# Carbosilane-Based Dendritic Polyols

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ABSTRACT: A divergent hydrosilation/Grignard-reaction sequence, followed by hydroboration of the allyl end groups was employed to prepare a series of novel dendritic carbosilane polyols. Dendrimers with 4, 12, 36, and 108 hydroxyl end groups have been prepared. The hydroboration reactions were monitored by $^1$H-NMR and MALDI-TOF and were quantitative in all cases. Using MALDI-TOF, the carbosilane dendrimers as well as the novel dendritic polyols have been characterized directly with respect to polydispersity. Whereas G2-OH consisted of mainly two species, the desired 36-ol (80%) and the 34-ol, G3-OH consisted of polyols with 92–108 hydroxyl groups. The dendritic polyols possess low glass transition temperatures (233–241 K) and thus constitute flexible polyols without polar interactions between the dendrons. The molecules appear suitable as chemically stable, flexible molecular scaffolds for the construction of unusual supermolecular architectures.

## Introduction

Due to their geometrical beauty and intriguing supramolecular properties, the interest in cascade molecules is increasing.[1-3] Currently, the focus in this area is shifting from the preparation of ever larger molecules to dendrimers showing unusual organization phenomena.[2-6] The use of dendrimers for controlled release of drugs as well as for highly selective membranes has been envisaged.[1,2,4] The preparation of rather perfect dendrimer molecules represents a synthetic challenge. This is particularly the case if one aims at surface functional dendrimers that offer the possibility of facile further attachment of functional oligomeric or polymeric building units. Such materials could be used as a "molecular scaffold" for the construction of unusual spherical macromolecular architectures.

To this end, three important prerequisites can be summarized: (i) a divergent synthetic route appears advantageous, as it allows surface functionalization of the dendrimers subsequent to dendrimer synthesis without the use of protecting groups; (ii) quantitative organic reactions (i.e. yield >99%) are required for each conversion step, i.e., for each new generation; and (iii) analytical tools that enable the characterization of the degree of structural perfection are crucial.

Dendritic polyols, i.e. spherical molecules with hydroxyl groups on the surface,[7] possessing an ideally lipophilic core and polar shell[8] are particularly intriguing in view of ordering phenomena in solution and the potential for unusual host/guest systems. A nonpolar interior may be suitable for inclusion and transport of lipophilic guests in an otherwise polar environment. An elegant, but synthetically demanding, divergent route to a dendritic polyol (arborol) with 36 end groups of this type has been described by Newkome et al. recently.[8]

Silicon chemistry offers a number of reactions with quantitative yields, which are suitable for dendrimer synthesis, such as replacement of chlorines in alkylchlorosilanes by Grignard reagents or hydrosilation. Carbosilane dendrimers[9-16] consist of alkyl groups linked to silicon atoms, that represent the branching points to the following generation. Carbosilane dendrimers are completely lipophilic due to the apolar nature of the Si–C bond and possess excellent chemical and thermal stability, which is explained by the thermodynamic stability of the Si–C bond (316 kJ/mol vs 354 kJ/mol for C–C).

In the current paper we describe a convenient, divergent synthetic route to lipophilic dendritic polyols, based on quantitative hydroboration of carbosilane dendrimers with allyl end groups. The novel polyols bear up to 108 hydroxyl groups on the surface. All dendrimers prepared are characterized with respect to polydispersity using MALDI-TOF mass spectroscopy (*M*atrix *A*ssisted *L*aser *D*esorption and *I*onization *T*ime *o*f *F*light Detection).

## Experimental Section

**General.** Solvents employed were generally of p.a. quality. THF was dried over Na. 9-BBN was purchased as a 0.5 M solution (Aldrich Chemical Co). All glassware was thoroughly dried and purged with Ar before use. All reactions described subsequently were carried out under Ar.

$HSiCl_3$ (Fluka) was distilled before use.

The combination of hydrosilation and Grignard reaction has been described in other articles recently.[9-13,15] Therefore, we only give a representative example of the slightly modified procedure for the preparation of G2, starting from G1. In contrast to refs 12 and 13 we have carried out the hydrosilation reaction in THF solution at 60 °C, because in our hands the reaction at ambient temperature was not successful.

