Synthesis of Novel Carbosilane Dendrimers Based on Pentaerythritol

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Novel pentaerythritol-based carbosilane dendrimers centered at carbon have been synthesised. Starting from tetraallyl ether based upon pentaerythritol as the core molecule, a succession of alternate Pt-catalyzed hydrosilylation of allyl groups with $HSiCl_3$ and allylations of SiCl groups thus introduced with $CH_2=CHCH_2MgBr$ in THF provided a divergent synthesis of three generations of carbosilane dendrimers in which the Si atoms are linked by $CH_2CH_2CH_2$ groups. The reaction conditions for hydrosilylation must be well controlled. After purification by chromatography on silica gel pure products for each generation were obtained. The IR, ^{1}H and ^{13}C NMR spectra and elemental analysis data are consistent with the proposed structures. The molecular weights of the resulting carbosilne dendrimers have been determined by vapor pressure osmometry.

Keywords   pentaerythritol, carbosilane dendrimer, hydrosilylation, allylation

Introduction

Over the past decade great interest has been developed in a group of macromolecules known as dendrimers, which represent a key stage in the ongoing evolution of macromolecular chemistry. Because of their distinct high-branched, well-defined, three-dimensional and treelike structures, dendrimers offer new and unique physical and chemical properties, they provide new models for basic and theoretical studies, and they are attractive scaffolds for a variety of high-end applications.[1,2]

There are mainly two methods for dendrimer synthesis, the convergent method and the divergent method,[1] of which the latter is the most common and efficient route to produce silicon based dendrimers. Among them, carbosilane dendrimers are well studied and can be synthesized by repetitive alkenylation-hydrosilylation cycles, first introduced by van der Made,[3] Roovers,[2,4] and Seyferth.[5,6] Silicon tetrachloride was used as a core in most cases to produce carbosilane dendrimers.[7] Carbosilane dendrimers with other cores, such as $(Me(CH_2=CH)SiO)_4$ and $((CH_2=CHCH_2O)$-$SiCH_2)_2$ have been reported by Kim's group.[8,9]

Introducing carbon as the central atom of carbosilane dendrimer is an interesting work. Pentaerythritol, with a center carbon, multi-functional groups and symmetrical structure, has been used for the synthesis of polyether dendrimers, polyamide dendrimers, polyamine dendrimers, and organometallic dendrimers,[10] nevertheless not for carbosilane dendrimer construction. As mentioned above, there are a few compounds which can be used as the core molecules of carbosilane dendrimers, such as $SiCl_4$ and siloxane. In general, carbon, as the central atom, is more stable than silicon. Due to their unique structure, pentaerythritol-based carbosilane dendrimer may offer novel properties and potential applications including that as scaffolds for the synthesis of new functional macromolecules. To the best of our knowledge, the carbosilane dendrimer with carbon being the center has not been reported. Herein we report the synthesis of these novel dendrimers based upon pentaerythritol.

Experimental

General

All reactions were carried out under an atmosphere of dry nitrogen unless otherwise noted. Solvents were purified by established procedures. Karstedt catalyst (platinum-divinyltetramethyldisiloxane complex in xylene) was prepared according to literature.[11] FT-IR spectra were measured on a Nicolet FTIR 5DX spectrophotometer. NMR spectra in $CDCl_3$ solution were recorded on a Japan Joel FX-90Q NMR spectrometer. A Perkin-Elmer 240C elemental analysis apparatus was employed. Vapor pressure osmometry (VPO) was performed with a Wescan in toluene at 50 ℃.

Pentaerythritol

Chin. J. Chem., 2004, Vol. 22, No. 11 **1367**

Allyl magnesium bromide

Allylmagnesium bromide was made in anhydrous THF by reacting magnesium metal coil with allyl bromide (1.1 mol equiv. to Mg) at room temperature. During the reaction the allyl bromide in THF was added dropwise into the flask containing magnesium and a small amount of allyl bromide in THF at a speed to keep the reaction system gently refluxing under dry nitrogen.

