
Silicon-Based Dendrimers

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This review focuses on dendrimers with Si-atoms as branching point, aiming at a comprehensive summary of the state of the art of the field. Carbosilane, siloxane, silane, silazane, and silatrane dendrimers are considered. The important features common to Si-based dendrimers are: (i) almost all of the Si-based dendrimers known at present are prepared divergently; (ii) most of the known Si-based dendrimers exhibit high flexibility, manifested by low glass transition temperatures; (iii) the use of Si as branching connectivity permits one to vary the branching multiplicity between 2 and 3, allowing one to tailor the density of the structures. Hyperbranched polymers based on silicon that fulfill the structural criterion are also considered, since it is likely that many of the applications discussed for structurally perfect dendrimers at present will eventually be realized with well-defined hyperbranched polymers obtained in one reaction step.

Keywords: Silicon, Dendrimers, Hyperbranched polymers, Synthesis, Application potential.

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1

Introduction

Since the first description of a “cascade” synthesis in the late 1970s by Vögtle et al. [1] and the seminal work by Tomalia et al. [2] and Newkome et al. [3] in the mid-1980s, dendrimers, perfectly branched, highly symmetrical tree-like macromolecules have evolved from a curiosity to an important trend in current chemistry. Amply demonstrated in this volume, a wide variety of dendrimer construction strategies has been developed on the basis of classical organic chemistry. The state of the art in the synthesis, nomenclature, and terminology in use as well as various unusual features of this still relatively young class of macromolecules have been summarized in excellent reviews by various authors [4–11].

Dendrimers based on heteroatoms offer several peculiar features, such as variable branching multiplicity, high flexibility, and unusual electro-optical properties. The main emphasis in this field to date has been placed on phosphorus- and silicon-based dendrimer topologies. Some of the developments in the general area of heteroatom-based dendrimers have been summarized in previous reviews, documenting the enormous increase in activity in recent years [12–14].

This review focuses on Si-based dendrimers, i.e., dendrimers with Si-atoms as branching point between the generations. We aim at a comprehensive summary of the state of the art in the field, focusing on carbosilane, siloxane, silane, silazane, and silatrane dendrimers. Only in a few cases, when analogies to other classes of dendrimers are important, are the respective works cited. Hyperbranched polymers that fulfill the structural criterion are considered in the final part of this review, since it is likely that many of the applications discussed for structurally perfect dendrimers will eventually be realized with well-defined hyperbranched polymers obtained in one reaction step, possessing a certain polydispersity and a randomly branched structure.

Silicon chemistry offers several quantitative (>99% yield) reactions suitable for the preparation of dendrimers. Most of the various classes of Si-based

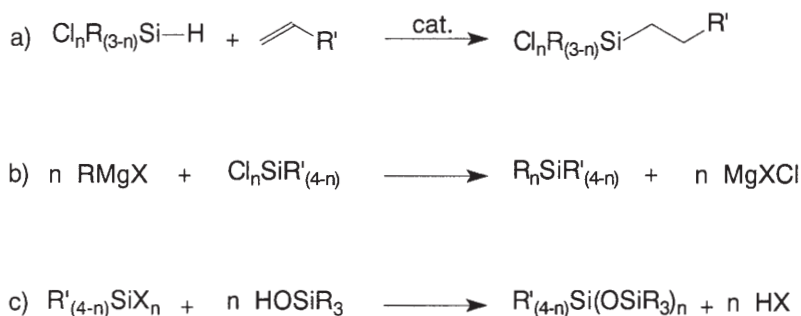


Fig. 1 a–c. Set of basic construction reactions used for the synthesis of most Si-based dendrimers

dendrimers known have been prepared on the basis of the relatively small set of reactions shown in Fig. 1, which comprises hydrosilylation, Grignard-reactions, and controlled condensation of silanols. In the case of silazane structures, the aminolysis of chlorosilanes replaces the hydrolysis used for the preparation of carbosiloxane structures. Complete conversion is an essential prerequisite for the construction of structurally perfect dendrimer molecules, since the preparation of higher dendrimer generations requires the transformation of a large number of functional groups at one macromolecule.

There are some important features common to all Si-based dendrimers: (i) almost all of the Si-based dendrimers known at present are prepared divergently; (ii) most of the known Si-based dendrimers exhibit high flexibility, manifested by low glass transition temperatures; (iii) the use of Si as branching connectivity permits to vary the branching multiplicity to a certain extent, rendering the structures ideal for the investigation of the correlation of the branching density with materials properties.

2 Carbosilane Dendrimers

2.1 Synthesis and Characterization

2.1.1 General Synthetic Strategy

Among the Si-based dendrimers, polycarbosilane structures, recently briefly reviewed [15], have received by far the strongest attention to date, due to their straightforward synthesis and the possibility to tailor the dendrimer structures by variation of (i) core functionality, (ii) branching multiplicity, and (iii) the segment length between the branch points, respectively. Furthermore polycarbosilanes are kinetically as well as thermodynamically very stable molecules owing to the dissociation energy of the Si-C bond (306 kJ mol^{-1}), which is similar to that of C-C bonds (345 kJ mol^{-1}) and the low polarity of the Si-C bond. So

far, almost all reported carbosilane dendrimers have been synthesized via the divergent approach. Generally, the synthesis starts from a core molecule possessing alkenyl groups with a hydrosilylation step using either trichlorosilane or dichloromethylsilane as hydrosilylation reagent, depending on the desired branching multiplicity. The following alkenylation step is usually carried out with either vinyl- or allylmagnesium halides, depending on the desired spacer length. Although hydrosilylation as well as Grignard reactions are well-known and widely studied reactions, they are not unproblematic for the construction of carbosilane dendrimers. It is obvious that the major problem in the divergent synthesis of dendrimers is the fact, that very high conversions have to be reached in each reaction step. Since the yields of Grignard reactions decrease with increasing size of the Grignard reagent, only short alkyl spacers between the branch points can be employed. The main problem associated with the hydrosilylation step lies in the control of the regioselectivity of the Si-H addition to an unsymmetrically substituted olefin. In the reaction of a terminal olefin $R'CH=CH_2$ with a silane of the structure R_3SiH , the α -adduct, $R_3SiCH(R')CH_3$, and the β -adduct, $R_3SiCH_2CH_2R'$, can be formed. Although the presence of both units in the hydrosilylation product should not affect the further growth of the dendrimer, usually the β -adduct is desired in order to obtain a dendrimer of maximum symmetry. The other problem related to the hydrosilylation step is the isomerization of the terminal double bonds in the case of allyl end groups. This isomerization leads to internal double bonds, which are no longer amenable to hydrosilylation and therefore this side reaction produces dendrimers with defective branching structure. The extent of isomerization depends strongly on the solvent used and can thus be disfavored by careful choice of the solvent. Depending on the chlorosilane used, the branching multiplicity of the dendrimers is either 2 or 3. As it has been shown by MALDI-TOF studies [16–18], a branching multiplicity of 2 leads to lower steric hindrance and hence more perfect structures can be obtained in higher generations ($> G_2$) than in the case of a branching multiplicity of 3. Unfortunately, in most reports on carbosilane dendrimers, MALDI-TOF mass spectrometry has not been employed, which renders it difficult to compare the perfection of the structures attained.

A typical reaction sequence leading to a carbosilane dendrimer of the first generation with allyl end groups and a branching multiplicity of 3 is shown in Fig. 2.

As early as 1978 Fetters et al. reported the use of a branched carbosilane structure that may be viewed as a dendrimer of the first generation with 12 end groups. This molecule was used for the preparation of a 12-arm star polymer [19]. However, van der Made et al. [20, 21], Zhou et al. [22, 23], and Muzafarov et al. [24] independently reported the first syntheses aiming at carbosilane dendrimers of various generations. Van der Made et al. used tetraallylsilane as core, trichlorosilane as hydrosilylation reagent, and allylmagnesium bromide as ω -alkenylation reagent to obtain dendrimers up to the fifth generation. The authors also report the use of undecenylmagnesium bromide to prepare dendrimers with a less dense structure. However, it has to be mentioned that the molecular weight and the structural perfection of these dendrimers were not substantiated by appropriate analytical methods. In addition, the use of long

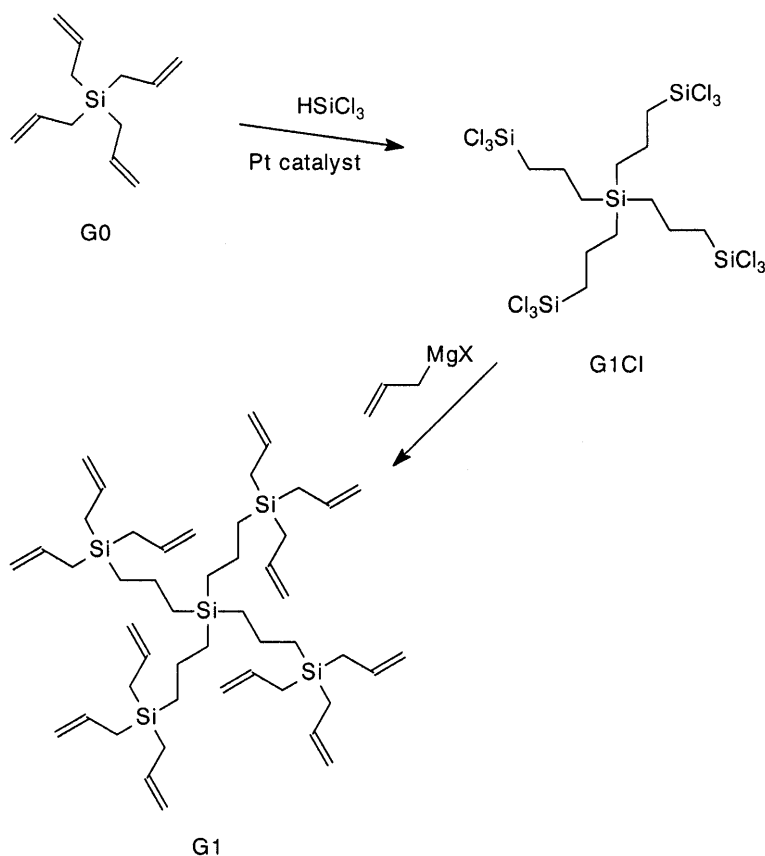


Fig. 2. Typical reaction sequence for the preparation of a G1 carbosilane dendrimer

