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Chapter 3*

Carbosilane Dendrimers

Jacques Roovers and Jianfu Ding

3.1 Introduction

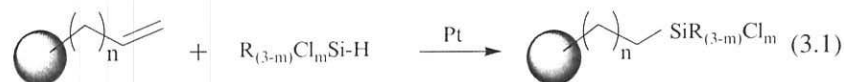
The concept of highly symmetrical, perfectly branched macromolecules prepared in a generational fashion was introduced in 1978 [1]. The synthesis of polylysine dendrimers [2] and the seminal research by Tomalia and Newkome in the mid-1980s established that such molecules could indeed be prepared [3, 4]. Tomalia et al. used trifunctional nitrogen branch points and Newkome chose tetrafunctional carbon branch points. These dendrimers contained ether, ester, amine and amide polar bonds.

Carbosilane dendrimers with a silicon branch point in an exclusively carbon-silicon skeleton are non-polar, inert, neutral and thermally and hydrolytically stable compounds. The absence of polar bonds facilitates the use of many derivatization reactions and creates the possibility of strong physico-chemical contrast between the core and the outer corona. The synthesis of carbosilane dendrimers is almost always by a *divergent* process from the core to the interior generations and to the periphery, with the number of reactions per dendrimer increasing geometrically with each generation (see Chapter 1). The divergent synthesis of carbosilane dendrimers consists of the generational repetition of a sequence of two clean, high-yield reactions: (a) hydrosilylation and (b) nucleophilic substitution by Grignard or organolithium reagents. The hydrosilylation reaction 3.1 introduces the branch juncture and creates the next generation:

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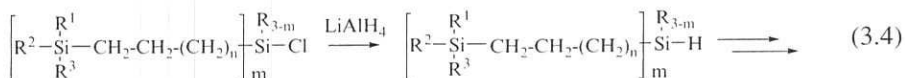
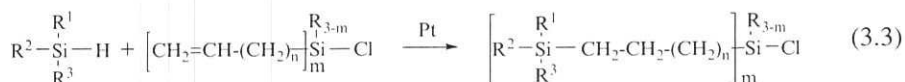


while the substitution reaction 3.2 introduces the branch:



where $n = 0$ (vinyl) or 1 (allyl) defines the length (2 or 3 methylene groups) of the branch and $m = 1, 2$ or 3 defines the functionality (i.e., multiplicity) of the branch point (i.e., juncture). Both reactions are performed with excess of the highly reactive hydrosilane and Grignard or organolithium compounds in order to promote quantitative conversions. Due to the high sensitivity of these reagents to oxygen, moisture, carbon dioxide, etc., these reactions have to be protected by high vacuum and/or Schlenk techniques.

In a *convergent* synthesis, a dendron containing the peripheral groups is repeatedly added via its focal group to a branched molecule and in the final step to a multifunctional core molecule (see also Chapter 1). A possible scheme for a convergent synthesis of a carbosilane dendron consists of the repetition of the following two reactions:



where the definitions of subscripts m and n are the same as for the divergent synthesis. The convergent approach has seldom been applied to carbosilane dendrimers.

Embryonic carbosilane dendrimers with 12 and 18 Si-Cl reactive peripheral (i.e., end) groups were described as early as 1978 and 1980 [5, 6]. The first synthesis of carbosilane dendrimers was reported almost simultaneously by three groups in the early 1990s [7–11], and several reviews of the field have been published previously [12–17].

3.2 Synthesis of Carbosilane Dendrimers

Dendrimers consist of a core, interior generational layers and the exterior or corona (see Chapter 1). These three elements of carbosilane dendrimers will be discussed separately in the following subsections. The core molecule is considered the zeroth generation (0G). A 1G dendrimer has but a core and a corona. In this chapter, dendrimers are named by their last generation and the multiplicity of each generation specifying the branching architecture is given in brackets. For example, 4G(4,3,2,2,2) is a fourth generation dendrimer with a tetrafunctional core and multiplicities 3,2,2,2 and 2 in the four consecutive generations. The number of end-groups is then given

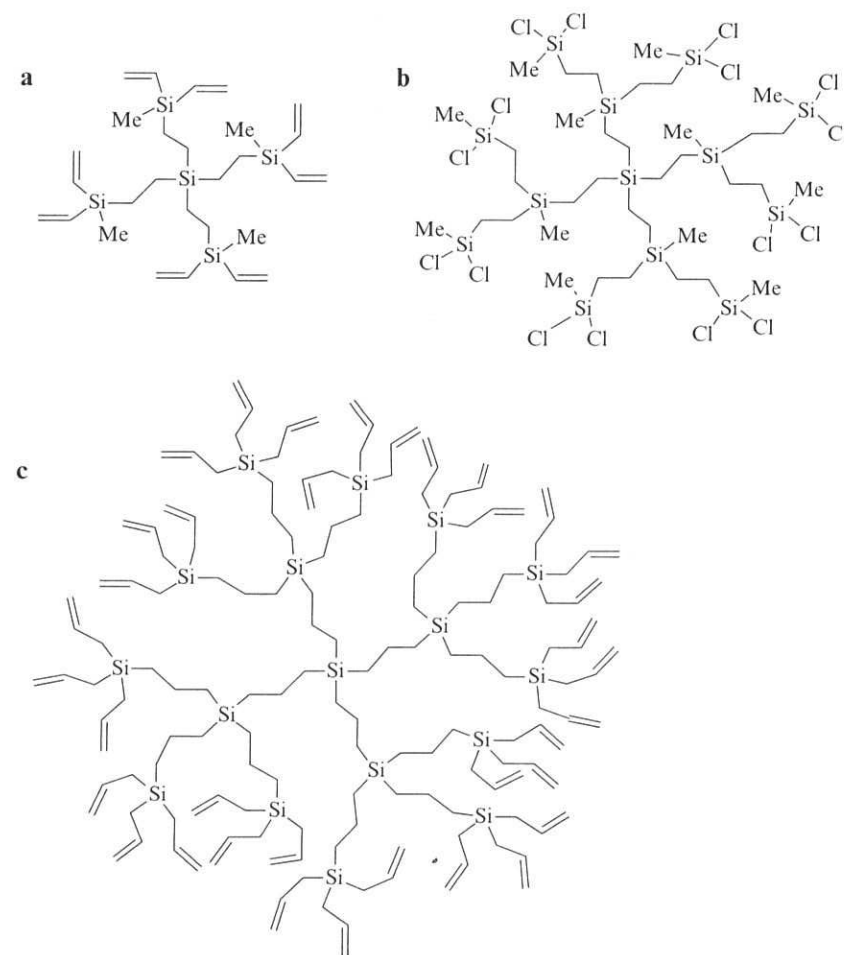


Fig. 3.1 Two dimensional representations of selected carbosilane dendrimers. **a:** 1G(4,2) dendrimer with ethenediyl (C_2) branches and vinyl end-groups; **b:** 2G(4,2,2) dendrimer with C_2 branches and Cl end-groups; **c:** 2G(4,3,3) dendrimer with propanediyl (C_3) branches and allyl end-groups. These representations do not include expected backfolding of a fraction of dendrimer branches.

by the product of all multiplicities, 96 in this example. The nomenclature is illustrated by three examples of dendrimers in Fig. 3.1.

3.2.1 Core Molecules

The inert core molecules that have been used in the divergent synthesis of classical carbosilane dendrimers are listed in Table 3.1.

Table 3.1 Classical carbosilane dendrimers

	Core	Branch point	Branch	Generation	References
1	Si(vinyl) ₄	HSiMeCl ₂	Vinyl	1G–5G (4,2,2,2,2,2)	[7, 18–20]
2	Si(allyl) ₄	HSiCl ₃	Allyl	1G–5G* (4,3,3,3,3,3)	[8, 9]
			Vinyl	1G–3G* (4,3,3,3)	
3	MeSi[OSiMe(allyl) ₂] ₃	HSiMeCl ₂	Allyl	1G–7G (3,2,2,2,2,2,2,2,2)	[10, 11]
4	Si(vinyl) ₄	HSiCl ₃	Vinyl	1G–4G* (4,3,3,3,3)	[21]
5	Si(allyl) ₄	HSiCl ₃	Allyl	1G–3G* (4,3,3,3)	[22]
5	MeSi(allyl) ₃	HSiMeCl ₂	Allyl	1G–5G (3,2,2,2,2,2)	[23]
7	[–CH ₂ Si(allyl) ₃] ₂	HSiMeCl ₂	Allyl	1G–3G* (6,2,2,2)	[24, 25]
3	c-[–Si(Me)(vinyl)O] ₄	HSiCl ₃ + HSiMeCl ₂	Allyl	1G–4G (4,3,2,2,2)	[26–29]
		HSiMeCl ₂	Allyl	1G–3G (4,2,2,2)	
9	Si ₈ O ₁₂ (vinyl) ₈	HSiCl ₃	Allyl	1G–2G (8,3,3)	[30]
		HSiCl ₃ + HSiMeCl ₂	Allyl	1G–2G (8,3,2)	
		HSiCl ₃ + HSiMe ₂ Cl	Allyl	1G–2G (8,3,1)	
10	Si(C≡CPh) ₄	HSiMeCl ₂	Ph-ethenyl	1G–3G* (4,2,2,2)	[31, 32]
	MeSi(C≡CPh) ₃	HSiMeCl ₂	Ph-ethenyl	1G–4G* (3,2,2,2,2)	
	Me ₂ Si(C≡CPh) ₂	HSiMeCl ₂	Ph-ethenyl	1G–5G* (2,2,2,2,2,2,2)	

*The dendrimer is sterically saturated

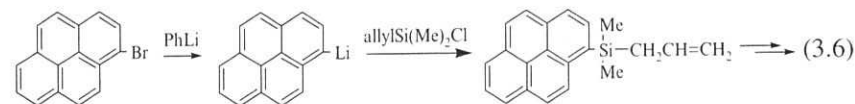
The first three rows of this table have historical relevance that already cover the common variation in chemistry and multiplicity of carbosilane dendrimers. The core molecules for most carbosilane dendrimers are vinyl or allylic compounds with functionality (i.e., multiplicity) from 2 to 8. A large core functionality reduces the number of steps required to produce a dendrimer with the desired number of peripheral groups but early steric saturation may set limits to this approach. The dendrimers marked with an asterisk in Table 3.1 have been confirmed to be sterically saturated. The synthesis of the next higher generation dendrimer was recorded to have failed catastrophically. Line ten in Table 3.1 should be particularly noted: the ethynyl triple bond can be selectively nonohydrosilylated with the resulting double bond being resistant to further hydrosilylation [31].

Core molecules have often been modified in such a way that a functional “handle” becomes available at the root of the dendron, as shown in Reaction Scheme 3.5. These core molecules are all of the (allyl)_{4–m}Si–X_m type, where m is almost always equal to one and X is compatible with the divergent hydrosilylation-Grignard substitution sequence of the dendron synthesis.

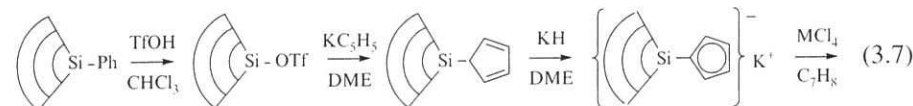


These core-functionalized dendritic molecules have also been called “wedges” [33, 34]. For example, Russian workers prepared carbosilane dendrons from a perylene

root starting from 3-bromoperylene [35] (see also Chapter 2). The subsequent dendron synthesis was extended to 6G(1,2,2,2,2,2,2):

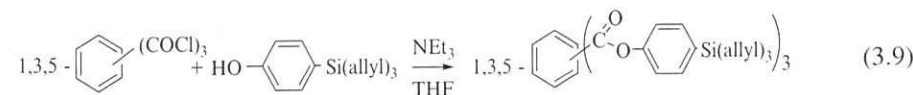
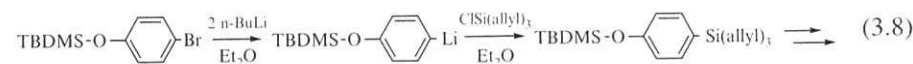


with 64 peripheral allyl groups. The effect of the dendron crowding around the perylene has been investigated by fluorescence studies [35, 36]. Kim et al. prepared dendrons starting from diallylmethylphenylsilane to 4G(2,3,3,3,3) and 5G(2,2,2,2,2,2,2), respectively [37]. In these prototypes the phenyl group can be displaced by triflic acid. The triflate is then a good leaving group for further modification [38]. The detailed reaction conditions for displacement of the phenyl ring with triflate have been described [39]. This procedure was followed by Andrés et al. for the direct attachment of a cyclopentadienyl ring onto the silicon focal atom of 1G, 2G and 3G dendrimers with fully saturated peripheral shells consisting of SiMe₂Bz groups [40]:



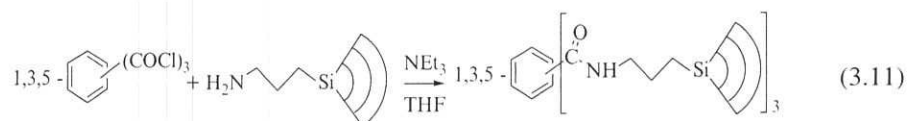
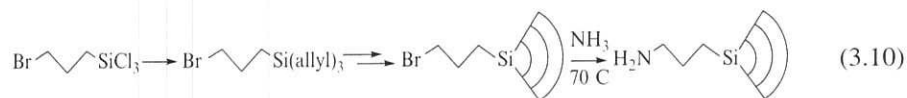
Coupling of 1G via its potassium salt with TiCl₄ and ZrCl₄ yields metal complexes that have catalytic activity. The coupling of 2G and 3G dendrimers, however, failed. An almost identical approach was also followed by Meder et al. [41].