**Preparation of G2.** In a three-necked flask equipped with reflux condenser, 3 g (3.75 mmol) of G1 (12-en) was dissolved in 40 mL of dry THF. Then 8.8 mL (87 mmol) of $HSiCl_3$ was added. At 0 °C 75 μL of PC-072 (Hüls; 1% in solution) was added; subsequently, the solution was warmed to 50–60 °C for 5 h. $^1$H-NMR spectra were recorded regularly to monitor the disappearance of the olefin protons. After removal of the remaining $HSiCl_3$ as well as THF, the subsequent Grignard reaction was carried out immediately. An allylmagnesium bromide solution in $Et_2O$ (450 mmol) was prepared according to standard procedures. The product of the first reaction step was dissolved in 40 mL of $Et_2O$ and slowly added to the Grignard solution. After refluxing for

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another 36 h, solvents were removed and G2 was purified by column chromatography. Yield: 6.17 g (62.6%).

**Preparation of G0-OH.** Tetraallylsilane (5 mL, 21 mmol) and 200 mL of THF were added in a 2 L three-neck flask. The solution was degassed three times and cooled to −10 °C. Then 400 mL of 9-BBN solution was added slowly (within 1.5 h) at −10 °C. The solution was stirred for 3 h at −10 and at 25 °C overnight. Subsequently, the reaction mixture was cooled to −10 °C again and 40 mL of a 6 M solution of NaOH was added. Immediately, 75 mL of an aqueous solution of $H_2O_2$ was added carefully (exothermic reaction). The reaction mixture was stirred for an additional 1 h at −10 °C, for 2 h at 40 °C, and for 1 h at 50 °C. After cooling to ambient temperature, the THF solution was decanted from the precipitated boronic acid and washed with a saturated solution of NaCl. The remaining $H_2O_2$ was destroyed by adding $FeSO_4$. $Fe^{3+}$ was removed by adding 0.5 M NaOH and precipitating $Fe(OH)_3$. Subsequently, the solvent was evaporated and the residue was heated with 500 mL of MeOH. The trimethyl ester of boronic acid and MeOH were distilled off. Remaining MeOH was removed in vacuo. Most of the cyclooctane-1,5-diol was distilled off under high vacuum ($10^{-4}$ Torr). The product was purified by recrystallization from toluene/butanol. Yield: 4.7 g (85%). $^1$H-NMR (DMSO-$d_6$, 300 MHz): $\delta$ 4.38 (t, 4 H), 3.3 (m, 8 H, impurity; water), 1.35 (m, 8 H), 0.4 (t, 8 H).

**Preparation of G1-OH.** G1 (1 g, 1.25 mmol) and 50 mL of THF were added in a 250 mL three-neck flask. After degassing and cooling to −10 °C, 60 mL of the 9-BBN solution was added within 20 min. The reaction mixture was stirred for 4 h at this temperature and additionally for 24 h at ambient temperature. Subsequently, the borane solution was cooled to −8 °C and 6 mL of a 6 M solution of NaOH was added, followed by addition of 12.05 mL of the aqueous solution of $H_2O_2$ (containing 30% $H_2O_2$). The solution was stirred at −8 °C for an additional 1 h, 2 h at 40 °C, and 1.5 h at 50 °C. After cooling to ambient temperature, the THF solution was decanted from the precipitated boronic acid and washed with a saturated solution of NaCl. After drying over $MgSO_4$, the solvent was evaporated. The residue was dissolved in 100 mL of MeOH and refluxed for 1 h. The trimethyl ester of boronic acid and MeOH was distilled off. The remaining MeOH was removed under high vacuum. Cyclooctane-1,5-diol was distilled off under high vacuum ($10^{-4}$ Torr), and G1-OH was further purified by dissolving the residue several times in THF/EtOH and precipitating the product by adding $CHCl_3$. Yield: 0.47g (37.6%). $^1$H-NMR (DMSO-$d_6$, 300 MHz): $\delta$ 4.31 (t, 12 H), 3.2 (m, 24 H, impurity; water), 1.1−1.3 (m, 32 H), 0.35 (t, 24 H), 0.45 (m, 16 H).

