Synthesis of novel starburst and dendritic polyhedral oligosilsesquioxanes

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The hydrosilylative reaction utilizing octakis(dimethylsiloxy)silsesquioxane and silsesquioxane disilanols bearing alkenylsilyl moieties produces a series of starburst-type giant silsesquioxanes and a second-generation dendritic molecule as well as a boron-containing one.

The synthesis of dendritic or starburst-type macromolecules,[1] including siloxane polymers,[2] is currently under extensive investigation because of their versatile potential utility. Especially, recent successes in the recovery of dendrimer-enlarged catalysts by the use of nano- or ultra-filtration techniques have boosted up expectations for industrial applications in the near future.[3] On the other hand, incompletely condensed silsesquioxanes and metal-containing silsesquioxanes have attracted much attention from the viewpoint of well-defined soluble model compounds of transition metal-containing siliceous heterogeneous catalysts.[4] One can expect the preparation of supports for the enlarged homogeneous catalysts with thermal and/or chemical tolerance by the arrangement of silsesquioxane silanols around the core. Note that cubic silsesquioxanes or spherosilicates have often been utilized as cores of starburst-type macromolecules.[5]

Here we report the synthesis of novel starburst-type and dendritic giant molecules with silsesquioxanes as peripheral building blocks based on a polyhedral spherosilicate core by a divergent synthetic method.

Octakis(dimethylsiloxy)silsesquioxane ($(\mathrm{HSi(CH_3)_2})_8$–$\mathrm{Si_8O_{12}}$, **1**) was allowed to react with ten equivalents of a silsesquioxane disilanol with a dimethylvinylsilyl group (**2**) in toluene solution in the presence of the Pt catalyst at room temperature for 24 h. Separation of lower molecular weight, unreacted **2** from the reaction mixture by preparative HPLC afforded a solution containing a starburst-type silsesquioxane (**3**) in 83% yield (Scheme 1).† The GPC analysis of the products shows very narrow molecular weight distribution (M_w = 4808, M_n = 4427, $M_\mathrm{w}/M_\mathrm{n}$ = 1.09) based on a polystyrene standard, however any attempts at MALDI-TOF mass spectroscopic analysis have not been successful. Note that even at such low polydispersity dendritic purity cannot be completely assured, since the ability to effect chromatographic separation of molecules with different degrees of condensation is often insufficient.[6] The GPC-derived molecular weight is, however, far below that expected (8695.5), while the ^{1}H NMR spectrum indicates the absence of defects (see below). Such discrepancy in GPC analyses using polystyrene standards has often been reported for dendritic polysiloxanes or polyethers of the 3rd to 5th or more generation,[7,8] and can be rationalized if the differences in hydrodynamic behaviour of the branched, more compact globular starburst macromolecules in comparison to the linear polystyrene standard are considered.[8a] The NMR spectra of **3** are very simple, reflecting the high symmetry of the molecule. Both ^{1}H and ^{13}C NMR spectra show that the spherosilicate core and peripheral silsesquioxanes are connected mainly by linear –$\mathrm{SiMe_2}$–$\mathrm{CH_2}$–$\mathrm{CH_2}$–$\mathrm{SiMe_2}$– linkages, together with a trace amount of regioisomeric branched connections.

A starburst-type silsesquioxane with sixteen Si–H groups (**4**) was synthesized in 70% yield by the reaction of silanol-terminated silsesquioxane **3** with 21 equivalents of chlorodimethylsilane in the presence of excess triethylamine in a benzene solution at room temperature. The ^{1}H NMR resonances for the 16 silanol groups completely disappeared, and those of 16 Si–H groups emerged.

The introduction of heteroatoms into the present starburst molecules offers interesting possibilities as enlarged homogeneous catalysts, with their local structure very close to that of zeolites or silica-supported catalysts. The reaction of a silsesquioxane **3** with 9 equivalents of dichlorophenylborane in the presence of excess triethylamine produced a boron-containing silsesquioxane **5** in 53% yield.

