Short survey

# Dendritic polysilanes

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## Abstract

Dendritic polysilanes consist of silicon chains that emanate from a silicon core and branch one or more times. First- and second-generation dendrimers have been prepared that possess longest chains up to 13 silicon atoms. Ultraviolet absorption occurs at a wavelength similar to that of straight polysilane chains of similar length. The intensity of electronic absorption, however, is enhanced on a molar basis compared with linear structures. The dendrimers are robust and often crystalline. Numerous crystal structures have been solved, providing unique information about polysilane conformations.
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## 1. Introduction

The important conducting, thermochromic, photonic, and nonlinear optical properties of polysilanes, which result from σ-conjugation along the silicon chain, may be vitiated by chemical instability, as the Si–Si bond is sensitive to both electrophiles and nucleophiles [1]. In order to circumvent this problem, a number of groups have examined alternative architectures to linear and cyclic polysilanes, including branched [2], hyperbranched/polysilyne [3], and dendritic variations. The entire lifetime of the study of dendritic polysilanes lasted only a few years, from the initial [4] to the most recent [5] report. Although the story is by no means complete, this review examines the rationale for the initial burst of activity, the results of the efforts of several groups, and the reasons for the decline in the activity.

## 2. Rationale

Dendritic molecules begin with a core atom or group, from which at least three wings emanate (if there were only two wings, the result would be chains or rings rather than dendrimers). The first atom on each wing then either serves as a branch point or leads linearly to another atom or group that serves as a branch point, which is attached to two or more new chains. When these new chains are linear, the molecule is classified as a first-generation (G1) dendrimer. When the new chains all lead to a second branch point, the molecule is classified as a second-generation (G2) dendrimer. Again, there can be any number of atoms between the first and second branch points. Further, analogous branching can lead to G3, G4, etc., dendrimers.

The advantages of dendrimers have been well-known for many years [6]. The specific advantages in the case of polysilanes are at least fourfold. (1) The process of multiple branching leads to a molecule with crowding around the periphery. The groups attached to silicon, such as methyl, are forced together and seek the surface of the molecule for steric relief. As a result, the surface becomes methyl rich, and the sensitive Si–Si bonds are sequestered and protected within. Attacking electrophiles or nucleophiles, prohibited from access to the interior of the dendrimer, encounter a relatively unreactive sphere of the methyl groups. Because the Si–Si bonds still can respond to light, heat, or unpaired electrons, it is likely that polysilane dendrimers will retain their favorable photonic, optical, thermal, and conductive properties. (2) The presence of multiple branching conveys redundancy to the structure. Thus,

molecular and bulk properties can survive even if one or more Si–Si bonds are cleaved. The redundancy also will enhance properties that are dependent additively on the presence of certain polysilyl pathways. (3) Solubility depends largely on the properties of the surface of the molecule, where interactions with solvent occur. Because the surface of these dendrimers consists largely of methyl groups, the molecules will tend to have very favorable solubility properties with organic solvents, despite their large size. The methods of solution NMR, therefore, should be readily applicable. (4) A dendrimer has an exact molecular weight, in contrast to the mixtures that typify linear polymers. One can expect to be able to isolate and characterize a molecule that has even a polymer-like molecular weight. Such molecules are likely to crystallize and hence be available for X-ray crystallographic analysis.

The simplest dendritic polysilanes possess four structural characteristics. (1) The core silicon atom may be attached to either three or four silicon atoms that begin the dendritic wings W. For tridendrons ($RSiW_3$) we assign the designation $c = 3$, and for tetradendrons ($SiW_4$) $c = 4$ (the group R is a nonsilyl substituent such as methyl). (2) The core may have any number of silicon atom spacers between it and the first branch point. When there are no spacer atoms, $s = 0$; when there is one spacer atom, $s = 1$, and so on. (3) The branching atom (Si*) may lead on to either two (–Si*$RSi_2$) or three (–Si*$Si_3$) additional silicon atoms. For twofold branching $b = 2$, and for threefold branching $b = 3$. (4) If there is only one branch point on each wing or dendron, the molecule is first generation (G1, $g = 1$). If a second branch point follows, the molecule is second generation (G2, $g = 2$), and so on.

Scheme 1 contains the four G1 dendrimers with no spacers between the core and the branch point ($s = 0$). Methyl groups are present on all silicon atoms to fill out
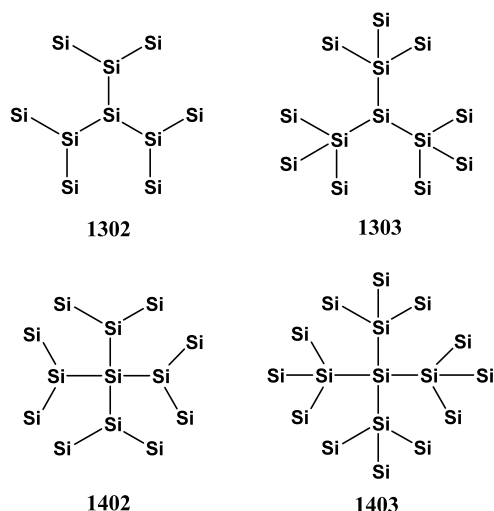
the valency to four but have been omitted to clarify the diagrams. Because the core can be threefold or fourfold ($c = 3$ or 4) and the branch point can be twofold or threefold ($b = 2$ or 3), there are four possible such molecules in the first generation ($g = 1$). In terms of these four defining quantities (*gcsb*), the molecules in Scheme 1 may be referred to as **1302**, **1303**, **1402**, and **1403**. Scheme 2 contains the four G1 dendrimers with a single-spacer silicon between the core and the branching point ($s = 1$). Again there are four possibilities, referred to as **1312**, **1313**, **1412**, and **1413**, and the methyl groups have been omitted. Scheme 3 illustrates the G2 dendrimer with a threefold core, one spacer, and twofold branching at both the first and second branching points, referred to as **2312**, again with the methyls omitted.