Tetraallyl ether based on pentaerythritol (0G)

Described as in reference 12. ^{1}H NMR (CDCl$_3$) δ: 6.03—5.67 (m, 4H), 5.30—5.06 (m, 8H), 3.94 (d, $J=6$ Hz, 8H), 3.46 (s, 8H); ^{13}C NMR (CDCl$_3$) δ: 136.25, 134.71, 71.98, 70.00, 44.99; IR (KBr) v: 3078, 2909, 2866, 1645, 1420, 1349, 1090, 993, 922 cm^{-1}. Anal. calcd for C$_{17}$H$_{28}$O$_4$: C 68.92, H 9.46; found C 68.85, H 9.40.

First generation carbosilane dendrimer (1G)

Into a 50 mL flask was added 1.5 g (5 mmol) of tetraallyl ether (**0G**), 3.0 mL (20 mmol, excess 50%) of HSiCl$_3$, 20 mL of anhydous THF, and five drops of Karstedt catalyst solution. The resulting mixture was stirred for 30 min at room temperature and subsequently for 4 h at 50 ℃. Volatiles were removed at reduced pressure, and 20 mL of fresh anhydrous THF was transferred to the flask through the vacuum system. Then this solution was dropwise added into freshly made allylmagnesium bromide (90 mmol, excess 50%) in 50 mL of THF. After completion of the addition, the reaction mixture was heated at reflux for 10 h. The mixture was cooled to room temperature and then poured into ice-cold saturated aqueous NH$_4$Cl. The aqueous layer was extracted twice with Et$_2$O, and the combined aqueous layers were washed twice with water and twice with saturated aqueous NaCl and dried over anhydrous MgSO$_4$. After the solvent was removed on the rotary evaporator, 5.0 g of residue was purified by flash chromatography on a silica gel column eluted with 1 ： 100 *V/V* EtOAc/petroleum ether leaving 2.5 g of pure oily product **1G** in 55% yield. ^{1}H NMR (CDCl$_3$) δ: 5.97—5.49 (m, 12H), 4.89—4.73 (m, 24H), 3.36 (m, 16H), 1.57 (m, 8H), 1.53 (d, $J=7.8$ Hz, 24H), 0.56 (m, 8H); ^{13}C NMR (CDCl$_3$) δ: 133.99, 113.43, 69.66, 70.48, 45.59, 23.61, 19.47, 7.54. Anal. calcd for C$_{53}$H$_{92}$O$_4$Si$_4$: C 69.03, H 10.18; found C 68.95, H 10.09.

Second generation carbosilane dendrimer (2G)

Into a 50 mL flask was added 1.8 g (2 mmol) of **1G**, 3.6 mL (36 mmol, excess 50%) of HSiCl$_3$, 20 mL of anhydous THF, and five drops of Karstedt catalyst solution. The resulting mixture was stirred for 30 min at room temperature and subsequently for 4 h at 50 ℃. Volatiles were removed at reduced pressure, and 20 mL of fresh anhydrous THF was transferred to the flask through the vacuum system. Then this solution was dropwise added into freshly made allylmagnesium bromide (110 mmol, excess 50%) in 50 mL of THF. After completion of the addition, the reaction mixture was

heated at reflux for 15 h. The mixture was cooled to room temperature and then poured into ice-cold saturated aqueous NH$_4$Cl. The aqueous layer was extracted twice with Et$_2$O, and the combined aqueous layers were washed twice with water and twice with saturated aqueous NaCl and dried over anhydrous MgSO$_4$. After the solvent was removed on the rotary evaporator, the 5.8 g of residue was purified by flash chromatography on a silica gel column eluted with 1 ： 200 *V/V* EtOAc/petroleum ether leaving 2.4 g of pure viscous product **2G** in 45% yield. ^{1}H NMR (CDCl$_3$) δ: 5.96—5.48 (m, 36H), 4.89—4.72 (m, 72H), 3.34 (m, 16H), 1.56 (m, 8H), 1.52 (d, $J=7.8$ Hz, 72H), 1.19 (m, 24H), 0.58 (m, 56H); ^{13}C NMR (CDCl$_3$) δ: 134.09, 113.39, 70.46, 69.70, 44.60, 29.59, 20.86, 19.65, 18.17, 17.39, 16.57. Anal. calcd for C$_{161}$H$_{284}$O$_4$Si$_{16}$: C 70.82, H 10.41; found C 70.50, H 10.18.