alkylmagnesium bromides for quantitative conversion at tetrahedral silicon has been reported to be problematic [25] and therefore dendrimers with perfect structure are unlikely. In contrast, Zhou and Roovers started from tetraallylsilane and built up dendrimers up to the fourth generation by hydrosilylation with dichloromethylsilane and alkenylation with vinylmagnesium bromide. This route leads to a slower increase of the number of branches and therefore to a more open structure compared to van der Made's approach. The molecular weights of each generation were determined by vapor pressure osmometry and laser light scattering, the results being comparable to the calculated values. Using SEC, Zhou and Roovers showed that there are no gross structural imperfections, such as dimers, in the dendrimers prepared. Furthermore, they showed that SEC is not well-suited for the judgment of the structural perfection of dendrimers, owing to the broadening of the SEC traces by diffusion and the insensitivity of the method to small imperfections in the globular topology. Muzafarov et al. reported the use of triallylmethylsilane as core, methyldichlorosilane in the hydrosilylation step, and allylmagnesium bromide in the alkenyla-

tion step [24]. However, experimental data were not given in this report. In a more recent publication by this group, carbosilane dendrimers obtained by similar reactions, however starting from tris(methyldiallylsiloxy)methylsilane have been described [26]. Dendrimers up to the seventh generation were obtained and characterized with respect to thermal properties.

Seyferth et al. presented a strategy that – starting from tetravinylsilane as the core molecule and using a succession of alternate hydrosilylations of the vinyl groups with trichlorosilane, followed by reaction of the silyl chloride end groups with vinylmagnesium bromide – provided four generations of carbosilane dendrimers. These represent the most dense structures available employing this approach [27]. In addition Seyferth et al. reduced the chlorosilanes of each generation with LiAlH_4 to the corresponding Si-H terminated dendrimers, which were employed as pyrolytic SiC precursors. The ceramic residue yields obtained after pyrolysis of these precursors in argon at 950 °C (TGA experiments) increased with generation number. For the fourth generation a yield of 66% was obtained, which is generally considered to be satisfactory in pre-ceramic polymer chemistry. However, the authors state unambiguously that in practice the utility of these materials as ceramics precursors is very limited due to the laborious synthesis.

Numerous reports on the synthesis of carbosilane dendrimers with allyl end groups have been published by Kim et al. [28–32], who used various core molecules containing allyl- or vinyl groups, for instance 2,4,6,8-tetramethyl-2,4,6,8-tetravinyltetrasiloxane, diallylphenylmethylsilane, 1,2-bis(triallylsilyl)ethane, and triallylmethylsilane. Kim et al. constructed the dendrimers with allylmagnesium bromide as Grignard reagent and either HSiCl_3 or HMeSiCl_2 as hydrosilylation reagent. Characterization of the dendrimers relies on NMR spectroscopy and elemental analysis only. In further publications these authors reported the synthesis of carbosilane dendrimers terminated with phenylethynyl, *p*-bromophenoxy and *p*-phenylphenoxy groups, respectively [33–38]. In some cases, the obtained products were characterized by MALDI-TOF mass spectrometry. In addition to carbosilane and siloxane cores, use of a glucose derivative as a chiral building unit for the construction of carbosilane dendrimers has been reported recently by Boysen and Lindhorst [39]. Tetra-*O*-allylglycosides were prepared and subjected to the hydrosilylation/Grignard reaction sequence to afford G1 dendrimers.

In recent work, van Leeuwen et al. developed a promising strategy for the divergent preparation of carbosilane-based dendrons with focal amine functionality (G1–G3). The approach is based on a bromopropyl-trichlorosilane core used for the dendrimer construction and subsequent reaction with ammonia under pressure to generate the focal amine functionality. Coupling of the amine with trimelic acid has been employed to obtain hybrid topologies with polar triamide core that may serve as a binding site for polar guests in the receptor-like structure [40, 41]. Jaffrès and Morris chose the polyhedral silsesquioxane octavinylpentacyclooctasiloxane as core and trichlorosilane, dichloromethylsilane, and chlorotrimethylsilane as hydrosilylation reagent [42]. Applying vinylmagnesium bromide as well as allylmagnesium bromide, a variety of dendrimers up to the second generation, differing in the number and the type of end groups,

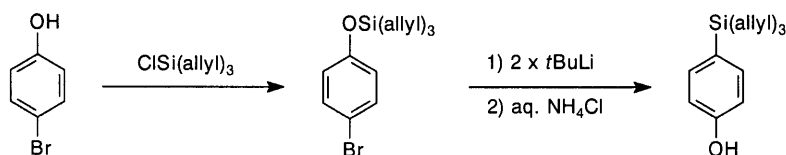


Fig. 3. Synthesis of 4-triallylsilylphenol by means of a low temperature (0 °C) [1,4]-silyl migration (Gossage, van Koten et al.)

was obtained. Characterization relies on NMR spectroscopy. In the case of the first generation possessing 24 vinyl groups, single crystals could be grown that were characterized by X-ray diffraction, showing disorder of the vinyl end groups in the crystal. The materials were used for the synthesis of silanol-terminated dendrimers (cf. Sect. 2.2.2).

A carbosilane dendrimer with a functionalizable core has recently been described by van Koten et al. [43, 44]. In an elegant way they obtained 4-triallylsilylphenol by means of a low temperature (0 °C) [1,4]-silyl migration from 4-(tri-allylsiloxy)phenyllithium which was obtained by lithiation of 4-(tri-allylsiloxy)bromobenzene (cf. Fig. 3). The use of the molecule obtained for the convergent synthesis of a carbosilane dendrimer has been demonstrated by the formation of [1,3,5-tris{4-(tri-allylsilyl)phenylester}benzene]. Furthermore novel trifurcate carbosilane dendrimers up to the second generation have been synthesized divergently, starting from the phenolic hydroxy group protected derivative of 4-triallylsilylphenol. These new materials were thoroughly characterized using NMR spectroscopy, SEC as well as mass spectrometry (ESI and MALDI-TOF).

Only recently an interesting study on carbosilane dendrimers using $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$ triple resonance 3-D NMR methods has been published by Tessier and co-workers [45, 46]. Starting from tetraallylsilane as core the authors obtained G0 by hydrosilylation with chlorodimethylsilane, followed by reduction using LiAlH_4 . In order to obtain G1 (designated G2 by the authors), tetraallylsilane was hydrosilylated with dichloromethylsilane. The resulting product was converted with vinyl Grignard reagent prior to hydrosilylation with chlorodimethylsilane. Subsequent reduction led to the desired second generation. The dendrimers were characterized using $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$ triple resonance, 3-D, and pulse field gradient NMR techniques. Signals from one-bond and two-bond connectivities among ^1H atoms coupled to both ^{13}C and ^{29}Si at natural abundance were detected selectively. The spectral dispersion and the atomic connectivity information present in the 3-D NMR spectra provided resonance assignments and a definitive structure proof.

2.1.2

Unusual Carbosilane Systems

Besides the carbosilane dendrimers with aliphatic units based on the repeating sequence of alternating hydrosilation and ω -alkenylation with Grignard reagents, only a few other systems have been developed: Nakayama and Lin

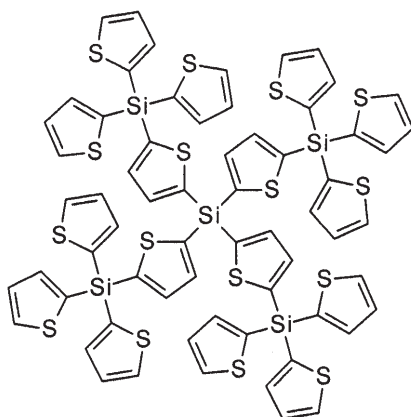


Fig. 4. Si-based dendrimer (G1) composed of thiophene rings connected by silicon (Nakayama and Lin)

synthesized the first generation of an organosilicon dendrimer composed of thiophene rings, connected by silicon [47]. The tetralithiation of tetra-2-thienylsilane followed by reaction with methyl tri-2-thienylsilyl ether gave the desired first generation, 5,5',5'',5'''-tetrakis[tri-2-thienylsilyl(tetra-2-thienyl)]silane which is shown in Fig. 4. The structures were confirmed using NMR spectroscopy and elemental analysis. It is noteworthy that the obtained dendrimer forms inclusion complexes with CCl_4 , CH_2Cl_2 , benzene, and acetone, when crystallized from these solvents.

Another so far uncommon carbosilane dendrimer has been obtained by Kim and Kim [48]. They started from tetrakis(phenylethynyl)silane and prepared dendrimers up to G3 via a repeated sequence of hydrosilylations with dichloromethylsilane and subsequent ω -alkynylations with lithium phenylacetylide. NMR and MALDI-TOF-MS support the successful synthesis. As expected, the glass transition temperatures are considerably higher than those of common carbosilane dendrimers based on alkenylation [49]. The obtained dendrimer possessing double bonds in the interior and triple bonds at the periphery has been used to prepare a dendritic Co complex whose properties are discussed below (Sect. 2.2.1) [50]. Another intriguing, recent development in this area are silylacetylene-dendrimers reported by Sekiguchi and coauthors [51]. These molecules, characterized by alternating silicon-acetylene units, were built up in a convergent type synthesis, that, however, is limited to G2 possessing 12 end groups. A crystal structure was obtained for G1, which shows a nearly planar structure due to the rigid acetylene units.

A hybrid dendrimer structure was obtained by Brüning and Lang by replacing the Grignard alkenylation step by an alcoholysis employing allyl alcohol [52]. As a core tetraallyloxysilane was used, which was hydrosilylated with dichloromethylsilane followed by the alkenylation with allylmagnesium bromide, yielding the first generation. Hydrosilylation resulted in the silylchloride-terminated second generation, which was subjected to alcoholysis with allyl alcohol. Accord-

ing to the authors the formation of uniform and analytically pure dendrimers was supported by NMR spectroscopy as well as elemental analysis.

