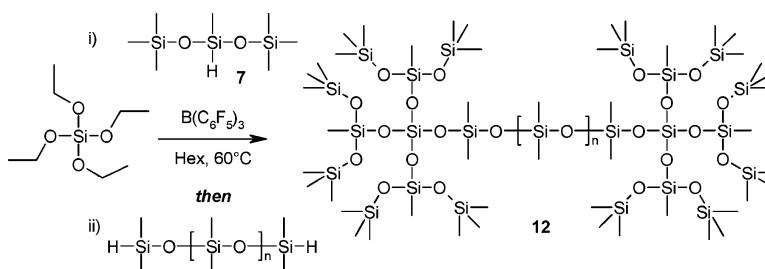


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Rapid Assembly of Complex 3D Siloxane Architectures

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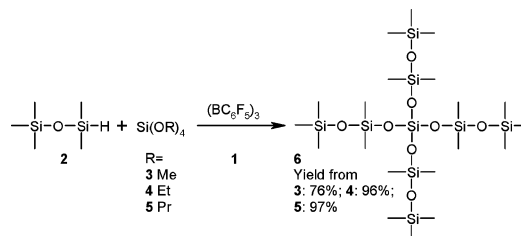
Constructing complex molecular assemblies with a high degree of precision has become a paradigm in modern macromolecular science. Advances in living polymerization (both ionic¹ and radical²) and the ongoing development of site specific catalysis to control polyolefin molecular architectures,³ for example, provide the synthetic chemist the ability to control MW, stereochemistry, copolymer distribution, and 3D architecture. An important consequence of this reaction control is production of more explicit structures with narrower property ranges and higher intrinsic value. Synthetic control has been achieved with condensation polymers too, notably through elegant synthesis of dendrimers using esters, amides, acetals, etc.⁴ However, the ability to control silicone architectures have been noticeably absent from these developments.

The reactivity of silicones toward strong electrophiles and nucleophiles, as well as their ability to undergo redistribution (re/depolymerization) reactions under both acidic and basic conditions considerably narrows the options available to the experimentalist attempting to make explicit 3D structures. Previous efforts have shown the ability to develop limited control over backbone stereochemistry,⁵ controlled copolymer synthesis using ring-opening polymerization of mixed cyclic silicone oligomers,⁶ and achieved the Herculean task of assembling a silicone dendrimer.^{7,8} However, these routes are not generic and, because of the intervention of acidic or basic conditions in the processes, are of limited practical application.

As with other polymers, it is desirable by efficient processes to make silicones with well defined architectures that have interesting properties. For example, 3D siloxane macrostructures, such as MQ resins,⁹ are condensation polymers of particular interest because of their ability to structure silicone interfaces.^{10,11} These are currently made by traditional condensation chemistry, which typically gives a broad distribution of polymer structures and, therefore, of properties. We have thus explored alternate strategies to prepare complex, highly branched silicone structures.

Tris(pentafluorophenyl)borane **1** is a strong Lewis acid catalyst that has been used in a number of organic and polymerization reactions.¹² This reagent has been found to strongly activate silicon–hydrogen bonds, facilitating a number of reactions such as the silylation of alcohols¹³ and hydrosilylation of carbonyls¹⁴ and thiocarbonyls.¹⁵ More recently, this compound has been found to catalyze the condensation of hydrosilanes with alkoxy-silanes to form new siloxane bonds $\text{Si}^1\text{H} + \text{Si}^2\text{OR} \rightarrow \text{Si}^1\text{OSi}^2 + \text{RH}$.¹⁶ Chojnowski has proposed that the reaction occurs after initial formation of borohydride and oxonium intermediates: a competing decomposition reaction of these intermediates leads to metathesis $\text{Si}^1\text{H} + \text{Si}^2\text{OR} \rightarrow \text{Si}^2\text{H} + \text{Si}^1\text{OR}$.¹⁶ Careful selection of starting materials allows for the exclusive formation of a new siloxane bond with the generation of the corresponding alkane. This reaction has been used to prepare siloxane polymers in both organic solution and aqueous emulsions.^{17,18} This new synthetic method permits the formation of polydisperse linear silicone polymers and inexplicit resins.