Third generation carbosilane dendrimer (3G)

Into a 25 mL flask was added 1.5 g (0.55 mmol) of **2G**, 3.0 mL (20 mmol, excess 50%) of HSiCl$_3$, 10 mL of anhydous THF, and five drops of Karstedt catalyst solution. The resulting mixture was stirred for 30 min at room temperature and subsequently for 6 h at 50 ℃. Volatiles were removed at reduced pressure, and 10 mL of fresh anhydrous THF was transferred to the flask through the vacuum system. Then this solution was dropwise added into freshly made allylmagnesium bromide (90 mmol, excess 50%) in 50 mL of THF. After completion of the addition, the reaction mixture was heated at reflux for 20 h. The mixture was cooled to room temperature and then poured into ice-cold saturated aqueous NH$_4$Cl. The aqueous layer was extracted twice with Et$_2$O, and the combined aqueous layers were washed twice with water and twice with saturated aqueous NaCl and dried over anhydrous MgSO$_4$. After the solvent was removed on the rotary evaporator, the 4.8 g of residue was purified by flash chromatography on a silica gel column eluted with 1 ： 500 *V/V* EtOAc/petroleum ether leaving 1.45 g of pure vircous product **3G** in 32% yield. ^{1}H NMR (CDCl$_3$) δ: 5.96—5.48 (m, 108H), 4.89—4.72 (m, 216H), 3.35 (m, 16H), 1.66 (m, 8H), 1.52 (d, $J=7.3$ Hz, 216H), 1.20 (m, 96H), 0.69 (m, 200H); ^{13}C NMR (CDCl$_3$) δ: 134.31, 113.13, 69.90, 70.61, 44.88, 29.65, 22.09, 20.97, 19.80, 18.35, 18.17, 17.87, 17.63, 16.77. Anal. calcd for C$_{485}$H$_{860}$O$_4$Si$_{52}$: C 70.98, H 10.49; found C 70.54, H 10.26.

Results and discussion

Synthesis of carbosilane dendrimers

In the controlled step growth approach, there should be two basic units for the construction of dendrimers: the initial core and the propagation units. The initial core contains more than two functional groups, which are used for the branch growth. The propagation unit always has two different functional groups. The resulting first generation is used as a new core and the reac-

tions of the first generation are repeated to yield the second generation. The third generation is made in the same manner. It should be noted that all reactions involed in each growth step should be quantitative without side reactions, since incomplete reactions or side reactions will cause structural defects and/or coupling between dendrimers. It is also obvious that the purity of each generation is very important for the subsequent growth of dendrimers.[2]

In our synthesis of carbosilane dendrimers, tetraallyl ether based upon pentaerythritol was chosen as the initial core molecule and trichlorosilane ($HSiCl_3$) was used as the propagation unit. The synthesis as shown in Scheme 1 started from the Pt-catalyzed hydrosilylation of the allyl groups of tetraallyl ether **0G** based upon pentaerythritol with trichlorosilane.[12] All the silicon chloride groups were then replaced by allylmagnesium bromide to give the first generation with twelve allyl groups connected to four silicon atoms.