2.2

Modification and Application Potential

2.2.1

Metal Complexes and Catalysis

One of the most promising applications of carbosilane dendrimers, based on their inertness, is the use as scaffolds for catalytically or redox active metal complexes. Dendrimer-bound catalysts combine the advantages of heterogeneous and homogeneous catalysis: on one hand they allow the accurate control of the number and structure of active sites, comparable to homogeneous catalysts, on the other hand they are conveniently removed from a product-containing solution using ultrafiltration as known from heterogeneous catalysts. This process can be carried out in a continuous manner, using a membrane reactor. The technique is considered to be promising for the synthesis of various fine chemicals. The first example of a homogenous catalyst based on a dendritic carbosilane scaffold was reported by van Koten et al. in 1994 [53, 54]. The authors connected 4-amino substituted 2,6-bis[(dimethylamino)-methyl]-1-bromobenzene (NCN-Br), a precursor for the potentially multidentate monoanionic 1-[C₆H₂(CH₂NMe₂)₂-3,5]⁻ (NCN) ligand, to the periphery of the zeroth generation with 4 chlorodimethylsilyl end groups and the first generation with 12 chlorodimethylsilyl end groups, respectively by a 1,4-butanediol linker. The first generation was obtained by hydrosilylating tetraallylsilane with trichlorosilane followed by alkenylation with allylmagnesium bromide. Conversion of the zeroth and first generation with chlorodimethylsilane led to the chlorodimethylsilyl derivatives. To achieve the connection between the scaffold and the NCN-Br ligands the 4-amino substituted NCN-Br was reacted with triphosgene to afford the isocyanate derivative, which was subsequently reacted with an excess of 1,4-butanediol. Reaction of the chlorodimethylsilyl functionalized dendrimers with the modified ligands yielded dendritic precursors with 4 and 12 binding sites for transition metals, respectively. The desired nickel containing dendrimers were produced by oxidative addition of these precursors to the zerovalent nickel complex Ni(PPh₃)₄. Figure 5 shows the dendritic nickel complex of the first generation.

The prepared dendrimers were successfully employed as homogeneous catalysts for the Kharasch addition reaction. Mechanistic considerations concerning the use of such diaminoarylnickel(II) complexes have been given in [55]. A drawback of the dendritic catalyst obtained in this fashion is the carbamate linker used, due to the additional synthetic steps required as well as the sensitivity towards organometallic reagents, such as alkyllithium or Grignard compounds. To improve the stability and to simplify the synthetic methodology, the attachment of the catalytic ligand-metal moiety directly to the outermost silicon atoms was targeted. Treating the biphosphinoaryl ligand 3,5-(Ph₂PCH₂)₂C₆H₃Br (PCP), a phosphorus analogue of the NCN ligand described above, with

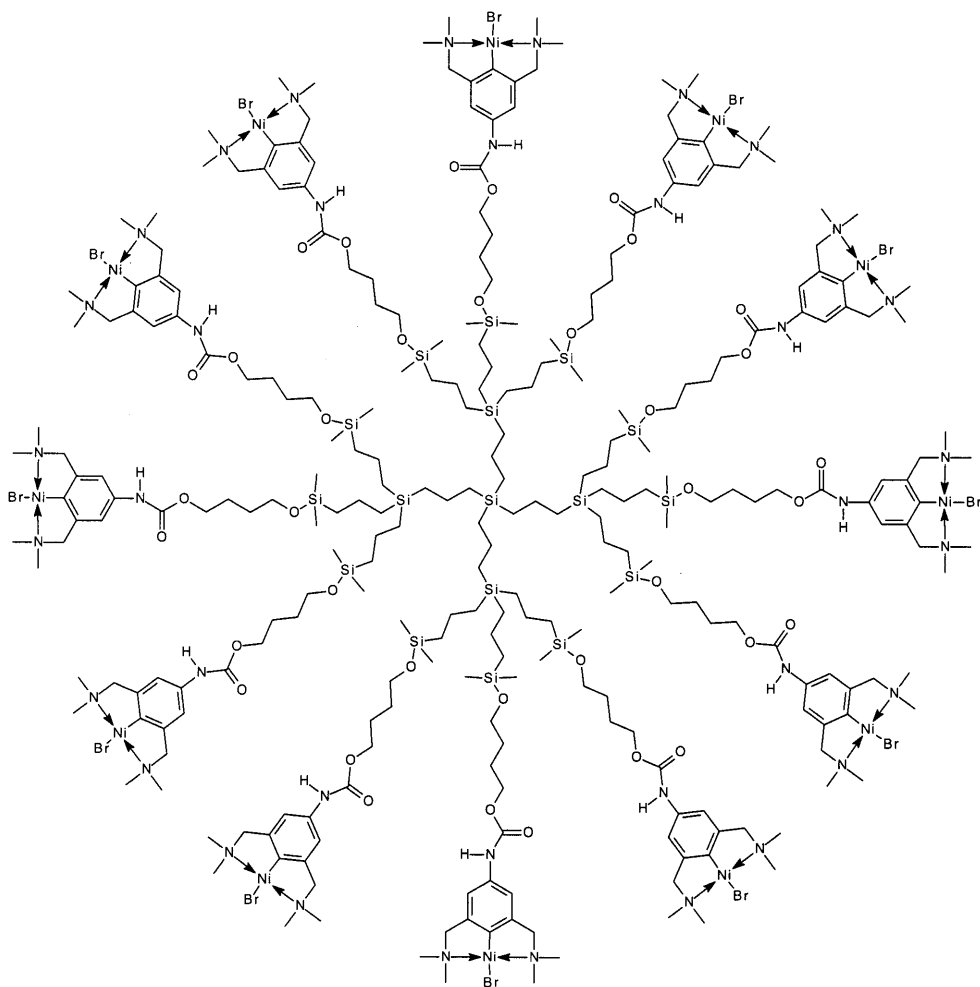


Fig. 5. Dendritic Ni-catalyst suitable for Kharasch addition reactions (van Koten et al.)

tert-butyllithium and quenching the resulting lithium derivative with chlorotrimethylsilane, van Koten et al. showed that this route allows a facile direct linking of these ligands to carbosilane dendrimers [56]. Furthermore it could be shown by model compounds that the incorporation of reactive Ru(II) PCP' complexes into carbosilane dendrimers can be accomplished by a ligand displacement of an NCN ligand, avoiding the use of the traditional precursor $\text{RuCl}_2(\text{PPh}_3)_3$, which leads to aryl-Si bond cleavage and hence to degradation of the carbosilane dendrimer. Dendritic carbosilanes functionalized with NCN-H end groups directly attached to the scaffold have been obtained via the reaction of a zeroth and a first generation dendrimer bearing chlorodimethylsilyl end groups with 3,5-bis[(dimethylamino)methyl]phenyllithium [57, 58]. Their multilithiated derivatives, representing the first examples of multilithiated den-

dimer systems with stable C-Li bonds, have been prepared by treatment with an excess of *tert*-butyllithium. These compounds can be used to introduce various metals via lithiation/transmetalation sequences. This has been exemplified by transmetalation of the tetralithiated, NCN derivatized zeroth generation carbosilane dendrimer with $\text{PtCl}_2(\text{SEt}_2)_2$ affording the desired Pt-metallated dendrimer. Further investigations concerning this new approach demonstrated its usefulness for the synthesis of (catalytically active) metal-containing carbosilane dendrimers [59].

A carbosilane dendrimer with 12 peripheral iodoarene groups has been prepared on the basis of carbosilane polyol precursors by van Koten et al. [60]. In this case, the iodoarene groups were attached to the polyols by esterification with 4-iodobenzoyl chloride. The obtained compound was reacted with $\text{Pd}(\text{dibenzylideneacetone})_2$ in presence of *N,N,N',N'*-tetramethylethylenediamine to yield periphery-palladated complexes. The prepared dendrimer represents the first example of an exclusively σ -bonded completely periphery-palladated dendrimer. In subsequent work, attachment of the iodoarene groups via esters was avoided, since the ester function appeared to prevent the transmetalation of the complex to a diorganopalladium(II) complex [61]. The reactivity of the dendritic organopalladium(II) and -(IV) complexes has been studied in detail and a crystal structure was obtained for the bipyridyl complex $[\text{PdMe}(\text{C}_6\text{H}_4(\text{OCH}_2\text{Ph})-4(\text{bpy}))]$.

Only recently, the first hydrovinylation of styrene carried out in a membrane reactor, catalyzed by Pd complexes with hemilabile P,O ligands attached to a carbosilane dendrimer has been reported by Vogt et al. [62]. A carbosilane dendrimer of the zeroth generation bearing four chlorodimethylsilyl end groups was converted with the protected lithium derivative of [4-bromo]-*tert*-butyldimethylsilylbenzyl ether to yield a dendritic polyol after deprotection. Coupling of this polyol with $\text{ClC}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ followed by reduction with trichlorosilane and subsequent reaction with $[(\eta^3\text{-C}_4\text{H}_7)\text{Pd}(\text{cod})]\text{BF}_4$ afforded the star-shaped Pd catalyst shown in Fig. 6. The dendritic catalyst proved to be active in the hydrovinylation of styrene with ethylene to 3-phenylbut-1-ene. However, isomerization to the E/Z mixture of the achiral 2-phenylbut-2-ene was also observed. To suppress this reaction, the hydrovinylation was carried out in a continuous process in a membrane reactor. This led to the highly selective conversion of styrene in low yields. The authors expect improved catalyst retention by nanofiltration membranes for the G1 dendrimer-supported Pd catalyst. In a recent publication van Leeuwen et al. reported the synthesis of phosphine functionalized carbosilane dendrimers and the corresponding palladium complexes as well as the use of the latter in the allylic alkylation reaction of allyl trifluoroacetate and sodium diethyl methylmalonate performed in a continuous flow membrane reactor [63]. Unfortunately, decomposition of the Pd-complex during the reactions complicated the analysis of the catalyst retention. Nevertheless, the authors were able to confirm that carbosilane dendrimers carrying catalytically active moieties are suitable for the use in continuous processes and that these molecules combine the advantages of homogeneous and heterogeneous catalysis. A remarkable result is the first X-ray analysis of a G2 carbosilane dendrimer.

