Chem. Mater. **1997,** *9,* 1475−1479

Thermal Properties of the Homologous Series of 8-fold Alkyl-Substituted Octasilsesquioxanes

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Received February 13, 1997. Revised Manuscript Received April 22, 1997[⊗]

The homologous series of 8-fold alkyl-substituted octasilsesquioxane has been prepared by hydrosilation of alkenes with octakis(hydridosilsesquioxane) $(HSiO_{3/2})_8$. Ethene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, and 1-decene were employed either in bulk or in toluene solution. The homologous series of 1,3,5,7,9,11,13,15-octaalkylpentacyclo$[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]$octasiloxanes, which are interesting model compounds for silsesquioxane-based materials was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, IR and mass spectroscopy, and elemental analysis. Melting points of the compounds were studied by DSC, revealing a strong decrease of the melting point from the octapropyl-substituted T_8 to the octapentyl derivative. Melting points for derivatives with longer *n*-alkyl chains showed an odd−even effect. TGA evidenced thermal stability under nitrogen up to temperatures between 200 and 400 °C and under air up to temperatures between 200 and 250 °C.

Introduction

Silsesquioxanes are polyhedral siloxane cages that are generally characterized by the formula $(RSiO_{3/2})_n$, where n is an even number (>4) and R may be hydrogen as well as inorganic or organic substituents. Polymeric branched and ladder-type siloxane structures may also be grouped in this class of compounds, although their stoichiometry does not precisely correspond to this formula, due to endgroups as well as nonhydrolyzed alkoxysilane units. A comprehensive review on this field was published by Voronkov and Lavrent'yev[1] and by Calzaferri recently.[2] Currently, silsesquioxanes meet increasing interest as building units for inorganic−organic hybrid materials, in which the incorporated inorganic segment is expected to contribute to unusual properties, such as thermal stability and abrasion resistance.[3] Furthermore, silsesquioxanes are considered to be interesting model compounds for silica surfaces.[4]

Silsesquioxanes are generally obtained via hydrolysis of trichlorosilanes or trialkoxysilanes.[5−17] Among the spherosiloxanes, the best studied compounds are the octasilsesquioxanes, with the general formula $R_8Si_8O_{12}$ (R_8T_8) that possess a cube-shaped Si_8O_{12} unit, often designated T_8[16,23] or T8.[18,19] Until recently, organo-substituted octasilsesquioxanes were generally prepared by hydrolysis of the respective organotrichloro- or trialkoxysilanes. However, only a few trichloro- or trialkoxysilanes form exclusively the cube-shaped molecule $(RSiO_{3/2})_8$ by this procedure. In most cases a mixture of different spherical silsesquioxanes as well as polymer structures are obtained. Pure 8-fold ethyl-, *n*-propyl-, and *n*-butyl-substituted T_8 were prepared in the late 1950s by Olsson, who isolated the octakis(alkylsilsesquioxane)s after repeated recrystallization from the mixture obtained after hydrolysis of the respective organotrichlorosilanes.[8]

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

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S0897-4756(97)00090-2 CCC: $14.00

Recently, an alternative route to organo-substituted octasilsesquioxanes has been developed by Calzaferri et al.,[20] which is based on the substitution of the hydrogen atom of $(HSiO_{3/2})_8$ with organic or inorganic groups. Synthesis of $(HSiO_{3/2})_8$ (in the following designated H_8T_8) was first described by Müller et al.[15] long ago and later improved by Frye and Collins[16] as well as Agaskar recently,[17] who demonstrated that controlled hydrolysis of $HSiCl_3$ can be used to prepare pure H_8T_8 with 17% yield. Meanwhile, several reports on hydrosilation of H_8T_8 have appeared.[21−25] Alkyl chains attached by this method include *n*-hexyl and *n*-decyl; however, no information on melting points and thermal properties of the compounds were given.