The hydrosilylation reaction, an addition reaction of a Si-H group to carbon-carbon unsaturated bond, has proved to be a very convenient method for forming silicon-carbon bonds. The advantages of using this reaction in the dendrimer synthesis are its high yields and minimal side reactions. The hydrosilylation of tetraallyl ether with trichlorosilane was carried out in THF at 50 ℃ under nitrogen with platium complex in xylene as the catalyst. Both trichlorosilane and anhydrous THF were distilled immediately before use. Excess trichlorosilane was used to enhance completion of the reaction.

The conversion of silicon chloride to allyl groups was performed by reacting the hydrosilylation product with allylmagnesium bromide in THF. After the hydrosilytion the excess trichlorosilane and solvent were removed at reduced pressure. The isolated product was redissolved in anhydrous THF. In general, this solution was then added to a freshly made Grignard reagent. It should be mentioned that we found that allylmagnesium bromide was easy to couple with allyl bromide to form 1,5-hexadiene (diallyl), which led to several failed

Scheme 1
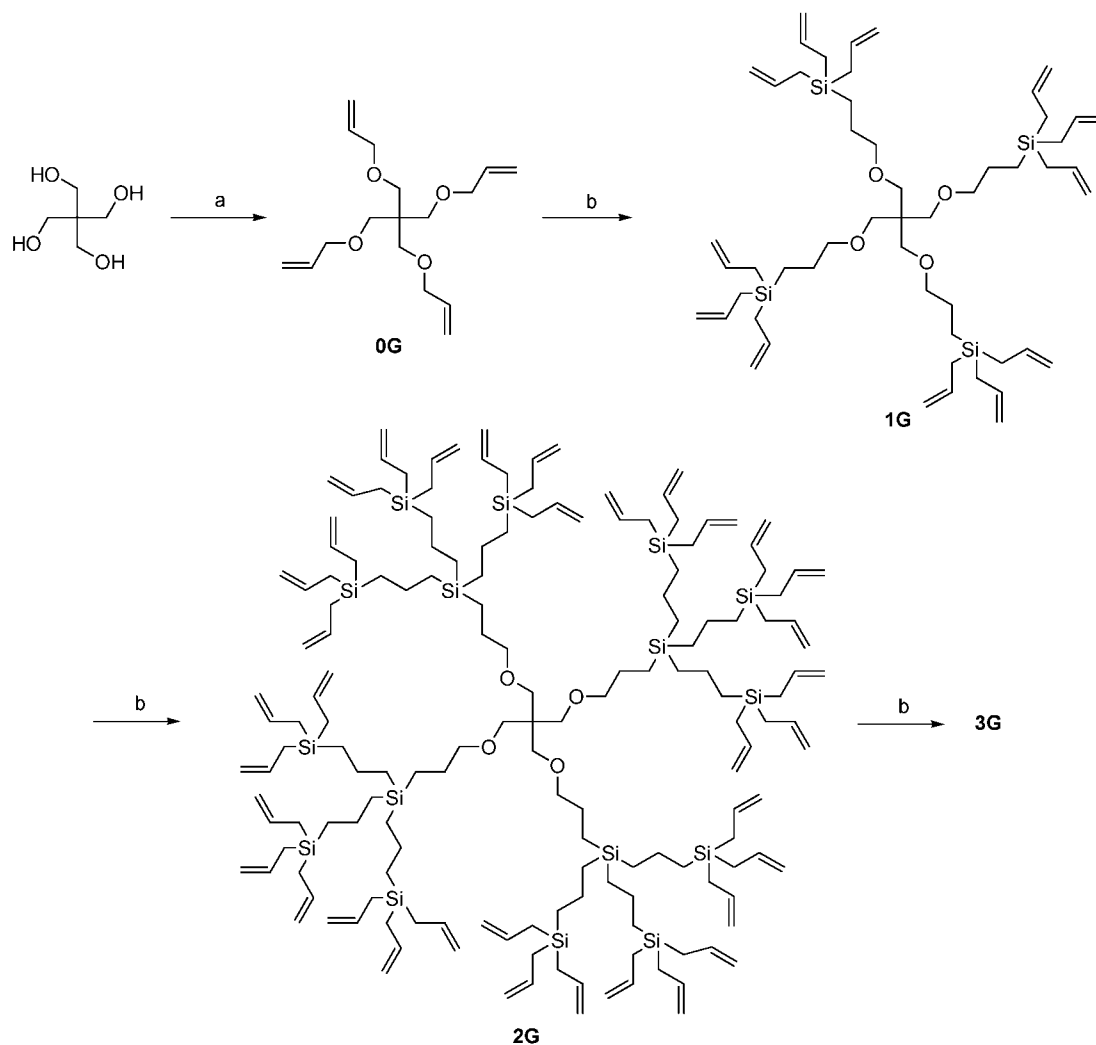
a. $CH_2=CHCH_2Br$, NaOH, THF;
b. 1) $HSiCl_3$, Karstedt catalyst, THF; 2) $CH_2=CHCH_2MgBr$, THF.