The first core modified dendrons used in the *convergent* synthesis of the next generation dendrimer were described in 1998 [42, 43]:

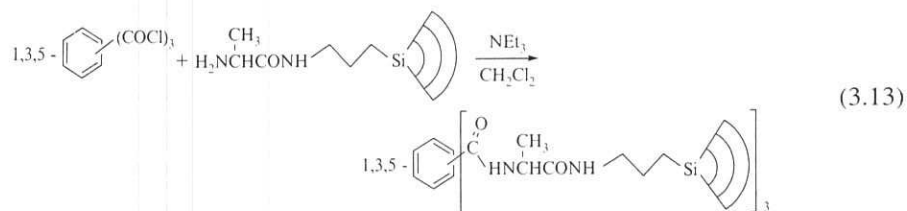
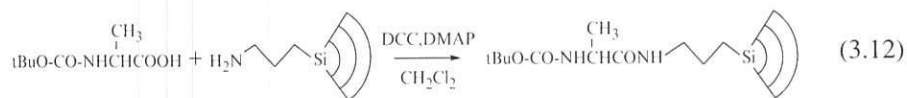


The convergent step is illustrated here with the 0G but has also been realized with 1G and 2G dendrons. The *tert*-butyldimethylsilyl protected phenol, which can be carried through the dendron synthesis, is then deprotected with tetrabutylammonium fluoride and linked with 1,3,5-benzenetricarbonyl trichloride to form mixed ester carbosilane dendrimers. A similar strategy has also been followed for a mixed amide carbosilane dendrimer [34]. Starting from the 3-bromopropyltrichlorosilane core the desired dendrimer is constructed as shown in Reaction Scheme 3.10. The bromide is converted to the primary amine in liquid NH₃ (15 bar) at 70°C and then

reacted with a multifunctional carbonyl chloride compound, as shown in Reaction Scheme 3.11:

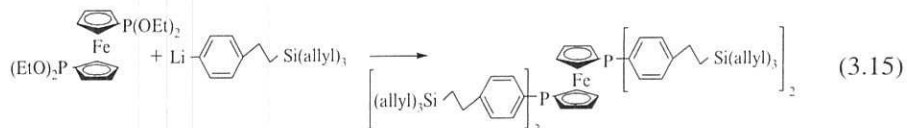
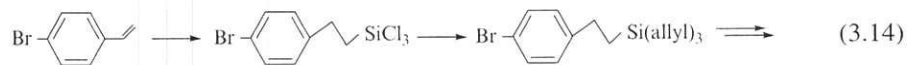


This amine functionalized 2G(3,3,3) dendron has also been used in a formation of highly efficient enantiopure intramolecular bidentate P,N-ligand on a 1,1'-binaphthyl [44]. Further modification of the functionalized core of a dendron prior to coupling into a dendrimer leads to materials with an active function in the direct vicinity of the core and surrounded by a hydrophobic shell. The incorporation of an alanyl group is illustrated in Reaction Scheme 3.13 [45]:

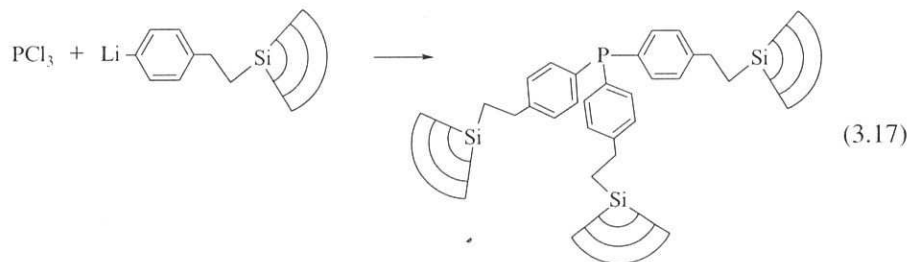
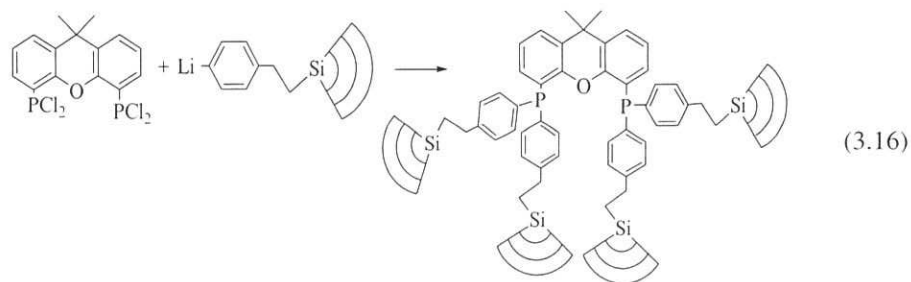


The influence of the dendrimer environment on the binding constants of acids with the amide bonds has been investigated.

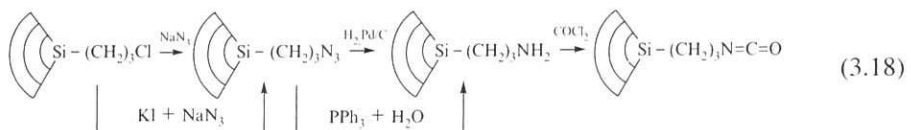
The first catalytically active carbosilane center was obtained by reacting a dendron containing a phenyllithium focal point with a ferrocenyl compound [46]:

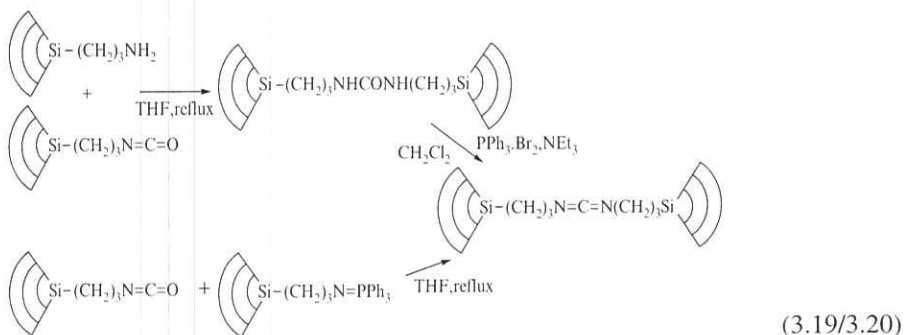


The example is given here for the 0G dendron. The coupling reaction with the ferrocenyl compound produces a 1G(4,3) dendrimer with 12 allyl groups. The 0G triallyl dendron (Reaction Scheme 3.14) was also expanded to 1G(3,3) and 2G(3,3,3) dendrons so that the final ferrocenyl-centered products are 2G(4,3,3) and 3G(4,3,3,3) dendrimers, respectively. The catalytic properties of carbosilane dendrimer-metal complexes are reviewed in Chapter 9. By the same procedure, P,O-ligands for Ni catalysts as well as a tridendrophosphine have been obtained [47, 48]:



A most detailed report concerning the synthesis of carbosilane carbodiimides and their use in the cyclization of dipeptides for the formation of seven-membered rings was published recently [49]. The reactions needed to convert the focal functional group into a carbodiimide require progressively more stringent conditions with increase of the dendrimer size. The carbodiimide is prepared convergently via the urea followed by dehydration with triphenylphosphine-bromine complex. For the 3G(2,3,3,3) dendron a direct coupling between the isocyanate and an activated amine gave a better (72%) yield (Reaction Scheme 3.20). The intramolecular cyclization of two different dipeptides with the dendritic carbodiimides doubled the yield when compared to the same cyclization with dicyclohexylcarbodiimide.





3.2.2 Interior Generations

Each interior generation (i.e., tier or layer) of a carbosilane dendrimer is made up of branch points introduced via a hydrosilylation reaction and branches introduced via an alkenylation step. These two reactions as applied to the synthesis of these dendrimers are next briefly reviewed.

3.2.2.1 Hydrosilylation

The homogeneous hydrosilylation reaction (see also Chapters 7 and 13 as well as the first book of this series: B. Marciniec, “*Hydrosilylation – A Comprehensive review on recent Advances*” is catalyzed by platinum compounds and is considered the more finicky step. General reviews are available [50, 51]. Either soluble Pt(IV) compounds such as Speier’s catalyst ($\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ in isopropanol) [52] or Lukevics’ catalyst $[(n\text{-Bu})_4\text{N}]_3\text{PtCl}_6$ [45, 48, 49, 53] or Pt(II) $[(\text{C}_8\text{H}_{17})_3\text{BzN}]_2\text{Pt}(\text{NO}_2)_4$ [54] are used. Alternatively, Pt(0) complexes such as Karstedt’s catalyst $[\text{Pt}-(1,3\text{-divinyltetramethyldisiloxane})_{1.5}]$ (PC072) [55] and the Silopren[™] (Platinum siloxane complex) [56] are used in a molar ratio of 10^{-5} to 10^{-3} relative to olefin. Exceptionally, Kim et al. used a heterogeneous Pt/C catalyst throughout most of their work [37].

It is generally believed that Pt(IV) and Pt(II) catalysts are first reduced to a more active Pt(0) complex by hydrosilane and that a common hydrosilylation mechanism operates [57]. Lewis has devoted considerable research to elucidate several details of the mechanism of Pt(0) catalyzed hydrosilylation, pointing out an initial induction period and the need for traces of oxygen; first, to create small active colloids, and later, to avoid formation of inactive Pt–Pt agglomerates [58]. Present understanding of the catalytic hydrosilylation mechanism, including its homogeneous/heterogeneous aspect, has been succinctly reviewed [59]. Hydrosilylation tolerates a wide variety of solvents such as benzene, hexane, diethylether, tetrahydrofuran (THF), dichloromethane and their mixtures with alcohols. Initial warming may be required in order to reduce the induction period but temperature control of the exothermic reaction is desirable in order to minimize side reactions. Detailed descriptions of

the best procedures for carbosilane dendrimer production have been given [7, 20, 21, 45, 60].

Hydrosilylation reactions are usually performed with excess (1.5-fold, in difficult cases up to 2.5-fold [60]) hydrosilane in order to drive the reaction to completion. The presence of electron withdrawing groups on silicon facilitates the reaction so that the rate order $\text{HSiCl}_3 \approx \text{HSi}(\text{Me})\text{Cl}_2 > \text{HSi}(\text{Me})_2\text{Cl} > \text{HSiEt}_3 \approx \text{HSiMe}_3$ is observed. The order $\text{HSiMeCl}_2 > \text{HSiMePh}_2$ has also been reported [61]. The general rule is that electron donating groups on the olefin and electron withdrawing groups on the hydrosilane increase the hydrosilylation rate [57]. Methylchlorosilanes are the most common branching agents for carbosilane dendrimers but HSiPhCl_2 has also been used [39]. The addition to the double bond is almost exclusively β or anti-Markovnikov which creates a linear branch. Occasionally, traces of α -addition are observed [21, 62]. As clearly indicated by the work of Iovel et al., α -addition occurs when less reactive hydrosilanes, e.g. $\text{HSi}(\text{aliphatic})_3$ compounds, are reacted at high temperature or without solvent [53]. Although α -addition changes the structure of the dendrimer, often little attention is paid to its complete elimination because α -placement does not immediately limit the growth. The number of Si–Cl bonds in the hydrosilane determines the multiplicity of the branch point. This multiplicity is often kept constant throughout the dendrimer synthesis but can also be changed at each generation (see also Chapter 1, Section 1.4). Kriesel and Tilley described a 4G(4,3,3,2) dendrimer with C_3 branches with 72 triethoxysilyl end-groups [63]. It was pointed out that branch point variation helps in the interpretation of NMR spectra of carbosilane dendrimers [64].

Hydrosilylation with $\text{HSi}(\text{Me})_2\text{Cl}$ serves one of two purposes. When used in an interior generation as a branch point with multiplicity of 1 it forms a $-\text{Si}(\text{CH}_3)_2-$ linker between consecutive linear branches and helps to decrease steric crowding [65, 66]. Alternatively, it is very often used in the last generation where it allows each chain end to be individually functionalized. Several examples of this use are described in Section 3.2.3.2 on the peripheral modification of dendrimers.

3.2.2.2 Substitution with Organometallics

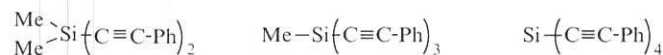
The nucleophilic substitution on Si–Cl with an excess of either vinylmagnesiumbromide or allylmagnesiumchloride or -bromide (Grignard reagents) is an alkenylation reaction. In conjunction with a further hydrosilylation step the former introduces C_2 (ethanediyl), the latter C_3 (propanediyl) branches in the reacting dendrimer generation. Introduction of longer ω -alkenyl chains with primary Grignard reagents has been proposed but no details have been reported [9]. It is suspected that in that case incomplete alkenylation due to steric hindrance and side reactions prevents efficient dendrimer formation [12, 67, 68] but the reactions of multiple Si–Cl groups on large dendrimers with $n\text{-BuLi}$ and methylmagnesiumbromide appear to proceed satisfactory [69].