Our interest was focused on the synthesis and thermal behavior of the homologous series of octa-*n*-alkyl-substituted T_8 derivatives, in the following designated as R_8T_8. On one hand, we were interested in a comparison of the melting points of octaalkyl-substituted octasilsesquioxane derivatives from the aforementioned direct hydrolysis of the respective organotrichlorosilanes with the compounds obtained from hydrosilation of H_8T_8. Furthermore some derivatives with alkyl chains have not been described yet. On the other hand, this series of compounds represents interesting models for silsesquioxane-based materials, with respect to thermostability in dependence of alkyl chain length. In this paper, we will describe the synthesis of 1,3,5,7,9,11,13,15-octaalkylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxanes, where alkyl is $[CH_3(CH_2)_n-]$ with $n = 1-9$. The compounds are characterized in detail with regard to purity and structure (^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, IR, elemental analysis) as well as thermal properties (DSC, TGA).

Experimental Section

Materials. Trichlorosilane (Aldrich), anhydrous ferric chloride, sodium dodecyl sulfate, sodium carbonate, calcium chloride (Fluka), hydrochloric acid (Riedel-De-Haen), and diethyl ether (Roth) were obtained in p.a. quality and used without further purification. Toluene (Roth) was extracted with concentrated sulfuric acid to remove thiophene and purified by distillation from sodium. For synthesis of H_8T_8, petroleum ether (technical grade) was used without purification. For filtration silica gel (Merck 60, 230−400 mesh) was employed. A solution of hexachloroplatinic acid (1 wt % Pt in diglyme) was used for hydrosilation reactions.

Methods. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker ARX 300 spectrometer operating at 300 MHz for ^{1}H, 75.4 MHz for ^{13}C, and 59.6 MHz for ^{29}Si, using TMS as internal standard in $CDCl_3$ at ambient temperature. IR spectra were measured with a Perkin-Elmer 1330 IR spectrometer. GC spectra were recorded with a GC 6000 Vega Series 2 controlled by an ICU 600 (Carlo Erba Instruments) using nitrogen as carrier gas, an Alltech capillary column (length 25 m, i.d. 0.25 mm) and the following heating rates: start 60 °C, 20 K/min to 100 °C holding 1 min), 20 K/min to 300 °C (holding 5 min). Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 thermal analyzer at heating rate 1 K/min. Thermogravimetric (TGA) investigations and differential thermoanalysis (DTA) were recorded on a Netzsch Simultaneous Thermo Analysis (STA) 409 controlled by a Netzsch TASC 412/2 unit. Nitrogen and air atmosphere (flow: 150 cm^3/min) with heating rates of 1 and 5 K/min, respectively, were employed. Melting points were determined on an Olympus Vanox-T, controlled by an Olympus AH-2. As heating element was used a RACZEK THM 600, controlled by a RACZEK TMS 90 unit. Mass spectra (CI) were recorded on a Finnigan MAT 44S with the data system Finnigan MAT SS 20.

Synthesis of 1,3,5,7,9,11,13,15-Octahydridopentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (1). Anhydrous $FeCl_3$ (80 g, 0.49 mol), 40 mL of HCl_{conc} (37 wt % in water), 3 g (10 mmol) of sodium dodecyl sulfate, and 1500 mL of petroleum ether were stirred vigorously for 30 min using a magnetic stirrer. Under vigorous stirring a solution of 80 mL (107.3 g, 0.79 mol) of $HSiCl_3$ or 145 mL (129.8 g, 0.79 mol) of $HSi(OEt)_3$ in 800 mL of petroleum ether was added dropwise to the flask in the course of 10 h. After additional stirring for 30 min, the petroleum ether layer was separated, dried and neutralized with Na_2CO_3 and $CaCl_2$. After filtration, the petroleum ether was reduced to a residual volume of 200 mL. After 30 min the precipitated crystals were collected and thoroughly washed with petroleum ether (2.5 mL × 4): yield 7.81 g (18.6%). ^{1}H NMR ($CDCl_3$) δ 4.23 ppm (s, Si−H). ^{29}Si NMR ($CDCl_3$) δ −84.70 ppm. MS (EI) *m*/*z* (%) 424 (27) [M$^+$].

With respect to the boiling point (bp) of the alkenes employed, two different procedures for hydrosilation were chosen. For alkenes with bp higher than 90 °C, the reaction was carried out in bulk; if the bp was lower than 90 °C, the reaction was carried out in toluene solution. Examples for both synthetic procedures to obtain the octakis(alkylsilsesquioxane)s $(RSiO_{3/2})_8$ with R = ethyl (**2**), propyl (**3**), *n*-butyl (**4**), *n*-pentyl (**5**), *n*-hexyl (**6**), *n*-heptyl (**7**), *n*-octyl (**8**), *n*-nonyl (**9**), and *n*-decyl (**10**) are given in the following.