Scheme 1. Effect of Steric Environment on Yield in Synthesis of **6**



We report that, by manipulating the local steric environment at both alkoxy- and hydrosilane and controlling reaction conditions, it is possible to rapidly assemble complex three-dimensional silicone assemblies in near quantitative yields under mild conditions; reactions can be performed in open, nondried flasks. The use of low molecular weight starting materials allows for the easy removal of excess reagent in vacuo, and catalyst removal can be achieved simply by stirring with neutral alumina followed by filtration. ²⁹Si NMR showed clear chemical shift differences between M, D, T, and Q units, permitting determination of both purity and structure. While competing metathesis reactions have been reported, they were not observed in our syntheses, suggesting they can be suppressed by judicious choice of reagents and reaction conditions. These observations thus allow us to begin to articulate synthetic rules that can be applied to ensure the assembly process is governed by condensation alone.

In the reaction of pentamethyldisiloxane **2** with $\text{Si}(\text{OR})_4$ (R = Me **3**, Et **4**, Pr **5**), the rate of reaction giving star siloxane **6** was found to inversely correlate with steric encumbrance at silicon (Scheme 1). This had a corresponding effect on yield, most clearly seen in the transition from **3** to **4**. The more controlled, milder reaction achieved through the use of bulkier alkoxy-silane **5** allowed the formation of the desired product in 97% isolated yield with no visible impurities, even in the crude material.

The steric environment of the reacting hydrosilane is also a strong mediator in the reaction rate and selectivity. For example, 1,1,1,3,3,5,5,5-heptamethyltrisiloxane **7** failed to react with **4** at room temperature. However, the use of less hindered **3** with similar catalyst loadings allowed the synthesis of branched siloxane **8** in 95% isolated yield, again with no visible impurities (Figure 1). To better establish the stability and purity of these compounds, a sample of **6** was chromatographed on silica. This resulted in a 96% recovery of material with no change or degradation according to ²⁹Si NMR.

Manipulation of temperature permits the exploitation of subtle effects of steric bulk on rate. The less hindered silane **3** reacted cleanly with **7** to give **8** in excellent yield (Scheme 2). By contrast, the reaction of **7** with **4** did not take place at room temperature, but proceeded cleanly at 50 °C. Under these conditions, however, only three of the ethoxy groups reacted, leading to the branched monoethoxy compound **9** (Scheme 3A). Even in the presence of excess **7**, no evidence of **8** was observed in the silicon NMR, and **9** was isolated in 98% yield. By contrast, less sterically hindered

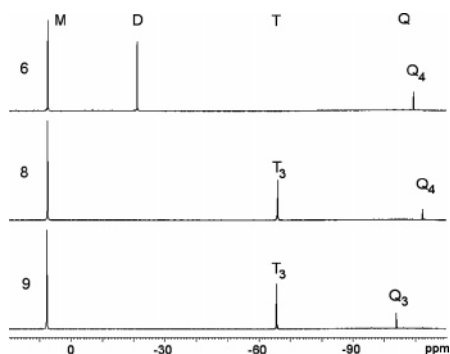
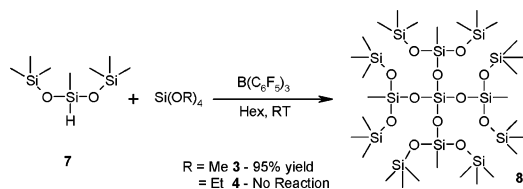
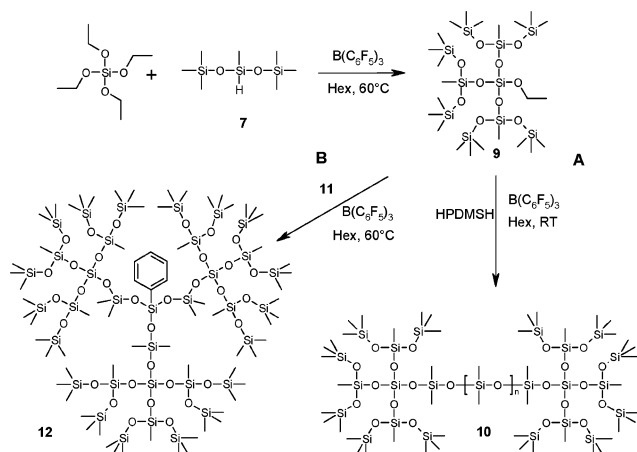