reactions. To avoid this disadvantage and the other side reactions, allyl bromide should be added dropwise and the vessel should be in water-bath or oil-bath, which made the reaction system keep lower temperature. After completion of the addition, the reaction mixture was heated at reflux for 10—20 h. The mixture was cooled to room temperature and then poured into ice-cold saturated aqueous NH_4Cl and extracted with Et_2O.

Each generation was purified by chromatography on a silica gel column eluted with a solution of ethyl acetate in petroleum ether. The isolated yields were 55%, 45% and 32% for **1G**, **2G**, and **3G**, respectively. All these pure products are either oily or viscous liquids. They are soluble in most organic solvents. The molecular characterization of each generation is summerized in Table 1.

Table 1 Molecular Information of the carbosilane dendrimers

Generation	Formula	Functionality	M_{calcd}	M^a
0G	$C_{17}H_{28}O_4$	4	296	282
1G	$C_{53}H_{92}O_4Si_4$	12	904	860
2G	$C_{161}H_{284}O_4Si_{16}$	36	2728	2610
3G	$C_{485}H_{860}O_4Si_{52}$	108	8200	7830

^{a} Vapor pressure osmometry (VPO) in toluene at 50 ℃.

^{1}H and ^{13}C NMR spectroscopy

In each step of the synthesis only perfect growth and pure products give simple, symmetric, and well-defined NMR spectra. For each generation, the exterior allyl protons and carbons are quite easily distinguished in both the proton and carbon NMR specrta, but the methylene groups, which include some types of hydrogens and carbons, give very complicated spectra.