Hydrosilation in Solution. Preparation of 1,3,5,7,9,11,13,15-Octaalkylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxanes 2−4. 1 (200 mg, 0.47 mmol) was dissolved in 20 mL of dry toluene, and 300 μL of Pt catalyst solution was added. The Ar atmosphere was replaced by the alkene atmosphere (ethene, propene, or butene), and the solution was refluxed for 16 h under stirring. The disappearance of the Si−H bond ($\nu = 2250$ cm^{-1}) was confirmed by IR spectroscopy. The cooled solution was filtered twice through a mixture of silica gel and charcoal (5:1). After removal of the solvent, the residue was dissolved in 5 mL of diethyl ether and several times filtered through silica gel until the solution became colorless. The solvent was evaporated, and the white product dried in vacuo.

2: sublimes at 252.4 °C; yield 272.1 mg (89.0%). ^{1}H NMR ($CDCl_3$) δ 0.58 (q, Si−CH$_2$-, 16H), 0.96 (t, −CH$_3$, 24 H). ^{13}C NMR ($CDCl_3$) δ 4.04 (Si−CH$_2$−), 6.49 ppm (−CH$_3$). ^{29}Si NMR ($CDCl_3$) δ −65.74 ppm. IR (KBr) ν 2960 cm^{-1}, 2940, 2920, 2900, 2880 (H−C−H), 1460 (CH$_3$), 1250 and 1230 (Si−C), 1100 (Si−O), 1010, 755, 690, 530, 460, 385 (Si−O). Anal. Calcd for $C_{16}H_{40}Si_8O_{12}$: C 29.63, H 6.22. Found: C 29.49, H 6.34. GC: 100%, r.t. 12.07 min. MS (CI) *m*/*z* (%) 649 (100) [M$^+$].

3: mp 212.0 °C; yield 273.9 mg (76.4%). ^{1}H NMR ($CDCl_3$) δ 0.59 (t, Si−CH$_2$−, 16 H), 0.94 (t, −CH$_3$, 24 H), 1.42 ppm (sext, CH$_2$, 16 H). ^{13}C NMR ($CDCl_3$) δ 14.39 (C-1), 16.34 (C-3), 17.33 ppm (C-2). ^{29}Si NMR ($CDCl_3$) δ −66.93 ppm. IR (KBr) ν 2960 cm^{-1}, 2930, 2870 (H−C−H), 1455 (CH$_3$), 1260 (Si−C), 1100 (Si−O), 550 (O−Si−O), 475 (Si−O). Anal. Calcd for $C_{24}H_{56}Si_8O_{12}$: C 37.89, H 7.42. Found: C 37.44, H 7.46. GC: 100%, r.t. 14.39 min. MS (CI) *m*/*z* (%) 761 (70) [M$^+$].

4: mp 69.5 °C; yield 314.2 mg (76.4%). ^{1}H NMR ($CDCl_3$) δ 0.60 (t, Si−CH$_2$−, 16 H), 0.87 (t, −CH$_3$, 24 H), 1.22−1.43 ppm (m, CH$_2$, 32 H). ^{13}C NMR ($CDCl_3$) δ 11.64 (C-1), 13.77 (C-4), 24.99 (C-2), 25.61 (C-3). ^{29}Si NMR ($CDCl_3$) δ −66.64 ppm. IR (KBr) ν 2950 cm^{-1}, 2920, 2860 (H−C−H), 1465, 1455 (CH$_3$), 1270, 1260 (Si−C), 1105 (Si−O), 550 (O−Si−O), 475 (Si−O). Anal. Calcd for $C_{32}H_{72}Si_8O_{12}$: C 44.02, H 8.32. Found: C 43.68, H 8.53. GC 100%, r.t. 17.97 min. MS (CI) *m*/*z* (%) 873 (100) [M$^+$].