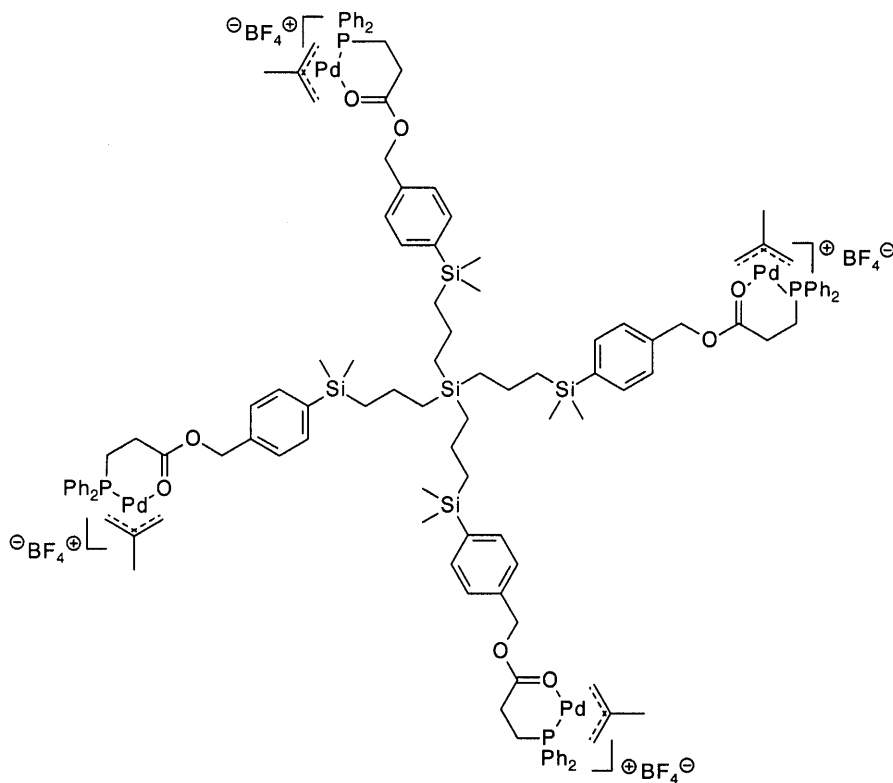


Fig. 6. G0-Pd catalyst used for the hydrovinylation of styrene in a membrane reactor (Vogt and van Koten)

A new concept in the use of functionalized carbosilane dendrimers as soluble supports is the ester enolate-imine condensation reaction leading to β -lactams, which has been developed by van Koten and co-workers [64]. In order to obtain a functionalized dendrimer suitable as a support in this reaction, the authors coupled dendritic chlorosilanes with a linker group, i.e., either [4-bromo]-*tert*-butyldimethylsilylbenzyl ether or (*S*)-[4-bromo]-*tert*-butyldimethylsilyl- α -methyl-benzyl ether. Desilylation afforded dendritic polyols, which were reacted with phenylacetyl chloride. In the zinc-mediated ester enolate-imine condensation the resulting dendrimers were treated with LDA and zinc chloride prior to addition of an imine. The reaction turned out to be highly *trans*-selective and led to high conversions. However, only a modest level of stereoselection was achieved.

Dendrimers offer interesting potential for electrochemistry, since they permit one either to isolate one single electroactive group internally or to load a large number of electroactive moieties on a single molecular nanoparticle [65]. The latter approach has been explored for carbosilane dendrimers in several laboratories and is based on the high redox-stability and flexibility of the carbosilane scaffold. The synthesis, characterization, and properties of redox-active carbo-

silane dendrimers containing ferrocenyl groups were reported by Casado and co-workers in several publications over the last few years, which have been summarized recently [66]. The electronic properties of these dendrimers containing a controlled number of equivalent redox centers render them promising materials for use in multielectron redox catalysis. The first example of this interesting class of organometallic dendrimers was published as early as 1994 by Cuadrado et al. [67]. Hydrosilylating tetraallylsilane with chlorodimethylsilane afforded the silyl chloride terminated G0. In order to obtain the corresponding first generation, tetraallylsilane was hydrosilylated using dichloromethylsilane followed by the allylation with allylmagnesium bromide. Subsequent hydrosilylation with chlorodimethylsilane yielded the targeted carbosilane dendrimer with eight silyl chloride end groups. The silyl chlorides have been replaced by reaction either with ferrocenyllithium resulting in direct attachment of the ferrocenyl groups to the outermost silicon atoms or with β -aminoethylferrocene resulting in ferrocenyl groups separated from the outermost silicon atoms via an ethylamino group. Electronic properties have been studied by cyclic voltammetry, revealing that the ferrocenyl moieties are noninteracting redox centers. Besides this, it was found that the dendrimers based on the first generation, i.e., eight ferrocenyl moieties, undergo "oxidative precipitation" upon oxidation to polycations. This results in thin films adsorbed on the Pt electrode surface. Further investigation concerning the preparation of electrode surfaces modified with dendrimers containing directly attached ferrocenyl groups revealed that the modified Pt electrodes are extremely durable and that the redox response is practically unchanged without loss of electroactive material [68]. More detailed cyclic voltammetry, differential pulse voltammetry, and bulk coulometry showed that the observed reversible oxidation waves represent a simultaneous multi-electron transfer of four or eight electrons respectively, as expected for four or eight independent reversible one-electron processes at the same potential. Carbosilane dendrimers containing electronically communicated ferrocenyl moieties have been obtained by one of the few convergent approaches to carbosilane dendrimers reported so far [69]. Cuadrado et al. prepared the G0-dendron diferrocenylmethylvinylsilane by reaction of ferrocenyllithium with dichloromethylvinylsilane. Further growth of this dendron was achieved by hydrosilylation with phenylchlorosilane followed by alkenylation with allylmagnesium bromide affording a dendron with four ferrocenyl units. Coupling these dendrons to tetrakis(dimethylsilylpropyl)silane via hydrosilylation resulted in carbosilane dendrimers containing 8 or 16 ferrocenyl moieties on the dendritic surface, respectively. The electrochemical behavior supports the existence of significant interaction between the two ferrocenyl units linked by the bridging silicon. In another study Losada et al. reported the synthesis of similar structures and their use as mediators in amperometric biosensors [70]. G0 bearing four ferrocenyl units was obtained by hydrosilylation of tetrakis(dimethylsilylpropyl)silane with vinylferrocene. Also the corresponding first generation has been prepared containing eight ferrocenyl moieties. The structure is depicted in Fig. 7.

Using these dendrimers, dendrimer/glucose oxidase/carbon-paste electrodes were constructed, whose electrochemical behavior has been investigated by cyclic voltammetry. Also the steady-state response of the ferrocene-mediated

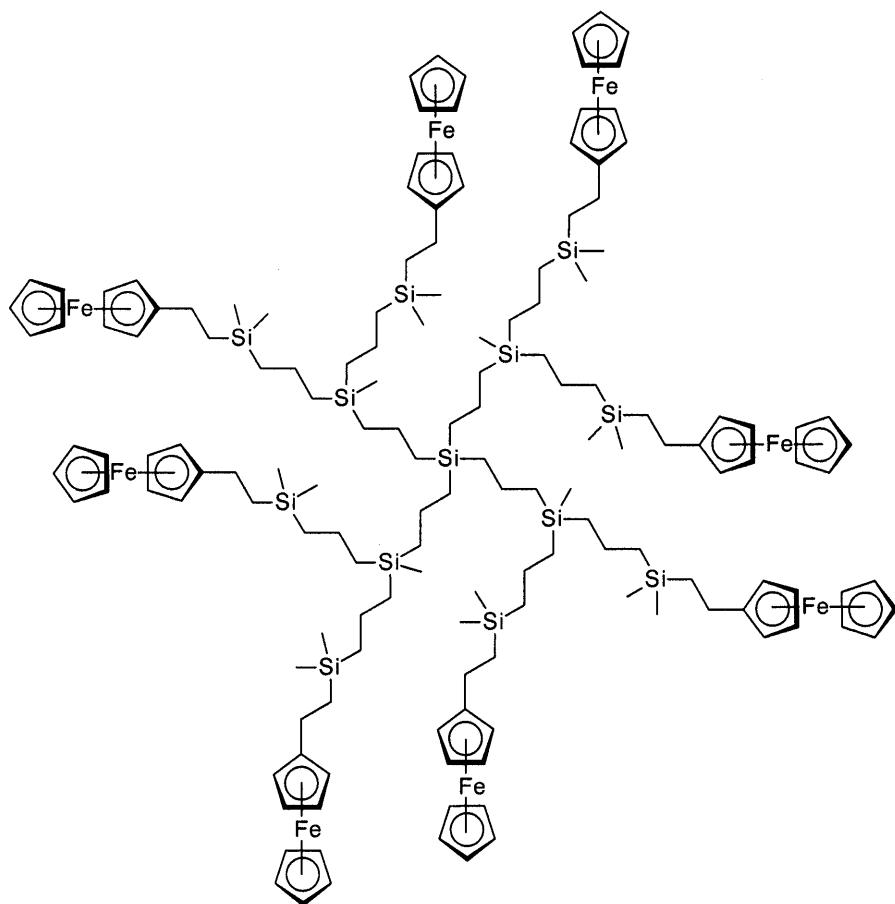


Fig. 7. Redox-active carbosilane dendrimer (G1), bearing 8 ferrocenyl units (Losada et al.)

glucose oxidase electrodes to glucose has been measured, demonstrating that ferrocenyl-functionalized dendrimers are capable of acting as mediators for carbon-paste electrodes. The results suggest that the flexibility of the dendritic mediator is an important factor in the ability to facilitate the interaction between the mediating species and the redox centers of glucose oxidase. Only recently, Losada et al. reported the use of Si-NH group containing dendrimers, the synthesis of which is described above [67], as anion receptors in solution and immobilized onto electrode surfaces [71]. Electrochemical investigations showed that the ferrocenyl functionalized dendrimer recognizes and senses anionic guests, i.e., HSO_4^- and H_2PO_4^- , via significant cathodic perturbations of the oxidation potential of the ferrocene couple. It has been demonstrated that the anionic guests are coordinated via hydrogen bonding interactions in the neutral state and electrostatic attractions after the electrochemical oxidation of the ferrocenyl moieties in the receptor. The impressive collection of ferrocenyl-

containing carbosilane dendrimers was further enlarged by Cuadrado et al. [72]. Dendrimers with similar branching structures but 1,3,5,7-tetramethylcyclotetrasiloxane as core were synthesized up to the second generation. As expected, in this case the ferrocenyl redox centers attached to the periphery behave as independent, electronically isolated units.