Further hydrosilylative reaction of **4** with silsesquioxanes bearing alkenylsilyl groups is expected to produce a second-generation dendritic giant molecule. The reaction of **4** with 20 equivalents of **2** in the presence of the Pt catalyst for 72 h successfully yields the expected polymeric product **6** with a yield of 63% (Fig. 1). Again ^{1}H, ^{13}C and ^{29}Si NMR analyses show a simple pattern irrespective of the large molecular weight of **6**, indicating its high symmetry. A PDI of 1.20 (M_w = 11 993, M_n = 9963) was indicated by GPC analysis of **6**, and is slightly larger than in the case of **3**. This implies the possibility of the presence of incompletely condensed species as well as species with regioisomeric connections, although there is no sign of residual silylhydrido groups in the NMR spectra.

In conclusion, starburst-type and the 2nd generation dendritic silsesquioxanes were synthesized from octakis(dimethylsiloxy)silsesquioxane and a silsesquioxane disilanol **2**. As far as we know, this provides the first example of a discrete starburst molecule in which both the core and branched moieties are composed of polyhedral oligosilsesquioxanes. The 2nd generation dendrimer **6** is considered to be large enough for separation by the nanofiltration technique[3] and is expected to be a material for recyclable "homogeneous" catalyst supports.

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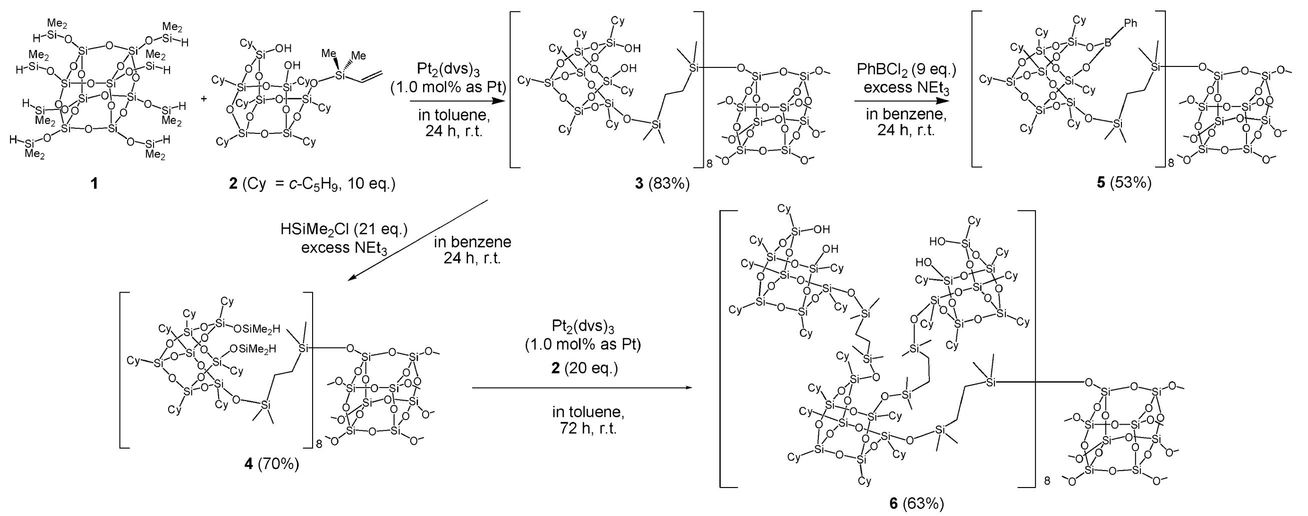

Scheme 1 Preparation of starburst and dendritic silsesquioxanes. The idealized structures of **3–6** are demonstrated.