Preparation of 1,3,5,7,9,11,13,15-Octaalkylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxanes 5 and 6. 1 (200 mg, 0.47 mmol) and 47.0 mmol of alkene (100-fold excess) were dissolved in 20 mL of dry toluene. Pt catalyst solution (300 μL) was added. Under stirring, the solution was heated to 90−95 °C for 16 h. The disappearance of the Si−H bond (ν = 2250

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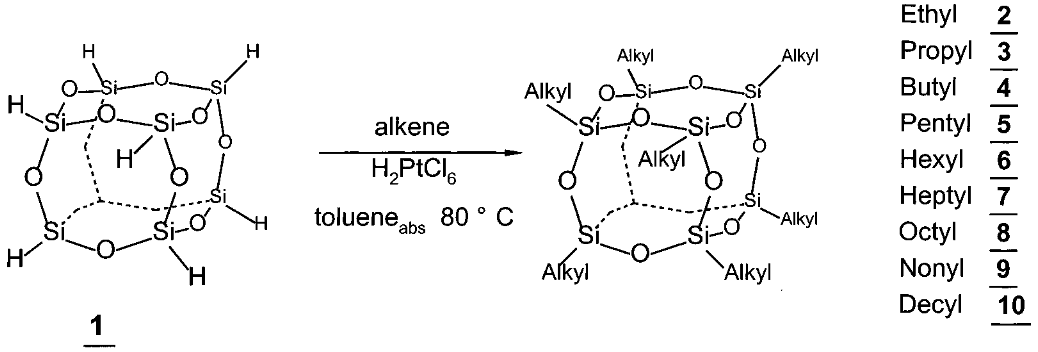
Scheme 1. Synthesis of the Octa(alkylsilsesquioxane)s 2−10



cm^{-1}) was confirmed by IR spectroscopy. After cooling to ambient temperature, the solvent was evaporated and the residue dissolved in 5 mL diethyl ether and twice filtered through a mixture of silica gel and charcoal (5:1) and then filtered several times through silica gel, until the solution became colorless. The solvent was evaporated and the white product dried in vacuo.

5: mp 24.0 °C; yield 405.7 mg (87.4%). ^{1}H NMR ($CDCl_3$) δ 0.59 (t, Si−CH_2−, 16 H), 0.86 (t, −CH_3, 24 H), 1.18−1.47 ppm (m, CH_2, 48 H). ^{13}C NMR ($CDCl_3$) δ 11.90 (C-1), 13.94 (C-5), 22.29 (C-2), 22.42 (C-4), 34.86 ppm (C-3). ^{29}Si NMR ($CDCl_3$) δ −66.63 ppm. IR (KBr) ν 2950 cm^{-1}, 2920, 2850 (H−C−H), 1460, 1455 (CH_3), 1265, 1250 (Si−C), 1100 (Si−O), 550 (O−Si−O), 470 (Si−O). Anal. Calcd for $C_{40}H_{88}Si_8O_{12}$: C 48.76, H 9.01. Found: C 48.58, H 8.99. MS (CI) *m*/*z* (%) 985 (100) [M$^+$].

6: mp 36.5 °C; yield 499.4 mg (96.6%; lit.[20] 90%). ^{1}H NMR ($CDCl_3$) δ 0.59 (t, Si−CH_2−, 16 H), 0.87 (t, −CH_3, 24 H), 1.18−1.44 ppm (m, CH_2, 64 H). ^{13}C NMR ($CDCl_3$) δ 11.98 (C-1), 14.10 (C-6), 22.56 (C-2), 22.75 (C-5), 31.57 (C-3), 32.34 ppm (C-4). ^{29}Si NMR ($CDCl_3$) δ −66.63 ppm. IR (KBr) ν 2950 cm^{-1}, 2920, 2850 (H−C−H), 1465, 1455 (CH_3), 1285, 1250 (Si−C), 1100 (Si−O), 560 (O−Si−O), 470 (Si−O). Anal. Calcd for $C_{48}H_{104}Si_8O_{12}$: C 52.53, H 9.56. Found: C 52.48, H 9.52. MS (CI) *m*/*z* (%) 1097 (100) [M$^+$].

Hydrosilation in Bulk. Preparation of 1,3,5,7,9,11,13,15-Octaalkylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxanes 7−10. **1** (200 mg, 0.47 mmol) was dissolved in 10 mL of alkene, and 300 μL of Pt catalyst solution was added. The solution was refluxed under stirring for 16 h. The disappearance of the Si−H bond (ν = 2250 cm^{-1}) was confirmed by IR spectroscopy. After cooling to ambient temperature, the solvent was evaporated, and the residue dissolved in 5 mL of diethyl ether, twice filtered through a mixture of silica gel and charcoal (5:1), and then filtered several times through silica gel, until the solution became colorless. The solvent was evaporated, and the white product dried in vacuo.