Jutzi and co-workers reported the preparation of a polyferrocene-branched dendrimer-like construct, which was obtained by hydrosilylation of decaallylferrocene with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{Me}_2)\text{H})]$ [73]. Although the structure is not based on silicon as branching point, it is based on a Si-containing spacer and has therefore been included in this review. The structure is shown in Fig. 8.

An interesting communication describing the synthesis of a core-functionalized carbosilane dendrimer has been published by van Leeuwen and co-workers [41]. Starting from *p*-bromostyrene, dendrons up to the third generation have been constructed by iterative hydrosilylation with trichloro-

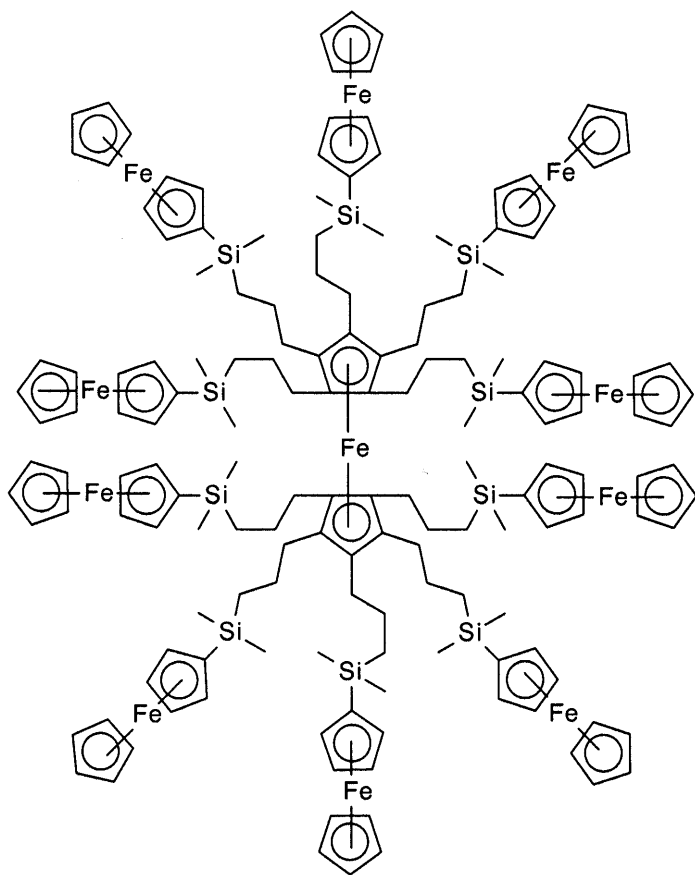


Fig. 8. Polyferrocene structure, obtained by hydrosilylation of decaallylferrocene with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{Me}_2)\text{H})]$ (Jutzi et al.)

silane and alkenylation with allylmagnesium bromide. The obtained dendrons were characterized by NMR spectroscopy, elemental analysis, FAB-, and MALDI-TOF-MS. After lithiation at the bromobenzene moiety, the dendrons were reacted with tetraethylferrocene-1,1'-diylbis(phosphonite), yielding the bidentate ligands with molecular weights up to 8567 g mol⁻¹. PdCl₂-complexes have been prepared by reaction of the different ligands with Pd(MeCN)₂Cl₂. In further experiments the catalytic activity of these unusual structures was tested in Pd-catalyzed allylic alkylation. All dendritic Pd complexes were found to be catalytically active. As expected, the rate of the reaction decreased when using the higher generation catalysts. Also, the selectivity of the allylic alkylation reaction was influenced by the generation: with increasing generation number of the dendrons, the selectivity decreased, which is tentatively explained by steric arguments, but also by a change in the polarity of the microenvironment.

Carbosilane dendrimers of the first generation peripherally functionalized with phenyl rings have been prepared by Cuadrado et al. [74]. The π -coordinating ability of the arene rings located at the dendrimer surface towards transition metals allows the synthesis of organometallic dendrimers containing η^6 -coordinated Cr(CO)₃ moieties at the periphery. The reaction of G0 with chromium hexacarbonyl afforded the desired dendritic tetranuclear complex. However, in the case of G1 only 4 of the 8 phenyl groups could be converted into the chromium complexes. Once more, cyclic voltammetric studies of metallated G0 revealed the tricarbonylchromium moieties to be noninteracting redox centers.

Organometallic carbosilane dendrimers (G0) with peripheral Si-cyclopentadienyl groups, Si-Co, and Si-Fe σ -bonds resulted from the reaction of tetrakis(chlorodimethylsilylpropyl)silane with alkaline cyclopentadienides, with LiAlH₄ followed by dicobalt octacarbonyl, and with Na⁺[(η^5 -C₅H₅)Fe(CO)₂]⁻, respectively [75]. All compounds were characterized by NMR and mass spectrometry.

Carbosilane dendrimers bearing acetylene-dicobalt hexacarbonyl units at the periphery have been reported by two groups: Seyferth et al. prepared small vinyl-terminated dendrimers based on previous work of this groups [27], which were then hydrosilylated with chlorodimethylsilane, followed by conversion with ethynylmagnesium bromide to yield carbosilane dendrimers with ethynyl groups at the periphery [76]. Reaction of these dendrimers with dicobalt octacarbonyl afforded the desired dendrimers with 4 (or respectively 12 in G1) acetylene-dicobalt hexacarbonyl complexes in the periphery. X-ray diffraction showed that the bond distances of the tetrahedrane cluster fall within the limits reported for other acetylene-dicobalt hexacarbonyl complexes. The reaction of dicobalt octacarbonyl with a dendrimer possessing two ethynyl substituents on each peripheral silicon atom failed. The authors attributed this failure to steric factors. Kim and Jung used dendrimers based on tetrakis(phenylethynyl)silane as core molecule with bis(phenylethynyl)methylsilyl end groups [48] to obtain the acetylenedicobalt hexacarbonyl terminated dendrimers [50]. Figure 9 shows the first generation. In contrast to Seyferth et al., apparently they did not encounter problems concerning the reaction of dicobalt octacarbonyl with the employed dendrimers possessing two phenylethynyl substituents on each peripheral silicon atom. However, a MALDI-TOF mass spectrum of the second

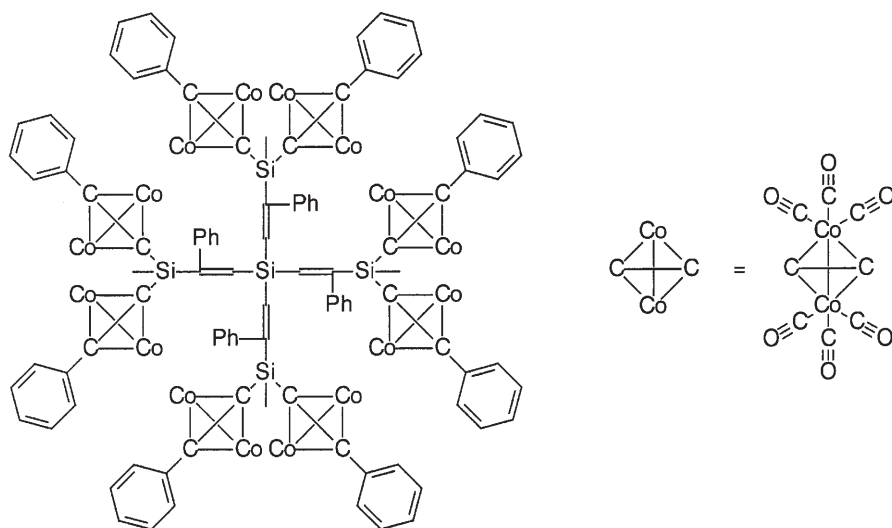


Fig. 9. Acetylene dicobalt hexacarbonyl terminated carbosilane dendrimers based on tetrakis (phenylethynyl)silane as core molecule (Kim and Jung)

generation ideally containing 32 dicobalt clusters could not be obtained. Similar work based on alkoxysilane dendrimers has been published by Lang and co-workers recently [77]. The results will be discussed in the alkoxysilane section of this review.

A very interesting report concerning the synthesis of highly charged organo-metallic carbosilane dendrimers and their characterization by mass spectrometry as well as X-ray diffraction was published by Tilley et al. [78]. They prepared G1 and G2 of benzyl-terminated dendrimers by hydrosilylation with trichlorosilane, followed by addition of benzylmagnesium chloride. The materials were characterized by NMR spectroscopy and MALDI-TOF-MS. Cationic ruthenium centers were introduced by the reaction of the corresponding benzyl terminated dendrimers with $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+\text{OTf}^-$. The structure of the first generation is shown in Fig. 10.

The authors' intention was to obtain charged, spherically shaped dendrimers, possessing cationic or anionic end groups for the construction of superlattice structures. In the case of G1, electrospray ionization Fourier transform-ion cyclotron resonance (ESI FT-ICR) mass spectrometry confirmed the formation of the perfect structure. Further support was obtained from the X-ray diffraction analysis. However, in the case of the second generation the ESI mass spectra revealed that a mixture of the perfect structure containing 36 Cp^*Ru^+ units and dendrimers with only 35 Cp^*Ru^+ units had been isolated. The hypothesis that steric congestion at the periphery prevented complete complexation of all 36 terminal benzyl groups was confirmed by preparing a second generation with 24 benzyl groups only. Reaction with $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+\text{OTf}^-$ led to the desired structure with 24 Cp^*Ru^+ units. A third generation dendrimer bearing 72 Cp^*Ru^+ units has also been prepared.