**Preparation of G2-OH.** G2 (0.95 g, 0.36 mmol) was dissolved in 50 mL of dry THF. The solution was degassed three times. At −10 °C, 60 mL of the 9-BBN solution was added. The solution was stirred for 3 h at −10 °C and subsequently for 60 h at ambient temperature. After cooling to −8 °C, 6 mL of a 6 M NaOH solution and subsequently 12.1 mL of a 30% $H_2O_2$ solution were added. Under slow elevation of the temperature the reaction mixture was stirred for another 4 h. After filtration and solvent removal the product was refluxed in methanol to convert boronic acid to the methyl ester. Cyclooctanediol and boronic acid ester were distilled off under high vacuum. Further purification of the product was achieved by several times dissolving the residue in THF/ethanol and precipitating it by adding $CHCl_3$. Final yield: 0.87 g of G2-OH (36-polyol). $^1$H-NMR (DMSO-$d_6$, 300 MHz): $\delta$ 4.45 (t, 36 H), 3.33 (m, 72 H, impurity; water), 1.2−1.5 (m, 104 H), 0.35−0.65 (m, 136 H).

**Preparation of G3-OH.** G3 (0.92 g, 0.11 mmol) and 50 mL of THF were added in a 250 mL three-necked flask. The solution was degassed three times and cooled to −16 °C. At this temperature 70 mL of the 9-BBN solution was added within 20 min. The solution was stirred for 1.5 h at low temperature and for 108 h at ambient temperature. After cooling to −10 °C again 7 mL of a 6 M solution of NaOH was added, immediately followed by 14.1 mL of a 30% aqueous solution of $H_2O_2$. The reaction mixture was stirred for 1 h at −10 °C, for 2 h at 40 °C, and for another 1 h at 50−60 °C. After cooling to ambient temperature, the precipitated boronic acid was removed and the THF solution was washed with a saturated solution of NaCl. Most of the product now could be isolated directly from a small phase that formed as an interlayer between the organic solution and the NaCl solution. The resulting oil was dried in vacuo. Further purification of the product was achieved by several times dissolving it in ethanol and precipitating it by adding $CHCl_3$. Yield: 0.52 g (47.5%). $^1$H-NMR (DMSO-$d_6$, 300 MHz): $\delta$ 4.45 (t, no fine structure, 108 H), 3.35 (m, 216 H, impurity; water), 1.28−1.51 (m, 320 H), 0.3−0.7 (m, 424 H).

**Methods. NMR.** Solution $^1$H-NMR spectra were recorded on a 300 MHz (Bruker) spectrometer in $CDCl_3$ (carbosilane dendrimers) and DMSO-$d_6$ (dendritic polyols). $^1$H-NMR chemical shifts are referenced to the signals of the solvents used.

**GPC.** A combination of PL columns (Polymer Laboratories), $10^5$, $10^4$, $10^3$, and 100 nm, was employed; DMF was used as solvent. All data are referenced to narrow polystyrene standards.

**Calorimetry.** A Perkin-Elmer DSC 7 was used to monitor glass transitions at scan rates of 5 °C/min. The instrument was calibrated with high-purity samples of indium and cyclohexane. Sample weights were typically chosen between 7 and 12 mg.

**MALDI-TOF.** All MALDI spectra were obtained using a REFLEX time-of-flight mass spectrometer (Bruker-Franzen, Bremen, Germany) operated at 30 kV accelerating voltage in reflector mode with positive ionization. For G2, 5-chloro salicylic acid together with silver trifluoroacetate was used; for G3 3-indolylacrylic acid with silver acetonylacetate was employed (solvent: $CH_2Cl_2$). G2-OH and G3-OH were dissolved in MeOH, DHB (2,5-dihydroxybenzoic acid) was used as matrix, and sodium acetate was added. The data were externally calibrated by means of ubiquitin.