7: mp 31.5 °C; yield 529.9 mg (92.3%). ^{1}H NMR ($CDCl_3$) δ 0.59 (t, Si−CH_2−, 16 H), 0.87 (t, −CH_3, 24 H), 1.19−1.45 ppm (m, CH_2, 80 H). ^{13}C NMR ($CDCl_3$) δ 11.98 (C-1), 14.10 (C-7), 22.71 (C-2), 22.80 (C-6), 29.03 (C-4), 31.81 (C-3), 32.64 ppm (C-5). ^{29}Si NMR ($CDCl_3$) δ −66.63 ppm. IR (KBr) ν 2910 cm^{-1}, 2850 (H−C−H), 1455 (CH_3), 1270 (Si−C), 1100 (Si−O), 560 (O−Si−O), 470 (Si−O). Anal. Calcd for $C_{56}H_{120}Si_8O_{12}$: C 55.55, H 10.01. Found: C 55.60, H 10.01. MS (CI) *m*/*z* (%) 1210 (100) [M$^+$].

8: mp 51.0 °C; yield 615.8 mg (87.0%). ^{1}H NMR ($CDCl_3$) δ 0.60 (t, Si−CH_2−, 16 H), 0.88 (t, −CH_3, 24 H), 1.21−1.44 ppm (m, CH_2, 96 H). ^{13}C NMR ($CDCl_3$) δ 11.97 (C-1), 14.11 (C-8), 22.71 (C-2), 22.80 (C-7), 29.26, 29.32 (C-4, C-5), 31.96 (C-3), 32.68 ppm (C-6). ^{29}Si NMR ($CDCl_3$) δ −66.64 ppm. IR (KBr) ν 2950 cm^{-1}, 2920, 2850 (H−C−H), 1465 (CH_3), 1270, 1255 (Si−C), 1110 (Si−O), 560 (O−Si−O), 470 (Si−O). Anal. Calcd for $C_{64}H_{136}Si_8O_{12}$: C 58.15, H 10.38. Found: C 57.87, H 10.63. MS (CI) *m*/*z* (%) 1331 (100) [M$^+$].

9: mp 47.6 °C; yield 587.7 mg (87.0%). ^{1}H NMR ($CDCl_3$) δ 0.58 (t, Si−CH_2−, 16 H), 0.86 (t, −CH_3, 24 H), 1.18−1.44 (m, CH_2, 112 H). ^{13}C NMR ($CDCl_3$) δ 11.97 (C-1), 14.11 (C-9), 22.72 (C-2), 22.80 (C-8), 29.39, 29.42, 29.59 (C-4 to C-6), 31.97 (C-3), 32.69 ppm (C-7). ^{29}Si NMR ($CDCl_3$) δ −66.64 ppm. IR (KBr) ν 2950 cm^{-1}, 2910, 2850 (H−C−H), 1460 (CH_3), 1275, 1260 (Si−C), 1105 (Si−O), 570 (O−Si−O), 480 (Si−O). Anal. Calcd for $C_{72}H_{152}Si_8O_{12}$: C 60.30, H 10.69. Found: C 60.30, H 10.69. MS (CI) *m*/*z* (%) 1435 (100) [M$^+$].

10: mp 60.5 °C; yield 686.8 mg (94.3%). ^{1}H NMR ($CDCl_3$) δ 0.60 (t, Si−CH_2−, 16 H), 0.88 (t, −CH_3, 24 H), 1.18−1.47 ppm (m, CH_2, 128 H). ^{13}C NMR ($CDCl_3$) δ 11.96 (C-1), 14.11 (C-10), 22.71 (C-2), 22.80 (C-9), 29.38, 29.42, 29.64, 29.73 (C-4 to C-7), 31.96 (C-3), 32.69 ppm (C-8). ^{29}Si NMR ($CDCl_3$) δ −66.65 ppm; IR (KBr) ν 2960 cm^{-1}, 2920, 2850 (H−C−H), 1468 (CH_3), 1270, 1255 (Si−C), 1105 (Si−O), 570 (O−Si−O), 480 (Si−O). Anal. Calcd for $C_{80}H_{168}Si_8O_{12}$: C 62.13, H 10.96. Found: C 61.88, H 10.96. MS (CI) *m*/*z* (%) 1547 (100) [M$^+$].

