogen 70/10 served as a sheath and auxiliary gas. The temperature of vaporizer was 400 °C, flow rate of acetonitrile 350 μl min^{-1}. The temperature of the heated capillary was 150 °C, the electric potential between the needle and the counter electrode was 6.0 κw. The samples with the concentration of 10^{-4} mol dm^{-3} in acetonitrile solution were introduced into the ion source through the Reodyne injector with the 5μl loop. Acetonitrile (Merck) was used for the gradient analysis. The data collection and treatment was fulfilled using the program *X* Calibur version 1.3.

MALDI experiments were carried out on an Ultraflex instrument (Bruker Daltonics) using dithranol and 2,5-dihydroxybenzoic acid (Bruker Daltonics) as matrices. Compounds under study were premixed with the matrix and supported on stainless targets.

Powder X-ray diffraction patterns of compounds under study were collected on a Bruker D8 Advance Vario diffractometer with copper radiation, Kα_1 monochromator (wavelength 1.54184 Å) and a LynxEye position sensitive detector in the 2θ range from 0.8 to 80° with an increment of 0.01° in 2θ. The X-ray diffraction patterns were analyzed using the TOPAS software.[1]

All-*cis*-(tetrahydroxy)(tetraphenyl)cyclotetrasiloxane **1**: mp 178–180 °C. ^{29}Si NMR (acetone-d$_6$) δ: –69.79 (s).

cis-cis-trans-(Tetrahydroxy)(tetraphenyl)cyclotetrasiloxane **2**: mp 174–176 °C. ^{29}Si NMR (acetone-d$_6$) δ: –70.05, –70.20, –70.35 (all s, intensity ratio 1 : 1 : 2).

cis-trans-cis-(Tetrahydroxy)(tetraphenyl)cyclotetrasiloxane **3**: mp 219–221 °C. ^{29}Si NMR (acetone-d$_6$) δ: –69.95.

All-*trans*-(tetrahydroxy)(tetraphenyl)cyclotetrasiloxane **4**: mp 248–250 °C. ^{29}Si NMR (acetone-d$_6$) δ: –70.66.

Synthesis of polyphenylsilsesquioxanes **5 -7**.

Monomer **1** (75 mg, 1.35×10^{-4} mol) was dissolved in toluene (3.10 ml). The solution was boiled at 110 °C for 2 h. The course of polycondensation reaction was monitored by IR and ^{1}H NMR spectroscopy until complete consumption of OH groups. Water from the reaction mixture was removed into a Dean–Stark trap. The solvent was removed *in vacuo* until a constant weight. Product **5** 70 mg, yield 95%, flow point above 290 °C.

IR (ν/ cm^{-1}): 493 (ν_s SiO), 697, 740 (Ph), 998, 1029, 1069 (Ph), 1133 (ν_{as}SiO), 1431 (Si-Ph), 1595 (Ph). ^{1}H NMR (C_6D_6 , 400 MHz) δ: 6.70–7.10 (m, 5H, Ph), ^{29}Si NMR (C_6D_6, 600 MHz) δ: –67.80 ÷ –70.00 (m), –76.32÷ – 80.10(m): MM = 1500 (GPC), APCI-MS, *m/z* 1309 [M+H], 1567 [M+H], 1825 [M+H] for structures A and 1447[M+H], 1705 [M+H], 1963 [M+H] for structures B.

Products **6** and **7** were synthesized analogously from monomers **2** and **3**.

Synthesis of cyclolinear polyphenylsilsesquioxanes **8–11**.

Monomer **1** (0.32 g, 5.78×10^{-4} mol) was dissolved in toluene (3.10 ml) and montmorillonite (0.24 g) was added. The solution was boiled at 110 °C for 2 h. The course of polycondensation

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[1] *TOPAS 4.2 User Manual*, Bruker AXS GmbH, Karlsruhe, Germany, 2009.

reaction was monitored by IR and ^{1}H NMR spectroscopy until complete consumption of OH groups. Water from the reaction mixture was removed into a Dean–Stark trap. Montmorillonite was filtered off and the solvent was removed *in vacuo* until a constant weight. Product **8** (0.28 g) was obtained in 95% yield, flow point above 290 °C.

IR (ν/ cm^{-1}): 495 (ν_s SiO), 696,730 (Ph), 1131 (ν_{as}SiO), 1431 (Si-Ph), 1462 (Ph), 1594 (Ph).

^{1}H NMR (C_6D_6) δ: 6.70–7.10 (m, 5H, Ph), ^{29}Si NMR (C_6D_6) δ: –76.32 (s), –78.32 (s): MM = 2100–16000 (GPC), d_1 = 12.20 Å.

Compounds **9** and **10** were synthesized analogously. Isomer **4** is insoluble in toluene at 110 °C; therefore, products **11** and **11'** were synthesized in solutions of anisole at 110 and 150 °C, respectively; product **11''** was synthesized in ditolylmethane at 200 °C.