## Results and Discussion

Recently, a detailed synthetic procedure for the preparation of carbosilane dendrimers based on an alternating hydrosilation/Grignard reaction sequence has been given by Roovers et al.,[9] who used carbosilane dendrimers as the core for the preparation of multiarm star polymers. In this case, monomethylated chlorosilanes were used and only two chlorines on silicon were replaced by vinyl groups. Van der Made et al. used $HSiCl_3$ for the hydrosilation reaction with subsequent replacement of all three chlorines by allyl groups to generate a dendrimer structure with higher density.[12-14] We have modified the synthetic conditions of this route, using the hydrosilation/Grignard reaction sequence to prepare carbosilane dendrimers with a branching degree of 3. Due to the relatively compact structures the polyols described subsequently can be expected to approach spherical geometry already at low generation numbers. Purification of the dendrimers by careful chromatography after each hydrosilation step was essential to separate the dendrimers from condensation products that become inavoidable in higher generations, resulting from unreacted SiCl bonds after the Grignard reaction during the aqueous workup. Carbosilane dendrimers with 4 (G0), 12 (G1), 36 (G2), and 108 (G3) allyl end groups were obtained using this synthetic approach.

The hydroboration reaction using 9-BBN with subsequent oxidation by $H_2O_2/OH^-$ formally leads to anti-Markovnikov addition of $H_2O$ at double bonds. The reaction has been used frequently for quantitative hydroxylation of the double bonds of 1,2- or 1,4-polybutadiene.[17-20] We have used 9-BBN for hydroboration of the allyl groups on the surface of the carbosilane dendrimers in order to avoid cross-linking side reactions. This functionalization route is illustrated in Figure 1, showing the synthesis of a dendritic polyol with 36 end groups.

Separation of the polyols from boronic acid and 1,5-cyclooctanediol is an important step in the synthesis of