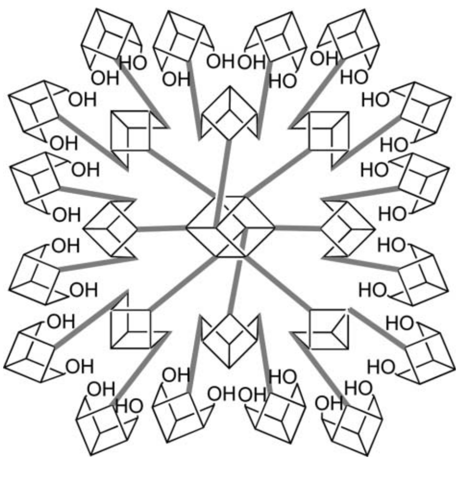

Fig. 1 Schematic drawing of the idealized structure of **6**.

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Notes and references

† Yields and assignments of **3–6** are based on the idealized structures.

Preparation of $Si_8O_{12}\{OSiMe_2(CH_2)_2SiMe_2[(c\text{-}C_5H_9)_7Si_7O_{10}(OH)_2]\}_8$ (**3**). Octakis(dimethylsiloxy)silsesquioxane (**1**, 0.102 mg, 0.10 mmol) was reacted with ten equivalents of **2** (0.959 mg, 1.0 mmol) in the presence of a $Pt_2(dvs)_3$ catalyst (1.0 mol% as Pt based on the number of connections) in toluene (10 cm^3) at room temperature for 24 h. Filtration through a Florisil column (*ca.* 100 mm thickness) after the reaction gave a clear solution. The product **3** was isolated by preparative HPLC. Yield 83%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 4.35 (br s, 16H, SiO*H*), 1.74–1.25 (br m, 448H, C*H*$_2$ of Cy), 0.99–0.91 (br m, 56H, C*H* of Cy), 0.49 (s, 32H, bridged C*H*$_2$), 0.14 (s, 48H, Si(C*H*$_3$)$_2$), 0.12 (s, 48H, Si(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ 27.61, 27.43, 27.34, 27.28, 27.25, 27.10, 27.03 (*C*H$_2$ of Cy), 23.74, 22.80, 22.43, 22.28, 22.23 (1 : 2 : 2 : 1 : 1 for *C*H of Cy), 8.97, 8.80 (bridged *C*H$_2$), −0.81, −1.18 (Si(*C*H$_3$)$_2$); $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M Cr(acac)$_3$, 25 °C) δ 13.30, 12.07 (*Si*Me$_2$), −56.72, −65.59, −66.35, −67.44 (2 : 2 : 1 : 1 : 2), −108.84 (Q$_4$–*Si*). Anal. calcd. for $C_{328}H_{648}O_{116}Si_{80}$ (8695.5): C, 45.31; H, 7.51. Found C, 45.12; H, 7.73.

$Si_8O_{12}\{OSiMe_2(CH_2)_2SiMe_2[(c\text{-}C_5H_9)_7Si_7O_{12}(SiMe_2H)_2]\}_8$ (**4**). Chlorodimethylsilane (55 mg, 0.58 mmol) in benzene (10 cm^3) was added to a stirred benzene solution (10 cm^3) of **3** (244 mg, 0.028 mmol) in the presence of excess triethylamine at room temperature for 24 h. After evaporation of the solvent the remaining solid was extracted with hexane (20 cm^3) to give a colorless filtrate. The reprecipitation of the filtrate afforded an off-white solid **4**. Yield 70%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 4.77–4.74 (br m, 16H, Si*H*(C*H*$_3$)$_2$), 1.74–1.46 (br m, 448H, C*H*$_2$ of Cy), 0.96–0.87 (br m, 56H, C*H* of Cy), 0.47 (s, 32H, bridged C*H*$_2$), 0.21 (d, ^3J = 2.6 Hz, 96H, SiH(C*H*$_3$)$_2$), 0.12, 0.11 (s, 96H, Si(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ 27.67, 27.61, 27.58, 27.29, 27.08, 26.97 (*C*H$_2$ of Cy), 24.53, 24.20, 23.63, 23.50, 22.42 (1 : 2 : 2 : 1 : 1 for *C*H of Cy), 9.06, 8.85 (bridged *C*H$_2$), 0.77 (SiH(*C*H$_3$)$_2$), −0.53, −1.16 (Si(*C*H$_3$)$_2$); $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M Cr(acac)$_3$, 25 °C) δ 13.20, 9.83 (*Si*Me$_2$), −5.39 (*Si*HMe$_2$), −66.18, −67.29, −67.95 (1 : 2 : 4), −108.87 (Q$_4$–*Si*). Anal. calcd. for $C_{360}H_{744}O_{116}Si_{96}$ (9626.1): C, 44.92; H, 7.79. Found C, 43.96; H, 7.80.