Carbosilane dendrimers with phenylethenyl branches have also been synthesized. The prototype reaction is illustrated by the formation of tetra(phenylethynyl)

silane from SiCl_4 and lithium phenylacetylene [31]. Hydrosilylation of tetra(phenylethynyl)silane with HSiMeCl_2 followed by substitution with lithium phenylacetylene provides the first generation [31]. It is noted that the phenylethenyl double bond is not further hydrosilylated:



The sequence had been repeated to 3G(4,2,2,2) but further hydrosilylation with HSiMeCl_2 failed. On the other hand, hydrosilylation with HSiMe_2Cl was successful. The limit of growth of pure phenylethenyl branched dendrimers was investigated starting from the following three core molecules with different multiplicities [32]:

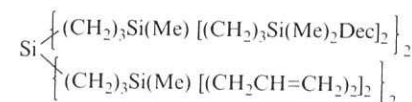


By generational reiteration from the di- tri- and tetrafunctional cores perfect 5G(2,2,2,2,2,2), 4G(3,2,2,2,2) and 3G(4,2,2,2) dendrimers with 64, 48 and 32 peripheral phenylethynyl groups, respectively, can be obtained and it was well established that further hydrosilylation was only partly successful. A larger trifunctional core, $\text{C}_6\text{H}_3[\text{Si(Me)}_2\text{vinyl}]_3$ branched with HSiCl_3 leads only to 2G(3,3,3) [70]. However, when mixed multiplicity is introduced higher generations become obtainable. Repetitive hydrosilylation-alkynylation of the previous 1G(3,3) dendrimer with HSiMeCl_2 affords a 5G(3,3,2,2,2,2) with 144 phenylethynyl end-groups.

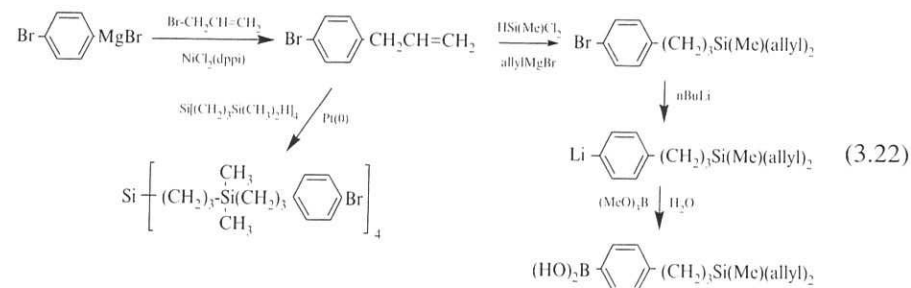
Probably the most efficient method to introduce peripheral phenylethynyl groups consists of preparing a standard carbosilane dendrimer with trimethylene (C_3) branches and decorating the final generation with phenylethynyl groups. In this way, 3G(6,2,2,2) and 4G(6,2,2,2,2) layered dendrimers with 48 and 96 phenylethynyls, respectively, were obtained [71]. In another variation, a double layer of phenylethynyl groups was added so that a 3G(4,3,2,2) dendrimer was formed [72]. This last dendrimer is interesting because not only is the chemistry changed in different generations but also the multiplicity is lowered. The phenylethenyl layer has also been placed exclusively in an interior generation [73]. A standard 3G(4,2,2,2) dendrimer with 32 Si-Cl bonds was first reacted with lithium phenylacetylene. The fourth generation was continued with a sequence of hydrosilylation with HSiMeCl_2 and alkenylation with allylmagnesiumchloride and the fifth generation was finally capped with 128 peripheral butyl groups, to yield the following structure:



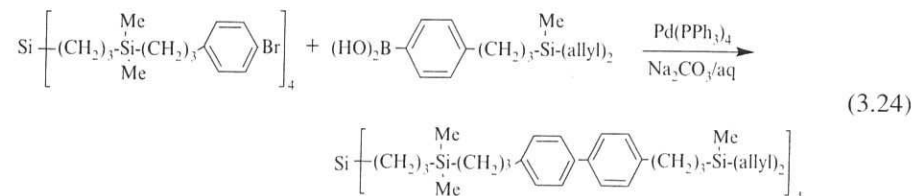
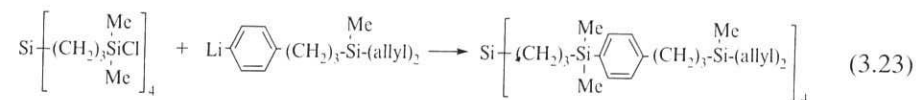
Very recently, a method was described for the synthesis of segmented carbosilane dendrimers that have two different pairs of dendrons emanating from the central silicon atom [60]:



Aromatic groups have been introduced into the branches of carbosilane dendrimers in order to expand the dimensions between the branch points, reduce the internal density, create larger cavities and relieve surface crowding [74]. The process was semi-convergent as the introduction of the phenyl or biphenyl (via Suzuki coupling) was always the last step in the synthesis. The construction of the dendrimers started from 1,4-dibromobenzene, and the building blocks were obtained via an interesting set of hydrosilylation/substitution reactions as shown in Reaction Scheme 3.22:



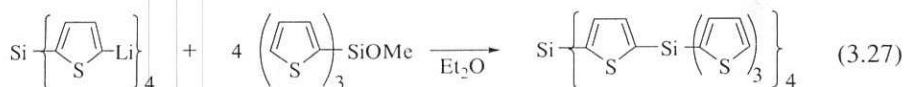
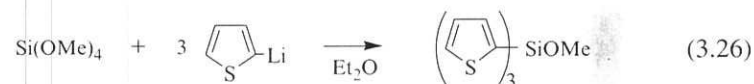
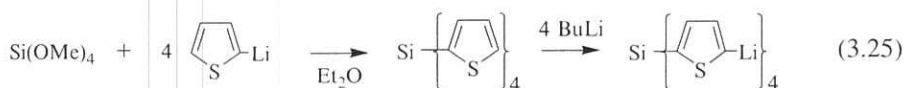
The final convergent formations of the phenyl and biphenyl branch are depicted for the 1G(4,2) dendrimer in the following reactions:



For the 2G(4,2,2) biphenyl analogue the same coupling reaction was employed starting with $(\text{HO})_2\text{B-C}_6\text{H}_4\text{-(CH}_2)_3\text{-Si(Me)[(CH}_2)_3\text{-Si(Me)(allyl)}_2]$.

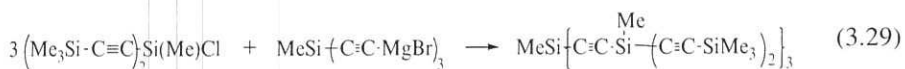
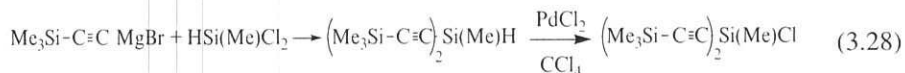
To conclude this section, we mention a few extraordinary carbosilane dendrimers whose chemistry and structure are not directly related to the classical ones. Interestingly, these examples are often based on silicon halide and organolithium coupling reactions. A carbosilane dendrimer with 16 thiophene rings, four functioning as branches and 12 as peripheral groups was prepared from tetra(2-thienyl)silane and tri(2-thienyl)methoxysilane with BuLi in 19% yield [75]. The basic

reaction was the controlled coupling of tetramethoxysilane with four and three 2-thienyllithium molecules, respectively:



Incomplete lithiation of tetrathienylsilane leads to partial dendrimers that have been isolated and identified [75].

Silylacetylene dendrimers with Si–C≡C repeat units were prepared convergently starting from trimethylsilyl acetylene Grignard reagent and methyldichlorosilane [76]. Conversion of the silicon hydride to silicon chloride allowed for coupling to a central trifunctional core:



The 1G dendrimer with matrix assisted laser desorption ionization-time of flight (MALDI-TOF) molecular weight $M = 850.8 (M + \text{Na}^+)$ and four Si and nine ethynyl branches was obtained in 48% yield. For the 2G dendrimer the $(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{SiMeCl}$ product of Reaction Scheme 3.28 was converted in four steps to $[(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{SiMeC}\equiv\text{C}]_2\text{SiMeCl}$ and then coupled to the same trifunctional Grignard core of Reaction Scheme 3.29. The 2G dendrimer had ten Si branch points and 21 ethynyl branches with MALDI-TOF molecular weight of 1836 $(M + \text{Na}^+)$ [76].

A completely different dense carbosilane dendrimer was prepared through a Si–C bond formation process. It consisted of trifunctional carbon branch points and Si(Me)_2 branches [77]:



The first generation compound had four carbon branch points and nine peripheral vinyl groups.

3.2.3 Peripheral (Corona; End-Groups) Modification

In this section we describe modification of the peripheral groups of carbosilane dendrimers. Such dendrimers modified with multiple functional groups are proposed for applications in catalysis (see Chapter 9), sol-gel processes (see Chapter 11), liquid crystalline materials (see Chapter 10), star polymers (Section *Star Polymers with Carbosilane Dendrimer Core*, pp. 54–57; see also Chapter 10 and Section 11.3) and biorecognition [78, 79].

3.2.3.1 Modification of Si–Cl End-Groups

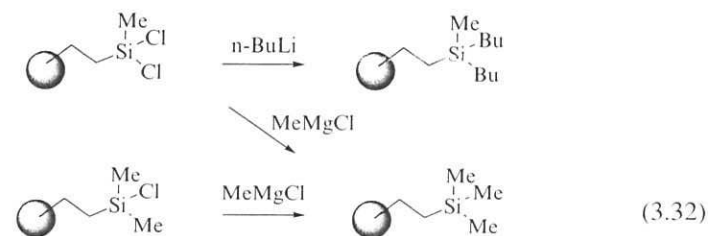
The very reactive Si–Cl bonds at the intermediate stage of the carbosilane dendrimer synthesis are ideally suited for introduction of multiple, compactly-placed functional groups. A large number of such transformations have been described. In this chapter, only Si–C compounds are described, while the reactions leading to carbosiloxane and carbosilazane compounds are described in Chapters 2 and 5.

The first modification to be considered is the reduction of Si–Cl bonds to Si–H bonds with LiAlH_4 in diethylether. The reaction was pioneered on SiCl_3 terminal groups in dendrimers up to 4G(4,3,3,3,3) affording a dendrimer with 324 Si–H bonds [21]:



The conversion is easily recognized by the ^1H NMR resonance of Si–H at 3.5 ppm and the ^{29}Si resonance at –53 ppm. The same reaction has also been applied to Si(Me)Cl_2 [80] and $\text{Si(Me)}_2\text{Cl}$ end-groups [16, 80–82]. Dendrimers with $\text{Si(Me)}_2\text{H}$ end-groups are reagents for “inverse hydrosilylation” reactions wherein the dendrimer carries multiple Si–H bonds. These applications are described in Section 3.2.3.3.

In order to obtain inert dendrimers, it is desirable to create a saturated aliphatic or aromatic external corona. This has been realized in a number of ways starting from the Si–Cl intermediates. For example, Tatarinova et al. reacted Si(Me)Cl_2 groups with $n\text{-BuLi}$ in hexane [69]:



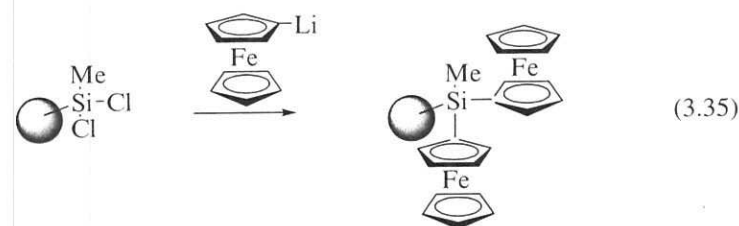
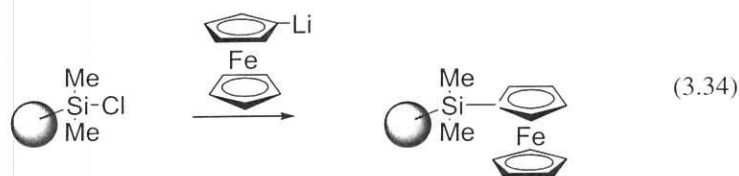
to obtain the product that required chromatographic purification. Others chose reactions of methylmagnesiumchloride with $\text{Si}(\text{Me})\text{Cl}_2$ [39] and $\text{Si}(\text{Me})_2\text{Cl}$ end-groups [48]. It is worth noting that the latter approach is preferred over the difficult direct hydrosilylation of allylic double bonds with gaseous trimethylsilane. Similarly, $\text{Si}(\text{Ph})\text{Cl}_2$ end-groups were converted to $\text{Si}(\text{Ph})(\text{Me})_2$ [39]. Terminal SiCl_3 and $\text{Si}(\text{Me})\text{Cl}_2$ were also treated with benzylmagnesiumchloride [83].

Functional groups linked to silicon via a stable Si–C bond are usually introduced by means of organometal, more specifically, organolithium chemistry. The use of organolithium compounds combined with a protection/deprotection strategy is practically inexhaustible. Seyferth et al. produced peripheral ethynyl groups that form $\text{Co}(\text{CO})_4$ complexes when treated with $\text{Co}_2(\text{CO})_8$ [84]:

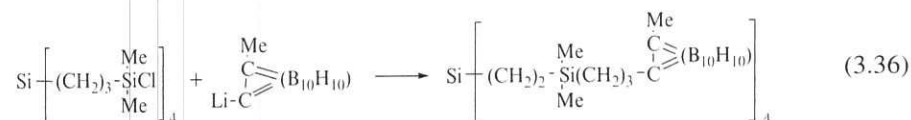


The same reaction was also applied when $\text{Si}(\text{Me})\text{Cl}_2$ was treated with $(\text{Ph})\text{C}\equiv\text{CLi}$ [85] and $\text{Si}(\text{Me})_2\text{Cl}$ with $[(\text{Ph})_2\text{PCH}_2]_2\text{C}(\text{CH}_3)\text{CH}_2\text{C}\equiv\text{CLi}$ or $\text{RO}(\text{CH}_2)_2\text{C}\equiv\text{C-Li}$ [41, 86].