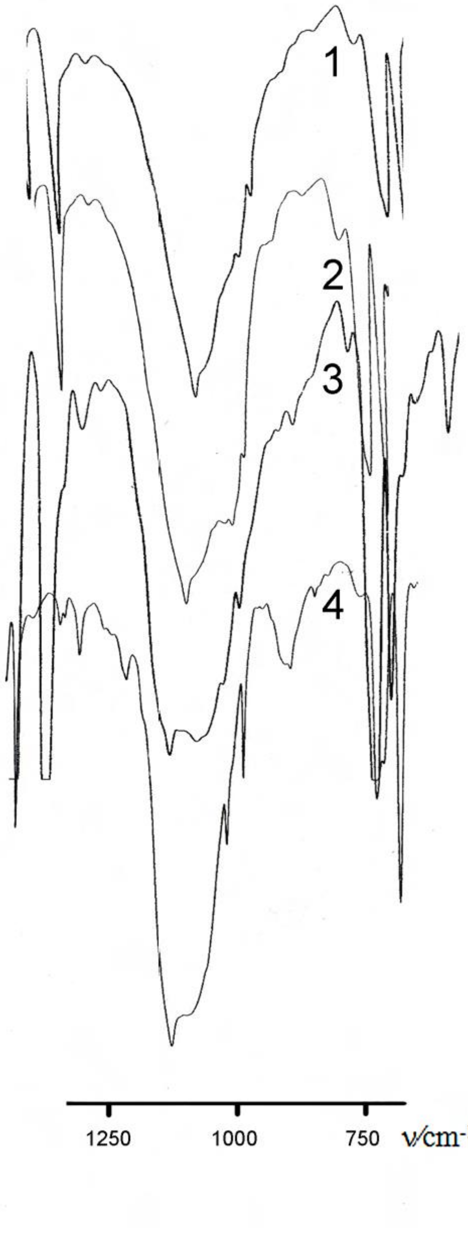

Figure S1 IR spectra of polymers (1) **8**, (2) **9**, (3) **10** and (4) **11**.

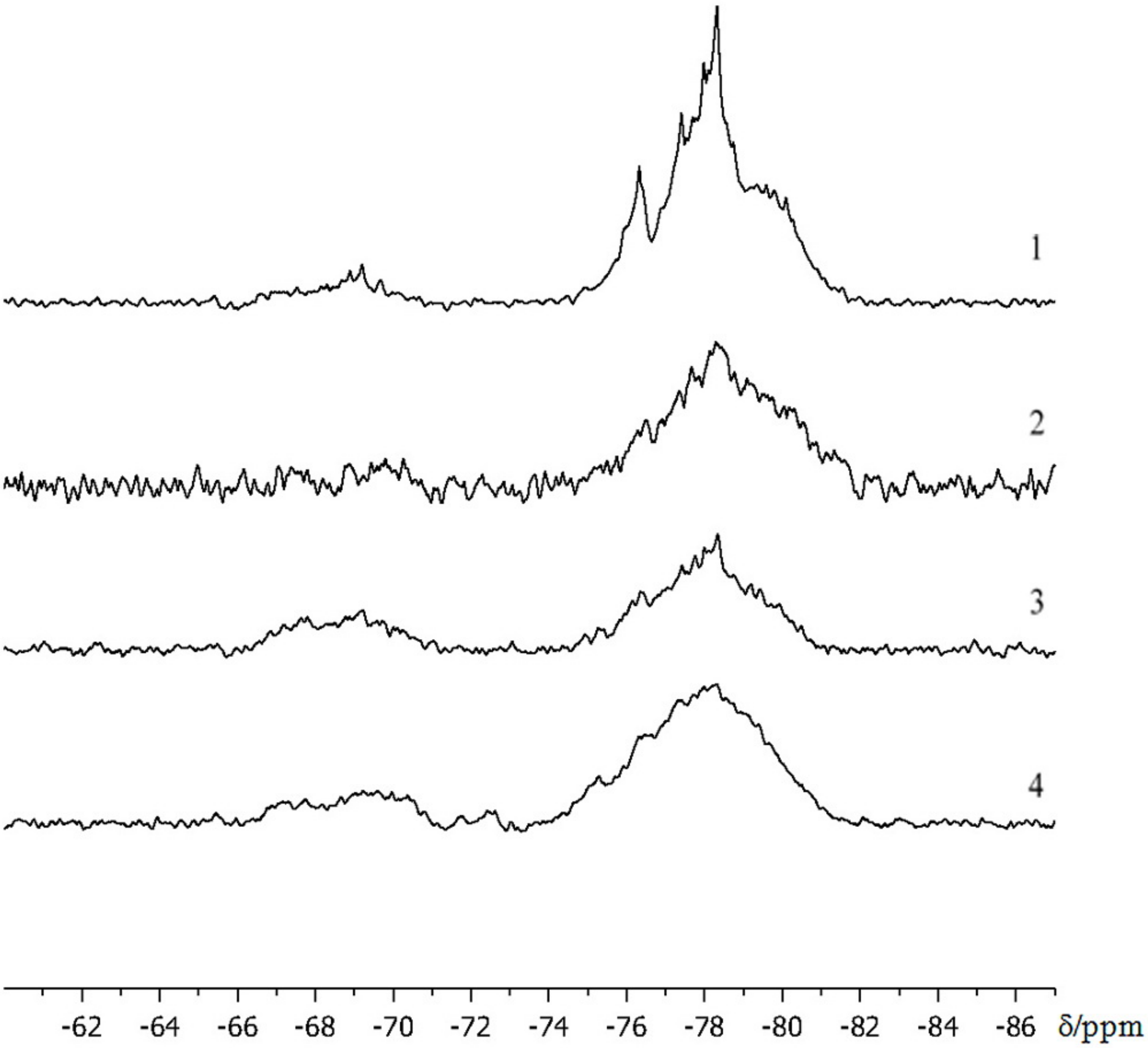

Figure S2 ^{29}Si NMR spectra of polymers (1) **8**, (2) **9**, (3) **10** and (4) **11**.