This numbering system applies only to entirely regular dendrimers. There are many structural deviations from regularity. The number of spacers between the core and the first branch point may not equal the number of spacers between the first and second branch points. The first branch point may be twofold, but the second branch point threefold. Not all substituents may be methyl.

For regular dendritic polysilanes that are fully defined by the four quantities *gcsb*, a number of numerical properties may be calculated directly [8]. The number $L$ of silicon atoms in the largest chain is given by Eq. (1) (the quantity is thus independent of the core and branching multiplicities).

$$L = 3 + 2g + 2gs \qquad (1)$$

The number $P$ of silicon atoms on the periphery is given by Eq. (2) and is independent of the number of spacer
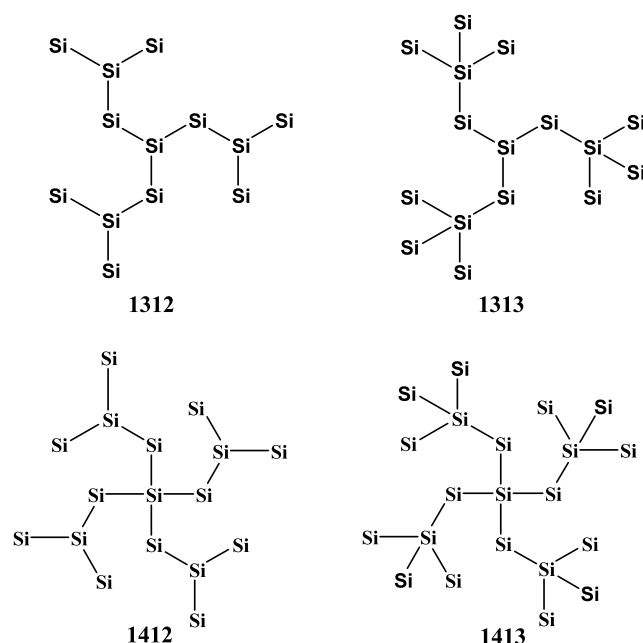


Scheme 1.



Scheme 2.

**2312**
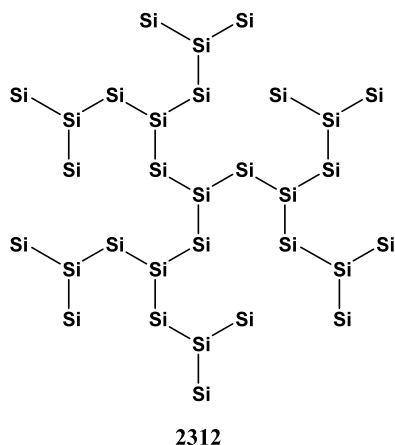
Scheme 3.

atoms.

$$P = cb^g \qquad (2)$$

The total number $T$ of silicon atoms present in the molecule is given by Eq. (3), in which the sum is necessary to recognize the various generations.

$$T = 1 + c\left[b^g + (1+s)\sum_{n=1}^{g} b^{(n-1)}\right] \qquad (3)$$

The molecular weight $M$ is readily calculated from from Eq. (4). All the equations are quite simple for first-generation dendrimers ($g = 1$).

$$M = 58T + 30 \qquad (4)$$

## 3. Synthetic approaches

Essentially, all the dendrimers have been assembled by variations on the halogen–metal exchange reaction. A metallosilane (Si–M) is allowed to react with a molecule in which a silicon atom is attached to a good nucleofugic-leaving group (Si–X) to produce the Si–Si bond and M–X as a byproduct. The set of molecules in Scheme 1 with only methyl substituents thus may be approached according to the methods of Scheme 4.

In the absence of spacers between the core and the branch point ($s = 0$), however, steric hindrance for the most part prohibited these reactions [7,8]. The only successful synthesis from these reactions was that of the
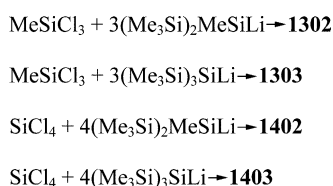
least hindered molecule **1302**, with a threefold core and a twofold branch point [8]. The other three dendrimers in Scheme 1 remain unknown.
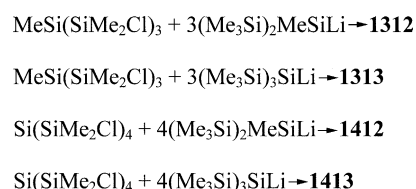
The addition of a spacer $SiMe_2$ ($s = 1$) should reduce steric repulsions between the groups on the core and branch points. Scheme 5 provides the methods for preparing the molecules in Scheme 2. These procedures were successful in all cases but the most sterically hindered (**1413**), which remains unknown [4,7–10].

