Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 4511–4519 **4511**
DOI: 10.1021/ma100315w

Structural Defects in Polyallylcarbosilane Dendrimers and Their Polyol Derivatives Characterized by NMR and MALDI-TOF Mass Spectrometry

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Received February 8, 2010; Revised Manuscript Received April 8, 2010

ABSTRACT: A series of polyallylcarbosilane dendrimers and carbosilane-based dendritic polyols up to third generation was analyzed by means of matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and multinuclear NMR spectroscopy to determine the character, origin, and number of structural defects. Besides occasionally reported α-hydrosilylation, several side reactions accompanying hydrosilylation, such as isomerization of terminal double bonds, were detected during the synthesis of carbosilane skeleton. Despite increased steric hindrance, internal double bonds react in subsequent addition reactions. Depending on the synthetic sequence applied, the retained reactivity of the internal double bonds can lead either to suppression of the defect in the next generation or to creation of more significant defects such as dendrimer dimers. Hydroboration of allyl groups using dicyclohexylborane proceeded with near quantitative conversion; a small amount of hydrolysis accompanying the following oxidation step producing nonreactive alkyl groups at the periphery was detected.

Introduction

Since their first synthesis in 1992,[1] carbosilane dendrimers have gained considerable attention because of their unique properties.[2] Nonpolar, highly flexible, and both chemically and thermally stable skeleton together with variability of the synthetic pathway and ease of peripheral functionalization make them suitable for many applications ranging from catalysis[3] to receptors and biomedicine.[4] However, despite numerous papers on the preparation and functionalization of carbosilane dendrimers, detailed information on the synthesis of the polyvinylcarbosilane or polyallylcarbosilane skeleton itself is scarce.[5,6] This applies even more to the full-scale characterization of products[7,8] that could disclose the character and extent of possible structural defects. These can vary in their impact ranging from small disturbance of the uniform structure to detrimental effect on polydispersity due to interference of the defect structure in subsequent reaction steps.

Carbosilane dendrimers are typically prepared via divergent approach, starting from a suitable core and growing the molecule outward by alternation of hydrosilylation of double bonds with chlorosilanes and nucleophilic substitution of chlorine with alkenylmagnesium halides.[2] Because the divergent synthesis leaves little space for the purification of products, high selectivity and quantitative conversion of each iteration step is needed.[9] In particular, hydrosilylation, which is known to be accompanied by various types of side reactions and to be highly sensitive to reagents and conditions applied,[10] requires careful optimization for each particular combination of silane and olefin type. For the development of the synthetic protocol, understanding of processes accompanying the reactions employed is crucial. For polyvinylcarbosilanes, several possible sources of defects were identified, such as α-hydrosilylation of the vinyl group leading to branched alkyl spacers in the structure[6] and "deactivation" of the branch by introducing ethyl instead of vinyl moiety during the reaction with Grignard reagent prepared from vinylbromide contaminated with ethylbromide.[8] For polyallylcarbosilanes, no specific defects were described; imperfect structures present in the published matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were ascribed to incomplete hydrosilylation.[7]

We have recently constructed a theoretical model of dendrimer formation to compare MALDI-TOF mass spectra of a small family of polyallylcarbosilane dendrimers with predicted values and thus confirm the validity of quantitative interpretation of MS data for dendrimers.[11] In this article, we present both qualitative and quantitative analysis of the MALDI-TOF mass spectra of two sets of polyallylcarbosilane dendrimers built on tetraallylsilane core and their polyol derivatives together with NMR characterization of the defect structures and the consideration of possible consequences these defects can have in the synthesis of more elaborated structures.

Experimental Section

General. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Diethyl ether was distilled from the solution of sodium benzophenone ketyl and stored under nitrogen. Borane−dimethylsulfide complex and cyclohexene were purchased from Aldrich and used without further purification. Functionalized dendrimers 2G-SiH_8[6,12] and 2G-$ArOH_8$[13] were prepared according to previously published methods. ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ (INEPT)

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Published on Web 04/22/2010

spectra were measured at 25 °C in $CDCl_3$ on Varian Mercury 300 spectrometer at 299.98, 75.44, and 59.60 MHz, respectively. Chemical shifts are reported in ppm relative to TMS and referenced to internal standard hexamethyldisilane (^1H, ^{29}Si) or residual solvent peak (^{13}C). Silicon atoms are numbered in ascending order from the core (Si^0) to the periphery, and carbon atoms are labeled according to generation (C^n stands for spacer atoms between Si^n and Si^{n+1}).

MALDI-TOF MS. The samples were prepared by the dried droplet method: tetrahydrofuran (THF) solutions of the dendrimer (10 mg/mL), matrix (anthracene-1,8,9-triol; 20 mg/mL), and ionizing agent (silver trifluoroacetate for polyallylcarbosilanes, sodium trifluoroacetate for polyols, 10 mg/mL) were mixed in the volume ratio 4:20:1, and 0.5 to 1 μL of the mixture was deposited on the target plate. MALDI TOF MS spectra were acquired with a Biflex III mass spectrometer (Bruker Daltonics) in the positive ion reflectron mode using delayed extraction and accelerating voltage 19 kV. The spectra were summed over 500 shots with a N_2 laser emitting at 337 nm and consisted of peaks from singly charged ions only because the spacing between adjacent isotopic peaks in all isotopic clusters was ~1 Da. The values of m/z were assigned using the external calibration with poly(ethylene glycol); no internal recalibration was applied.

Preparation of Polyallylcarbosilane Dendrimers. Polyallylcarbosilane dendrimers were prepared by standard iterative procedure starting from tetraallylsilane as a core and alternating hydrosilylation of double bonds with either dichloromethylsilane or chlorodimethylsilane in the presence of Karstedt catalyst and nucleophilic displacement of chlorine by allylmagnesium bromide. The procedure was optimized on the basis of previously published methods.[1,5,6] To our knowledge, spectroscopic data for only some of the lower generation dendrimers of these structural types are available in literature,[12,14] so we include here full characterization for the whole series of structures prepared.

1G-Cl_8. ^1H NMR: δ 0.69 (m, 8H, CH_2Si^0); 0.78 (s, 12H, CH_3Si^1); 1.20 (t, $^3J_{HH}$ = 7.9 Hz, 8H, CH_2Si^1); 1.55 (m, 8H, $Si^0CH_2CH_2CH_2Si^1$). ^{13}C NMR: δ 5.4 (CH_3Si^1); 15.8 (CH_2Si^0); 17.3 ($CH_2CH_2CH_2$); 25.9 (CH_2Si^1). ^{29}Si NMR: δ 1.50 (Si^0); 32.04 (Si^1).

1G-$Allyl_8$. ^1H NMR: δ −0.01 (s, 12H, CH_3Si^1); 0.55 (m, 8H, CH_2Si^0); 0.63 (m, 8H, $CH_2CH_2Si^1$); 1.33 (m, 8H, $Si^0CH_2CH_2CH_2Si^1$); 1.55 (ddd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.3 Hz, $^4J_{HH}$ = 0.9 Hz, 16H, CH_2CH=); 4.84 (tdd, $^3J_{HH}$ = 10.0 Hz, $^2J_{HH}$ = 2.1 Hz, $^4J_{HH}$ = 0.9 Hz, 8H, =HC$H_{cis\text{-}H}$); 4.86 (tdd, $^3J_{HH}$ = 16.8 Hz, $^2J_{HH}$ = 2.1 Hz, $^4J_{HH}$ = 1.3 Hz, 8H, =HC$H_{trans\text{-}H}$); 5.78 (tdd, $^3J_{HH}$ = 16.8 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 8.1 Hz, 8H, =CH−). ^{13}C NMR: δ −5.8 (CH_3Si^1); 17.5 (C^0); 18.1 (C^0); 18.4 (C^0); 21.5 (CH_2CH=); 113.1 (=CH_2); 134.8 (=CH−). ^{29}Si NMR: δ 0.19 (Si^1); 0.57 (Si^0). MALDI-TOF MS: m/z 803.16; calcd m/z 803.32 ($(M+Ag)^+$; monoisotopic values).