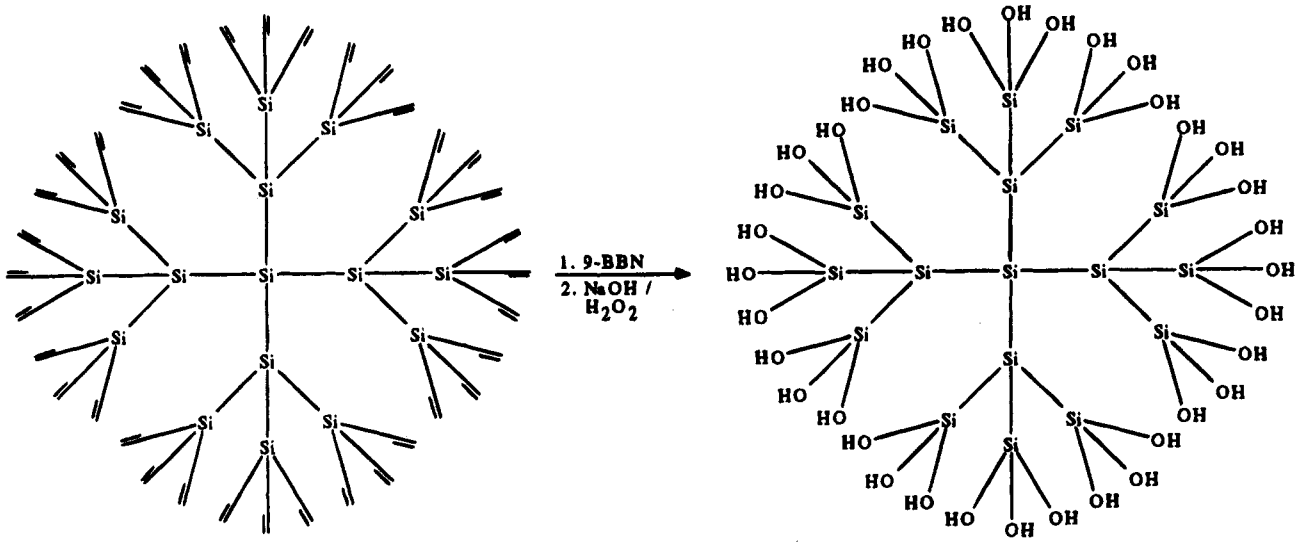


**Figure 1.** Hydroboration of the 36-en (G2) to prepare the dendritic 36-polyol (G2-OH) (— designates a $C_3H_6$ unit).

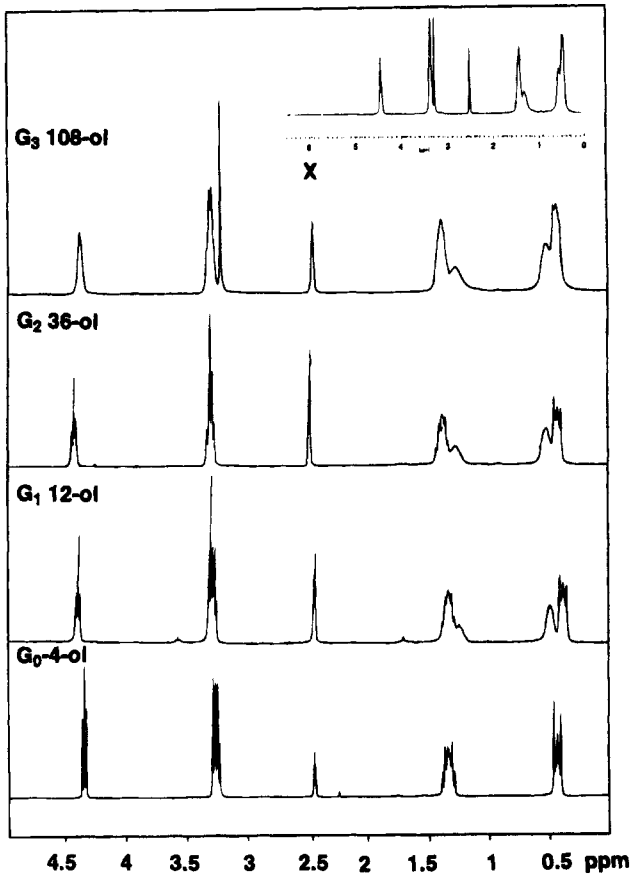


**Figure 2.** $^1$H-NMR spectra of 4-, 12-, 36-, and 108-polyols (X = DMSO signal).

the carbosilane polyols. The boronic acid formed as a product after the hydroboration oxidation procedure has to be separated from the polyols to avoid gelation.[20] This was achieved by converting boronic acid to the respective methyl ester by refluxing with an excess of methanol. The main fraction of cyclooctane-1,5-diol could be removed in vacuo. After repeated precipitation, the pure dendritic polyols were obtained. (For details see the Experimental Section).

Figure 2 shows the $^1$H-NMR spectra of the dendritic polyols from G0-OH to G3-OH. The spectra reflect the transition from a small organic molecule with sharp, narrow lines to a polymer like structure with slightly different chemical environments for nuclei in different generations. This results in broader, unstructured resonances. In addition, restricted mobility of the respective protons in the outer shells may play a role. The NMR spectra evidence the disappearance of the resonances of the olefin protons at 4.8 and 5.7 ppm (this spectral region was generally not shown in the spectra but is exemplified for the 108-polyol in the inset in Figure 2). Neither in the NMR spectra of the carbosilane dendrimers (not shown here) nor for the respective polyol signals evidencing hydrosilation could Markovnikov orientation be discerned.

Although NMR spectroscopy is a valuable tool for monitoring growth and subsequent surface modification reactions of the dendrimers, the sensitivity of the integration was not sufficient for an assessment of structural perfection of the dendrimers at the stage of G2 and G3.