Sekiguchi et al. [11] developed a more flexible synthesis, which could be extended to the second generation. Instead of using only methyl groups in the reactions of Schemes 4 and 5, they placed phenyl groups strategically at the termini of their building blocks. The phenyls could be converted to a nucleofuge and could serve to generate new polysilyl chains. This procedure required development of innovative synthetic methods for preparing complex silyllithium compounds [12]. Their synthesis of the G2 dendrimer **2312** (Scheme 3) is laid out in Scheme 6 (TfO = triflate). This molecule remains the only example of a regular second-generation dendritic polysilane. It contains 31 silicon atoms, has a nominal molecular weight of 1813, and possesses a longest polysilane chain with 11 silicon atoms.
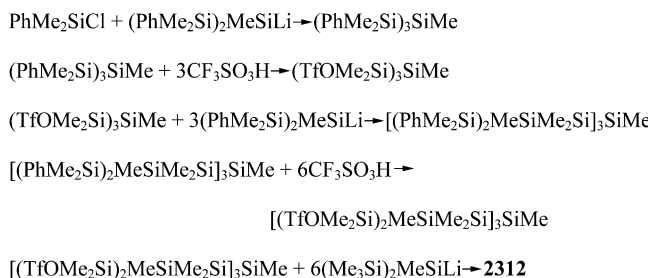
Further examples of dendritic polysilanes were obtained as low yield byproducts of these and related reactions, including the molecules in Scheme 7 [8,10,13]. Molecules **1** and **2** are related to **1312**, in which the core methyl has been replaced, respectively, by hydrido (also called **1312-H**) or by dimethylsilyl (**1312-SiMe₂H**). Molecule **3** is a double-cored dendrimer in which each core leads without a spacer to a twofold branch point.

All the synthetic methods to produce these dendritic polysilanes are classified as divergent. The syntheses begin with the core silicon and methodically add groups to incorporate the various spacers, branch points, and terminal groups. The largest dendritic silane prepared to date, however, was synthesized using a convergent methodology [13].

This molecule, **4**, and its synthesis are illustrated in Scheme 8. Molecule **4** is formally second generation with 31-silicon atoms total ($T$), a nominal molecular weight of 1833, and 13 silicon atoms in the longest chain. It has a threefold core. Each wing begins with a single spacer silicon that leads to the first branch point. Branching is irregular, as this threefold branch silicon leads to two terminal trimethylsilyl groups and to one new chain.

$MeSiCl_3 + 3(Me_3Si)_2MeSiLi \rightarrow \mathbf{1302}$

$MeSiCl_3 + 3(Me_3Si)_3SiLi \rightarrow \mathbf{1303}$

$SiCl_4 + 4(Me_3Si)_2MeSiLi \rightarrow \mathbf{1402}$

$SiCl_4 + 4(Me_3Si)_3SiLi \rightarrow \mathbf{1403}$

Scheme 4.

$MeSi(SiMe_2Cl)_3 + 3(Me_3Si)_2MeSiLi \rightarrow \mathbf{1312}$

$MeSi(SiMe_2Cl)_3 + 3(Me_3Si)_3SiLi \rightarrow \mathbf{1313}$

$Si(SiMe_2Cl)_4 + 4(Me_3Si)_2MeSiLi \rightarrow \mathbf{1412}$

$Si(SiMe_2Cl)_4 + 4(Me_3Si)_3SiLi \rightarrow \mathbf{1413}$

Scheme 5.

$PhMe_2SiCl + (PhMe_2Si)_2MeSiLi \rightarrow (PhMe_2Si)_3SiMe$

$(PhMe_2Si)_3SiMe + 3CF_3SO_3H \rightarrow (TfOMe_2Si)_3SiMe$

$(TfOMe_2Si)_3SiMe + 3(PhMe_2Si)_2MeSiLi \rightarrow [(PhMe_2Si)_2MeSiMe_2Si]_3SiMe$

$[(PhMe_2Si)_2MeSiMe_2Si]_3SiMe + 6CF_3SO_3H \rightarrow$

$$[(TfOMe_2Si)_2MeSiMe_2Si]_3SiMe$$

$[(TfOMe_2Si)_2MeSiMe_2Si]_3SiMe + 6(Me_3Si)_2MeSiLi \rightarrow \textbf{2312}$

Scheme 6.



Scheme 7.

This new chain leads via two spacer silicons to the second branch point. This threefold branch silicon leads to three terminal trimethylsilyl groups. Molecule **4** is the largest pure polysilane isolated and characterized to date.

These dendrimers, generally, are available in multi-gram quantities. Even the largest dendrimer **4** was produced in yields of over 4 g. Efforts to move onto higher generations, however, have been thwarted by the dilemma of decreased yields in divergent syntheses and increased steric effects from surface crowding. Although improved syntheses may be developed, today the longest chain remains 13 silicon atoms and the highest generation G2.