Results and Discussion

Synthesis. Pure octakis(hydridosilsesquioxane) (**1**) was synthesized via a slightly simplified procedure, using technical grade petroleum ether instead of the solvent mixture of toluene, methanol, and hexane isomers described by Agaskar.[17] Partial solvent removal permitted isolation of H_8T_8 by fractionating crystallization and enabled us to separate it from the mixture containing H_8T_8 and $H_{10}T_{10}$. The final yield of pure H_8T_8 obtainable by this modified procedure was 18.6%. Similar yields were obtained when $HSi(OEt)_3$ was employed under the same conditions.

The octakis(alkylsilsesquioxane)s $(RSiO_{3/2})_8$ with R = ethyl (**2**), propyl (**3**), *n*-butyl (**4**), *n*-pentyl (**5**), *n*-hexyl (**6**), *n*-heptyl (**7**), *n*-octyl (**8**), *n*-nonyl (**9**), and *n*-decyl (**10**) were prepared via hydrosilation with **1** as shown in Scheme 1.

Depending on the 1-alkene boiling point (bp), two different procedures for hydrosilation were chosen. If the bp was higher than 90 °C, hydrosilation was carried out in bulk, if the bp was lower than 90 °C, the reaction was performed in toluene solution. For the gaseous alkenes ethene, propene, and butene the argon atmosphere was replaced by the alkene atmosphere. Completion of the reaction was monitored by the disappearance of the Si−H signal in IR spectra. All reactions were run overnight (at least 16 h reaction time), which was sufficient in all cases for complete substitution. After evaporation of solvent or residual alkene the octakis(alkylsilsesquioxane)s were purified by dissolution in diethyl ether and filtration through a mixture of silica gel/active charcoal (5:1) until the solutions were colorless. After evaporation of the solvent the obtained white products were dried under reduced pressure. Yields were in the range of 76−98%.

Elemental analysis confirmed the molecular composition $(RSiO_{3/2})_n$ in all cases. One single peak in the ^{29}Si NMR spectra (Figure 1, i.e., ethyl-T_8) evidenced that the

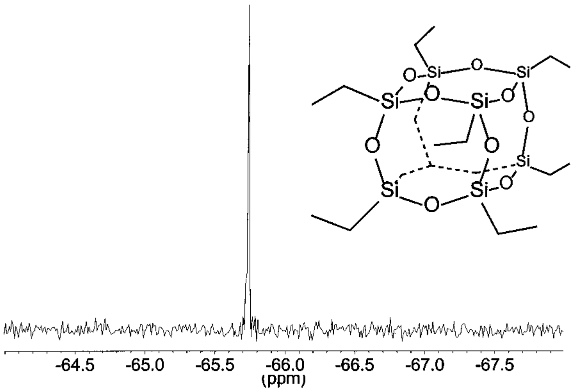


Figure 1. ^{29}Si NMR spectrum of ethyl-T_8 (**2**).

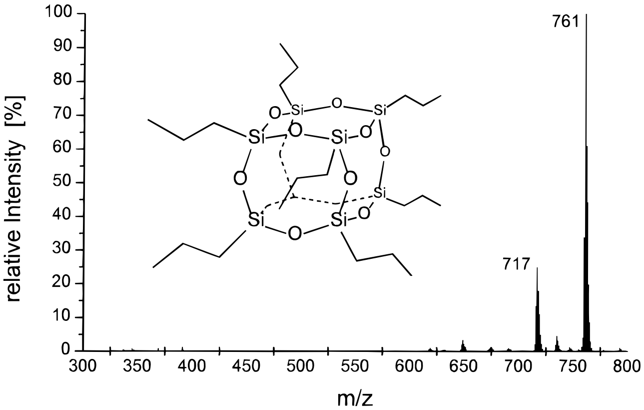


Figure 2. Mass spectrum of propyl-T_8 (**3**).

products were uniform and completely substituted. For the case of partial substitution additional resonances would be expected.[24] Except for **2** (−65.74 ppm) and **3** (−66.93 ppm) all alkyl-T_8 derivatives show a signal at −66.64 (±0.01) ppm.