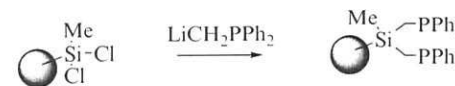
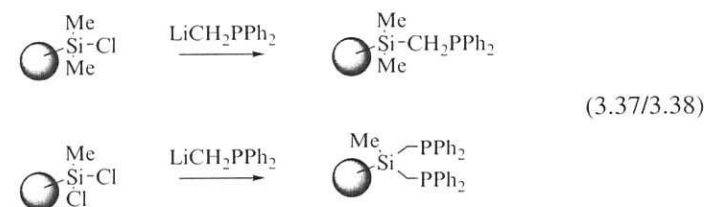
The ferrocenyl group was introduced by reaction of mono- and disubstituted silicon with ferrocenyllithium (see also Chapter 8) [87–89]:



In the monosubstituted dendrimer all ferrocenyl groups have identical redox properties but electronic coupling occurs in the disubstituted dendrimers [89]. A similar method for preparing dendrimers peripherally substituted with carboranes has also been described [90]. 1-Methyl-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$ carborane was easily lithiated with *n*-BuLi and then reacted with the 1G (4,1) dendrimer:



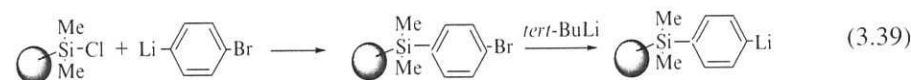
Another example involves the attachment of diphenylmethylphosphine groups via the easily formed lithiummethyl reagent in the presence of tetramethylethylenediamine [91–97]:



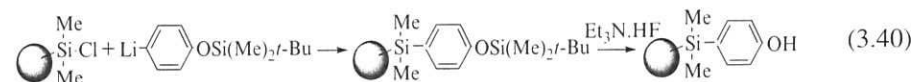
The phosphines are ligands for organometallic compounds and many of the resulting metallodendrimers have been assessed for their catalytic properties (see Chapter 9) [92, 97–99]. An optically active phosphorus center has also been introduced [65].

A wide variety of functionalized phenyl rings has been placed on the periphery of carbosilane dendrimers. The phenyl ring creates a rigid 5 Å extension of the dendrimer branch. This work has been driven by the search for effective complexing agents for homogeneous multifunctional organometallic catalysts and is often limited to 2G(4,3,3) dendrimers. In almost all cases, branch extension is on a terminal $-\text{Si}(\text{Me})_2\text{Cl}$ group and the required lithium (occasionally, Grignard reagent) is prepared *in situ* from the phenylbromide or phenyliodide precursor by lithium-halogen exchange with one equivalent of *n*-butyllithium or *t*-butyllithium.

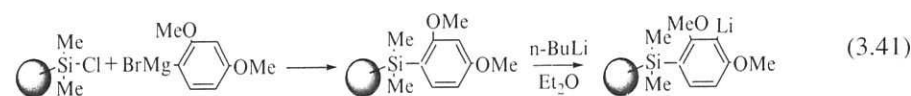
Monolithiation of *para*-dibromobenzene and substitution of Si–Cl leads to carbosilane dendrimers with 4-bromophenyl groups [100]. The 4-bromo substituent itself can be converted quantitatively to the 4-lithiophenyl, a versatile reagent for reactions with many electrophiles, including $\text{Cl-P}(\text{C}_6\text{H}_5)_2$, $\text{Cl-P}(\text{C}_6\text{H}_{11})_2$ [100, 101], R-CO-R and R-COH [100]:



Phenol groups are introduced after protection with *tert*-butyldimethylsilyl groups which can be cleanly cleaved with $\text{Et}_3\text{N}\cdot\text{HF}$ [100]:

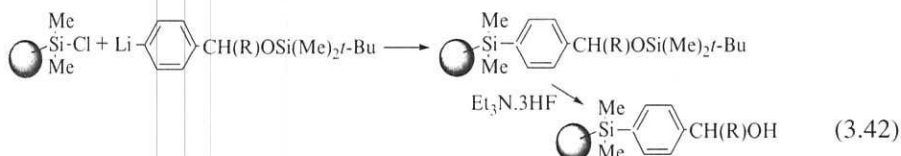


Dimethoxy substituted phenyl rings are introduced via reaction with 2,4-dimethoxyphenylmagnesiumbromide [102]:



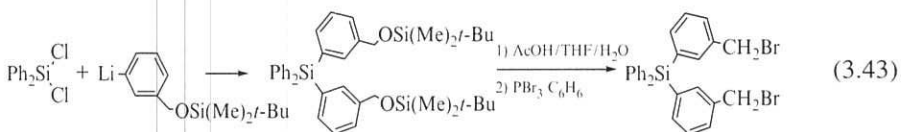
The resulting carbosilanes can be directly lithiated at the 3-(*meta*) position where the lithium atom is strongly stabilized by the two neighboring methoxy groups. However, the related 3,5-dimethoxytolyl group, when attached to carbosilane dendrimers, is simultaneously lithiated at the benzyl position.

Introduction of hydroxyl groups requires prior protection with *tert*-butyldimethylsilyl groups. The general scheme for R = CH₃ or H is [103–105]:

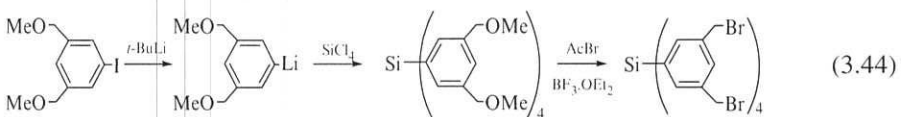


The hydroxyl group is another versatile starting point for further modification, such as esterification or conversion of the hydroxymethyl group to a bromomethyl group [106].

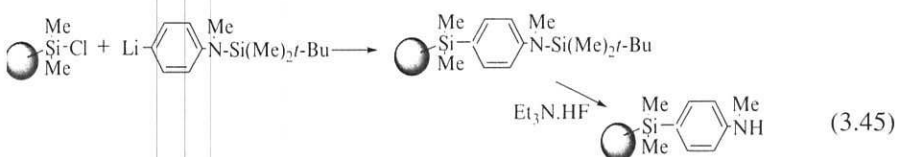
A special case involves the modification of (Ph)₂SiCl₂ at the 0G(2) level with 3-hydroxymethylphenyl groups and conversion to the benzyl bromide groups [107]:



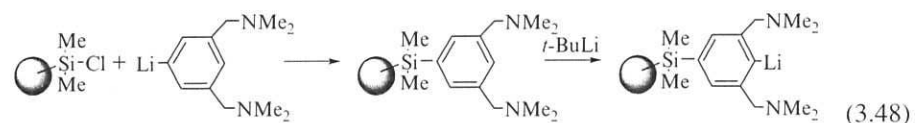
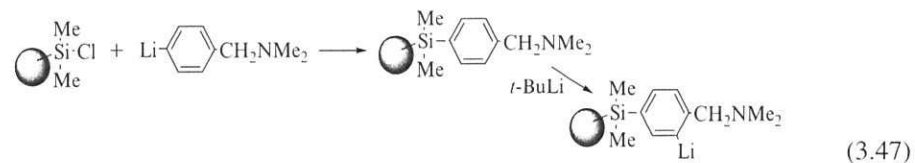
3,5-Di(methoxymethyl)phenyliodide is the starting point for introduction of 3,5-di(methoxymethyl)phenyl groups that can be converted cleanly to benzyl bromide groups [108]:



Anilino substitution of peripheral Si-Cl groups proceeds by a similar strategy after primary and secondary amines are protected [100, 109, 110]:

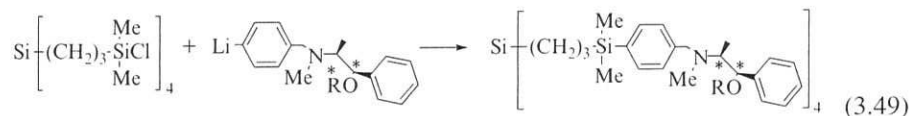


Tertiary amines can be introduced directly, monoamines starting from 4-[(dimethylamino)methyl]phenylbromide and diamines starting from 3,5-[[bis(dimethylamino)methyl]phenyl]bromide [111–114]:

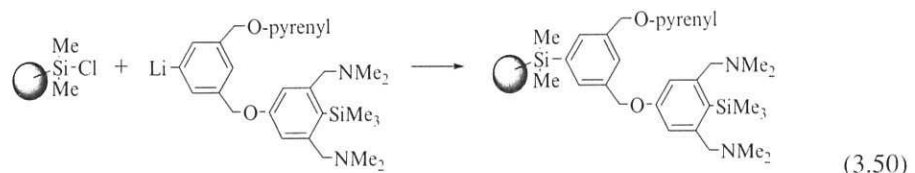


In both cases, lithiation of the position ortho to the tertiary amine functions has been studied extensively for further attachment of catalytic metal centers.

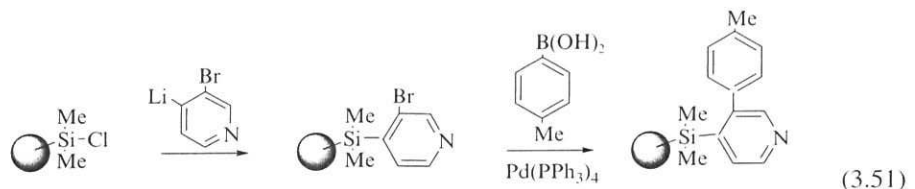
A special case is the introduction of chiral 1R,2S-N-(4-bromobenzyl)-O-(*tert*-butyldimethylsilyl)ephedrine [115, 116] for the construction of carbosilane dendrimers with chiral ligands that are used in the enantioselective addition of dialkylzinc to phosphonylimines:



Post modification steps on dendrimers are preferably kept to a minimum in order to optimize the yield of the final product. This is illustrated with the placement of a complex peripheral group on a 2G(4,3,3) dendrimer [117]:

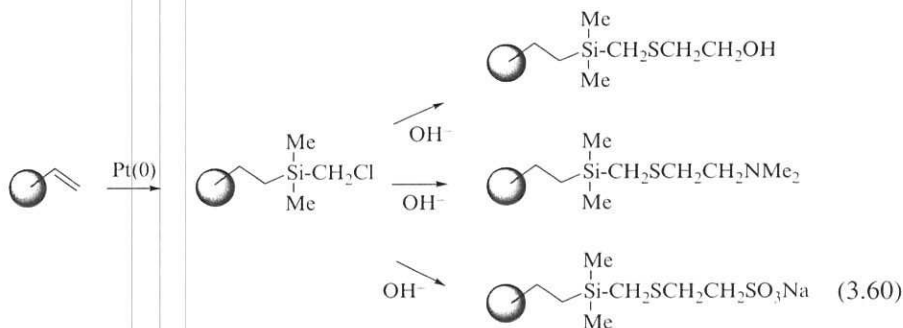


A 1G(4,3) dendrimer was decorated with *meta*-bromopyridine [118], and the resulting compound was used as a reagent for multiple Suzuki coupling reactions with *para*-tolylboronic acid:



Moreover, one extra generation is added to the dendrimer in the process. After deprotection, the polyhydroxy dendrimers were good initiators for anionic polymerization of ethylene oxide [137].

In another approach, vinyl terminated dendrimers were first converted to alkylchloride derivatives by the hydrosilylation with $\text{HSiMe}_2\text{CH}_2\text{Cl}$ [62]. The CH_2Cl group was then reacted under basic conditions with numerous thiol compounds to introduce a variety of functional groups:

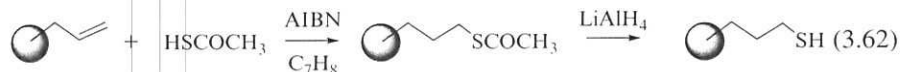


The same procedure was also used to introduce thioglycolic acid, its ethylester and various perfluoroalkyl groups [138]. Hydroxyl terminated carbosilane dendrimers are soluble in methanol and ethanol but not in water [62, 133]. The charged dendrimers with $-\text{SO}_3^-\text{Na}^+$ and $-\text{NHMe}_2^+\text{Cl}^-$ groups are water soluble [62].

The radical addition-hydrogen abstraction reaction was performed with a large excess of thio-compound and used to form a perfluoroalkyl corona around a carbosilane core [139]:



The contrast between carbosilane and fluoroalkyl groups leads to liquid crystalline mesophases for 1G to 3G(4,3,3,3) materials. The same reaction with thiolacetic acid was used to introduce terminal thiol groups [140]:



The hydrogen abstraction-addition reaction, initiated with azobisisobutyronitrile (AIBN) as the initiator at 50°C , has also been used to attach phosphines HPR_2 ($\text{R} = \text{Et}, \text{Ph}$) to vinylsilane double bonds [141, 142].