## 4. Crystallography

Because these dendrimers, unlike synthetic polymers, have a precise molecular structure, most were able to be crystallized and characterized by X-ray crystallography, including **1302** [8], **1312** and its hexaphenyl analogue [14], **1313** [4,8,9], **2312** [11], **1** [8], **3** [13], and **4** [13]. When materials failed to crystallize, recourse was made to mass spectrometry, which was critical in demonstrating the formation of **1412** [8,10] and **2** [10]. NMR spectroscopy, of course, was important in the characterization of all the dendrimers in solution. The development of $^{29}Si–^{29}Si$ INADEQUATE was of particular use in studying the structures of **1302** [15] and **4** [16]. This method provides proof for the sequential connectivity of Si–Si bonds through analysis of double-quantum coherence and provides assignments of $^{29}Si$ resonances to specific silicon atoms.

Bond lengths and bond angles for the most part are unremarkable (torsional angles are discussed in a later section). All the silicon atoms are attached to four nonhydrogen atoms, except for the case of the core atom in **1**. The longer Si–Si bonds, however, generally relieve steric interactions. As a result, Si–Si bond lengths are close to the value of 2.340 Å for hexamethyldisilane [17] and bond angles are within 7° of tetrahedral. Bending force constants for the Si–Si–Si bond angle permit these relatively large excursions from tetrahedrality without introducing appreciable strain.

When four silicon atoms are attached to a silicon (this arrangement is called quaternary), steric effects are heightened because of the larger number of substituents in the general vicinity of the quaternary silicon. The only structures considered herein that contain quaternary silicons are molecules **1313** [4,8] and **4** [13]. In **1313**, strain around the crowded periphery is reduced by flattening of the molecule. The largest observed distortion is enlargement of the Si–Si–Si angle between the core, spacer, and branch silicons to the remarkable value of 130.4(1)°. Angle strain around the spacer atom then is alleviated by decreasing the Me–Si(spacer)–Me angle to 97.8(3)°. In the large dendrimer **4**, again strain in the periphery is reduced by flattening around the core. In this case, the average angle between the core, spacer, and branch silicons is 128.8°. In C–C–C structures, such an expanded angle would introduce prohibitive strain, but, in Si–Si–Si structures, the lower bending force constants permit overall reduction in steric strain by means of this deformation.

## 5. NMR spectroscopy

Most of these molecules contain only methyl hydrogens and carbons. As a result, the $^1H$ and $^{13}C$ spectra uninformatively contain only a few peaks, closely spaced at very low frequency. The $^{29}Si$ spectra, however, provide critical structural information, because there is a variety of silicon atoms in all the structures. Silicon atoms are considered to be primary, secondary, tertiary,
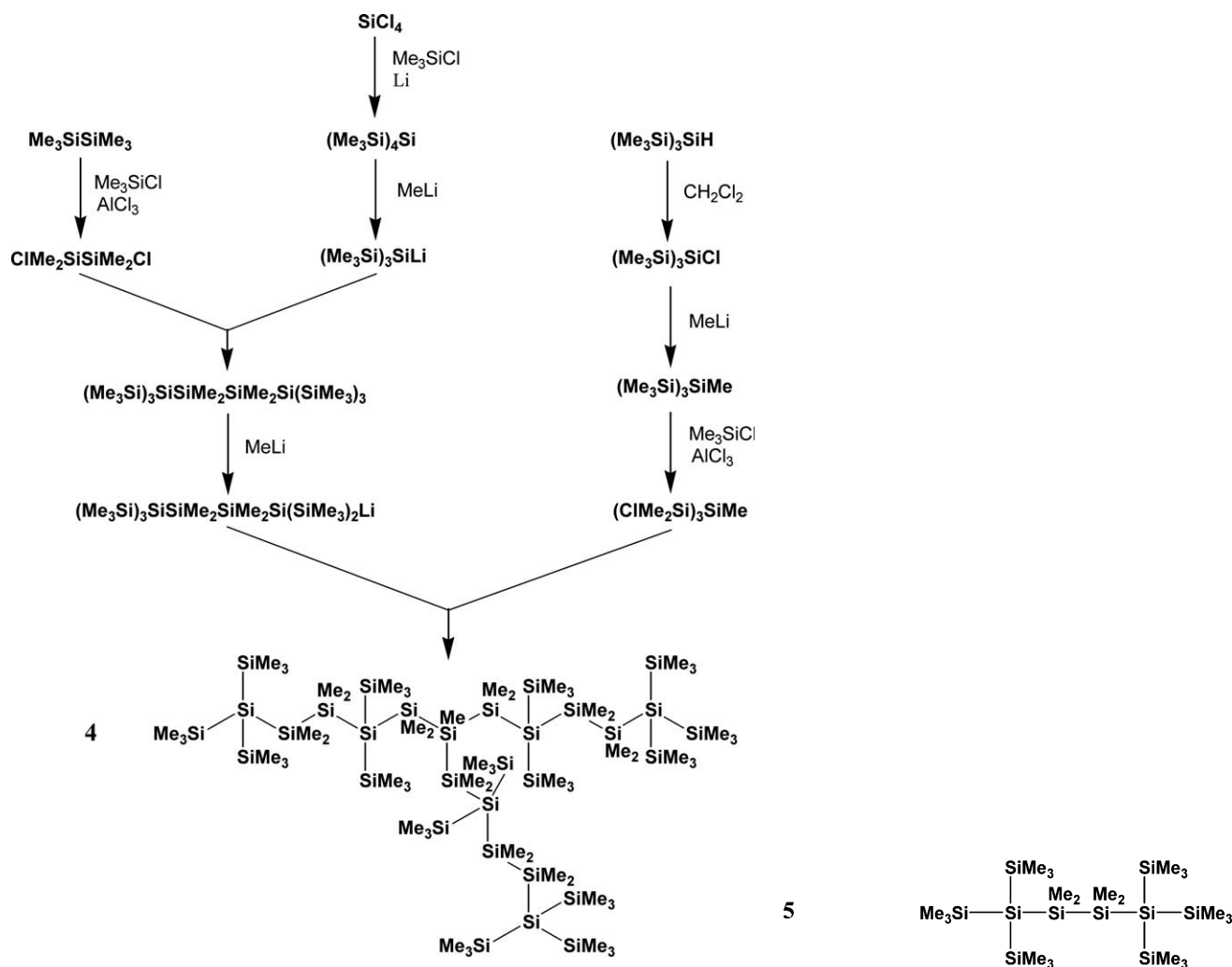
Scheme 8.