2G-Cl_{16}. ^1H NMR: δ −0.02 (s, 12H, CH_3Si^1); 0.61 (m, 32H, $CH_2Si^{0,1}$); 0.77 (s, 24H, CH_3Si^2); 1.18 (m, 16H, CH_2Si^2); 1.31 (m, 8H, $Si^0CH_2CH_2CH_2Si^1$); 1.54 (m, 16H, $Si^1CH_2CH_2CH_2Si^2$). ^{13}C NMR: δ −5.1 (CH_3Si^1); 5.5 (CH_3Si^2); 17.3 (C^1); 17.5 (C^1); 17.6 (C^0); 18.5 (C^0); 18.8 (C^0); 25.9 (CH_2Si^2). ^{29}Si NMR: δ 0.53 (Si^0); 1.46 (Si^1); 32.15 (Si^2).

2G-$Allyl_{16}$. ^1H NMR: δ −0.07 (s, 12H, CH_3Si^1); −0.01 (s, 24H, CH_3Si^2); 0.59 (m, 48H, $CH_2Si^{0,1,2}$); 1.34 (m, 24H, $Si^{0,1}CH_2CH_2CH_2Si^{1,2}$); 1.55 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 0.9 Hz, 32H, CH_2CH=); 4.84 (m, 16H, =HC$H_{cis\text{-}H}$); 4.85 (m, 16H, =HC$H_{trans\text{-}H}$); 5.78 (tdd, $^3J_{HH}$ = 16.7 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 8.2 Hz, 16H, =CH−). ^{13}C NMR: δ −5.7 (CH_3Si^2); −5.0 (CH_3Si^1); 17.7 (C^0); 18.0 (C^1); 18.2 (C^1); 18.6 (C^0); 18.8 (C^1); 19.1 (C^0); 21.5 (CH_2CH=); 113.0 (=CH_2); 134.8 (=CH−). ^{29}Si NMR: δ 0.46 (Si^0); 0.24 (Si^2); 0.98 (Si^1). MALDI-TOF MS: m/z 1811.94; calcd m/z 1812.07 ($(M+Ag)^+$; monoisotopic values).

2G-Cl_8. ^1H NMR: δ −0.05 (s,12H, CH_3Si^1); 0.40 (s, 48H, CH_3Si^2); 0.57 (m, 32H, $CH_2Si^{0,1}$); 0.89 (m, 16H, CH_2Si^2); 1.30 (m, 8H, $Si^0CH_2CH_2CH_2Si^1$); 1.45 (m, 16H, $Si^1CH_2CH_2CH_2Si^2$). ^{13}C NMR: δ −5.0 (CH_3Si^1); 1.9 (CH_3Si^2); 17.6 (C^0); 17.7 (C^1); 18.1 (C^1); 18.6 (C^0); 19.0 (C^0); 23.5 (CH_2Si^2). ^{29}Si NMR: δ 0.53 (Si^0); 1.24 (Si^1); 31.16 (Si^2).

2G-$Allyl_8$. ^1H NMR: δ −0.07 (s, 12H, CH_3Si^1); −0.02 (s, 48H, CH_3Si^2); 0.57 (m, 48H, $CH_2Si^{0,1,2}$); 1.33 (m, 24H, $Si^{0,1}CH_2CH_2CH_2Si^{1,2}$); 1.51 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 1.2 Hz, 16H, CH_2CH=), 4.81 (m, 8H, =HC$H_{cis\text{-}H}$); 4.83 (m, 8H, =HC$H_{trans\text{-}H}$); 5.77 (tdd, $^3J_{HH}$ = 16.7 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 8.2 Hz, 8H, =CH−). ^{13}C NMR: δ −4.9 (CH_3Si^1); −3.6 (CH_3Si^2); 17.7 (C^0); 18.4 (C^1); 18.6 (C^0); 18.8 (C^1); 19.2 (C^0); 19.7 (C^1); 23.4 (CH_2CH=); 112.6 (=CH_2); 135.2 (=CH−). ^{29}Si NMR: δ 0.52 (Si^0); 0.70 (Si^2); 0.99 (Si^1). MALDI-TOF MS: m/z 1603.73; calcd m/z 1603.95 ($(M+Ag)^+$; monoisotopic values).

3G-Cl_{16}. ^1H NMR: δ −0.07 (s, 12H, CH_3Si^1); −0.04 (s, 24H, CH_3Si^2); 0.40 (s, 96H, CH_3Si^3); 0.57 (m, 80H, $CH_2Si^{0,1,2}$); 0.89 (m, 32H, CH_2Si^3); 1.31 (m, 24H, $Si^{0,1}CH_2CH_2CH_2Si^{1,2}$); 1.45 (m, 32H, $Si^2CH_2CH_2CH_2Si^3$). ^{13}C NMR: δ −5.0 ($CH_3Si^{1,2}$); 1.9 (CH_3Si^3); 17.7 (C^2); 18.1 (C^2); 18.4 (C^0); 18.5 (C^1); 18.6 (C^0); 18.8 (C^1); 18.9 (C^1); 19.2 (C^0); 23.5 (CH_2Si^2). ^{29}Si NMR: δ 0.52 (Si^0); 0.96 (Si^1); 1.27 (Si^2); 31.09 (Si^3).

3G-$Allyl_{16}$. ^1H NMR: δ −0.07 (s, 36H, $CH_3Si^{1,2}$); −0.02 (s, 96H, CH_3Si^3); 0.57 (m, 112H, $CH_2Si^{0,1,2,3}$); 1.32 (m, 56H, $Si^{0,1,2}CH_2CH_2CH_2Si^{1,2,3}$); 1.51 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 1.2 Hz, 32H, CH_2CH=), 4.82 (m, 16H, =HC$H_{cis\text{-}H}$); 4.84 (m, 16H, =HC$H_{trans\text{-}H}$); 5.77 (tdd, $^3J_{HH}$ = 16.6 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 8.2 Hz, 16H, =CH−). ^{13}C NMR: δ −5.0 (CH_3Si^1); −4.9 (CH_3Si^2); −3.6 (CH_3Si^3); 18.3 (C^2); 18.6 (C^1); 18.8 (C^2); 18.9 (C^1); 19.0 (C^1); 19.7 (C^2); 23.4 (CH_2CH=); 112.6 (=CH_2); 135.2 (=CH−); C^0 carbon peaks are too weak for proper assignment. ^{29}Si NMR: δ 0.43 (Si^0); 0.70 (Si^3); 0.94 (Si^1); 1.02 (Si^2). MALDI-TOF MS: m/z 3418.87; calcd m/z 3419.29 $(M+Ag)^+$.