In order to define the dendritic polyols molecularly, SEC and MALDI-TOF mass spectroscopy were employed. So far, generally, no mass spectroscopical assessment of the perfection of carbosilane dendrimers has been carried out. Although size exclusion chromatography (SEC; calibrated to narrow polystyrene standards) is widely used for the characterization of linear macromolecules and also employed to determine the polydispersity of dendrimers, dendrimers in general can not be characterized by SEC, as they do not fit universal calibration curves. An example for the use of SEC with suitable dendritic standards was given by Wörner and Mülhaupt.[21] We have characterized all carbosilane dendrimers and dendritic polyols with SEC, using common PS standards. Generally, SEC showed a monomodal, narrow molecular weight distribution. The polydispersity $M_w/M_n$ remained unchanged in going from G1 to G3. Whereas the molecular weights of the allyl-terminated carbosilane dendrimers were underestimated by a factor of 1.2–2, most probably due to the compact structure of these molecules in comparison to the coiled conformation of the polystyrene standard, the molecular weights of the dendritic polyols were grossly overestimated by SEC. This may be explained by the large hydrodynamic volume of the molecules due to the incompatibility of the surface groups with the core or little interaction with the SEC column due to the polar surface of the molecules.

The MALDI-TOF technique has recently found broad application in the area of biopolymers, such as peptides and proteins.[22] The method is based on laser desorption