or quaternary according to whether they are attached to (are alpha to), respectively, one, two, three, or four silicon atoms (alternatively, are attached to three, two, one, or zero carbon or hydrogen atoms).

Table 1 displays the $^{29}$Si chemical shift data for molecules **1302**, **1312**, **1313**, **2312**, **1**, **3**, **4**, and a nondendritic but branched molecule (**5**) [8], arranged according to substitution patterns. The ranges are roughly $-9$ to $-11$ for primary silicons, $-25$ to $-30$ for secondary silicons, $-40$ to $-80$ for tertiary silicons, and $-112$ to $-128$ for quaternary silicons. These broad ranges depend on the number of beta silicons in addition to the number of alpha silicons. This relationship was not previously recognized in the literature. The quaternary silicons then comprise subgroups $Q^1$ with one beta silicon and a shift of about $-125$ and $Q^2$ with two beta silicons and a shift of about $-112$ (there is, however, only one datum for this latter category). The tertiary silicons comprise $T^1$ with a shift of about $-80$, $T^2$ with a shift of about $-75$, $T^3$ with a shift of about $-65$, and $T^6$ with a shift of about $-44$

(there currently are no data for $T^4$ or $T^5$). Thus, both Q and T silicons exhibit monotonic trends dictated by the number of beta silicons. The subgroups are remarkably consistent. The secondary silicons comprise $S^4$ with values of about $-29$ and $S^5$ with values of about $-26$. The S ranges are too small to be useful in drawing structural distinctions. The primary silicons comprise $P^2$ with values of about $-11$ and $P^3$ with values of about $-9$.

It should be noted that the values for the core and branch silicons in **3**, both of which are tertiary silicons, were not distinguished in the literature [13]. The authors had no basis at that point without carrying out Si–Si 2D INADEQUATE experiments. The empirical ranges quoted herein now provide a basis for their assignment, by counting the number of β silicons. There are two sets of chemical shifts reported for **1312** [14,15], differing consistently by 3–4 Hz. The empirical classification in Table 1 now provides for a preference between these two sets. The values of Sekiguchi and coworkers [14] are entirely consistent with other data and are included in

Table 1
Silicon-29 chemical shifts according to substitution patterns

| | |
|---|---|
| Quaternary | Mono-$\beta$ ($Q^1$) $-124$ [a], $-127.3$ [b], $-128$ [c] |
| | Di-$\beta$ ($Q^2$) $-112.5$ [d] |
| Tertiary | Mono-$\beta$ ($T^1$) $-80.1$ [e], $-80.7$ [f], $-80.4$ [g] |
| | Di-$\beta$ ($T^2$) $-76.3$ [h], $-74.8$ [i] |
| | Tri-$\beta$ ($T^3$) $-69.6$ [j], $-62.3$ [k], $-64.8$ [l], $-66.3$ [m], $-66.1$ [n] |
| | Hexa-$\beta$ ($T^6$) $-44.4$ [o], $-43.8$ [p] |
| Secondary | Tetra-$\beta$ ($S^4$) $-26.7$ [q], $-30.0$ [r], $-30.0$ [s], $-29.1$ [t], $-27.7$ [u], $-29.8$ [v] |
| | Penta-$\beta$ ($S^3$) $-26.7$ [w], $-25.5$ [x] |
| Primary | Di-$\beta$ ($P^2$) $-11.3$ [y], $-11.0$ [z], $-11.4$ [aa], $-10.3$ [bb], $-11.3$ [cc] |
| | Tri-$\beta$ ($P^3$) $-9.4$ [dd], $-9.1$ [ee], $-9.6$ [ff] |