^{13}C NMR spectra evidence that no Markovnikov addition (β-addition) took place. This is in agreement with data reported in literature.[25] Only the expected number of signals appeared in the spectra. ^{1}H NMR spectroscopy supplements the characterization.

Mass spectroscopy (Figure 2, i.e., propyl-T_8) proves that 8-fold substitution of H_8T_8 to octakis(alkylsilsesquioxane)s was successful. High-purity compounds were obtained. Additionally the spectra show, that the R_8T_8 possess high stability toward fragmentation. Besides the molecule peak, there are only signals for the fragments with one arm missing.

Thermal Properties. Melting points (mp) of the octaalkylsilsesquioxanes (R_8T_8) have been determined by microscopy, DTA and DSC. The values obtained by the different methods were in good agreement. The mp's of **3**−**10** (filled circles) as well as data reported in literature[5,7,8] before for the respective compounds prepared by hydrolysis of the organotrichlorosilanes (open circles) are plotted in Figure 3.

Unexpectedly and in contrast to data reported before,[8] microscopic study and DTA/TGA measurements showed that **2** sublimates even under ambient conditions. We were unable to observe a melting peak in the DTA, but a peak did appear at 252.4 °C, where the material showed an abrupt weight loss of 100%. **3**−**10** show very interesting melting behavior. **3** (212.0 °C) exhibits a relatively high melting point, for **4** (69.5 °C) and **5** (24.0 °C) the mp's decrease. For derivatives with longer *n*-alkyl chains from **5** to **10** the mp's show a clear odd−even effect with the compounds with odd number of carbon atoms exhibiting generally lower melting points. Similar behavior is well-known from the melting points of several other homologous series. Clearly, from the trends observed, for short alkyl chains, the T_8 unit determines the packing of the molecules, whereas for longer *n*-alkyl chains the flexible alkyl chains control the packing in a most probably layered type of packing, as found for octakis(9-oxazolinyldecyl)silsesquioxane recently.[28]

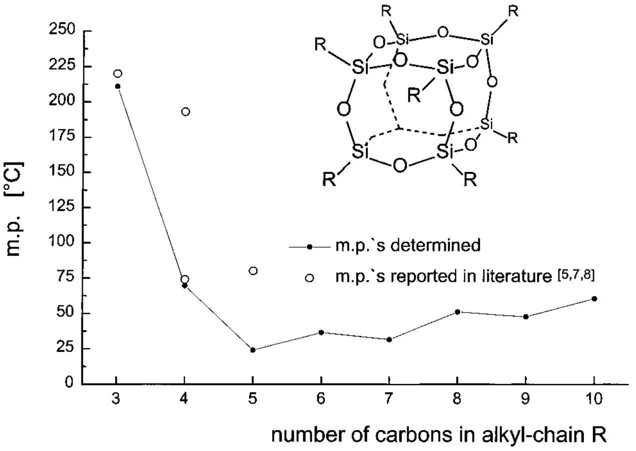


Figure 3. Melting points of the octakis(alkylsilsesquioxane)s **3**−**10**.

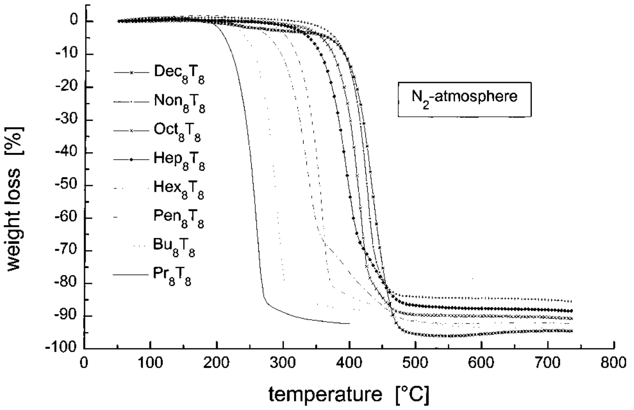


Figure 4. TGA-traces of **3**−**10** under N_2 atmosphere.