Preparation of 2G-OH_8. Borane−dimethylsulfide complex solution (3.60 mL of 2 M solution in diethylether, 7.20 mmol) was diluted with diethylether (15 mL) and cooled to −10 °C. A solution of cyclohexene (1.18 g, 14.4 mmol) in diethylether (5 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature with simultaneous stirring until the white precipitate of dicyclohexylborane appeared (1 h). The suspension was then cooled again to −10 °C, and a solution of 2G-allyl$_8$ (1.00 g, 0.60 mmol) in diethylether (5 mL) was added dropwise. The reaction mixture was stirred for 1 h at −10 °C, for 1 h at 0 °C, and for additional 40 h at room temperature. Subsequently, methanol (0.1 mL) was slowly added to decompose excess Cy_2BH, the reaction mixture was stirred for 1 h and the volatiles were removed in vacuo. The residue was redissolved in fresh diethylether (20 mL) and cooled to −10 °C. Aqueous NaOH solution (3 mL of 3 M solution) was added upon cooling with subsequent dropwise addition of H_2O_2 (2.2 mL of 30% solution). The reaction mixture was stirred for 1 h at −10 °C; then, it was allowed to warm up and was refluxed for 2 h. The organic layer was separated, and the aqueous layer was extracted with diethylether. Combined organic extracts were washed with saturated aqueous NaCl solution and dried with $MgSO_4$. The volatiles were evaporated, and the byproduct (cyclohexanol) was distilled off in vacuo. The product was obtained as a whitish very viscous oil (0.80 g, 73%). ^1H NMR: δ −0.07 (s, 12H, CH_3Si^1); −0.02 (s, 48H, CH_3Si^2); 0.48 (m, 16H, $CH_2CH_2CH_2OH$); 0.56 (m, 48H, $CH_2Si^{0,1,2}$); 1.32 (m, 24H, $Si^{0,1}CH_2CH_2CH_2Si^{1,2}$); 1.54 (tt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.7 Hz, 16H, CH_2CH_2OH); 2.20 (bs, 8H, OH); 3.57 (t, $^3J_{HH}$ = 6.7 Hz, 16H, CH_2OH). ^{13}C NMR: δ −4.9 (CH_3Si^1); −3.3 (CH_3Si^2); 10.9 ($CH_2CH_2CH_2OH$); 17.7 (C^0); 18.4 (C^1); 18.6 (C^0); 18.8 (C^1); 19.2 (C^0); 20.0 (C^1); 27.1 (CH_2CH_2OH); 65.7 (CH_2OH). ^{29}Si NMR: δ 0.98 (Si^1); 2.23 (Si^2); Si^0 not observed. MALDI-TOF MS: m/z 1663.71; calcd m/z 1664.12 ($(M+Na)^+$; monoisotopic values).

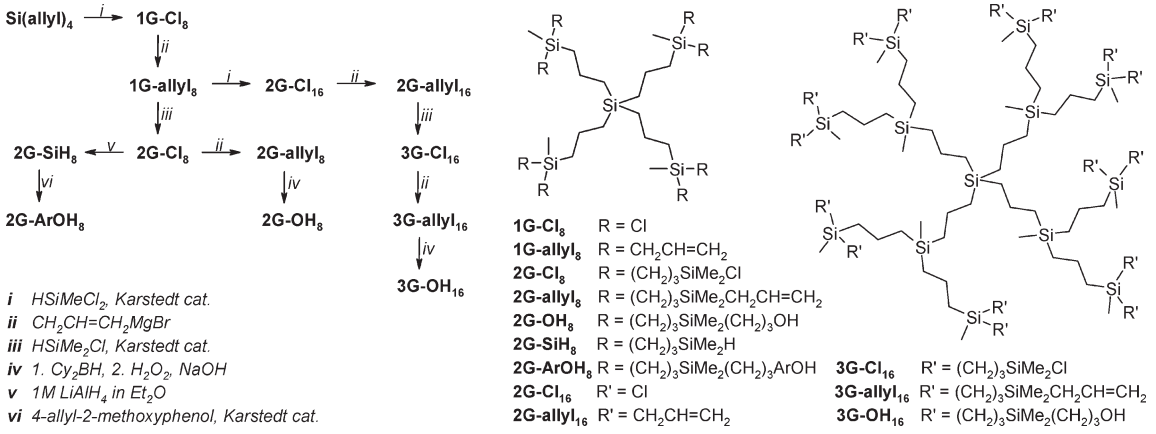

Figure 1. Overview of synthesis, structures, and notation of dendrimers.

Preparation of 3G-OH$_{16}$. This dendrimer was prepared by a method analogous to that described above for 2G-OH$_8$, starting from 3G-allyl$_{16}$ (1.00 g, 0.30 mmol) and dicyclohexylborane prepared from borane−dimethylsulfide complex (3.60 mL of 2 M solution in diethylether, 7.20 mmol) and cyclohexene (1.18 g, 14.4 mmol). The crude product containing cyclohexanol was dispersed in methanol (4 mL), which was then slowly distilled off to remove possible traces of boric acid in the form of methyl borate (azeotropic distillation).[15] The byproduct (cyclohexanol) was then distilled off in vacuo. The product was obtained as a yellowish very viscous oil (1.00 g, 93%). ^{1}H NMR: δ −0.07 (s, 36H, $CH_3Si^{1,2}$); −0.02 (s, 96H, CH_3Si^3); 0.48 (m, 32H, $CH_2CH_2CH_2OH$); 0.56 (m, 112H, $CH_2Si^{0,1,2,3}$); 1.32 (m, 56H, $Si^{0,1,2}CH_2CH_2CH_2Si^{1,2,3}$); 1.55 (tt, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.6 Hz, 32H, CH_2CH_2OH); 2.19 (bs, 16H, OH); 3.57 (t, $^3J_{HH}$ = 6.6 Hz, 32H, CH_2OH). ^{13}C NMR: δ −4.9 ($CH_3Si^{1,2}$); −3.3 (CH_3Si^3); 10.9 ($CH_2CH_2CH_2OH$); 18.4 (C^2); 18.5 (C^1); 18.8 (C^2); 18.9 (C^1); 19.0 (C^1); 20.0 (C^2); 27.1 (CH_2CH_2OH); 65.7 (CH_2OH); C^0 carbon peaks are too weak for proper assignment. ^{29}Si NMR: δ 0.94 (Si^1); 0.99 (Si^2); 2.22 (Si^3); Si^0 not observed. MALDI-TOF MS: m/z 3622.51; calcd m/z 3622.65 $(M+Na)^+$.

Results and Discussion

Defect Analysis of Polyallylcarbosilane Skeleton. The synthesis and structure of the dendrimers under study are summarized in Figure 1. Polyallylcarbosilane dendrimers were prepared according to literature procedures.[1,5,6] To obtain products of sufficient quality; the procedure of hydrosilylation had to be optimized. During the optimization, many batches of dendrimers were prepared that differed in the type and amount of defects present in their structure; products enriched in a specific type of defect greatly helped its identification because the signals of impurity became clearly visible in ^{13}C and ^{29}Si NMR spectra.

Because of the nature of divergent synthesis involving multiple transformations on a single molecule, even small overall amount of defects introduced in one reaction step can cause a serious decrease in dendritic purity. The conversion of a particular reaction is often checked only by NMR, and signals corresponding to impurities can easily go unnoticed because of their low intensity and coincidence with other signals when they are not expected and searched for.