Allyl terminated dendrimers are good substrates for direct introduction of terminal hydroxyl groups to form a hydrophilic shell around the hydrophobic skeleton and for use in further modifications. The first carbosilane-based dendritic polyols, sometimes also called *arborols* (see [21] of Chapter 1), were obtained via direct hydroboration followed by alkaline H_2O_2 oxidation of peripheral allyl groups

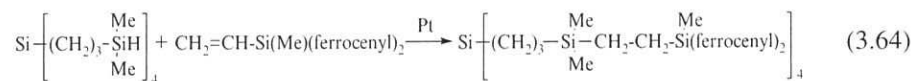
[22, 143, 144]. The reactions must be carried out carefully in order to avoid potential crosslinking [145]:



The MALDI-TOF analysis of 3G(4,3,3,3) dendrimer with a polyol corona revealed dendrimers with 94 to 108 hydroxy groups, in agreement with the analysis of the multifunctional allyl parent. The same method was followed by others to prepare 4G(4,2,2,2,2) and 2G(8,3,3) polyols [30, 146]. Treatment of the 2G polyol with carbonyl chloride was used to introduce mesogenic groups [147, 148]. Subsequent modification of hydroxyl groups to bromopropyl, iodopropyl, azidopropyl, and aminopropyl has also been described [144, 149]. These dendrimers offer gateways to further derivatization; for example, with saccharides [150, 151].

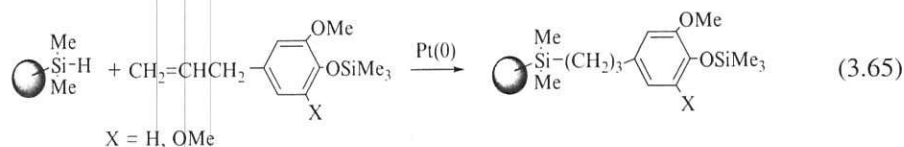
3.2.3.3 Modification of Si-H End-Groups

The Si-H peripheral groups are introduced into carbosilane dendrimers by reaction of Si-Cl functionalized precursors with LiAlH_4 in diethylether. The Si-H bond is relatively stable when care is exercised and it is often used as a starting function for further dendrimer functionalization via hydrosilylation when functional molecules with vinyl or allyl double bonds are available. We call this approach “*inverse hydrosilylation*” in contrast to the classical divergent hydrosilylation with $\text{HSiR}_n\text{X}_{3-n}$ compounds. Preliminary studies of inverse hydrosilylation were described in 1993 and 1995 for the addition of vinylferrocene to octakis(dimethylsiloxy)octasilsesquioxane [152] and to tetramethylcyclotetrasiloxane [153], respectively (see also Chapter 8). The approach was first systematically applied to the construction of bis(ferrocenyl)silyl substituted carbosilane dendrimers [89]:

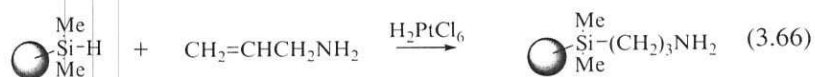


and a larger 1G tetraferrocenyl compound was also used. Such inverse hydrosilylation can be considered the final step in a convergent dendrimer synthesis.

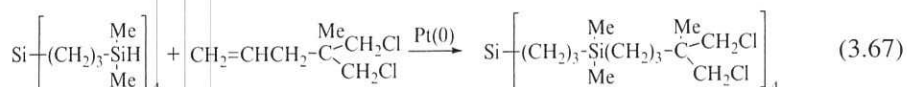
The same reaction has been applied to modify the carbosilane dendrimer periphery when vinyl or allyl substituted functional compounds are easily available. In most cases substitutions are limited to the 0G(4) compound and product purification is often indicated. Arévalo et al. carefully studied the hydrosilylation of eugenol, $\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_3(\text{OCH}_3)\text{OH}$, with Et_3SiH and established that the phenolic groups require trimethylsilyl protection in order to prevent side reactions including O-silylation and simultaneous isomerization of allyl to propenyl [154–156]. Reaction in a minimum amount of THF at 70°C for 9 h provided a 90–95% yield and could then be extended to 3G(4,2,2,2) dendrimers [154]:



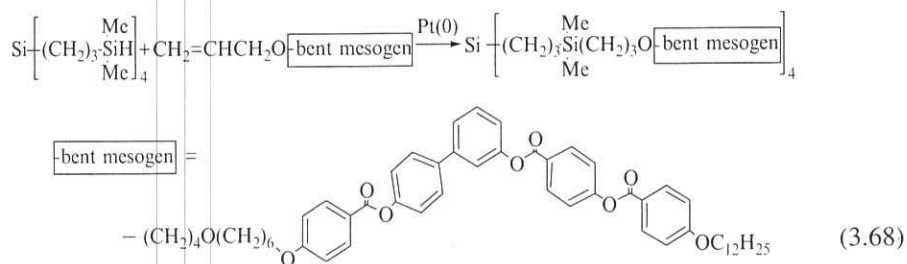
Primary amines were directly introduced via hydrosilylation with excess allylamine in a minimum amount of THF at 120°C giving moderate 80% yield for 0G(4) and 55% yield in the case of the 1G(4,2) dendrimer. N-silylation is a possible side reaction here. However, it was not studied in detail [157]:



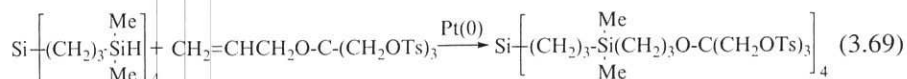
Findeis and Gade used inverse hydrosilylation as an alternative to modification of Si-Cl with Li-C≡C-R so that no triple bonds appear in the dendrimer. However, the reaction was performed only on the 0G(4) model [86]:



Allyloxy substituted reagents seem particularly suited for inverse hydrosilylation, as shown by a comparison of their effectiveness with that of α-alkenyl substituted reagents [158]:

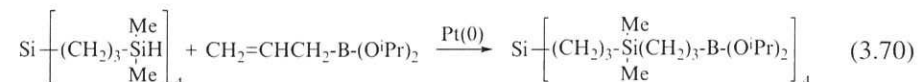


The yields for introduction of four bent-core mesogens (see also Chapter 10) into 0G(4) and 16 bent-core mesogens into 2G(4,2,2) dendrimers were 32% and 39%, respectively. Similarly, ionophores, either triethyleneglycol or crown ethers (15-crown-5, 18-crown-6), with allyloxy handles were introduced into 0G(4) or 1G(4,2) dendrimers [159–161]. The same reaction was used to attach the monoallylether of pentaerythritol suitably protected with tosylates [162]:

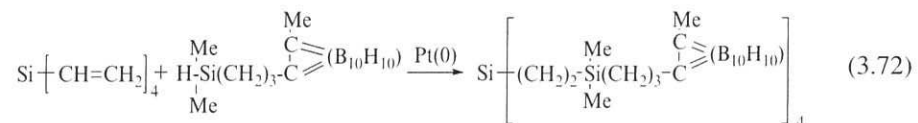
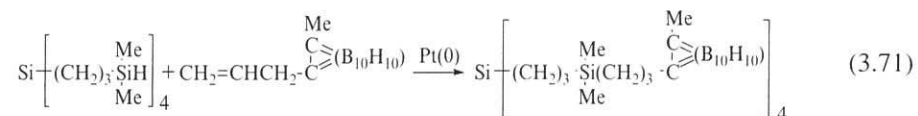


The complete reaction creates a mixed carbosilane-Newkome-type dendrimer [135] and the protecting tosylate groups are versatile leaving groups that facilitate further derivatization; for example, by thiocyanate to form thiol end-groups [162].

Allyl diisopropoxyboron reacted quantitatively with 0G(4) dendrimer, as shown in Reaction Scheme 3.70 [163]:



In a recent study of end-functionalization of carbosilane dendrimers with carboranes, hydrosilylation and inverse hydrosilylation have been closely compared:



When 1-phenyl or 1-methyl-2-allyl-1,2-*closo*-carborane was added to a 0G(4) carbosilane hydride, as shown in Reaction Scheme 3.71, the yield was 36%. On the other hand, when the same carboranes were first hydrosilylated with HSi(Me)₂Cl and then reduced with LiAlH₄ [164], hydrosilylation of tetraallylsilane failed but hydrosilylation of tetraallylsilane gave 99% yield [165] (see Reaction 3.72). Direct reaction of the Si-Cl terminated 0G dendrimer with 1-methyl-2-lithio-1,2-*closo*-carborane has also been performed [90], as shown in Reaction Scheme 3.36.

Overall, the available evidence suggests that inverse hydrosilylation is a reaction with limited yield that can only be applied effectively to low generation multifunctional hydrides after carefully establishing reaction conditions. There are several possible reasons for this, including the bulky size of the hydride which may limit the formation of the active Pt intermediate, and the impossibility of using excess hydride which prevents promoting the yield in the usual fashion.

Finally, it should be mentioned that the Si-H bond can be easily converted to Si-Metal as shown in the following example [166]:



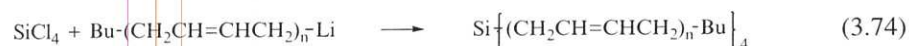
3.2.3.4 Carbosilane Dendrimer-Polymer Hybrids

In this section we deal with two types of dendrimer-linear polymer hybrids (sometimes also referred to as architectural copolymers), including: (a) carbosilane

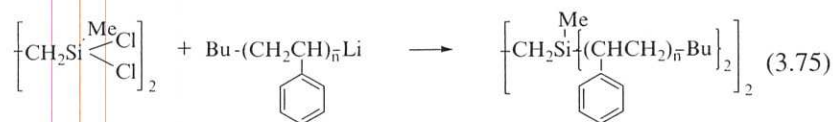
dendrimers to which linear polymers chains are attached, usually referred to as *star polymers* (see also Section 11.3), and (b) linear polymers decorated with pendant carbosilane dendrons, the so-called *dendronized polymers* (see also Section 8.2.2.5). Three general reviews of such dendrimer-polymer hybrids can be found in the literature [167–169].

Star Polymers with Carbosilane Dendrimer Core

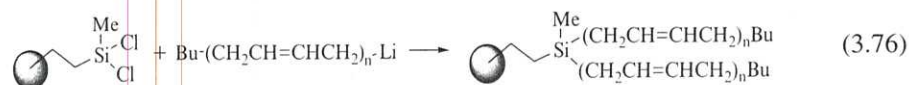
Derivatization of dendrimers with linear polymers is an efficient use of expensive dendrimers because of the large molecular mass increase that is realized in the process. Moreover, the resulting star polymers have unusual colloidal properties [170]. The chemically inert carbosilane dendrimers are uniquely suited for modification with anionic living polymers. The basic reaction involved in this process is exemplified with polybutadienyllithium:



It has been shown that this reaction is essentially free of side reactions when performed in hydrocarbon solvents [171, 172]. Earlier work led to two crucial observations: (1) Si–Cl bonds on a single Si atom are successively substituted, and (2) in the substitution, the least sterically hindered anion is favored, i.e. polybutadienyllithium over polyisoprenyllithium over polystyryllithium, independent of the molecular weight [173, 174]. Even in the least favorable case, coupling of polystyryllithium with dendrimers containing multiple –Si(Me)Cl₂ end-groups is successful [173]:

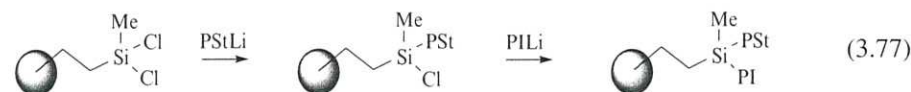


3G(4,2,2,2), 4G(4,2,2,2,2) and 5G(4,2,2,2,2,2) C₂ carbosilane dendrimers with –Si(CH₃)Cl₂ end-groups have been reacted with excess polybutadienyllithium [19, 20, 175, 176]:



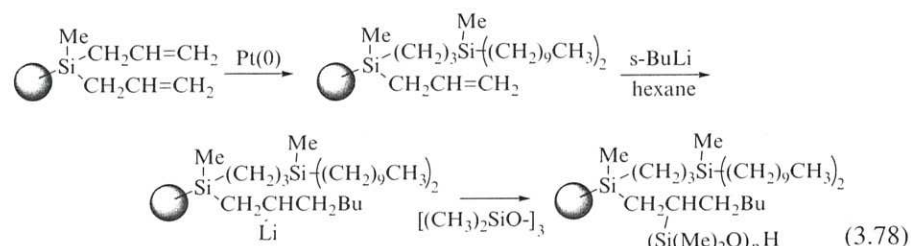
In this reaction, narrow molecular weight distribution (MWD) linear polymers are transformed into narrow MWD star polymers with 32, 64, and 128 arms, respectively.

Application of successive substitution of multiple Si–Cl bonds on one silicon atom has led to miktoarm star polymers (ABC, A_nB_m, etc.) [174, 177]:



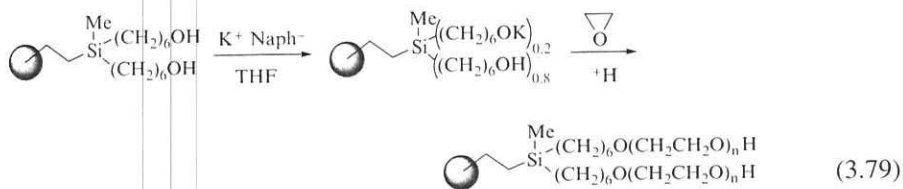
A 2G(4,2,2) dendrimer with 16 Si–Cl bonds is first reacted with 0.5 equivalents of the sterically demanding polystyryllithium followed by the addition of a 30% excess polyisoprenyllithium. The intermediate eight-arm star polymer and the final star blockcopolymer were fully characterized. The same scheme was also followed with a 2G(3,2,2) dendrimer [178]. The special placement of the blocks influences the microphase behavior of the miktoarm stars.