As shown in Figure 1, the ^{1}H spectrum of **0G** shows allyl protons at δ 5.85, 5.18, and 3.94, and the methylene protons (attached to the center carbon) give peak at δ 3.46. The ^{1}H spectrum of **1G** shows allyl protons at δ 5.73, 4.81, and 1.53. There are three types of methylenes: one is attached to the center carbon and the oxygens, one is between the other two methylenes and another is close to the silicon, which give peaks at δ 3.36, 1.57, and 0.56, respectively. For **2G** and **3G**, the pattern of these allyl protons does not change, but there are four types of methylenes. The methylenes between the other two methylenes can be divided into two types: one is close to the oxygens and the center carbon, and the other is between the two silicons, which give peaks at δ 1.57 and 1.19, respectively. Furthermore, these peaks become broader as the molecular weight becomes larger.
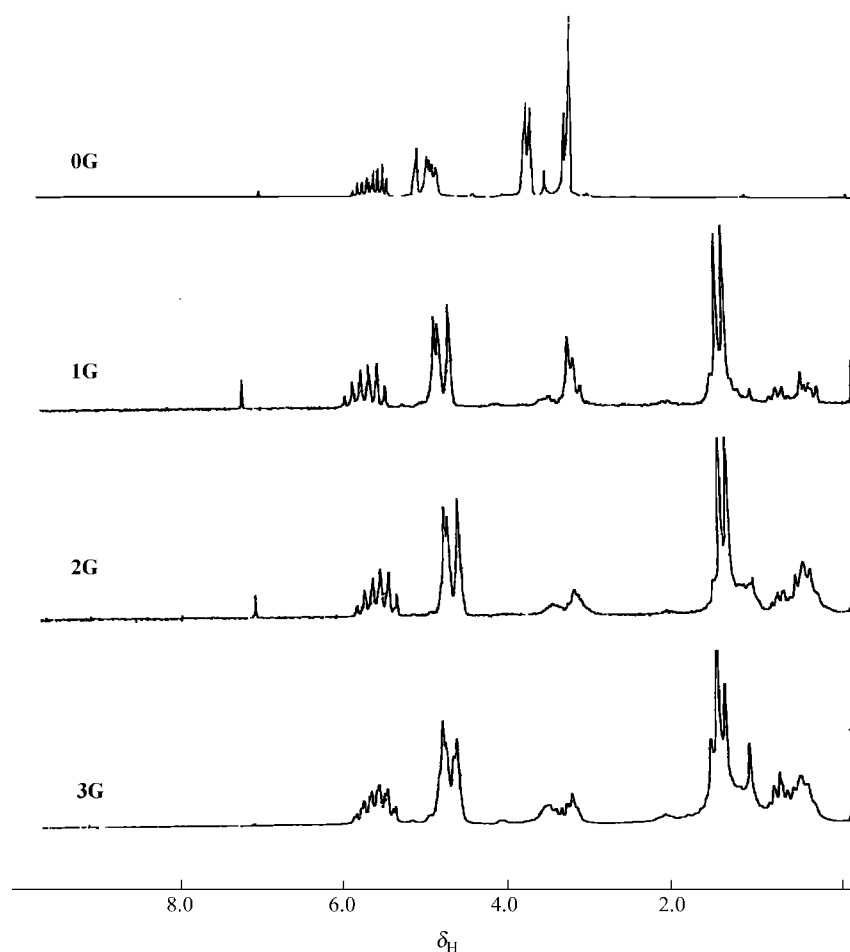

Figure 1 ^{1}H NMR spectra of the carbosilane dendrimers.

The ^{13}C NMR spectra of all the generations are also quite similar, as shown in Figure 2. For **0G**, the three allyl carbons are found at δ 134.71, 136.25, and 71.98, the carbon close to the center carbon is found at δ 70.00, and the center carbon is found at δ 44.99. For **1G**, the three allyl carbons are found at δ 133.99, 113.43, and 19.47. For **2G**, they are at δ 134.09, 113.39, and 19.65. For **3G**, they are at δ 134.31, 113.54, and 19.80. The methylene carbons are more complicated. For **1G**, there are four types of methylene carbons. The methylene carbons between the center carbon and the oxygens are at δ 69.66 and those attached to methylenes and the oxygens are at δ 73.92. The methylene carbons between the other two methylenes are at δ 23.61 and those close to the silicons are at δ 7.54. The center carbon is at δ 45.59. For **2G** and **3G**, there are more types of methylene carbons. The methylene carbons attached to the center carbon and the oxygens are at δ 69.70 for **2G**, δ 69.90 for **3G**. The methylene carbons attached to methylene and the oxygens are at δ 70.46 for **2G**, δ 70.61 for **3G**. The methylene carbons between the other two methylenes, and close to the oxygens and the center carbon are at δ 29.59 for **2G**, δ 29.65 for **3G**. The methylene carbons between the other two methylenes, and close to the two silicons are at δ 20.86 for **2G**, δ 20.97 and 22.09 for **3G**. The methylene carbons close to the

silicon are at δ 18.17, 17.39, and 16.57 for **2G**, δ 18.35, 18.17, 17.87, 17.63, and 16.77 for **3G**. The center carbon is at δ 44.60 for **2G**, δ 44.88 for **3G**. As the dendrimer grows bigger, the concentration of the carbons connected to the center carbon becomes lower, and the intensity of the peak at δ 70 for these carbons decreases from **1G** to **3G**.