As can be seen from Figure 2, most defects are formed during the hydrosilylation step of the iteration cycle. Because the hydrosilylation product cannot be purified because of its high moisture sensitivity, the defects are translated into the next reaction step. Defect A, unreacted allyl group, can be identified only from the NMR spectra of the chlorosilyl "half-generation" dendrimer because after the subsequent allylation, its signals would become completely hidden under the signals of next generation allyl groups. In fact, this kind of defect was seldom observed in the NMR spectra during optimization, and its presence was probably due to the use of partially decomposed catalyst. Much more common was the defect E, caused by isomerization of the terminal double bond to the internal one, more sterically hindered and as such less susceptible to hydrosilylation. These two defects are characterized by the same loss of molecular weight so they cannot be distinguished in the mass spectra. It is possible that part of the defects ascribed by Lorenz et al. to incomplete conversion of hydrosilylation[7] is actually due to isomerization. Signals of internal double bonds are downfield from those of allyl groups in ^{1}H NMR spectra, and they can be easily distinguished because of their different multiplicity. (See Table 1, entry 1−3.) Because both E and Z isomer can be formed, two sets of peaks are usually observed, the one of E isomer being predominant. With higher amount of isomerization, the number of different sets of signals increases because of varying chemical environment of particular defects. The lower limit of detection generally increases with dendrimer generation, and it is affected by many factors such as sample concentration and setup of the NMR experiment, but in typical ^{1}H spectra, it amounts to several tenths of a percent. Double-bond isomerization also has notable influence on the adjacent silicon atom, shifting its signal by nearly 9 ppm to higher field.

Because the coordination ability of internal double bond is lower than that of allyl group, the stabilization of the active catalyst is worse, and it tends to decompose, leaving the internal double bonds unreacted. However, it is possible to convert the internal double bonds to desired hydrosilylation product by adding fresh catalyst to the reaction mixture and prolonged heating. The course of the reaction has to be monitored by NMR, and additional portions of the catalyst must be added when necessary. In the presence of THF, only the desired γ-adduct is formed, which means that the hydrosilylation is preceded by migration of the double bond back to the terminal position. Still, the method should be used only when the amount of isomerization is low because long heating of the reaction mixture with decomposed catalyst has a negative influence on the overall purity of the dendrimer.

α-Hydrosilylation was previously reported to accompany the hydrosilylation step in the synthesis of polyvinylcarbosilanes when the reaction was carried out without a solvent.[6] We have observed that the regioselectivity of hydrosilylation of allyl groups by dichloromethylsilane is also solvent-dependent, and two end-group regioisomers are formed in

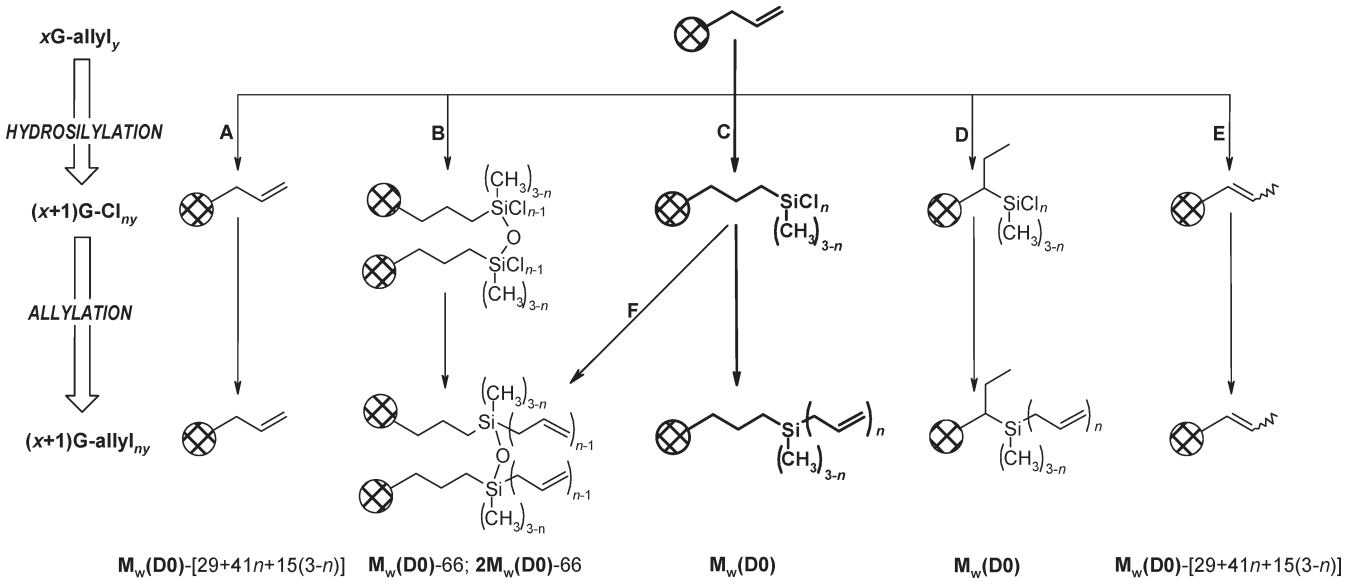

Figure 2. Possible pathways for introduction of defect structures in one iteration cycle and the impact of defects on the molecular weight. M_w(D0) stands for the molecular weight of perfect dendrimer of the $x + 1$ generation, ⊗ represents the interior of the dendrimer, and n denotes the branching multiplicity. (A) incomplete conversion of hydrosilylation; (B) hydrolysis of chlorosilane and condensation of the resulting silanol to either intra- or intermolecular disiloxane; (C) desired pathway; (D) α-hydrosilylation; (E) isomerization of the double bond (both E and Z isomers are possible); (F) incomplete conversion of allylation (subsequent aqueous workup causes hydrolysis of unreacted chlorosilyl groups).

Table 1. Overview of NMR Spectra of Regular End Groups and Defects Detected by NMR Spectroscopy