Figure 1. Stacked ^{29}Si NMR plot showing purity and diagnostic peak distribution for compounds **6**, **8**, and **9**.

Scheme 2. Assembly of Branched Siloxane **8**



Scheme 3. Synthesis of Monoethoxy Branched Siloxane **9** and Branched Terminal Poly(dimethyl)siloxane **10**



terminal Me_2SiH groups reacted efficiently: **9** was grafted to hydrosilane-terminated poly(dimethyl)siloxanes (PDMS) to create branch terminated silicone **10**.

The degree of control over the synthesis of structures such as **10** is necessarily limited by the polydispersity of the starting hydride functional siloxane. To more fully demonstrate the potential of this reaction to construct a well-defined higher molecular weight siloxane, **9** was reacted in hexanes with phenyltris(hydridodimethylsilyloxy)silane **11** in the presence of **1** at 60°C to form large branched siloxane **12** in 94% yield (Scheme 3B). This synthesis of an atomically precise 2600 MW symmetrical branched siloxane was achieved in two steps from commonly available starting materials in 92% overall yield. Currently, there is no other technology available to facilitate the synthesis of such complex silicone structures in a comparable manner.

These condensation reactions typically have an induction time, during which, according to Chojnowski,¹⁶ activation of the hydrosilane occurs. However, once reaction is initiated, there is generally an exotherm of sufficient severity that low molecular weight reagents are readily volatilized. This is believed to be the source of the lower yield, for example, of **6** from **3**. While it is

possible to mitigate this effect by efficient cooling, it is more practical to design reagents of appropriate steric bulk such that efficient, yet selective, reaction can occur. As an example, the formation of **9** (Scheme 3) occurs cleanly under the conditions described. However, it was not possible to stop the reaction at either intermediate stage $((\text{R}_2\text{R}'\text{SiO})_n\text{Si}(\text{OR}'')_{4-n}, n = 1, 2)$. Nor could the methoxy analogue of **9** be prepared cleanly from TMOS—that reaction instead produces **8**.

The effect of hydrosilane sterics is more pronounced. The reactivity of $\text{R}_3\text{SiOMe}_2\text{SiH}$ is significantly higher than $(\text{R}_3\text{-SiO})_2\text{MeSiH}$, permitting the selective formation of **9**, but also its facile reaction to give **12**.

The exquisite control exhibited by these systems relies on careful choice of thermal reaction conditions and appropriate steric bulk on both alkoxy silane and hydrosilane reagents. The reactions with more reactive groups can be rather energetic (*note: methane or other alkanes are released, which could constitute a fire/explosion hazard*) and, if not properly controlled, lead to reduced yield as a consequence of volatilized starting materials. However, these reactions indicate that by appropriately balancing reagents and reaction conditions direct condensation can be favored over metathesis reactions leading to complex 3D branched silicones selectively and in high yield. This process also opens new routes to controlled silicon-based materials, including MQ and polyhedral oligomeric silsesquioxane resins (T_n , POSS). In addition to synthesizing these nonfunctional materials and developing empirical rules for synthetic control, we will exploit the functional group tolerance of $\text{B}(\text{C}_6\text{F}_5)_3$ to prepare functional silicon-based structures with the same high degree of specificity.

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Supporting Information Available: Experimental procedures and characterization of new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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