In addition to the “grafting to” reactions described above, a “grafting from” approach using carbosilane dendrimers with multiple lithiated sites has also been proposed. However, multifunctional lithium compounds are notoriously insoluble in hydrocarbon solvents due to their great tendency to associate intermolecularly. Nevertheless, an ingenious method has been devised to decorate the interior of carbosilane dendrimers with an exact number of C–Li sites for initiation of the polymerization of styrene and polar monomers [179, 180]:



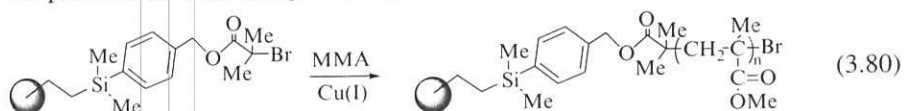
The allylic end-groups of a 2G(4,2,2) and 3G(4,2,2,2) dendrimer were first hydrosilylated with 0.5 equivalents of didecylmethylsilane and then the remaining allyl groups were reacted with *sec*-BuLi in the presence of a stoichiometric amount of tetramethylethylenediamine (TMEDA). The solubility of the resulting octa- and hexadecalithium initiators was explained by a reduction of the lithium association and/or by a preference for intra-dendrimer association. However, on polymerization of hexamethylcyclotrisiloxane the living polydimethylsiloxane solutions formed physical gels indicating that the –Si(Me)₂OLi end-groups associate outside the dendrimer cores. Note that this type of initiator leads to somewhat broader molecular weight distribution polymers (M_w/M_n ranging between 1.2 and 1.3). The method was expanded to 3G(3,2,2,2) and 5G(3,2,2,2,2,2) dendrimers for the preparation of 12 and 48-arm polydimethylsiloxane stars [181]. Intrinsic viscosities of the stars clearly revealed their size contraction relative to linear polymers but the contraction factors showed unusual molecular weight dependence [181].

This grafting-from method was also used to prepare 8, 16 and 32-arm poly(ethylene oxide) star polymers [137, 182]:



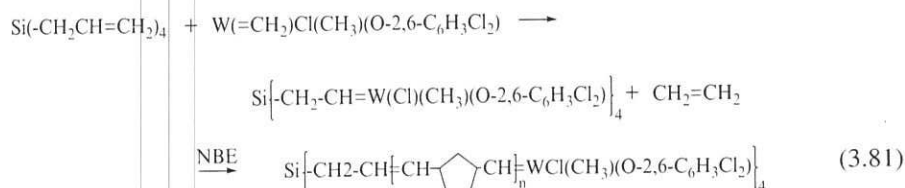
In this case, a fraction of the peripheral hydroxyl groups was converted to potassium alkoxide with potassium naphthalene in THF. This prevented ionic association and consequent insolubility of the initiator. The rapid exchange of potassium ions between CH_2OK and CH_2OH groups relative to the propagation step guaranteed narrow molecular weight distribution star polymers.

The 0G and 1G dendrimers with 2-bromoisobutyrate end-groups were used for the initiation of the pseudo-living radical polymerization of methyl methacrylate in the presence of Cu(I) complex [183]:



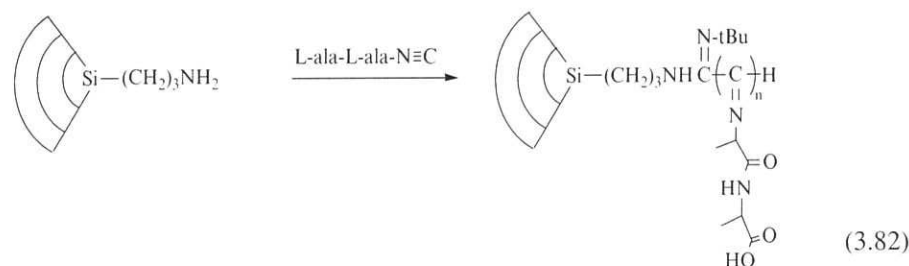
This process works well and yields narrow MWD star polymers provided the initiator concentration is relatively high and monomer conversion is kept below 30%. At higher conversion, coupled star polymers appear due to chain termination by recombination. Incompletely substituted dendrimers are poor initiators, possibly because the unreacted allyl groups on the dendrimer participate in the polymerization.

Carbosilane dendrimers have also been modified with ring opening metathesis (ROMP) initiator sites. In a prototype reaction, tetraallylsilane was treated with a tungsten carbene in an olefin metathesis reaction:



and successfully used to initiate the polymerization of norbornene (NBE) [184]. The molecular weight and molecular weight distribution increased rapidly after the propagation step due to dismutation of the living ends. The arm coupling of stars results in high molecular weight and highly branched materials. Multiple Ru-carbenes on 0G (tetraallylsilane) and 1G(4,2) dendrimer were excellent initiators for norbornene [185, 186]. A combination of end-group analysis and size exclusion chromatography (SEC) indicated that narrow molecular weight distribution star-branched polymers were obtained [186].

In an exceptional case, the amine-functionalized focal point of a dendron was reacted with a nickel complex to form a carbene polymerization initiator for L-alanine L-alanine isocyanide [187]:

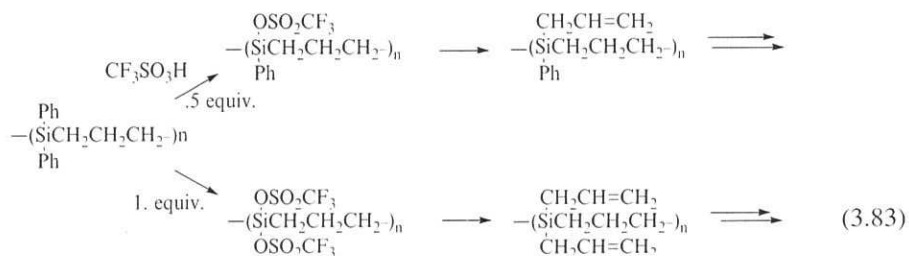


Isocyanide polymers are characterized by a substituent on every chain carbon. The resulting dense packing and the interaction of the functional groups in the side chains lead to stiff, rod-like, helical polymers. In the presence of Ag^+ ions the block copolymers composed of flexible spherical carbosilane dendrimers and rigid polyisocyanides self-assemble into discrete nanoarrays. On irradiation of some third generation arrays the Ag^+ ions were reduced to metallic silver that was predominantly oriented as [111] silver crystals.

Carbosilane Dendronized Polymers

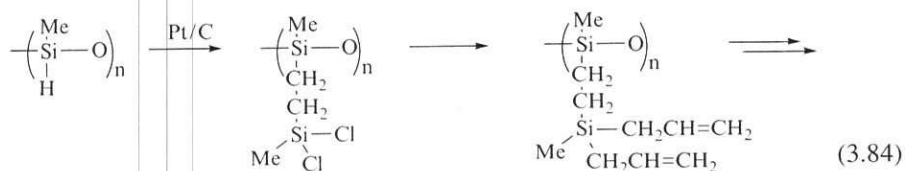
Most carbosilane dendronized polymers have been obtained by growing the dendrons from every repeat unit or from a fraction of repeat units of a linear polymer chain. In a sense, the linear polymer chain serves as a multifunctional core for these dendrons. Dendronized monomers have also been polymerized into dendronized polymers to ensure that an identical dendron is attached to every repeat unit of the resulting polymer.

Kim and collaborators developed a method to grow carbosilane dendrons from a linear carbosilane polymer [38, 188]. This is a unique design as both polymer-core and dendrons have similar chemical compositions. The linear carbosilane polymer ($n \geq 10$) was obtained by the self-hydrosilylation of diphenylallylsilane, following which one or both phenyl rings were displaced by triflic acid in toluene at -78°C :



The triflate is a good leaving group for alkenylation with allylmagnesium bromide. Further construction of the dendronized polymer through reiteration of hydrosilylation and alkenylation reactions led to a linear singly or doubly dendronized polymer with 3G(2,3,3,3) dendrons, each carrying 27 peripheral allyl groups. Analysis of such polymers, however, is difficult as the dendrons and the polymer backbone have the same chemical composition.

Dendronized polysiloxanes with carbosilane dendrons to the second generation (four allyl groups) were prepared from poly(methylhydrosiloxane) [189]:

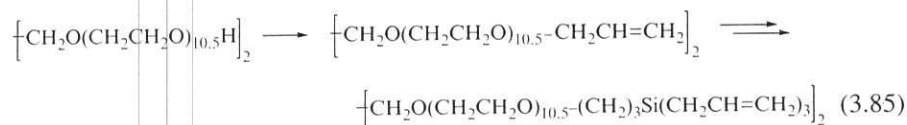


The presence of methyl groups on the polymer backbone is a convenient marker for quantitative ^1H NMR and SEC analyses which can prove the polymer molecular weight integrity. The same poly(methylhydrosiloxane) linear polymer was also dendronized with trichlorosilane and alkenylated with allylmagnesium bromide [190]. The 1G(1,3) dendronization yielded 100% conversion while the 2G(1,3,3) conversion was limited to 84%. Molecular weight and radii of gyration from small angle neutron scattering (SANS) in THF-d_8 were obtained for narrow molecular weight distribution fractions of the linear precursor and the 1G and 2G dendronized polymer. Since dendronization is known to stiffen the linear polymer backbone, the exponent ν in

$$\langle R_g^2 \rangle = K \cdot M_w^{2\nu} \quad (\text{E.3.1})$$

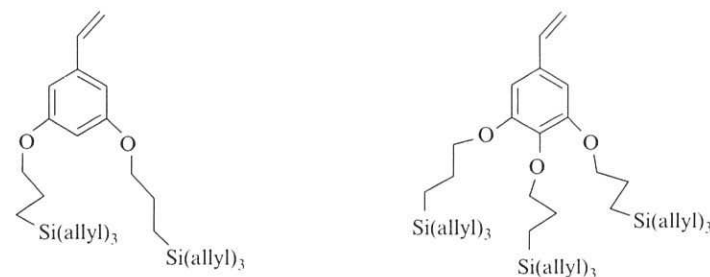
increased from 0.53 (typical for linear polymers in good solvent) to 0.84 and 0.93 for the 1G and 2G dendronized polymers, respectively. Note that the last value was near unity which is characteristic of rod-like polymers. Similarly, the persistence length, a good measure of backbone stiffness, increased from 14 to 44 Å for the 1G and to 200 Å for the 2G dendronized polymer.

Chang and Kim synthesized and characterized a triblock copolymer in which carbosilane dendrons were constructed on the chain-ends of a narrow molecular weight distribution poly(ethylene oxide) (PEO) ($M_w = 1,000$, degree of polymerization (DP) = 22) [191]. The PEO was diallylated and cycles of hydrosilylation with HSiCl_3 and alkenylation with allylmagnesiumbromide were repeated on each end to build 3G(1,3,3,3) dendrons with 27 allyl groups:



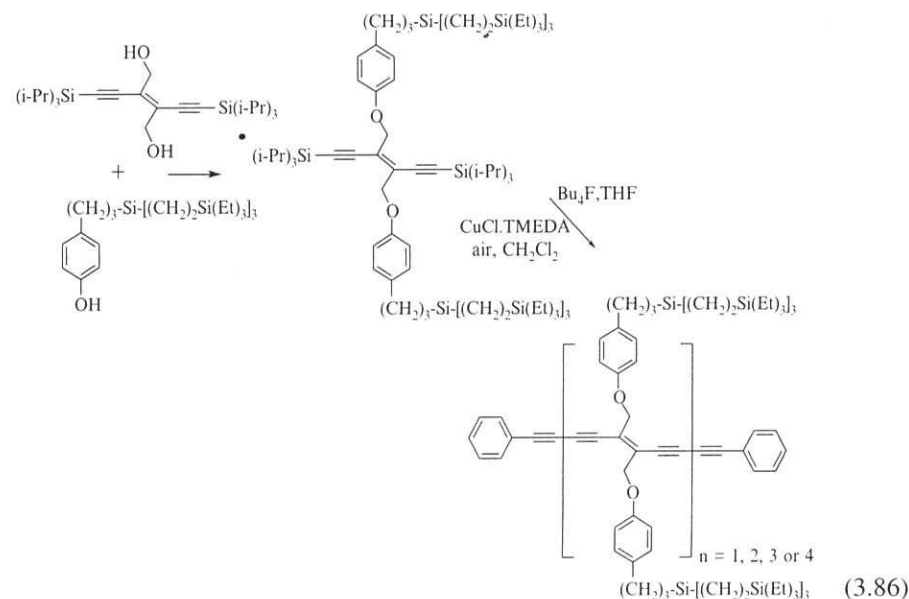
This synthesis offered an excellent opportunity to assess the perfection of the reactions since the 12, 36 and 108 CH_2 hydrogens of the terminal allyl groups in the 1G, 2G and 3G dendrons could be compared to 88 hydrogens of the central polymer chain in the ^1H NMR spectrum. The use of monomolecular PEO would avoid possible changes in these ratios due to potential molecular weight fractionation during the dendron synthesis. MALDI-TOF data confirmed the synthesis, but the polydispersity of the primary chain ($m_0 = 44.05$) made assignments of defects (e.g. missing allyl group, $m_0 = 42.08$) difficult. The absence of coupled products was verified by SEC. These amphiphilic materials – the 3G product had 80% carbosilane content – formed micelles in water. The crystallization/melting behavior of the PEO chains was strongly affected by the increase in dendrimer generation, due to increasing isolation of the PEO chains.