	end group	nuc.	n	significant signals[a]
1	D−^{a}Si(^{b}Me)$_{3-n}$(^{c}CH$_2$^{d}CH=^{e}CH$_2$)$_n$	^{1}H	2	*b* −0.01 (s); *c* 1.55 (ddd 8.2/1.2/0.9); *e* 4.84 (m); *d* 5.78 (tdd 16.7/10.3/8.2)
			1	*b* −0.02 (s); *c* 1.51 (ddd 8.2/1.2/1.2); *e* 4.82 (m); *d* 5.77 (tdd 16.7/10.2/8.2)
		^{13}C	2	*b* −5.7; *c* 21.5; *e* 113.1; *d* 134.8
			1	*b* −3.6; *c* 23.4; *e* 112.6; *d* 135.2
		^{29}Si	2	*a* 0.2
			1	*a* 0.7
2	D−^{a}Si(^{b}Me)$_{3-n}$(^{c}CH=^{d}CH^{e}CH$_3$)$_{E\text{-isomer}}$	^{1}H		$b_{n=1}$ 0.01 (s); *e* 1.82 (dd 6.2/1.6); *c* 5.60 (qd 18.5/1.6); *d* 6.05 (qd 18.5/6.2)
		^{13}C		$b_{n=1}$ −4.8; *e* 22.8; *c* 128.9; *d* 143.1
		^{29}Si		*a* −7.4
3	D−^{a}Si(^{b}Me)$_{3-n}$(^{c}CH=^{d}CH^{e}CH$_3$)$_{Z\text{-isomer}}$	^{1}H		*e* 1.77 (dd 6.8/1.5); *c* 5.45 (qd 14.1/1.5); *d* 6.46 (qd 14.1/6.8)
		^{13}C		*e* 22.8; *c* 127.9; *d* 143.7
		^{29}Si		*a* −9.1
4	D−^{a}Si^{b}CH$_2$^{c}CH$_2$^{d}CH$_2$^{e}Si(^{f}Me)$_{3-n}$Cl$_n$	^{1}H	2	*b* 0.64 (m); *f* 0.77 (s); *d* 1.18 (m); *c* 1.54 (m)
			1	*f* 0.40 (s); *b* 0.57 (m); *d* 0.89 (m); *c* 1.45 (m)
		^{13}C	2	*f* 5.5; *b* 17.3; *c* 17.5; *d* 25.9
			1	*f* 1.9; *b* 17.7; *c* 18.1; *d* 23.5
		^{29}Si	2	*a* 1.5; *e* 32.1
			1	*a* 1.2; *e* 31.2
5	D−^{a}Si^{b}CH(^{c}CH$_2$^{d}CH$_3$)^{e}Si(^{f}Me)Cl$_2$	^{1}H	*	*b* 0.39 (dd 6.4/4.2); *f* 0.82 (s); *d* 1.09 (t 7.3); *c* 1.70 (m)
		^{13}C	*	*f* 7.6; *d* 17.6; *c* 18.5; *b* 19.6
		^{29}Si	*	*e* 32.3
6	[D−^{a}CH$_2$^{b}CH$_2$^{c}CH$_2$^{d}Si(^{e}Me)Cl]$_2$−O	^{1}H	*	*e* 0.79 (s)
		^{13}C	*	*e* 5.3; *a* 16.5; *b* 19.3; *c* 25.1
		^{29}Si	*	*d* 31.8
7	[D−^{a}Si(^{b}Me)(^{c}CH$_2$^{d}CH=^{e}CH$_2$)]$_2$−O	^{1}H		*b* 0.16 (s)
		^{13}C		*b* −2.8; *c* 23.8; *e* 114.1; *d* 133.5
		^{29}Si		*a* 10.2
8	[D−CH$_2$CH$_2$CH$_2$^{a}Si^{b}Me$_2$]$_2$−O	^{1}H		*b* 0.12 (s)
		^{13}C		*b* −2.2
		^{29}Si		*a* 9.4
9	D−CH$_2$CH$_2$CH$_2$^{a}Si^{b}(Me$_2$)−OH	^{1}H		*b* 0.13 (s)
		^{13}C		*b* −0.1
		^{29}Si		*a* 17.7
10	D−^{a}Si^{b}CH$_2$^{c}CH$_2$^{d}CH$_2$^{e}Si(^{f}Me$_2$)^{g}H	^{1}H		*f* 0.06 (d 3.7); *b* 0.57 (m); *d* 0.65 (m); *c* 1.38 (m); *g* 3.89 (sp 3.7)
		^{13}C		*f* −4.3; *b* 18.2; *d* 18.9; *c* 19.0
		^{29}Si		*e* −14.1; *a* 1.2
11	D−^{a}Si(^{b}Me$_2$)^{c}CH$_2$^{d}CH$_2$^{e}CH$_2$^{f}OH	^{1}H		*b* −0.02 (s); *c* 0.48 (m); *d* 1.54 (tt 8.5/6.7); *f* 2.20 (bs); *e* 3.57 (t 6.7)
		^{13}C		*b* −3.3; *c* 10.9; *d* 27.1; *e* 65.7
		^{29}Si		*a* 2.2
12	D−^{a}Si^{b}CH(OH)^{c}CH$_2$^{d}CH$_3$	^{1}H		*d* 1.02 (t 7.3); *b* 3.27 (dd 10.0/4.0)
		^{13}C		*d* 11.7; *c* 26.8; *b* 66.9
		^{29}Si		*a* 1.5

[a] In case of defects, only well-resolved signals, which do not overlap with major structure peaks, are given. Depending on generation, branching pattern, and chemical environment, ^{1}H shifts can vary by 0.01 to 0.04 ppm, ^{13}C shifts by 0.1 to 0.4 ppm, and ^{29}Si shifts by 0.1 ppm from those reported here. Values for the second generation are given where possible; the first generation signals are marked with asterisk.

the ratio of approximately 10:1 when the reaction is performed in nonpolar media. The presence of donor solvent such as THF or diethylether in the reaction mixture prevents the formation of unwanted end-group isomer, which was identified as 1-(dichloromethylsilyl)propyl group from the NMR spectra (Table 1, entry 5). Just as in the hydrosilylation of vinylsilanes, the silyl group adds to the α-carbon, and compound with two geminal silyl groups is formed, which is consistent with the large influence of this defect on the NMR spectra of neighboring dendritic branches. Unlike the vinyl analog, the formation of α-adduct in the hydrosilylation of allyl group is a two-step process, migration of the double bond being its first step. That may be the reason why α-addition to allylsilanes is less extensive than that to vinylsilanes.

α-Addition does not change either the molecular weight or the number of peripheral functions of the defect molecule, so it does not affect the dendrimer growth in a major way, but it affects the symmetry of the molecule, and because of the large influence on the adjacent branches, it spoils the simplicity of the NMR spectra and impedes their unambiguous interpretation. However, this type of defect was observed only in the synthesis of the first generation dendrimer because of the fact that the small amount of THF retained in the dendrimer structure after the first iteration cycle can suppress the formation of α-adducts in the following hydrosilylation, even when it is performed in nonpolar media.

Considering the susceptibility of the Si−Cl bond to hydrolysis, the presence of disiloxane bridges, either intra- or intermolecular, in the molecule can be expected, at least when the branching multiplicity $n = 2,3$. These can be introduced from the silane used in the hydrosilylation step, they can appear when handling the moisture sensitive "half-generation" dendrimers, or eventually they can arise from incomplete allylation, which is followed by the hydrolysis of the reaction mixture. Nonchlorinated disiloxanes (and silanols in case of $n = 1$) give rise to specific signals in ^{29}Si NMR spectra that can hardly be mistaken (Table 1, entries 6−9). However, the presence of a small amount of these defects is best detected from proton signals of methyl group adjacent to siloxane because of higher signal-to-noise ratio of ^{1}H NMR spectra.

Intermolecular siloxane bridges nearly double the molecular weight of affected molecules, so their impact on dendrimer polydispersity is much higher than that of other defects. At the same time, however, the large difference in size between perfect and defect structures makes the separation of this type of defect molecules possible (at least in principle), for example, by gel permeation chromatography (GPC). Intramolecular siloxane bridges create molecular loops in the structure and introduce "dead end" branches, whose further growth is inhibited so the defects deepen in subsequent iteration cycles. Fortunately, the disiloxane bridge is chemically very stable, so it cannot interfere in a majority of reactions that can be used for periphery functionalization of carbosilane dendrimers.

The sensitivity of NMR experiment does not allow the detection of a defect present in amounts smaller than several tenths of a percent; the limit for identification of unknown defect is even higher. Because of the multiple functionality that amplifies the number of defect molecules compared with the fraction of defect end groups, mass spectrometry is far more sensitive to defects in divergently synthesized dendrimers. Soft ionization technique of MALDI MS ensures that the molecules stay intact and defect structures cannot be mistaken for fragment ions. Moreover, from high-resolution mass spectra, exact molecular composition of particular structures can be deduced.

MALDI-TOF mass spectra of regularly branched dendrimers (branching multiplicity $n = 2$ in all generations) show a simple pattern illustrated by Figure 3a. The difference between isotopic multiplets corresponds to the loss of a repeat unit, diallylmethylsilane (126 Da), which can be a result of defects A or E. A similar pattern was observed with related dendrimers of higher branching multiplicity ($n = 3$), only the mass difference was respectively higher, corresponding to triallylsilane (152 Da).[7] Except for the peak of perfect dendrimer (m/z 1812), only the peak at m/z 1686 can be assigned unambiguously; it corresponds to one defect in the outer layer. Other peaks correspond to molecules with different combinations of defects, for example, the one at m/z 1560 to a molecule with two defects in the outer layer or to a molecule with one defect in the inner layer, which had reacted in the second iteration cycle.