[a] **1313**, branch, Ref. [8].
[b] **4**, branch atom 6, Ref. [13].
[c] **5**, branch, Ref. [8].
[d] **4**, branch atom 3, Ref. [13].
[e] **2312**, second branch, Ref. [11].
[f] **1**, branch, Ref. [13].
[g] **1312**, branch, Ref. [14].
[h] **1302**, branch, ref [8].
[i] **3**, branch, Ref. [13].
[j] **1313**, core, Ref. [8].
[k] **2312**, core, Ref. [11].
[l] **2312**, first branch, Ref. [11].
[m] **1312**, core, Ref. [14].
[n] **4**, core atom 1, Ref. [13].
[o] **1302**, core, Ref. [8].
[p] **3**, core, Ref. [13].
[q] **2312**, first spacer, Ref. [11].
[r] **2312**, second spacer, Ref. [11].
[s] **1312**, spacer, Ref. [14].
[t] **4**, spacer atom 4, Ref. [13].
[u] **4**, spacer atom 5, Ref. [13].
[v] **5**, spacer, Ref. [8].
[w] **1313**, spacer, Ref. [8].
[x] **4**, spacer atom 2, Ref. [13].
[y] **2312**, periphery, Ref. [11].
[z] **1302**, periphery, Ref. [8].
[aa] **1312**, periphery, Ref. [14].
[bb] **3**, periphery, Ref. [13].
[cc] **1**, periphery, Ref. [8].
[dd] **1313**, periphery, Ref. [8].
[ee] **4**, periphery atom 7, Ref. [13].

the table. The spectrum is reproduced in the literature in a 2D representation [15]. Translation of the scale in this reference by 3–4 Hz brings all the values into consonance. The reliability of the correlations indicated in Table 1 thus can pinpoint questionable chemical shifts down to 3–4 Hz.

Table 1 includes two values from the molecule **1** (**1312-H**), which carries hydrido instead of methyl on the core silicon, an exception to all other structures in the table. The chemical shifts for the core and spacer silicons of **1** were excluded, as they lack methyl, respectively, at the $\alpha$ and $\beta$ positions (replaced by hydrido). It would be expected that this structural alteration would influence the $^{29}$Si chemical shifts. Indeed, the core silicon resonates at $\delta$ $-104$, a value that falls into no recognizable

pattern. The spacer silicon, however, resonates at $\delta$ $-32.1$, a position that is quite appropriate for $S^4$, although on the high side (Table 1). The values for the branch and periphery silicons were included, as hydrido at the $\gamma$ or $\delta$ positions should have vanishingly small effects.

## 6. Electronic spectra

Interest in the electronic properties of polysilanes has driven much of the synthetic activity in this field. Unlike polymers composed of linked, saturated alkyl groups (polyalkenes such as polystyrene), which lack extensive electronic delocalization, and unlike polymers composed of linked double bonds (polyalkynes), which engage in $\pi$-delocalization, polymers composed of linked, saturated silyl groups are capable of exhibiting delocalization through their $\sigma$-bonds [1]. The subject has been examined theoretically up to pentasilanes [18]. $\sigma$-Delocalization results in absorption in the ultraviolet at an increasingly higher wavelength as the polysilane chain increases, reaching an asymptote at about $Si_{18}$, for which $\lambda_{max}$ is 296 nm [19]. Maximum delocalization, generally, is considered to occur when tetrasilane segments are in *anti* rather than *gauche* conformations [18]. Whereas linear polysilanes can exist in all-*anti* arrangements, dendritic polysilanes are prohibited structurally from that arrangement. Conformational considerations are examined in Section 7.

Table 2 summarizes the electronic absorption data for dendritic and analogous linear polysilanes. Despite the absence of all-*anti* conformations, the dendrimers closely parallel the linear polysilanes [20] in the position of electronic absorption ($\lambda_{max}$). For longest chains of 5, 7, 11, and 13 silicon atoms, the value of $\lambda_{max}$ moves monotonically to the red, respectively, 240, 266–272, 279, and 283 nm. The extinction coefficients, however, offer the most significant electronic enhancement of dendritic vis-à-vis linear polysilanes. On a per silicon basis, dendritic polysilanes exhibit more intense absorption than linear polysilanes by a factor of 2–10 (Table 2). It is likely that this enhancement results from the redundancy of pathways in the dendrimers. Whereas a

Table 2
Electronic absorption spectra

| | $\lambda_{max}$ (nm) | $\varepsilon$ $(10^{-5})$ | Longest Si chain | Source |
|---|---|---|---|---|
| **1302** | 240 | 0.25 | 5 | [8] |
| **1312** | 269 | 0.49 | 7 | [11] |
| **1313** | 272 | 3.4 | 7 | [4,8] |
| Linear $Si_7Me_{16}$ | 266 | 0.3 | 7 | [20] |
| **2312** | 279 | 0.96 | 11 | [11] |
| Linear $Si_{12}Me_{26}$ | 264, 285 | 0.43, 0.43 | 12 | [19] |
| **4** | 260, 283 | 1.80, 1.16 | 13 | [13] |

given linear polysilane contains only a single pathway (irrespective of conformation), the dendrimers offer several pathways with the same longest chain. The redundancy in **1302** and **1312** is 12, that in **1313** is 27, and that in **2312** is 48. Each of these pathways absorbs light to some extent, depending on its exact conformation (Section 7). The resulting enhanced absorption is the sum of all the components within the molecule.