Dendronized polymers can also be obtained by the polymerization of dendronized monomers. Méry et al. described anionic polymerization of 1G carbosilane dendronized styrenics with different multiplicities [192]:



In principle, this method assures structurally perfect polymers with potentially narrow MWD. Best polymerization results have been obtained with potassium naphthalene initiation in THF at -78°C . The propagation step was limited to $\text{DP} \leq 30$ for the bis-substituted monomer, and to $\text{DP} \leq 10$ for the tris-substituted monomer. Steric crowding was presumably responsible for this limitation.

Diederich and his collaborators have decorated a tri(acetylene) monomer ($\text{C}\equiv\text{C} \text{---} \text{CR}=\text{CR} \text{---} \text{C}\equiv\text{C}$) with Fréchet-type polybenzylether dendrimers [193] and with a variety of carbosilane dendrimers. Polymerization of the latter under end-capping conditions with phenylacetylene produced a series of oligomers [119]:



The UV-Vis spectra indicated that insulating dendritic wrapping did not alter the electronic properties of these polyacetylene molecular wires.

3.3 Carbosilane Dendrimer Characterization

The sequence of reactions used in dendrimer synthesis suggests a particular chemical structure that requires verification by analytical methods commonly used in organic chemistry. However, the repeated catenation of "identical" building blocks lends dendrimers a polymeric character, and creates analytical difficulties not otherwise encountered in macromolecules. As a consequence, analytical methods of polymer science with their statistical approach, must often compliment more rigorous methods, especially for high generation dendrimers. The products of the hydrosilylation reaction stage, with their multiple reactive Si-Cl bonds, are not usually analyzed beyond qualitative observation by ^1H NMR that all olefinic double bonds have reacted [21, 24]. Quantitative analysis is, therefore, limited to the carbosilane dendrimer generations with vinyl, allyl or other stable end-groups.

Organic chemistry methods, including elemental analysis and quantitative absorption spectroscopies (UV-Vis, IR), are limited in their capability to confirm dendrimer structures and detect defects because dendrimer compositions tend towards asymptotes with increasing generation. Generally, a property, X_i , associated with one, some or all dendrimer subunits with mass m_i , drifts to a limiting value with increasing generation:

$$\lim_{G \rightarrow \infty} X = (\sum X_i m_i) / (\sum m_i). \quad (\text{E.3.2})$$

For example, elemental composition is often inconclusive since it rapidly approaches its asymptote at generation 2 or 3 as the composition of the core, internal subunits and end-units of carbosilane dendrimers are very similar [24, 28].

Similarly, in quantitative ^1H NMR intensity ratios also tend to asymptotes. A signal associated with the core will tend to zero with increasing generation. In some cases, a marker, such as phenyl groups [39, 60], perylene [35] or a polymer chain attached to the core [191], allows useful comparison of the core and periphery proton signals to higher generations. In all cases, attention to quantitative spectrum acquisition (pulse power, relaxation times and digitalization of signals) is required. Broadening of resonances associated with atoms at or near the core is commonly observed and makes their detection and quantification more difficult. A complete structural analysis of 1G(4,1) and 2G(4,2,1) C_2 carbosilane dendrimers with $-\text{Si}(\text{CH}_3)_2\text{H}$ end-groups was accomplished with a high resolution 600 MHz spectrometer based on the intensity of the Si resonances as the primary assignment and $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$ three-dimensional analysis for full identification of all resonances [81]. A similar study was also made with 1G(4,1) and 2G(4,2,1) C_1 dendrimers with phenyl end-groups [194]. Note that such analysis

remains limited to 2G dendrimers in which the core, first and second generation Si atoms have different substituents. Complete resolution of higher generation dendrimer spectra requires introduction of chemical variation, such as $-\text{Si}(\text{C}_6\text{H}_5)_2$ branch points [39] or $-\text{CH}=\text{CH}(\text{C}_6\text{H}_5)_2$ branches [73].

It has been remarked that ^1H and ^{13}C spectra of carbosilane dendrimers should be clean and not contain *traces* of spurious resonances, the presence of which indicates structural defects. For example, proton resonances at 0.1–0.2 ppm from tetramethylsilane indicate the presence of methoxysilane groups ($\text{CH}_3-\text{O}-\text{Si}-$) originating from the methanolysis of Si-Cl bonds [7, 28]. α -Addition in the hydrosilylation step is most easily recognized by spurious resonances in the ^{13}C spectrum and can be quantified by the doublet at 1.00 ppm assigned to CH_3 protons in $-\text{SiCH}(\text{CH}_3)\text{Si}-$ units [21, 62, 152]. Isomerization of the allylic double bond has been observed under some hydrosilylation conditions. The resulting propenyl group is then immune to further hydrosilylation [119].

Fast atom bombardment mass spectroscopy (FAB-MS) is the most commonly used method for identification of low molecular mass (0G–2G) carbosilane dendrimers [49, 166, 195]. A careful study of the fragmentation products is required in order to identify possible incomplete dendritic compounds [48]. Electron spray ionization (ESI) mass spectroscopy [83] and atmospheric pressure chemical ionization (APCI) mass spectroscopy [80] have also been used.

Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectroscopy has proven ideally suited for the analysis of high molecular mass carbosilane dendrimers and their derivatives because of its mass range and resolution. Under ideal conditions, the mass spectra consist exclusively of positively ionized parent species: $[\text{M}^+]$, $[\text{M} + \text{Na}]^+$, $[\text{M} + \text{Ag}]^+$ etc. dependent on the added salt. The first published MALDI-TOF data probed the perfection of 2G(4,3,3) and 3G(4,3,3,3) carbosilane dendrimers with allyl terminal groups. In the 2G dendrimer, two species were observed, one with the expected 36 allyl groups and the other with 34 allyl groups [M-152], which corresponded to one defect in the hydrosilylation step. In the 3G dendrimer about ten species were observed. They were spaced by 152 mass units down from the perfect dendrimer with 108 allyl groups. From random probability considerations [62, 196] it was concluded that the hydrosilylation reactions were 97.3% and 96.6% complete for the 2G and 3G dendrimers, respectively [22, 143]. The defective species had therefore a kinetic rather than thermodynamic origin. These results were further confirmed by the MALDI-TOF spectra of the hydroxypropyl derivatives. Beside the perfect structure, species from one and two missing hydrosilylation reactions (out of a possible 32) were also observed at the 3G level in dendrimers with $\text{Si}(\text{Me})(\text{Bz})_2$ end-groups [83].

Allgaier et al., on the other hand, concluded that the pairwise reduction in the number of end-groups was due to the incorporation of ethyl end-groups into the dendrimer, as a result of the use of vinylbromide contaminated with 1% ethylbromide in the alkenylation step [19]. Mass spectra with identified masses of dendrimers with 14, 15 and the correct 16 PPh_2 groups were also observed [197]. In another example, the product of the hydrosilylation reaction had 15 out of 16 bent mesogens, the remaining Si-H of the dendrimer being converted with methanol into SiOMe

during chromatographic purification [158]. In principle, lower mass ions that are due to defects caused during the synthesis should differ from the parent ion by multiples of the monomer mass. Their relative intensity should follow statistical rules [196].

Instructions for obtaining MALDI-TOF spectra of carbosilane dendrimers with multiple polar end-groups were given [62, 198]. Fragmentation processes are rare but tend to become more frequent in the spectra of high generation dendrimers and dendrimers with large polar substituents [62, 97, 114, 199]. In most cases, fragmentation occurs in the substituents and, therefore, does not disprove the integrity of the carbosilane dendrimer skeleton. Occasionally, ions are observed that seem to arise from the loss of $(\text{Me})_2\text{Si} = \text{CHCl}$ and $\text{CH}_3\text{CH}_2\text{Si}(\text{Me})_2\text{CH}_2\text{Cl}$ which suggests true fragmentation at the C–Si bond of the dendrimer but may also be evidence for incomplete dendrimer construction [62]. Missing allyl groups have also been reported [45]. In such cases recourse to evidence from ^1H NMR or other analytical method may be required to decide the case. Compared to synthetic defects, fragmentation products are expected to exhibit a more random relative intensity distribution that can be manipulated by changing parameters of the spectroscopy.

Size exclusion chromatography (SEC) fractionates samples according to their hydrodynamic volume but does not provide the high resolution of the MALDI-TOF technique. The elution trace of a high quality carbosilane dendrimer should be narrow and result in a small apparent polydispersity index that essentially measures the axial dispersion of the chromatographic system at the size of the dendrimer. In all cases this polydispersity will be narrower than that of the best narrow-distribution polymer from a living polymerization. SEC is commonly used to qualitatively assess the monodispersity of carbosilane dendrimers. It is most useful for quick detection of higher and much lower molecular mass species [60, 73]. The presence of higher molecular mass species (dendrimer dimers, trimers and/or multiplets) is most likely due to trace hydrolysis (with formation of intermolecular Si–O–Si bonds) at the intermediate Si–Cl rich stage of the synthesis [19, 97]. This result also suggests simultaneous intramolecular hydrolysis that is nearly impossible to detect at low levels. Flash chromatography on silica gel is the standard purification method [7, 20] but preparative SEC has also been used to purify carbosilane dendrimers [60]. Ultimately, combined NMR and MALDI-TOF analyses are the best way to prove the structure of the purified dendrimer.

In principle, the universal calibration of SEC applies to carbosilane dendrimers, i.e. the elution volume depends on the product $M[\eta]$ where the standard calibrant is polystyrene [7]. The only exception to this appears to be dendrimers with perfluoro end-groups where clear deviations from universal calibration were observed [123].

3.4 Properties of Carbosilane Dendrimers

3.4.1 Molecular Dimensions of Carbosilane Dendrimers

The molecular size of dendrimers, including carbosilanes, places them at the lower end of the nanoscopic size domain (see Chapter 1). While much research has been

Table 3.2 Core-to-periphery dimensions of carbosilane dendrimers (nm)^a

Generation	C ₃ – allyl end-groups	C ₂ – vinyl end-groups
0G Tetraallylsilane	0.395	
Tetravinylsilane		0.276
1G	0.95	0.70
2G	1.50	1.13
3G	2.06	1.56
4G	2.61	1.99
5G	3.17	2.41
6G	3.72	2.84
7G	4.27	3.27

^aValues are calculated assuming fully stretched all-trans configurations.

devoted to the synthesis and functionalization of carbosilane dendrimers, the study of their physical properties has considerably lagged behind. However, the general knowledge (although still somewhat controversial) about size, conformation, density profiles and dynamics of other types of dendrimers should, properly adjusted, also be applicable to carbosilanes. Table 3.2 lists the core-to-periphery distances of the fully stretched all-trans configurations of single arms of the two common types of carbosilane dendrimers [9, 190]. These calculated lengths are based on tetrahedral (109.5°) bond angles and on 0.154 nm C–C and 0.185 nm C–Si bond lengths.

The obtained dimensions are equivalent to the contour lengths of linear polymer chains and can be compared to the crystallite lengths per backbone carbon (0.126 nm) in aliphatic chains. Note that the core-to-periphery is the largest dimension in the dendrimer that is independent of the core and branch functionalities. Clearly, most real core-to-periphery distances in dendrimers are reduced by one or more \pm gauche configurations at the branch points and in the branches. Experimentally measured dimensions, like the radius of gyration, R_g , from small angle X-ray scattering (SAXS) or small angle neutron scattering (SANS), or the hydrodynamic radius, R_H , from self-diffusion, or R_v from intrinsic viscosity measurements, are therefore considerably smaller.

Radii of gyration of a number of carbosilane dendrimers in solution have been determined by SAXS or SANS [200–202]. The scattering profiles (scattering intensities as a function of scattering vector q or angular dependence) were matched to different particle models. It was concluded that some anisotropy was present, as well as some local density variations [202]. No observable solvent effects (in benzene, chloroform) were detected. Experimental R_g data are collected in Table 3.3.

Based on $R_H = (5/3)^{1/2} R_g$, the internal mass density of carbosilane dendrimers in solution was determined to be of the order of 0.6–0.7 g/cm³ [200], a value later corrected to 0.7–0.8 g/cm³ [202]. In the case of a peripherally substituted trifluoropropyl dendrimer, indirect evidence indicates that peripheral Si–O–Si(CH₂CH₂CF₃)₃ groups reside mostly in the corona [200]. This may be due to the chemical contrast

Table 3.3 Experimental dimensions of C₃ carbosilane dendrimers in solution (nm)

Sample	MW ^a	R _g ^b	D ₀ ^c	R _h	[η] ^d	R _v
5G(3,2,...)-allyl	11,971	1.4	3.04	1.43		
6G(3,2,...)-allyl	24,093	1.9	2.28	1.89		
7G(3,2,...)-allyl	48,337	2.3	1.74	2.46		
1G(4,2,...)-allyl	696		4.5 ^e	0.89	—	—
2G(4,2,...)-allyl	1,704		3.6 ^e	1.12	3.0	0.93
3G(4,2,...)-allyl	3,720		2.9 ^e	1.38	3.7	1.30
4G(4,2,...)-allyl	7,752		2.2 ^e	1.89	3.5	1.63
3G(3,2,...)-butyl	3,315		2.18 ^f	0.99		
4G(3,2,...)-butyl	6,705		1.82 ^f	1.19		
5G(3,2,...)-butyl	13,539		1.49 ^f	1.45		
3G(4,2,...)-butyl	4,299		4.3	1.0	3.6 ^g	1.36
4G(4,2,...)-butyl	8,946		3.3	1.3	4.0 ^g	1.78
5G(4,2,...)-butyl	17,906	2.0	2.55	1.7	4.2 ^g	2.28
6G(4,2,...)-butyl	36,122	2.5	2.07	2.1	3.6 ^g	2.74
7G(4,2,...)-butyl	72,554	3.0	1.70	2.5	4.6 ^g	3.75
8G(4,2,...)-butyl	145,421				3.8 ^g	4.44
9G(4,2,...)-butyl	291,155 ^h				4.3 ^g	5.83

^aCalculated molecular weight.