Molecular weight determination

The molecular weights of each generation were determined by vapor pressure osmometry (VPO). All the results are summarized in Table 1. As seen in Table 1, the experimental molecular weights are very comparable to their calculated values within the experimental errors.

Conclusion

A series of novel carbosilane dendrimers were synthesised via a divergent growth. In the synthesis, tetraallyl ether based upon pentaerythritol was used as the initial core molecule. Two important reactions are involved in the synthesis: hydrosilylation and allylation. These dendrimers have been characterized by IR, NMR spectra, elemental analysis, and VPO.
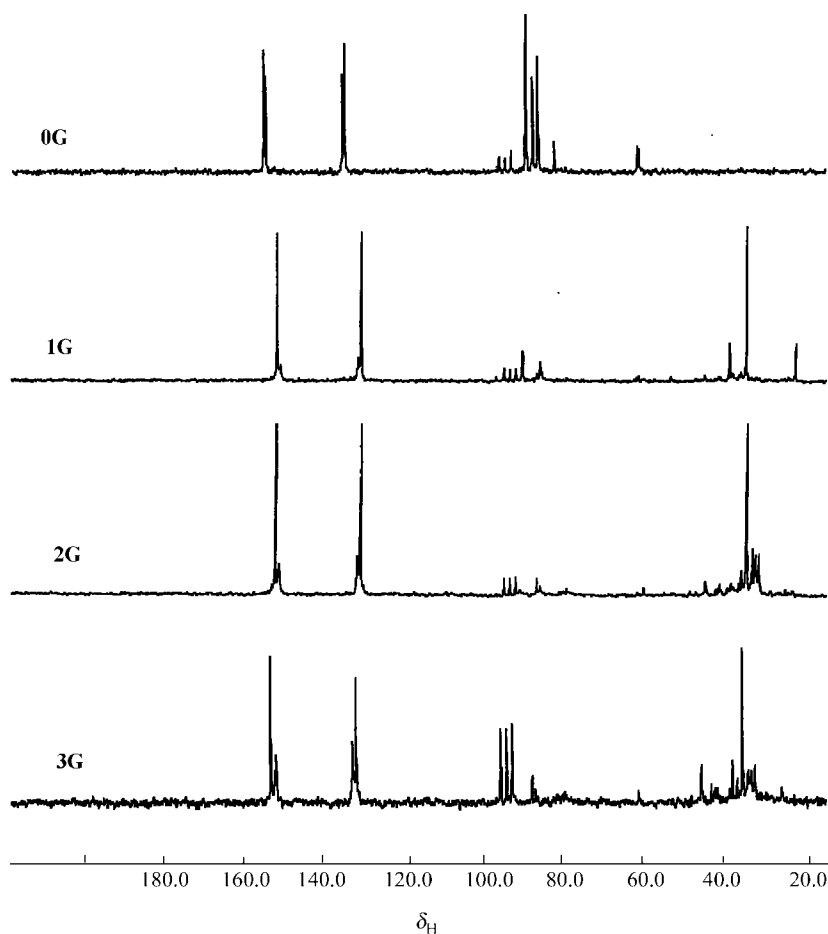

Figure 2 ^{13}C NMR spectra of the carbosilane dendrimers.

Pentaerythritol

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This is the first report for the synthesis of pentae-rythritol-based carbosilane dendrimers with central atom being carbon, which is different from conventional carbosilane dendrimers. These dendrimers may show new physical and chemical properties. They are expected to lead potential applications. Moreover, our route offers a unique flexibility: not only the degree of branching can be adjusted by replacing $HSiCl_3$ with $HSiCl_2Me$ or $HSiClMe_2$, but also the length of the branches can be varied. As an additional benefit the reactive Si-Cl end groups allow an easy functionalization of the dendrimer surface for the preparation of a diversity of novel materials, such as liquid crystalline dendrimers. Further research into the properties and functionalization of these dendrimers is now under way.

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