Emission spectra of polysilanes have been studied by several authors [5,8,9,21]. The most thorough study of dendritic polysilanes has been that of Watanabe et al. [5]. Fluorescence spectra in general are quite weak at room temperature. The increase in fluorescence quantum yields and lifetimes with lower temperatures has been attributed to a decrease in nonradiative processes such as Si–Si cleavage [21]. In their study of the nondendritic (G0) molecule (Me₃SiMe₂Si)₃SiMe and of the dendrimers **1312** and **2312**, Watanabe et al. [5] found two bands in time-resolved emission spectra. The lower wavelength band increased in the order 340, 350, 380 nm for the three systems, and the higher wavelength band increased in the order 450, 460, 470 nm. The increase in wavelength is due to enhanced σ-conjugation, much as with the absorption spectra. The authors attributed the presence of two bands to the existence of two distinct emissive centers in the molecules. The lower wavelength band was caused by emission from the excited state from the linear Si–Si chains. The broader band at longer wavelength was caused by emission from excitation at the branch points (even the G0 system has a single branch point). Similar phenomena have been observed in branched, network, and ladder polysilanes [22].

## 7. Polysilane conformations

The conformations for butane fragments in hydrocarbons have normally been described in terms of *gauche* and *anti* arrangements (Scheme 9), in which the CH₃/CH₃ torsional angles are about 60° and 180°, respectively. Michl and coworkers [18] found that polysilanes have three rather than two conformational families: *gauche*, *ortho* (for orthogonal), and *anti*, also depicted in Scheme 9. Repulsive 1,4 interactions between substituents split the original *gauche* family with CH₃/CH₃ torsional angles close to 60° (their calculated value at the HF/6–31G* level was 65.4°) into two families. The authors retained the term *gauche* for the conformation with the smaller SiMe₃/SiMe₃ torsional angle (53.7° calculated for octamethyltetrasilane) and assigned the name *ortho* to the conformation with the larger, nearly orthogonal SiMe₃/SiMe₃ torsional angle (calculated 92.0°). They found that repulsive 1,3 interactions between substituents lowered the torsional angle for the *anti* conformation significantly (calculated 163.5°). The regime of three conformational families
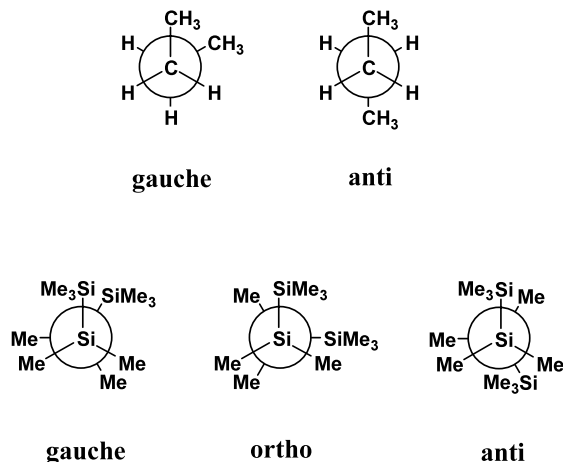


Scheme 9.

was suggested not only for polysilanes but also for highly methylated or halogenated hydrocarbons [18]. Experimental evidence was slower in coming, originally from vibrational experiments [23]. Extensive evidence was not forthcoming until several X-ray structures were published for dendritic polysilanes, in which the three-conformation regime proved to be the norm [8,13].

Dendrimer **1302** [8] possesses three wings that are nonequivalent in the crystal. The longest polysilane chain contains five silicons and is defined conformationally by two tetrasilane dihedral angles (a single dihedral angle defines the geometry for each Si–Si–Si fragment). The molecule contains 6 *gauche* tetrasilane fragments (dihedral angles in the range 30°–33°), 12 *ortho* fragments (93°–103°), and 6 *anti* fragments (131°–133°). As predicted, the *gauche* range is well below 60° and the *anti* range is well below 180°. There is no all-*anti* (AA) pentasilane arrangement, nor is there an all-*gauche* (GG) arrangement. Instead, the molecule is composed of a mix of *gauche/ortho* (GO), *gauche/anti* (GA), *ortho/ortho* (OO), and *ortho/anti* (OA) arrangements.