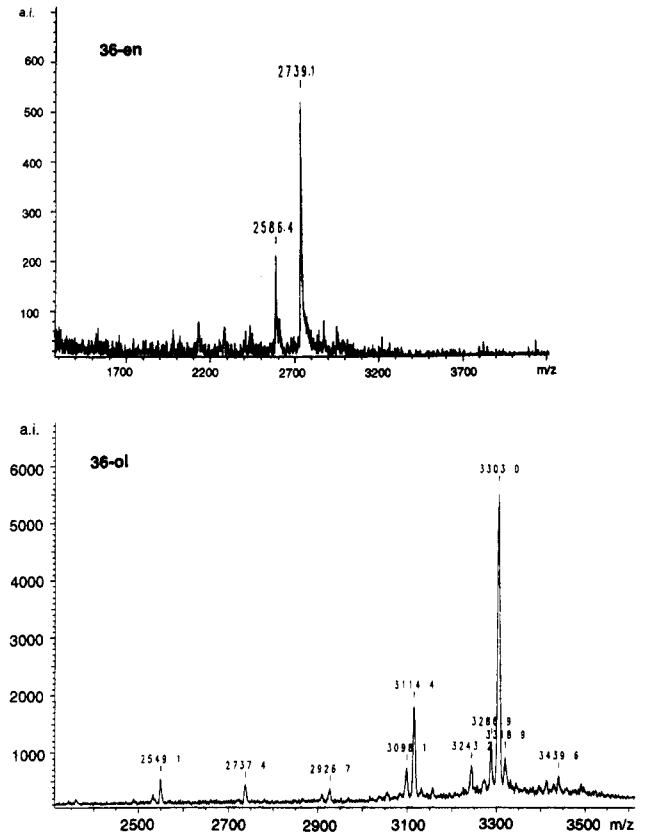


**Figure 3.** a,b MALDI-TOF spectra of (top) G2 (34 and 36 allyl end groups) and (bottom) 36-polyol (G2-OH).

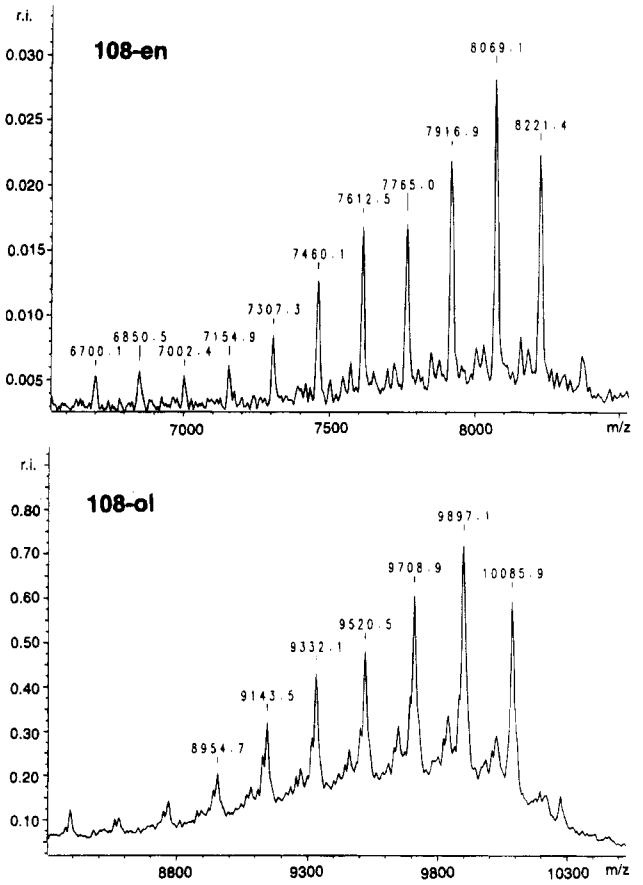


**Figure 4.** a,b MALDI-TOF spectra of (top) G3 (94–108 allyl end groups) and (bottom) 108-polyol (G3-OH).

of molecules dissolved in a suitable matrix (usually organic acids). The potential of MALDI-TOF for the direct analysis of molecular weight distributions of synthetic macromolecules is explored intensely at present.[22] One of the key problems encountered with linear macromolecules, the presence of chain entanglements, is absent for dendrimers. Thus, MALDI-TOF is a highly valuable method for the analysis of the structural perfection of dendrimers. This is demonstrated by the recent investigation of polyacetylene dendrimers and polyesters using MALDI-TOF with excellent results.[23,24]

The MALDI-TOF spectrum of G2 (36-en, Figure 3) shows mainly two signals that are clearly due to the 36-arm dendrimer and a 34-arm dendrimer molecule. The $m/z$ value of the dominant signal (2739.1−107.9 for Ag, see the Experimental Section) corresponds to the calculated value of $m/z$ 2629.4. The formation of the 34-arm dendrimer molecule (smaller signal) is due to incomplete hydrosilation of the 12-arm carbosilane dendrimer, that formally leads to the loss of one $Si(allyl)_3$ unit. The difference of 152.8 amu between the signals reflects the mass difference between carbosilane dendrimers with 34 and 36 end groups, respectively. No signals are observed between these peaks, which confirms clearly that fragmentation of allyl groups on the molecular surface does not affect the analysis. Thus, from the MALDI-TOF spectrum it can be concluded that G2 consists of approximately 80% of the desired, perfect 36-en dendrimer and 20% of dendrimer molecules with one defect resulting from incomplete hydrosilation. Small amounts of dendrimer molecules with 28−32 end groups, that appear in the respective spectrum of the 36-polyol (Figure 3) are badly resolved.

The MALDI-TOF spectrum of the G2-OH (36-polyol) shows the same pattern and demonstrates the presence of mainly two species, the 34- and 36-polyol (the mass of Na has to be subtracted from the $m/z$ values measured in the case of the polyols, see the Experimental Section). This is clear evidence for the quantitative conversion during hydroboration of the dendrimer surface. The mass difference of 188 amu between the respective signals of the polyols again represents exactly the mass of the missing unit in the case of the incomplete hydrosilation reaction of G1 (12-en). If the MALDI-TOF data are interpreted from the viewpoint of polymer chemistry, the results translate to a $M_w/M_n$ value of 1.01 for the dendritic polyol with 36 end groups.

Clearly to be seen from the MALDI-TOF spectra (Figure 4), G3 (108-en) and, consequently, G3-OH are characterized by a broader distribution of dendrimers with 92−108 end groups. The most abundant species possesses 106 end groups. The molecular weight distribution observed with MALDI-TOF translates to 1.03 in this case. Again the occurrence of the same pattern in the two spectra evidences that the surface modification of G3 (108-en) via hydroboration/oxidation proceeded quantitatively.

Whereas the G0-OH (4-polyol) was obtained as a crystalline white solid, the higher generation polyols were obtained as transparent, highly viscous liquids after purification. G1-OH and G2-OH crystallized extremely slowly within a period of 2 months storage at ambient temperature. The crystals formed showed birefringence and a broad melting endotherm at 60−80 °C. Further work on this unusual solid behavior is in progress. No crystallization was observed for G3-OH. All dendritic polyols were very soluble in alcohols and pyridine in contrast to the lipophilic, allyl-substituted carbosilane dendrimers that could only be dissolved in apolar solvents. However, even G3-OH (108-polyol) was practically insoluble in water.