^bIn C₆D₆ and CDCl₃ from Figure 5 of [200], Table 1 and Figure 5 of [201] and table of [202].

^c10⁶ cm²/s in CDCl₃ at 303 K from Figure 7 of [208] and Figure 18 of [207].

^dcm³/g in CHCl₃ at 294 K from table of [210].

^eIn CHCl₃ at 298 K from table of [210].

^fIn CCl₄ at 293 K from Figure 2 of [209].

^gIn toluene [69].

^hMW = 295,600 by light scattering (LS) in toluene [69].

between the peripheral groups and the dendrimer core which may have led to an enthalpically driven internal microphase separation. A similar conclusion was also drawn from SANS data [203].

A molecular dynamics simulation did not directly assess the dimensions of carbosilane dendrimers but probed the size of the internal cavity as a function of the branch length of the 0G shell and its accessibility for different size molecules through the corona [204]. For a 5G(3,2,2,2,2,3) dendrimer with C₃ branches and terminal methyl groups (M_w = 9,373) in CCl₄ this yielded R_g = 1.65 nm [205, 206]. The radial density had a maximum at the core, a plateau of 0.6 g/cm³ between r = 0.5 and 1.3 nm and a tail reaching to r = 2.6 nm which was slightly less than the core-to-periphery distance of 2.9 nm estimated for a fifth generation dendrimer with methyl end-groups. Although the methyl groups were found mostly in the peripheral zone (1.6–2.6 nm), some were found in all regions of the structure as a result of backfolding of the branches. Zhang et al. performed molecular dynamics simulations on 2G(8,3,n) dendrimers with n = 1, 2 or 3 hydroxypropyl terminal groups [30]. They found that the large octafunctional core promoted a small asymmetry

(less than 1.15), and noted that hydroxyl groups were found in all parts of the dendrimer with R_g = 0.97, 1.02 and 1.08 nm for n = 1, 2 and 3, in agreement with increasing number of hydroxypropyl groups.

Self-diffusion and intrinsic viscosity measurements allow determination of an equivalent-sphere hydrodynamic radius via the Stokes-Einstein and Einstein relations, respectively:

$$R_H = kT/6\pi\eta_s D_0 \quad (\text{E.3.3})$$

and

$$R_v = \{3[\eta]M/10\pi N_A\}^{1/3} \quad (\text{E.3.4})$$

For equal density spheres, which is a good approximation for high generation dendrimers, R_H ≈ R_v = (5/3)^{1/2} R_g is expected. The self-diffusion coefficient, D₀, was measured by Pulsed-Field Gradient NMR in either chloroform [207, 208] or carbon tetrachloride [209]. The data and corresponding R_H values are collected in Table 3.3. The R_H data are internally consistent; for example, 5G(3,2,2,2,2)-allyl and 5G(3,2,2,2,2)-butyl have approximately the same dimensions, while all butyl dendrimers with a trifunctional core are slightly smaller than the same generation butyl dendrimers with a tetrafunctional core. Unfortunately, comparison of R_H with R_g, where possible, is less satisfactory. Hydrodynamic radii (R_v), based on intrinsic viscosity measurements of the first four generations of dendrimers with tetrafunctional cores, C₃ branches and allyl end-groups are also given in Table 3.3 [210]. R_v values of the corresponding dendrimers with tetrafunctional cores, C₂ branches and vinyl end-groups are 1G (M_w = 528) 0.48, 2G (M_w = 1,312) 0.74, 3G (M_w = 2,880) 1.06 and 4G (M_w = 6,016) 1.48 nm, respectively [7]. Therefore, the C₂ dendrimers are smaller than C₃ dendrimers and all radii are less than the calculated core-to-periphery lengths of Table 3.2. It should be noted that there is no evidence that generational evolution of intrinsic viscosities of carbosilane dendrimers shows a maximum as reported for polyamidoamine, PAMAM, and benzylether dendrimer series [211, 212]. Indeed, where data are available, the experimental radii scale approximately as M^{1/3} indicating that internal density of the dendrimers is little changed with generation number. The spherical nature and relatively constant density of carbosilane dendrimers, even at low generations, have also been deduced from molecular mechanics simulations [213].

Other studies of dimensions were performed on highly functionalized carbosilane dendrimers. In these cases, the properties tend to be dominated by the large mass of the peripheral groups and their individual and collective properties. In many cases, microphase separation is observed [214]. In one interesting analysis, the thickness of the corona of mesogenic groups was estimated by subtracting the experimental radius of the carbosilane core from the overall dendrimer radius [210, 215]. On the assumption that the presence of the corona had no effect on the dendritic core size it was concluded that the corona density was about one half that of the dendrimer proper.

3.4.2 Dynamics of Carbosilane Dendrimers

Carbosilane dendrimers are very flexible molecules as indicated by their low glass transition temperatures (T_g). The most extensive measurements were reported by Lebedev et al. on C_3 dendrimers by means of adiabatic vacuum calorimetry [216–219]. The data obtained are collected in Table 3.4.

The glass transition region was about 10 K wide and the ΔC_p ($\text{JK}^{-1} \text{mol}^{-1}$) was proportional to the molecular weight. Previous differential scanning calorimetry (DSC) determinations of T_g gave similar results for 3G to 7G dendrimers [11]. A T_g of 175 K was originally obtained for a 3G(1,2,2,2)-allyl dendrimer with a perylene core [35]. The 1G dendrimer of each series had a somewhat lower T_g , but the T_g of the higher generation dendrimers became rapidly constant. The dendrimers with multiplicity 3 [22, 139] had a 10 K higher T_g than the corresponding dendrimers with multiplicity 2. Most importantly, T_g was strongly affected by the end-groups of the dendrimer. As seen from Table 3.4, the T_g of the dendrimers with butyl end-groups [219] was about 10 K higher than the T_g of dendrimers with allyl end-groups, despite their lower core multiplicity [216–218]. Larger differences were observed when the end-groups were changed to hydroxyl groups. Polyols 1G(4,3), 2G(4,3,3) and 3G(4,3,3,3) had T_g of 233, 239 and 241 K, respectively, 50–60 K higher than the parent dendrimers with allyl end-groups [22, 139]. This large difference was ascribed to hydrogen bonding of the hydroxyl groups. All carbosilane dendrimers functionalized by multiple large substituents had T_g s that were mostly determined by the thermal properties of their substituents. In no case have two glass transitions been observed in calorimetric measurements.

A single T_g , related to both components, was also observed in carbosilane–dendrimer hybrids. For example, the T_g of poly(methylsiloxane) is 129 K, but it increased to 179 K when dendronized by 0G(3)-allyl groups and to 205 K when

Table 3.4 Glass transition temperatures of C_3 carbosilane dendrimers

Dendrimer	T_g/K	Reference
1G(4,2)-allyl	154	[216, 217]
2G(4,2,2)-allyl	172	
3G(4,2,2,2)-allyl	173	[218]
4G(4,2,2,2,2)-allyl	172	
5G(4,2,2,2,2,2)-allyl	162	
6G(4,2,2,2,2,2,2)-allyl	180	
7G(4,2,2,2,2,2,2,2)-allyl	181	[139]
1G(4,3)-allyl	170	
2G(4,3,3)-allyl	184	[22, 139]
3G(4,3,3,3)-allyl	188	
3G(3,2,2,2)-butyl	179.8	[219]
4G(3,2,2,2,2)-butyl	186	
5G(3,2,2,2,2,2)-butyl	186	
6G(3,2,2,2,2,2,2)-butyl	186	

dendronized by 1G(3,3)-allyl [190]. When dendronizing polystyrene oligomers, carbosilane dendrons had the opposite effect and lowered the T_g [192]. Polystyrene ($T_g \approx 343 \text{ K}$) dendronized with a 0G3,5-di-(γ -triallylsilyl)propyloxy groups had a T_g of 243 K and when dendronized with 0G3,4,5-tri-(γ -triallylsilyl)propyloxy groups T_g dropped to 223 K. Such changes were qualitatively explained by the weighted molecular mixing of components with low (carbosilane) and high (polystyrene) T_g s. Clearly, the available data were insufficient to establish a mixing rule [220] and to recognize more specific effects due to dendron structure.

The melting temperature, T_m , of poly(ethylene oxide) dendronized at both ends with carbosilane dendrons decreased from 317 K to 307, 273 and 260 K for generation OG, 1G and 2G, respectively [191]. This change was not correlated with lamellar thicknesses of the crystallites.

Dynamic mechanical spectra of carbosilane dendrimers (20% in an immiscible polystyrene matrix) revealed a strong loss peak at about 210 K (at 150 Hz) with a large Vogel-Fulcher type activation energy assigned to the α (T_g) transition in agreement with a T_g of 175 K by DSC. A weaker relaxation process was observed at 165 K (at 150 Hz) with an Arrhenius-type activation energy dependence. No specific molecular process was assigned to this β relaxation, but it was observed that incorporation of *n*-decyl end-groups shifted the relaxation to lower temperatures [221]. Both signals had a dielectric counterpart. Merger of the dielectric α - and β -processes has also been suggested [222].

High resolution NMR spectra obtained on 600 MHz instruments provided sufficient resolution to resolve all resonances in 1G(4,1) and 2G(4,2,1) C_3 dendrimers with phenolic end-groups [194] and 1G(4,1) and 2G(4,2,1) C_2 dendrimers with $\text{Si}(\text{CH}_3)_2\text{H}$ end-groups [81]. All resonances were assigned by means of their generational intensities and via two-dimensional $^1\text{H}/^{13}\text{C}$ analysis [194] or three-dimensional $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$ analysis [81]. An investigation of the T_1 spin lattice relaxation times in toluene- d_8 showed that T_1 increased with the radial distance of the atom from the core. The slower average motions experienced by the atoms near the core were possibly due to the higher density in the core [194]. It is not established that this conclusion is general or that it depends on the quality of the solvent. Nevertheless, a similar conclusion was also reached in a T_1 study of poly(propylene imine) dendrimers [223].

In favorable cases, the spin echo technique of quasi-elastic neutron scattering (NSE) has allowed probing internal (segmental) dynamics of polymers and this method was, therefore, also applied to some carbosilane dendrimers with perfluoro- $-\text{SCH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ end-groups [214]. In the case of 1G(4,3), 2G(4,3,3) and 3G(4,3,3,3) dendrimers, the available q and time ranges were such that only center of mass diffusion was observed. This is in agreement with observations on bare PAMAM dendrimers in which no internal motions were detected by NSE [224]. In one particularly large 4G dendrimer ($R_g = 2.7 \text{ nm}$, $R_H = 4.9 \text{ nm}$) with an extended core and 324 (theoretical) perfluoro end-groups, additional relaxation processes were also observed. Since the maximum of the effective diffusion coefficient $D_{\text{eff}} = (\tau q^2)^{-1}$ coincided with the minimum in the structure factor in the Kratky representation ($S(q) = I'q^2$) it was argued that the additional processes involved shape changes on

the surface of the dendrimer [214], but it could not be excluded that internal density fluctuations were responsible [225]. Introduction of long chains between branch points was required to make internal motions observable [225].

Molecular dynamics simulations are a natural tool to probe intramolecular mobility of carbosilane dendrimers. Mazo et al. have shown that a one-barrier mechanism with an activation energy that does not exceed that of the isolated local environment governs the conformational transition between *trans* and *gauche* conformers [205]. It was shown that, in good solvents, the frequency of the transitions was only mildly dependent on the radial position of the bond [206]. In poor solvents, where the internal density approached the bulk density, the end-groups were clearly more mobile than internal ones. The effect of temperature decrease was most prominent in poor solvents as all transitions were frozen out and fluctuations became local – a signature of the liquid-to-glass conversion.

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Chapter 4

Polysilane Dendrimers

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4.1 Introduction

Polysilanes, $-(Si)_n-$, are polymers that contain catenated silicon atoms, and their chemistry has attracted considerable interest during the last 30 years because of their electronic, optical, structural, and chemical properties [1]. In particular, the σ -conjugation of the $-Si-Si-$ backbone has attracted much attention compared with analogous carbon polymer systems. Although, in contrast to the numerous reports on polysilanes with linear main chains, little attention has been devoted to their branched counterparts; hyperbranched polysilanes [2], ladder polysilanes [3], and organosilicon nanoclusters [4] have nevertheless been described. However, with the exception of ladder polysilanes, the precise structures of these branched polymers have not been sufficiently elucidated. This chapter deals with polysilane dendrimers from the initial [6] to the most recent report [20]. These dendrimers, which contain silicon atoms attached to three or four other silicon atoms, exhibit some interesting properties compared with their linear homologues [5]. As in other chapters of this book, the “1G(4,3) end-group” nomenclature system (see Fig. 4.1) is used. In this system, 1G denotes generation 1, the first number in parentheses denotes the branching functionality of the core (in this example a tetradendron dendrimer with first digit 4); the following superscript represents the number of spacer silicon atoms between the core and the next branching point; the following numbers represent functionalities of the silicon atoms in each subsequent generational layer; and finally the end-groups are specified by their chemical formulas.

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