Dendrimers with lower branching multiplicity in the outmost layer show more complicated spectra (Figure 3b,c). The structure contains not only two types of repeat units and so the defects in the outer and inner layers can be distinguished but also two other types of defects not observed in the NMR spectra. The structures proposed for defects are shown in Figure 3d.

The drop of 58 Da compared with the dominant peak corresponds to a loss of $(CH_3)_2Si$ fragment and so to the replacement of $-(CH_2)_3Si(CH_3)_2CH_2CH{=}CH_2$ sequence in the peripheral layer of the molecule with a purely aliphatic chain $-(CH_2)_4CH{=}CH_2$. This defect could be due to hydrochlorination of the double bond taking place under hydrosilylation conditions, utilizing hydrochloric acid inherently present in chlorosilanes used for hydrosilylation and possibly catalyzed by Karstedt catalyst itself or some product of its decomposition. Chloropropyl group thus generated would react in the next step with allylmagnesium bromide to form the proposed structure. The aliphatic spacer can be either linear or branched depending on the regioselectivity of hydrochlorination. However, there is no evidence of the branched spacer in the ^{13}C NMR spectra, in contrast with the presence of several unassigned methylene peaks.

The occurrence of the molecule with higher-than-expected molecular weight is rather surprising. The excess of 74 Da corresponds to a $(CH_3)_2SiO$ fragment that could be incorporated into the dendrimer skeleton in case the chlorodimethylsilane used in the hydrosilylation step contained (chlorodimethylsiloxy)dimethylsilane. Considering that hydrosilanes can undergo disproportionation and redistribution reactions under certain conditions,[16] its presence can be explained by the following reaction sequence.

$$2HSiMe_2Cl \rightarrow H_2SiMe_2 + SiMe_2Cl_2$$

$$SiMe_2Cl_2 + H_2O \rightarrow SiMe_2ClOH + HCl$$

$$SiMe_2ClOH + HSiMe_2Cl \rightarrow HSiMe_2OSiMe_2Cl + HCl$$

Fortunately, these latter two types of defects have negligible effect on the dendrimer properties, retaining the high chemical and thermal stability and low polarity of the perfect structure and not even modifying the number and type of end groups.

Mass spectra of 2G-allyl$_8$ and 3G-allyl$_{16}$ also confirm the ability of isomerized or unreacted allyl groups (defects A and E) to participate in subsequent iteration cycles, which

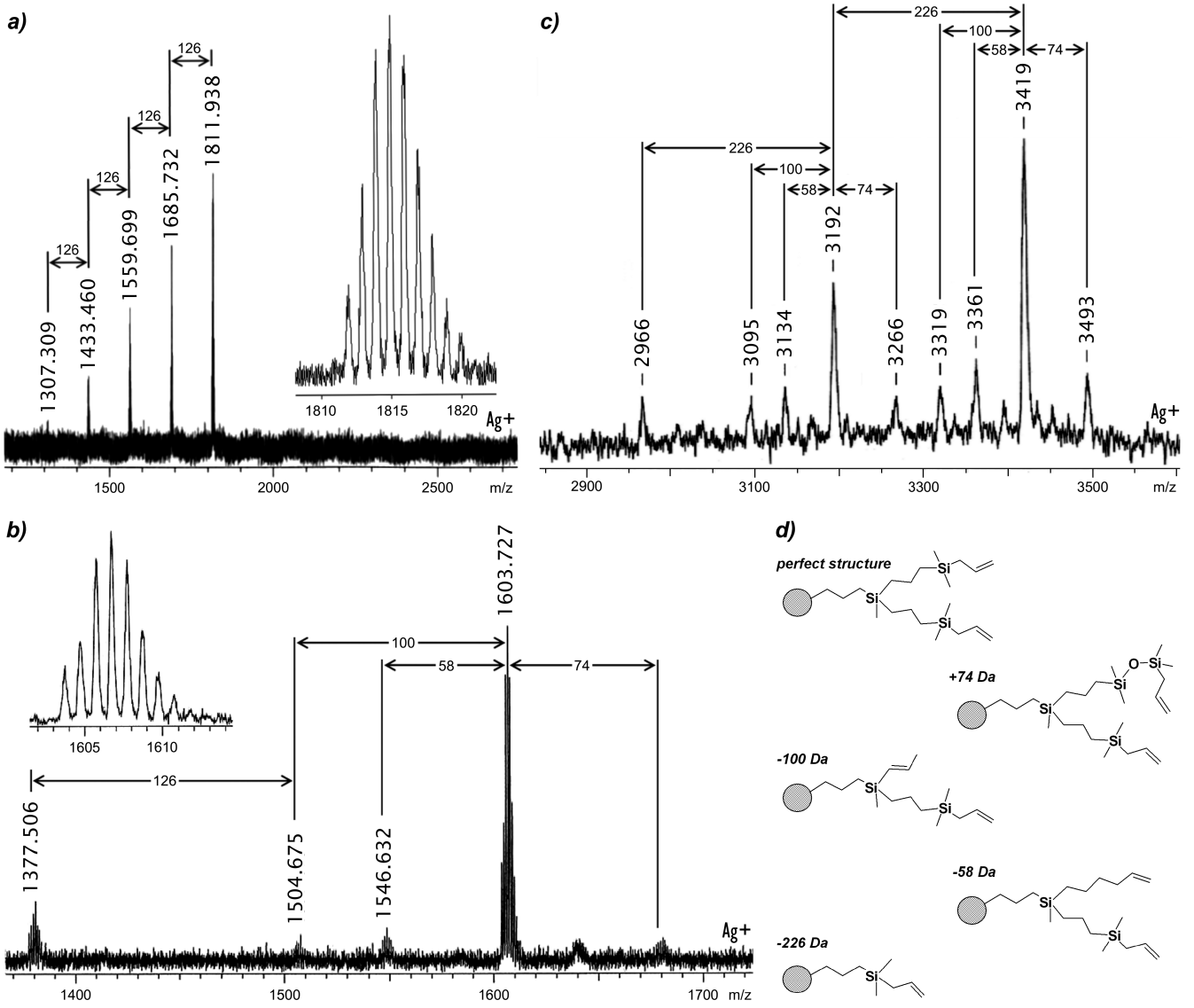

Figure 3. MALDI-TOF mass spectra of polyallylcarbosilane dendrimers and their interpretation; insets showing isotopic multiplets of dominant peaks are included in the high-resolution spectra. (a) Mass spectrum of 2G-allyl$_{16}$; (b) mass spectrum of 2G-allyl$_8$; (c) mass spectrum of 3G-allyl$_{16}$; and (d) structures of affected branches proposed for the defects observed in mass spectra of 2G-allyl$_8$ and 3G-allyl$_{16}$.

can decrease the impact of these defects on the structure of higher dendrimer generations. This is fully consistent with the results previously obtained from a theoretical model for 2G-allyl$_{16}$, where the conversion of defects was calculated to be as high as 83%.[11] In the case of 2G-allyl$_8$ (Figure 3b), the peak corresponding to a molecule bearing unreacted defect from the first generation (loss of 326 Da) is not even apparent in mass spectrum, whereas there is a rather intensive signal (m/z 1378) assigned to a molecule with one defect from the first iteration cycle, which had reacted in the subsequent hydrosilylation/allylation sequence.

The presence of dimeric or oligomeric structures was never detected in MALDI-TOF mass spectra. However, responsiveness of the method is known to be a function of molecular weight depending on the experimental conditions.[17] Also, the broadening of isotopic distribution with increasing molecular weight results in a decrease in relative intensity of particular isotopic peaks and flattening of the isotopic multiplet so that the signal-to-noise ratio decreases. A small amount of high-molecular-weight impurities can therefore easily go unnoticed.