From a materials science oriented point of view the series of octaalkylsilsesquioxanes represents interesting model compounds with respect to the effect of a gradual increase of the organic fraction on the thermal stability of silsesquioxanes in general. Thermogravimetry (TGA) was employed to study thermal degradation of the series under N_2 atmosphere (Figure 4) as well as under air (Figure 5).

Clearly, under nitrogen atmosphere, with increasing alkyl chain length, the onset of the weight loss was found to shift to higher temperatures (166 °C for **3**, 355 °C for **10**). The total weight loss of all R_8T_8 derivatives at 500 °C exceeded 80% and is thus larger than the organic fraction of the materials. We assume that this might be due to evaporation of the compounds under

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(27) Schneider, O. *Thermochim. Acta* **1988**, *134*, 269−74.

(28) Müller, P.; Mülhaupt, R., manuscript in preparation.

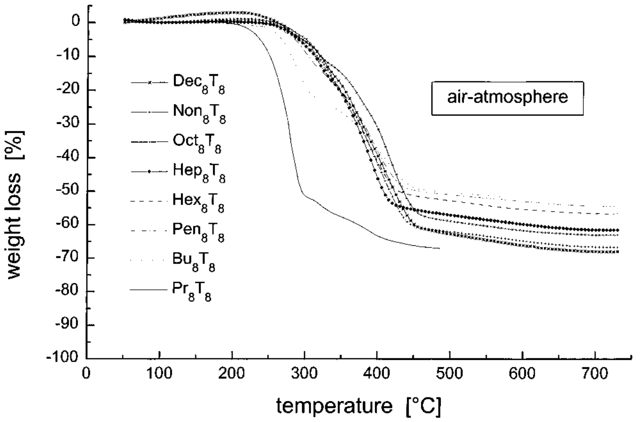

Figure 5. TGA traces of **3**−**10** under air.

nitrogen atmosphere; however, decomposition and rearrangement under formation of larger siloxane structures also plays a role, evident in the incomplete weight loss. Other authors mentioned sublimation of silsesquioxane cage molecules and cage fragments under nitrogen and argon atmosphere too.[26]

Under air the series also showed increasing weight loss with increasing alkyl chain length; however, for **5**−**10** the onset of the decomposition was found at lower temperatures than under nitrogen atmosphere. A slight, initial weight increase occurred above 100 °C, which we explain by oxidation and partial cross-linking of the material also found by Lichtenhan.[26] The total weight loss increased with increasing length of the alkyl chains. The total weight loss at 500 °C under air was generally lower than under nitrogen atmosphere, which is in agreement with the formation of a cross-linked network structure.

In summary, these data permit the tentative conclusion that under air a continuous decrease of the fraction of organic units under simultaneous cross-linking of the Si−O−Si scaffold occurred. During this cross-linking procedure a small fraction of organic substituents is trapped in the network and leads to lower weight loss than calculated for complete split-off of the alkyl groups. Also, the incorporation of oxygen in the course of the cross-linking reaction with siloxanes increased the residual weight. The simultaneous occurrence of the split-off of alkyl chains and oxidation processes under air leading to a silicate network is in agreement with data known from the curing of methylsilicone resins.[26,27]

Conclusion

H_8T_8 was prepared in a slightly simplified procedure according to the method of Agaskar. The homologous series of octaalkyl-substituted octasilsesquioxanes was prepared by hydrosilation with H_8T_8 in good yields. The compounds were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, elemental analysis, and mass and IR spectroscopy. Investigation of the melting points of the homologous series showed high melting points for compounds with short alkyl chains and relatively low melting points with odd−even effect for alkyl chains longer than four methylene units. Unexpectedly, ethyl-T_8 could be sublimated even under ambient conditions. It has furthermore been demonstrated that the materials are useful model compounds to study thermal stability and cross-linking of silsesquioxanes in dependence of the organic fraction. Unexpectedly, the total weight loss for all compounds was lower under air than under nitrogen, leading to the tentative conclusion that concurrent with the elimination of the alkyl chains a network structure is formed, which incorporates a fraction of the alkyl chains. This conclusion may have general implications for the thermostability of silsesquioxane-based materials.

Acknowledgment. C.B. and A.T. acknowledge financial support by the Graduiertenkolleg of the SFB 60. H.F. gratefully acknowledges support from the "Fonds der Chemischen Industrie" as well as the DFG.

CM970090F