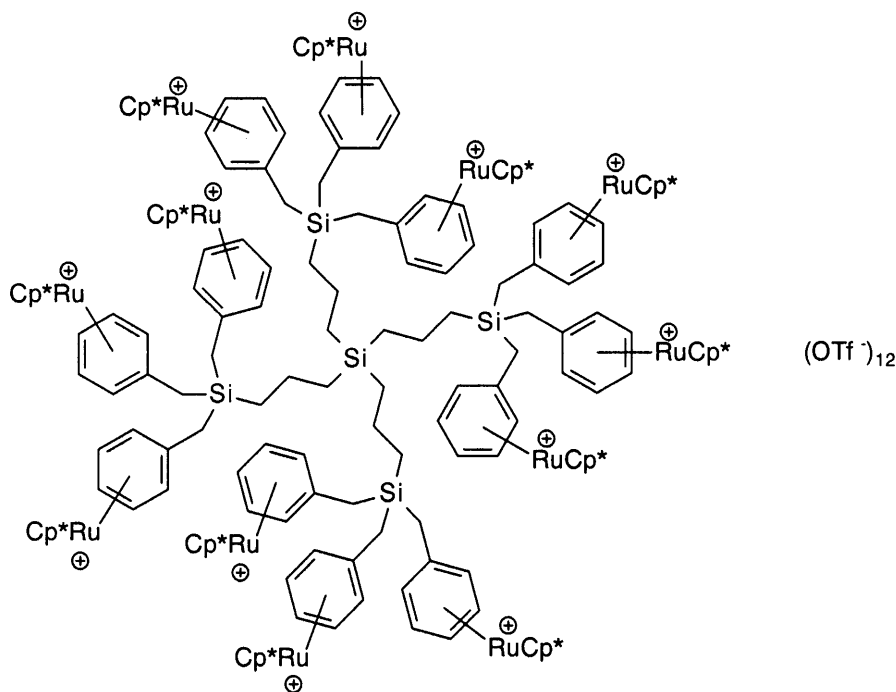


Fig. 10. Benzyl-terminated dendrimers with $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+ \text{OTf}^-$ complexes (Tilley et al.)

Attachment of transition metal clusters represents another novel facet of carbosilane dendrimer chemistry. The mixed gold/iron cluster fragment $[\text{AuFe}_3(\text{CO})_{11}]$ has been attached to a phosphino-terminated G1 carbosilane dendrimer by Rossell et al. [79]. In this manner, dendrimers with high metal density on the periphery can be obtained.

Seyferth et al. patented the preparation of group 4 metal-containing carbosilane dendrimers and their use as catalysts for the polymerization of olefins and silanes [80, 81]. As an example, polyethylene was prepared using a methylaluminumoxane-activated catalyst prepared by the reaction of a second generation carbosilane dendrimer with a vinyl derivative of a zirconocene.

2.2.2

Dendritic Carbosilane Polyols

Dendritic carbosilane polyols are intriguing materials, since they represent a versatile platform for the construction of a variety of unusual dendrimer-based polymer architectures. Therefore, this class of carbosilane dendrimers is reviewed in a separate section. Possessing a completely hydrophobic scaffold in combination with strongly polar end groups, the dendritic carbosilane polyols are expected to resemble micelles in their behavior.

Our group reported the first synthesis of these compounds [18, 82]. We prepared a series of carbosilane dendrimers, which were converted into dendritic

carbosilane polyols by hydroboration using 9-BBN and subsequent oxidation with $\text{H}_2\text{O}_2/\text{OH}^-$. This formally led to quantitative anti-Markovnikov addition of H_2O to the terminal double bonds of the carbosilane dendrimers. The second generation of the prepared carbosilane dendrimer bearing peripheral hydroxy groups is depicted in Fig. 11.

The dendritic polyols were characterized by NMR spectroscopy and MALDI-TOF mass spectrometry, demonstrating not only the quantitative hydroboration/oxidation reaction, but also the suitability of the MALDI-TOF mass spectrometry for the molecular characterization of dendritic structures in general. Glass transition temperatures of the carbosilane dendrimers with allyl end groups indicated high flexibility (-100°C to -80°C). Glass transition temperatures and flow temperatures of carbosilane dendrimers were also determined by Muzafarov et al., confirming this result [26]. These authors showed that the T_g s for dendrimers with a branching multiplicity of 2 were in the range of -90°C to -80°C , becoming constant above the fourth generation. In contrast, the

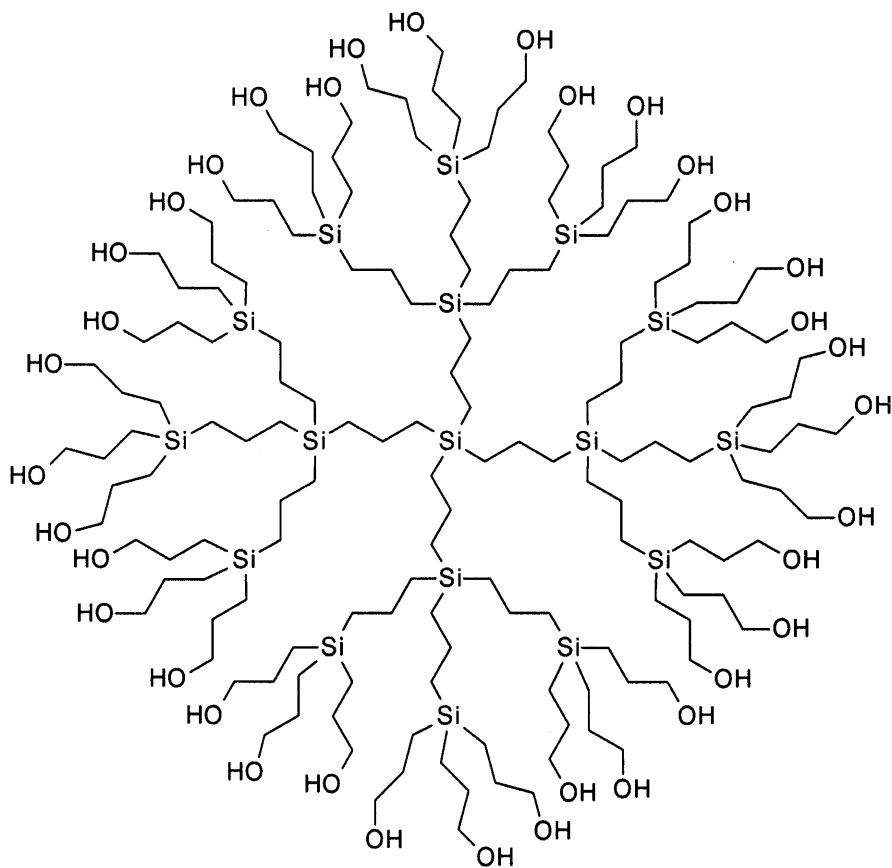


Fig. 11. Dendritic carbosilane polyol (G2) obtained by hydroboration/oxidation of allyl-terminated carbosilane dendrimers (Frey et al.)

glass transition temperatures of the dendritic polyols prepared in our group are approximately 60 K higher (-30°C to -40°C). This strong increase is explained by hydrogen-bonding, resulting in a network-like structure and by a possible exclusion of the polar hydroxyl end groups from the lipophilic carbosilane interior.

In an alternative approach, Getmanova et al. obtained dendritic carbosilane polyols by hydrosilylation of an allyl-terminated carbosilane dendrimer with an organosilane bearing a trimethylsilyl protected hydroxyl group [83, 84]. Hydrolysis of the trimethylsiloxy groups afforded the desired polyols. IR spectroscopic investigation in bulk and solution showed that the hydrogen-bond network formed in both cases is rather sensitively dependent on temperature and concentration. Sheiko et al. studied the spreading of these hydroxy functional materials at the air/water interface [85, 86]. The dendrimers formed a monolayer on the interface. Depending on the molecular area, three equilibrium states have been identified: (i) over a remarkably broad range of molecular areas a stable monolayer was formed; (ii) upon compression of the monolayer with decreasing molecular area a transition into a bilayer structure occurred, which is considered to be a first-order transition; (iii) finally, an isotropic liquid film was formed. In the same work a carbosiloxane dendrimer was also investigated (cf. Sect. 3.2). Sheiko and co-workers also employed tapping mode scanning force microscopy to examine the hydroxy-functional dendrimers [87]. The dendrimers showed two types of wetting behavior, depending on the substrate used. Due to preferential adsorption of the hydroxyl groups, the dendrimer displayed autophobic spreading on mica, whereas a substrate coated with a semifluorinated polymer was only partially wetted. On both substrates, submicrometer-size droplets were observed.

Comparison of the measured microscopic contact angles and macroscopic values revealed a difference, which was explained by deformation of the droplets caused by the tapping tip.

In an elegant approach, using nucleophilic reactions of mercapto-substituted amphiphiles and carbosilane dendrimers bearing (chloromethyl)silyl groups on their terminal branches, Krska and Seyferth obtained amphiphilic dendrimers with hydrophobic carbosilane cores and, among others, hydroxyl groups at the periphery [88]. The synthesis and properties of these compounds will be discussed in more detail in Sect. 2.2.4 dealing with host-guest chemistry.

Only recently Comanita and Roovers reported an alternative synthetic approach to dendritic carbosilane polyols [89]. Hydrosilylation of vinyl-terminated carbosilane dendrimers, synthesized by successive hydrosilylation and nucleophilic displacement starting from tetravinylsilane, methyldichlorosilane, and vinylmagnesium bromide [22], with bis-(6-(2-tetrahydropyranyloxy)hexyl)methylsilane led to the THP-protected polyols. After deprotection, the desired polyols with 4, 8, 16, and 32 hydroxy groups (G0–G3), respectively, were obtained. The purity of the compounds was established via NMR-spectroscopy and SEC.

Kuzuhara et al. used carbosilane polyols, using the approach of Terunuma et al. [90], to attach cyclodextrin moieties to a core molecule [91]. Although only G0 has been reported so far, the methodology should be applicable to carbosilane dendrimers of higher generations as well.