As previously confirmed through the comparison between experimental data and data obtained from the theoretical model of the formation of defects, quantitative interpretation of the MALDI-TOF mass spectra of carbosilane dendrimers gives credible results in limited range of m/z.[11] Because of the fact that the molecular composition of particular defect structures of a given generation is very similar and the same holds for the width and shape of respective isotopic multiplets, it is possible with slight inaccuracy to use the intensity of the most intense peak of each isotopic multiplet for the calculation instead of multiplet integral. Using this approximation, aggregate conversion of a given iteration cycle can be easily obtained from the spectra. Aggregate conversion of the last iteration cycle, ξ, which is particularly interesting for the optimization of synthesis, was obtained from the ratio between the intensity of the perfect molecule peak, I_{D0}, and the sum of intensities of the peaks corresponding to structures with just one defect, I_{D1}, which is given by

$$\sum I_{D1}/I_{D0} = f(1-\xi)\xi^{f-1}/\xi^{f} \qquad (1)$$

where f stands for the number of groups reacting in the given iteration cycle, for example, for 1G-allyl$_8$ $f = 4$, for both

Table 2. Aggregate Conversions[a], as Calculated from MALDI-TOF Mass Spectra Presented in Figure 3

dendrimer	f	ξ	$\xi_A + \xi_E$	ξ_G	ξ_H
2G-allyl$_{16}$	8	91.6%	8.4%		
2G-allyl$_8$	8	97.0%	0.9%	1.2%	0.9%
3G-allyl$_{16}$	16	96.2%	1.0%	1.5%	1.3%

[a] ξ: aggregate conversion to desired product; ξ_A: fraction of unreacted allyl groups; ξ_E: conversion of isomerization; ξ_G: conversion to defect characterized by the loss of 58 Da; ξ_H: conversion to defect characterized by the excess of 74 Da.

2G-allyl$_{16}$ and 2G-allyl$_8$ $f = 8$, and for 3G-allyl$_{16}$ $f = 16$. Therefore, ξ can be calculated according to eq 2

$$\xi = f/(\sum I_{D1}/I_{D0} + f) \quad (2)$$

In the case of 2G-allyl$_8$ and 3G-allyl$_{16}$, where more than one type of defect is apparent in the spectra, the amount of particular defect is also of interest. Knowing the aggregate conversion of the iteration cycle, the conversion to particular defect ξ_x is obtained from the intensity of corresponding peak I_{D1x}.

$$I_{D1x}/I_{D0} = f\xi_x\xi^{f-1}/\xi^f \quad (3)$$

$$\xi_x = (\xi/f)(I_{D1x}/I_{D0}) \quad (4)$$

Conversions calculated from the spectra in Figure 3 are presented in Table 2. Low conversion values found for the defects characterized by loss of 58 Da and by excess of 74 Da (ξ_G and ξ_H) are consistent with the fact that these defects were not identified in NMR spectra. Also, the approximation of integrals by maximum intensities gives aggregate conversion very close to that previously calculated using integration,[11] as can be seen for 2G-allyl$_{16}$ (91.6 vs 91.2%). For comparison, aggregated conversions calculated according to eq 2 from the published MALDI-TOF mass spectra of higher branching polyallylcarbosilane dendrimers, 2G-allyl$_{36}$ and 3G-allyl$_{108}$,[7] amount to 97 and 96%, respectively. The conversion of the first iteration cycle can also be estimated from the spectrum of 2G-allyl$_{36}$ as equal to 95%.

Synthesis and Analysis of Dendritic Polyols. The majority of carbosilane dendritic polyols is prepared using two strategies. The first one involves reduction of peripheral chlorosilyl groups, typically with $LiAlH_4$, followed by hydrosilylation of suitable unsaturated (and usually protected) alcohol with dendritic hydrosilane thus obtained. This strategy enables incorporation of a wide range of alcohols, including substituted phenols, onto the dendrimer periphery. The second possibility is the hydroboration/oxidation procedure, applied to carbosilane dendrimer of any generation with double bonds on the periphery. This strategy yields simple structures ending with short hydroxyalkyl groups.

The first strategy is more flexible but also more prone to produce materials of high polydispersity because of many possible side reactions. Whereas the concurrent O- and C-silylation can be easily avoided by the protection of unsaturated alcohol used, other pathways leading to dendrimer dimers and oligomers are inherently present in the reaction sequence. Any chlorosilyl group that has not reacted in the reduction step would hydrolyze during the reaction mixture workup to form silanols and disiloxanes. In fact, we have detected signals of both silanols and disiloxanes in the NMR spectra of all hydrosilane dendrimers prepared by the common procedure introduced by Seyferth et al.,[6] even when using ether solution of $LiAlH_4$ instead of solid hydride. Silanols that prevailed in freshly synthesized materials slowly condensed to disiloxanes, forming structures identical to defect F (Figure 2, $n = 1$). Under hydrosilylation conditions of the next step, silanols can also undergo O-silylation, the resulting product being identical to that mentioned above. Finally, any defect structure containing unsaturated bond present in the starting chlorosilyl dendrimers (defects A and E) is able to undergo hydrosilylation.

All three pathways can produce both inter- and intramolecular bridges. The polydispersity of 2G-ArOH_8, prepared according to a published procedure[13] by hydrosilylation of eugenol with 2G-SiH_8, was high according to GPC (data not shown here), indicating the presence of intermolecularly bridged structures. Whereas no peaks with higher-than-expected molecular weight were detected in MALDI-TOF mass spectra, intramolecular bridges due to hydrosilylation of defect E, present in the starting chlorosilane dendrimer and persisting after the reduction step, were clearly apparent (Figure 4a).

For hydroboration of carbosilane dendrimers, 9-borabicyclononane is mostly used. However, during the subsequent oxidation step, 1,5-cyclooctanediol is formed as a byproduct, of which complete removal from the dendritic polyol is rather complicated because of its high boiling point.[7] Therefore, we have chosen another reagent, in situ prepared dicyclohexylborane, which was also previously applied to carbosilane dendrimers.[18] The hydroboration of 2G-allyl$_8$ and 3G-allyl$_{16}$ using dicyclohexylborane gave satisfactory results with conversion of allyl groups exceeding 99% according to NMR analysis. The hydroboration products were not isolated, and they were immediately oxidized to desired dendritic polyols 2G-OH_8 and 3G-OH_{16}. The density of hydroxyl groups on the periphery of 2G−OH_8 and 3G−OH_{16} is lower than that of related structures prepared previously by Lorenz et al.[7] so they are not soluble in alcohols but they are well soluble in moderately polar solvents such at diethylether or chloroform.

As confirmed by NMR, hydroboration proceeded with high conversion not only on peripheral allyl groups but also on isomerized interior double bonds (if present in the starting dendrimer). Considering the substitution of double bond with electrondonating trialkylsilyl group, we have expected the formation of 1-hydroxypropyl group, which was consistent with the observed multiplicity of corresponding signals in the ^{1}H NMR spectrum (Table 1, entry 12). No side reactions related to hydroboration were detected, but the subsequent oxidation step was accompanied by basic hydrolysis of intermediate alkylboranes to alkanes. This reaction is well apparent in ^{29}Si NMR spectrum, where the replacement of 3-hydroxypropyl group at silicon by propyl group causes a shift of the corresponding signal by ~0.9 ppm to higher field. The products formed under hydroboration−oxidation conditions are summarized in Figure 5.