$Si_8O_{12}\{OSiMe_2(CH_2)_2SiMe_2[(c\text{-}C_5H_9)_7Si_7O_{12}BPh]\}_8$ (**5**). Dichlorophenylborane (35 mg, 0.22 mmol) in dry benzene (5 cm^3) was added to a solution of **3** (217 mg, 0.025 mmol) in dry benzene (5 cm^3) in the presence of excess triethylamine and stirred at room temperature for 24 h. After the solvent was evaporated, the resulting solid was extracted with hexane (15 cm^3). The product **5** was obtained by reprecipitation from the filtrate. Yield 53%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.81–7.26 (br m, 40H, *Ph*), 1.83–1.49 (br m, 448H, C*H*$_2$ of Cy (c-C_5H_9)), 1.26–0.86 (br m, 56H, C*H* of Cy), 0.24 (m, 32H, bridged *C*H$_2$), −0.02, −0.20 (s, 96H, Si(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ 135.58, 131.03, 127.37 (*Ph*), 27.54, 27.47, 27.33, 27.25, 27.14, 27.10, 27.03, 26.98, 26.95 (*C*H$_2$ of Cy), 23.93, 23.03, 22.84, 22.37, 22.05 (1 : 2 : 2 : 1 : 1 for *C*H of Cy), 8.76, 8.56 (bridged *C*H$_2$), −1.01, −1.21 (Si(*C*H$_3$)$_2$); $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M Cr(acac)$_3$, 25 °C) δ 13.08, 10.10 (*Si*Me$_2$), −63.67, −64.88, −66.97, −67.76 (1 : 1 : 1 : 4), −108.94 (Q$_4$–*Si*). Satisfactory elementary analysis was hampered by the formation of a carbidic species during the combustion.

The second generation dendrimer (**6**). A starburst silsesquioxane with sixteen silylhydride groups (**4**, 0.804 mg, 0.083 mmol) was reacted with 20 equivalents of **2** (1.60 mg, 1.7 mmol) in the presence of a $Pt_2(dvs)_3$ catalyst (1.0 mol% as Pt based on the number of connections) in toluene (10 cm^3) at room temperature for 72 h. The product **6** was isolated by preparative HPLC. Yield 63%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 4.23 (br s, 32H, SiO*H*), 1.75–1.48 (br m, 1344 H, C*H*$_2$ of Cy), 1.00–0.85 (br m, 168 H, C*H* of Cy), 0.55–0.45 (br m, 96 H, bridged C*H*$_2$), 0.15 (s, 144 H, Si(C*H*$_3$)$_2$), 0.12 (s, 144 H, Si(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C) δ 27.76–26.96 (*C*H$_2$ of Cy), 23.79, 22.88, 22.50, 22.36, 22.30 (1 : 2 : 2 : 1 : 1 for *C*H of Cy), 9.56, 9.40, 8.98 (bridged *C*H$_2$), −0.20. −0.40, −0.76, −1.11 (Si(*C*H$_3$)$_2$); $^{29}Si\{^1H\}$ NMR (76 MHz, $CDCl_3$, 0.02 M Cr(acac)$_3$, 25 °C) δ 13.12, 12.28, 9.54 (*Si*Me$_2$), −56.39, −65.38, −66.12, −67.18, −67.65 (*Si* in silsesquioxane cages), −108.42 (Q_4–*Si*). Satisfactory elementary analysis was hampered by the formation of a carbidic species during the combustion.

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