Silanol functionalized carbosilane dendrimers were obtained by Morris and co-workers [92]. Although silanol groups are, in general, hydrolytically unstable,

these molecules are of interest since they may be used to mimic silica surfaces to study the attachment of catalytically active metals to silanol groups. To obtain silanol derivatives, the vinyl end groups of the dendrimers were hydrosilylated with chlorodimethylsilane. Subsequently, the silyl chloride was reduced, using LiAlH_4 . Catalytic hydrolysis employing water over Pd/C yielded the desired silanol-functionalized carbosilane dendrimer. The compounds were characterized by NMR spectroscopy and CHN microanalysis. According to the authors, even upon standing for 6 months in air the dendrimers showed little evidence for intermolecular condensation.

Earlier disclosed patent literature by researchers at Bayer A.-G. had also described the synthesis of carbosilane dendrimers with silanol end groups and their use for the preparation of coatings with improved scratch resistance and toughness [93–95]. These materials were prepared by hydrolysis of chlorosilyl terminated dendrimers of low generations. Compared to ethoxysilyl or methoxysilyl end group containing dendrimers, the prepared dendritic silanols are considered to be advantageous because they do not release ethanol or methanol upon condensation.

As already mentioned above, due to their chemical stability carbosilane polyols permit a wide variety of modification reactions on the dendrimer periphery. For instance, the polyols can be coupled with mesogenic, i.e., rigid, units. This has been used to prepare dendritic liquid crystalline polymers, discussed in the following section.

2.2.3

Dendritic Liquid Crystalline Polymers (DLCP)

Carbosilane dendrimers were among the first dendrimers whose solid state properties and mesophase formation have been considered. Currently, there is growing interest in the combination of branched structures and mesogenic units, motivated by the fact that the globular shape might reduce the bulk viscosity, and hence the switching times of such materials. Coupling of the flexible, dendritic carbosilane scaffolds with rigid mesogenic units as end groups results in dendritic liquid crystalline polymers (DLCPs). It is a peculiarity of this class of LC polymers that the attachment of mesogenic units to the flexible carbosilane dendrimer scaffold leads to a structural conflict between preferential anisotropic order of the mesogenic units and the spherosymmetry of the dendrimer. The construction principle demonstrated first for carbosilane dendrimers has meanwhile also been realized for poly(propyleneimine) and PAMAM dendrimers [96, 97].

The first work on dendrimers with a large number of mesogenic end groups was reported by our group [82, 98, 99]. Carbosilane dendrimers with 12, 36, and 108 cholesteryl end groups were prepared via esterification of dendritic carbosilane polyols with cholesteryl chloroformate. Self-assembled ultrathin films of carbosilane dendrimers with these mesogenic units at the periphery, obtained after deposition on mica surfaces, were studied with atomic force microscopy [100]. At high dendrimer concentrations, flat, homogeneous films of 2–4 dendrimer layers were found. For low concentrations, a single dendrimer monolayer

exhibiting an irregular cellular pattern of holes was observed. Interestingly, the third generation dendrimer, i.e., the highest generation examined in this study, did not show dewetting or reorientation upon annealing, which was ascribed to lower molecular mobility. In further studies we investigated the influence of (i) generation, (ii) spacer length, and (iii) type of mesogen coupled to the dendrimer on the phase behavior of the dendritic liquid crystalline polymers [101–103]. We attached cyanobiphenyl units to dendritic carbosilane polyols of G0 to G2 via esterification of the hydroxyl end groups, obtaining DLCPs with the mesogenic groups connected by spacers of different length to dendritic scaffolds of different generations. In Fig. 12 a dendrimer of this type is depicted,

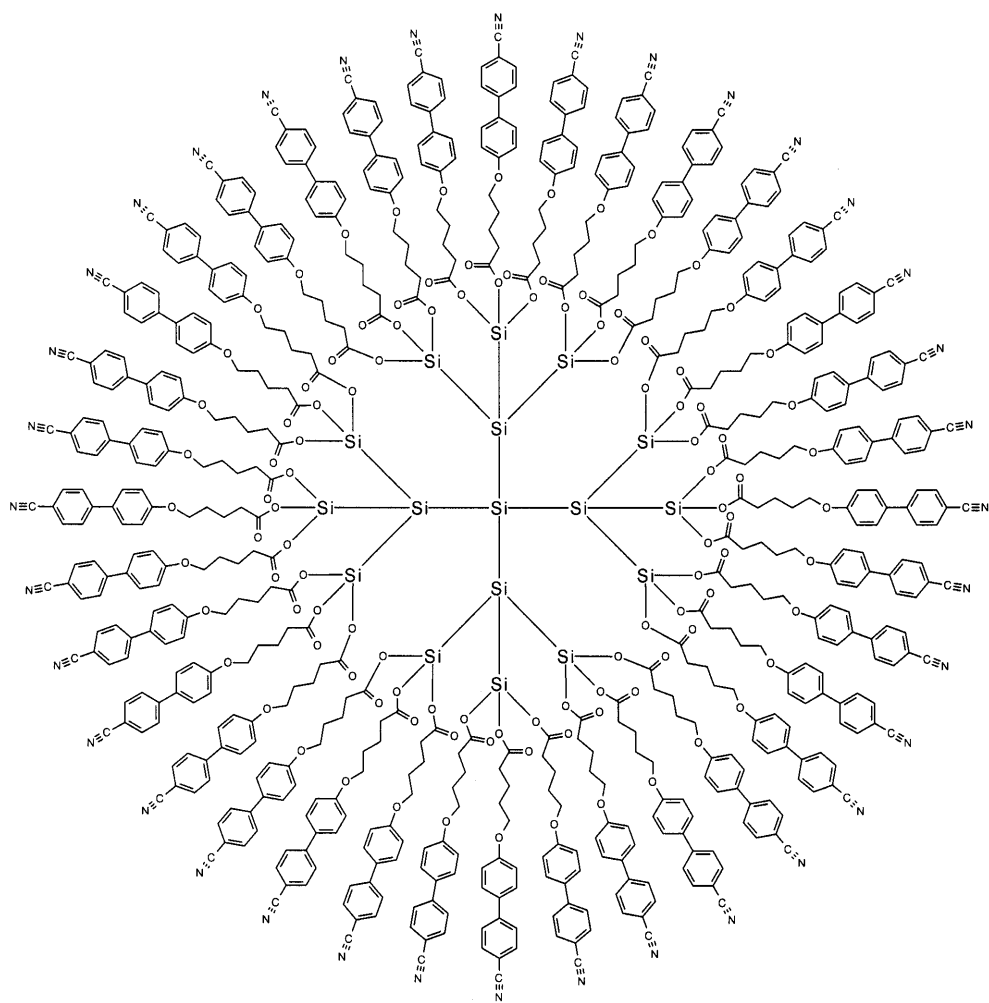


Fig. 12. Dendritic liquid crystalline dendrimer (DLCP) bearing 36 cyanobiphenyl moieties that are attached to the scaffold via a short spacer (Frey et al.) (— represents C_3H_6)

bearing 36 cyanobiphenyl moieties that are attached to the scaffold via the short spacer. The DLCPs were characterized by polarizing microscopy, DSC, WAXS, and SAXS with respect to their thermotropic phase behavior. All of the DLCPs except for G1 develop layered (smectic) structures, which are explained by separate ordering of the calamitic surface groups and the core which, however, requires a deformation of the dendritic scaffolds in order to adjust to the smectic order. Reducing the spacer length and/or increasing the number of end groups (i.e., the generation number) complicates the formation of well-developed smectic phases. Furthermore, if dendrimer scaffolds with a branching multiplicity of 3 are used, in higher generations (usually above G2) no liquid crystalline phases were observed [104]. This is explained by the dense packing of the mesogens at the dendrimer surface, disabling the formation of smectic layers.

Concurrent to the evolution of higher order within the smectic layers on cooling G1 and G2, microphase separation of the dendritic carbosilane scaffolds from mesogen and spacer-containing domains occurs. From SAXS data the resulting morphology is concluded to be lamellar with a periodicity showing distinct increase with generation. Thus, surprisingly, these LC-materials, although being composed of constitutionally isotropic molecules, are capable of developing nanophase-separated morphologies in a certain analogy to block copolymers. This is supported by TEM-images (Fig. 13), showing a lamellar morphology with stained mesogen-rich domains of 2–3 nm thickness and domains containing the dendrimer cores [105].

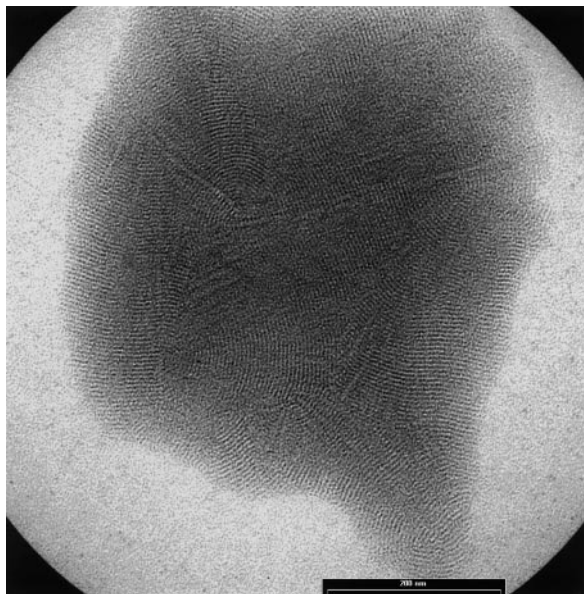


Fig. 13. TEM-image of the nanophase-separated morphology of a liquid crystalline dendrimer with mesogenic cyanobiphenyl end groups; mesogen-rich domains are stained preferentially and appear dark; scale-bar: 200 nm (Thomann et al.)