The presence of hydrolytic products in the structure of dendritic polyols was also confirmed by MALDI-TOF MS analysis (Figure 4b). Although it is not possible to distinguish this defect characterized by loss of 16 Da from unreacted allyl group (loss of 18 Da) because of low resolution in the spectrum of 3G-OH_{16}, from the high-resolution spectrum of 2G-OH_8 it is clearly evident that the defect caused by hydrolysis predominates. The same defect, albeit in lower amount, can be observed in MALDI-TOF mass spectrum of similar second-generation dendritic polyol synthesized by Lorenz et al., although the authors claim quantitative conversion of the hydroboration−oxidation sequence.[7] In the spectrum of 3G-OH_{16}, it is also possible to find defects

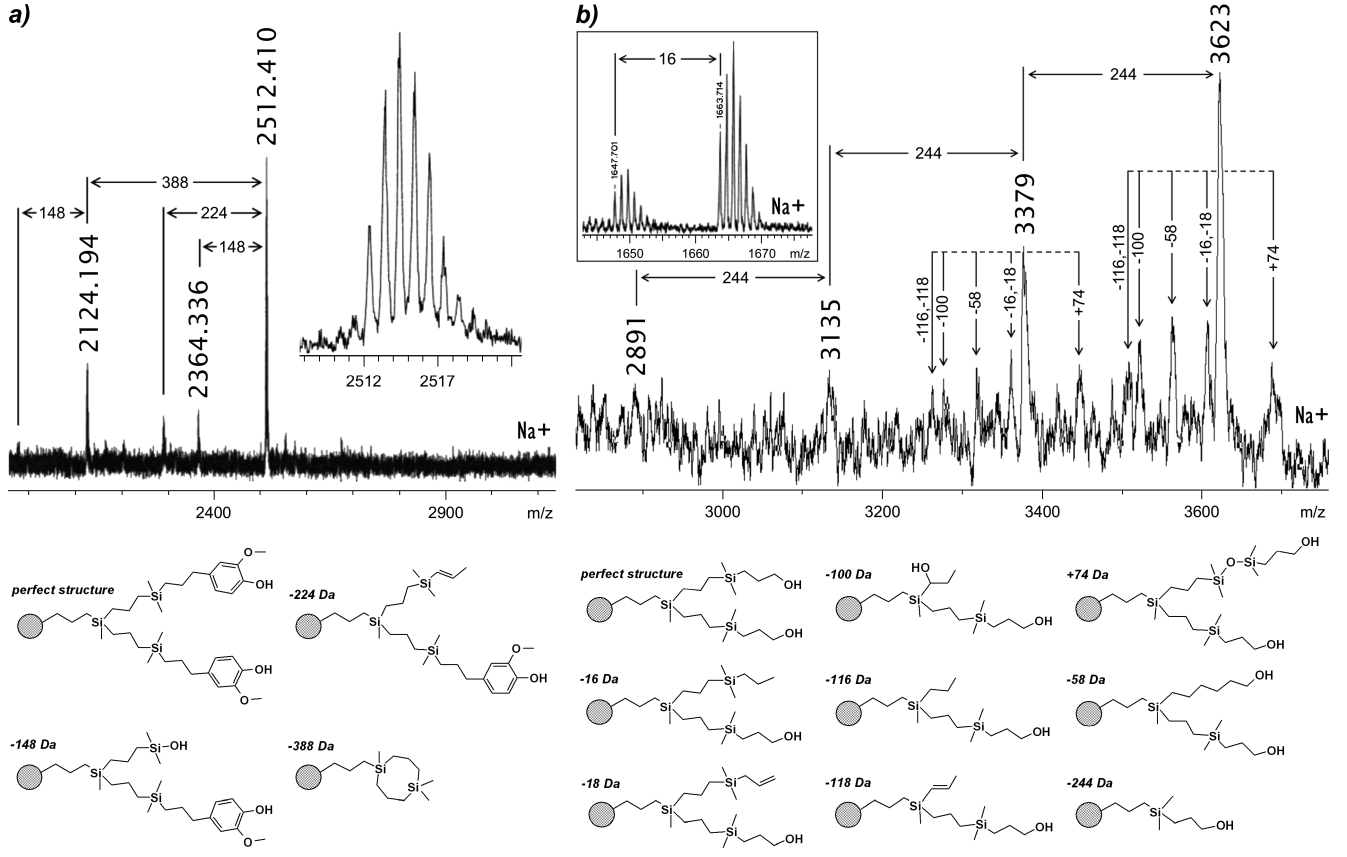

Figure 4. MALDI-TOF mass spectra of dendritic polyols and their interpretation including structures of affected branches proposed for the defects. (a) Mass spectrum of 2G-ArOH_8 with inset showing isotopic multiplet of dominant peak and (b) mass spectrum of 3G−OH_{16}, with inset showing segment of mass spectrum of 2G−OH_8.

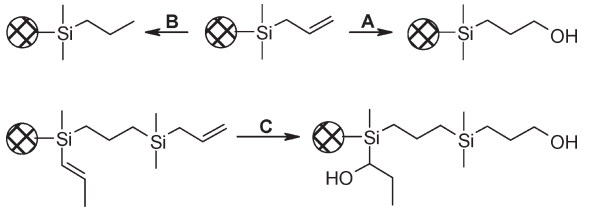

Figure 5. Reactions occurring under hydroboration−oxidation conditions. (A) Desired course of reaction sequence; (B) hydroboration followed by hydrolysis of intermediate borane; (C) reaction on defect branch yielding secondary alcohol.

identical to those present in the starting 3G-$allyl_{16}$ (peaks +74, −58, and −100 Da, cf. Figure 3c). The mass difference from the corresponding dominant peak stays unchanged after the hydroboration−oxidation sequence, which implies that these defects do not affect the number of double bonds on the dendrimer periphery. This fact further supports the correctness of proposed structures. By contrast, each defect in the preceding (second) generation lowers the number of functional groups on the periphery by one, which causes the increase by 18 Da (one molecule of water) in the difference between dominant peaks corresponding to lower generation defects upon going from 3G-$allyl_{16}$ to 3G-OH_{16}.

The conversion of allyl to 3-hydroxypropyl groups, as calculated from the mass spectra in Figure 4b, was 95.9 and 98.1% for 2G-OH_8 and 3G-OH_{16}, respectively. According to the high-resolution spectrum of 2G-OH_8, the remaining fraction consists mainly of propyl groups formed by hydrolysis, which are nonreacrive and would not interfere in further functionalization of the dendrimer.

Conclusions

Combined multinuclear NMR and MALDI-TOF MS analysis was used for the determination of structure, origin, and amount of defects present in divergently synthesized polyallylcarbosilane dendrimers and their polyol derivatives. The main part of defects characterized by missing repeating units in MS spectra was ascribed to isomerization of allyl groups under hydrosilylation conditions. Isomerized double bonds retain some reactivity toward hydrosilylation, which can, on one hand, contribute to suppression of the impact of defects on the structure of higher generations; on the other hand, it is a possible source of dendrimer dimers and oligomers when such defect structure is reduced to hydrosilyl-functionalized dendrimer and used in hydrosilylation of an unsaturated substrate. Insensitivity of MALDI-TOF MS for high-molecular-weight impurities was observed so that their absence has to be confirmed by complementary NMR and GPC analyses. The defects incorporated into the structure due to impurities present in reagents used are of small importance because they do not alter either polarity or functionality of the dendritic molecule. The presented summary of significant NMR signals of a range of impurities as well as simplified equations for quantitative analysis of MS spectra may help in further optimization of synthesis of structurally related dendrimers.

Acknowledgment. We thank the Ministry of Education, Youth and Sport of the Czech Republic (grant LC06070) and to Academy of Sciences of the Czech Republic (grant AV0Z40500505) for financial support.

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