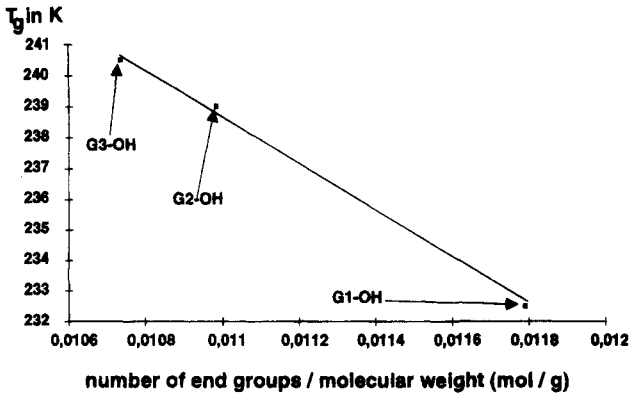


**Figure 5.** Glass-transition temperatures vs $n_e/M$ of the polyols.

Generally, the glass transition temperatures of dendrimers of the same constitution are determined by the ratio of the number of end groups $n_e$ to the number of branching points $n$,[25] which affect the glass transition in an opposite way. Whereas the number of branching points leads to an increase of $T_g$, due to the decreased flexibility of the chain segments in the neighborhood, the number of end groups lowers the $T_g$, which is explained by the larger conformational flexibility of end groups in comparison to segments of the dendrimer core.[25] The ratio $n_e/n$ approaches a limiting value at higher generations, which also marks the limiting $T_g$ value. According to a proposal made by Fréchet et al.,[26] this effect of the number of $n_e$ and $n$ leads to a linear relationship between $T_g$ and $n_e/M$ ($M$ = molecular weight of the dendrimer). For the dendritic carbosilane polyols described in the current paper, the observed glass transitions plotted vs $n_e/M$ also displayed a linear dependence. Clearly to be seen from Figure 5, the expected relationship, already demonstrated for various benzyl phenyl ether dendrimers,[26] is also found in the dendritic carbosilane polyols.

In addition, the surface polarity and hydrogen-bonding strongly affect the glass transition of the novel polyols in comparison to the carbosilane dendrimers. A dependence of the glass transition temperature of benzyl phenyl ether dendrimers on the polarity of the surface groups has been observed already.[26] Whereas the $T_g$ of G3 (108-en) is observed at 185 K, G3-OH (108-polyol) exhibits a $T_g$ at 241 K. This strong increase of $T_g$ is certainly related to hydrogen-bonding, but may also be influenced by exclusion of the polar hydroxyl units from the lipophilic carbosilane core, leading to extension of the molecular scaffold. Further experiments are under way to investigate this $T_g$ variation in detail.

## Conclusions

A divergent hydrosilation/Grignard reaction sequence, followed by end-group hydroboration has been employed to prepare a series of novel dendritic carbosilane polyols. Using MALDI-TOF, for the first time the dendritic carbosilanes as well as the novel polyols have been characterized directly with respect to molecular weight distribution. The data show clearly that the Grignard reaction as well as the ensuing surface hydroboration reaction are quantitative, whereas the hydrosilation reaction step resulted in almost quantitative conversion in higher generations. The dendritic polyols constitute lipophilic, flexible arborols with weak intramolecular interactions. These compounds may conveniently be used as molecular scaffolds for the construction of unusual molecular architectures. The chemical stability of the dendrimer core permits a wide variety of modification reactions on the dendrimer shell that may be carried out by simple condensation with acyl chlorides or addition reactions of isocyanates.

From a polymer physical point of view it is intriguing that the molecules contain an inner compartment whose polarity is completely different from the hydrophilic shell. This should lead to unusual viscosity behavior in solution.

Further work on surface modification of the dendrimers, e.g., aiming at the preparation of liquid crystalline dendrimers with spherically coupled mesogens, is in progress.

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