Dendrimer **1312** [14] contains only *anti* (143°–162°) and *ortho* (82°–95°) conformations. The longest chains of seven atoms are defined by four tetrasilane dihedral angles, such as OOAO, OOAA, OAOO, and AOAA. There is no all-*gauche* or all-*anti* fragment. These same authors [14] also reported the structure of the hexaphenyl analogue of **1312**: MeSi[SiMe₂SiMe(SiMe₂Ph)₂]₃. Like **1312**, this molecule possesses no *gauche* conformations. They found many *ortho* (83°–102°) and *anti* (157°–164°) conformations. In addition, there are numerous tetrasilane fragments with dihedral angles in the low end of the *anti* range (138°–142°), which they labeled as a distinct conformation E. The heptasilane

fragments then were found to be OAOE, OAOO, OOAE, OOAO, EAOE, EAOO, EOAO, and EAOE. The theoretical studies of Michl and coworkers [18], however, did not find evidence for a fourth conformational family. It should be noted that all the conformations designated as *anti* in **1302** have dihedral angles of $131°–132°$, in the E range of Sekiguchi and coworkers. Further theoretical work is necessary before the E conformation can be validated.

Dendrimer **1313** [8] contains three wings that are crystallographically equivalent, reducing the total number of distinct conformations. The longest polysilane chain contains seven atoms and is defined by four tetrasilane dihedral angles. The AAAA, OOOO, and GGGG conformations are absent. Again, there are mixes such as OAGG and AAGG. The nine total sets of four are composed of 15 *gauche* fragments ($42°–64°$), 6 *ortho* fragments (all $88°$), and 15 *anti* fragments ($157°–173°$). In the large dendrimer **4**, there are polysilane chains of varying length, the longest of which contains 13 atoms. There are a few AAA and many GGG hexasilane pieces, but no conformationally homogeneous larger fragments. There are fewer *ortho* fragments than in the smaller dendritic polysilanes. Neither **1313** nor **4** possesses any tetrasilane fragments that would be classified as E conformations. Molecule **1**, however, has dihedral angles of $132°$, $147°$, $151°$, $154°$, $169°$, and $177°$. Some of these may correspond to the E conformation of Sekiguchi and coworkers [14].

The collection of X-ray structures of dendritic polysilanes thus has provided massive evidence for the existence of at least three polysilane conformational families, including the novel *ortho* family. We classified the families as *gauche* when the dihedral angle was in the range $29°–73°$, *ortho* in the range $80°–106°$, and *anti* in the range $131°–179°$, but these definitions are subject to revision. Although these ranges are somewhat arbitrary, it is noteworthy that no tetrasilane fragments fell in the intermediate regions. Sekiguchi and coworkers [14] split the third range into E ($131°–142°$) and *anti* ($157°–180°$). It is not clear whether the angles of $147°$, $151°$, and $154°$ in **1** would be E or *anti* in this classification.

In light of superior σ-delocalization in all-*anti* arrangements and the presence of *gauche* and *ortho* arrangements in all these dendrimers, it is of interest that the intensity of ultraviolet absorption is stronger in dendrimers than in linear silanes (Table 2). We attributed this general trend to the presence of many redundant pathways in the dendrimers. If these pathways, however, are more *gauche* or *ortho* than *anti*, some attenuation of absorption would be expected. It is possible that there are more *gauche* and *ortho* pieces in the linear polysilanes than expected, since there are no known crystal structures for such molecules. Comparisons between linear and dendritic polysilanes then become more apt. The relationship between conformation and ultraviolet absorption is not yet fully understood.

## 8. Summary

Dendritic polysilanes form a viable and robust alternative to linear polysilanes in the search for useful electronic materials. To date, the third order nonlinear, conducting, and many other such properties of the dendrimers have not been measured. Structural maturity of dendritic polysilanes has not yet been reached. Whereas only a single second-generation dendrimer has been prepared, G4 and higher dendrimers are not uncommon in other families. Molecule **4** is the largest known dendritic polysilane in terms of molecular weight and length of the longest polysilane chain. With a nominal molecular weight of 1833, it is still far smaller than other dendrimers. The smaller dendrimers, such as **1313**, do not describe a sphere in the crystal, but **4** approximate to one, as expected for larger dendrimers. The roughly perpendicular distances between antipodal terminal methyl groups in **4** are 1.74, 1.70, and 1.65 nm, approximating a sphere with nanometer dimensions [13]. Its longest wavelength absorption occurs at 283 nm, still short of the asymptotic value of ca. 296 nm expected if the longest chain were to reach 18 or higher. The dendritic nature of these molecules provided a number of excellent crystal structures, which in turn generated a wealth of previously unavailable structural information about polysilanes.

Thus, some but not all of the objectives have been achieved in the exploration of dendritic polysilanes. Clearly, synthetic difficulties have prevented rapid development of the field. All the syntheses, whether divergent or convergent, have relied on the use of silyl anionic reagents. Although these reagents are critical in the formation of Si–Si bonds, they also react with the Si–Si bond by both anionic and radical pathways [10]. Expansion of the field to higher generations of dendritic polysilanes would require development of new methods for the formation of Si–Si bonds. To simulate the procedures employed to reach higher generations in other dendrimer families, these new methods would need to be high yield and easily adapted to repetitive application. Absent such methods, the field of dendritic polysilanes will have to consolidate its current synthetic successes with examination of the electronic properties of existing systems. A modest and achievable goal would be to prepare dendrimers with longest chains of 18 silicons or higher, even of only first- or second-generation structure. Such molecules would achieve the asymptotic value of absorption in the ultraviolet spectrum, might exhibit superior electronic materials properties, and should possess the crystallinity of other dendrimers.

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