Shibaev and co-workers used cyanobiphenyl, methoxyphenyl benzoate, and cholesteryl groups as mesogenic units [106] in a number of works on liquid crystalline dendrimers. Generally, dendrimers with a branching multiplicity of 2 have been used by this group. The mesogenic units were coupled to carbosilane dendrimers bearing eight allyl groups by hydrosilylation. The LC properties of the obtained dendrimers were determined by polarizing optical microscopy in combination with DSC-measurements and X-ray diffraction. It could be shown that the type of the mesophase depends essentially on the chemical nature of the mesogenic group attached. Furthermore, a phase transition between two different smectic phases (S_C and S_A) was observed for the cyanobiphenyl-terminated dendrimer. In further work the electric birefringence (Kerr effect) and the dielectric polarization of the prepared DLCPs have been measured [107]. In accordance with the Kerr law, the dielectric polarization was found to be proportional to the second power of the electric field. It was shown that the electric birefringence of DLCP solutions is mainly determined by the electro-optical properties of the mesogenic groups oriented in the electric field independently of the scaffold. Shibaev and co-workers also prepared liquid crystalline carbosilane dendrimers containing terminal cyanobiphenyl groups up to the fifth generation [108] using dichloromethylsilane as branching reagent. The cyanobiphenyl groups were attached to the dendritic scaffold via a spacer consisting of 11 methylene units. In preliminary experiments all obtained dendrimers exhibited birefringence over a wide temperature range. The phase behavior of the fifth generation of the above described series of carbosilane liquid crystalline dendrimers has recently been studied in detail [109]. Polarizing optical microscopy, DSC, and X-ray diffraction revealed an unusual phase behavior. At room temperature the dendrimers form a lamellar (smectic A) phase which develops in-plane ordering above 40 °C. Above 121 °C the material transforms into a more disordered mesophase, probably a disordered hexagonal columnar phase. Since lower generations of liquid crystalline dendrimers form smectic (layered) structures only, this behavior shows that the dendrimer core becomes significant for the structure of the LC phase. Furthermore the existence of a smectic mesophase up to the fifth generation shows that the structural conflict between the mesogenic units and the sphericosymmetry of the scaffold is less pronounced in these carbosilane dendrimers with a branching multiplicity of 2, compared to structures possessing a branching multiplicity of 3 [102].

Smectic phases have also been found for carbosilane dendrimers substituted with mesogenic units based on azobenzene by Zhang et al. [110]. In subsequent work these authors reported on the attachment of further mesogenic units [111] and formation of nematic as well as cholesteric phases. Terunuma et al. recently reported the synthesis of cyanobiphenyl-terminated carbosilane dendrimers based on triallylphenylsilane as a core [90]. The prepared DLCPs were characterized by DSC and polarizing optical microscopy. X-ray diffraction data were not given. In a subsequent report, the same authors reported carbosilane dendrimers with mesogens bearing a chiral tail (G1, G2; branching multiplicity 3). Again, the materials exhibited smectic A phases only. Interestingly, these dendrimers could be used as chiral dopants, leading to the formation of Sc^*

phases. The response times for switching of these phases in electric fields increased with molecular weight, as commonly seen in the case of ferroelectric liquid crystals [112].

Besides classical calamitic mesogens, perfluoroalkyl groups ($-\text{C}_6\text{F}_{13}$) have been attached to carbosilane dendrimers in our group [113]. The attachment of the perfluorinated alkyl groups to the allyl end groups of the dendrimers was performed via free radical addition of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-*n*-octyl mercaptane, which affords the corresponding fully thioether-functionalized end groups. Perfluorinated dendrimers of G0 to G3 with 4, 12, 36, and 108 perfluoroalkyl end groups, respectively, have been prepared. As an example, G2 is shown in Fig. 14.

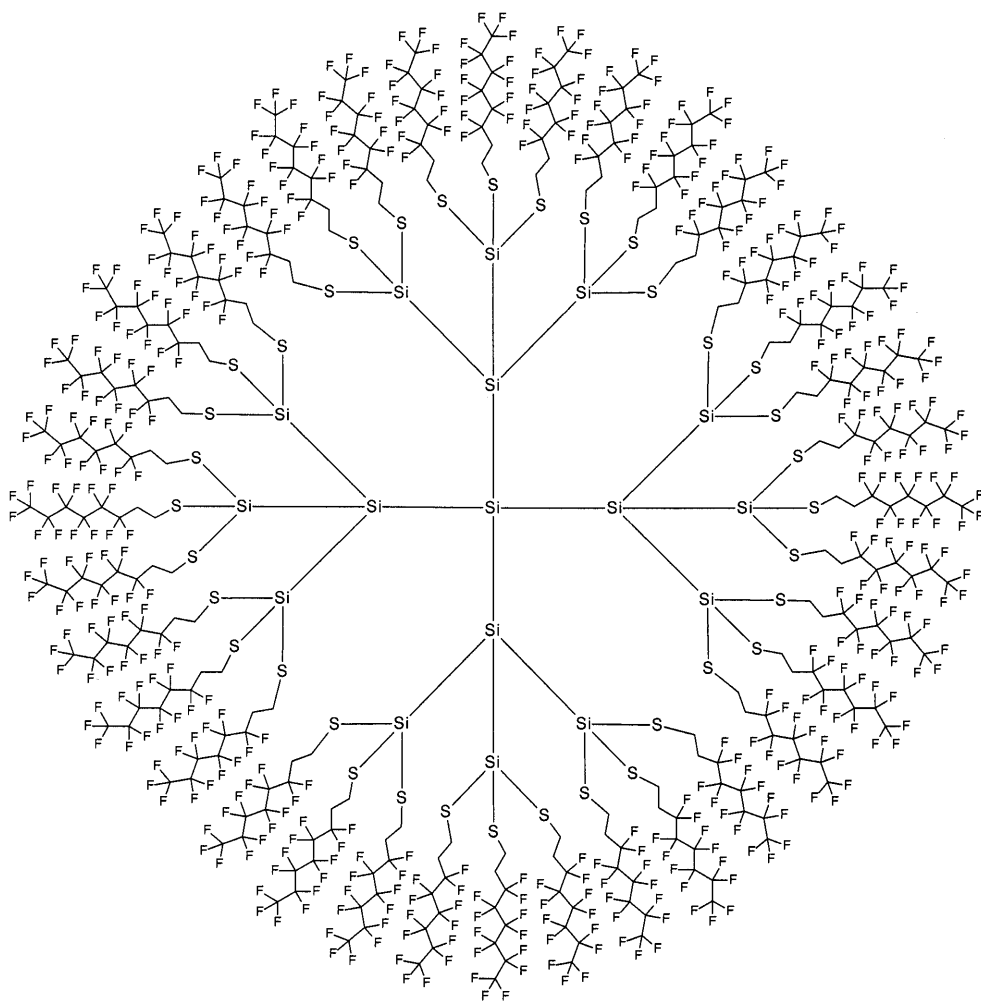


Fig. 14. Perfluorinated carbosilane dendrimer (G2) with 36 perfluoroalkyl end groups (Frey et al.) (— represents C_3H_6)

The “fluorophilic” periphery of these dendrimers is immiscible with the “lipophilic” carbosilane structure. Such core-shell-type dendrimers also exhibit generation-dependent mesophase formation. Whereas G0 was obtained as a crystalline material that did not show the formation of a mesophase, G1 formed a highly ordered smectic phase at low temperature. The layered structure of G2 was considerably less well developed and G3 displayed a WAXS pattern that indicated a hexagonally packed array of cylindrical domains. This generation-dependent thermal behavior is ascribed to the increasingly dense packing of perfluorohexyl groups on the dendrimer surface. The obtained dendrimers have been studied in further detail by Stühn et al. using X-ray scattering techniques as well as quasielastic neutron scattering [114]. As a result of the microphase separation between the end groups and the carbosilane core, the perfluorinated dendrimers form generation-dependent superstructures. It has been found that the helical end groups tend to arrange in layers between the carbosilane domains, the layers possessing a local order similar to that observed in the crystalline state of perfluorinated alkanes. Independent of the generation number the dendrimer core has to deform to adjust to the order of the end groups. Furthermore, segmental dynamics, as studied with quasielastic neutron scattering, revealed a dynamic heterogeneity caused by the demixing of end groups and dendrimer core. Only recently Stühn and co-workers examined the dielectric relaxation in these perfluorinated carbosilane dendrimers [115]. The dendrimers showed a fast relaxation with an Arrhenius-type temperature dependence and an activation energy of 17 kJ mol^{-1} . In all generations a dominant α -process was found, which was split into a slow and a fast part. For G1 a transition from a smectic to a nematic state was observed at -15°C . This transition is observed in the dielectric relaxation as a discontinuous increase of the relaxation times for both components of the α -process. Further studies concerning the dielectric relaxation of carbosilane dendrimers with cyanobiphenyl end groups have also been carried out [116]. An unusually narrow α -process was observed, indicating a clear separation between the relaxation times of the dendrimer scaffold and the end groups. The distortion of the dendrimer scaffold as a consequence of the smectic order within the end groups was reported to be responsible for a shift of its relaxation times.

In summary, carbosilane dendrimers have permitted one to obtain a detailed understanding of the behavior of end-group induced liquid crystallinity in flexible dendrimers. In most cases, the topology leads to smectic phases. Key parameters for the supramolecular order developed are the branching multiplicity as well as the spacer length between mesogen and dendrimer.

2.2.4

Host-Guest-Chemistry and Solubilization Properties

Due to their structural density gradient leading to inner cavities and their fixed spherical topology, dendrimers with an amphiphilic structure are regarded as micelle-analogues. The first dendrimer that acts like a micelle of usual amphiphiles was reported by Newkome et al. [117]. Newkome et al. prepared a carboxylate-terminated hydrocarbon dendrimer, which shows solubilization behavior

for apolar molecules in polar media, yet no critical micelle concentration was observed. As already mentioned above, carbosilane dendrimers are similarly well-suited for application in the field of host-guest-chemistry and solubilization, since they likewise possess a completely hydrophobic scaffold. In addition the route to these dendrimers is flexible, permitting to control the size of the inner cavities. This has been demonstrated by our group in a molecular force field study concerning the host properties of carbosilane dendrimers [118]. Based on these results, the dimensions of the inner cavities can be controlled from 5–15 Å by variation of the branching multiplicity and/or spacer length. The density of the periphery has also been investigated. It was found that the higher generations possess a dense outer shell with holes in the range of 2–3 Å. On the basis of the results obtained, predictions concerning the size of molecules that can be trapped inside the dendrimers are possible. Besides, the calculations showed that with increasing generation number the tendency of the dendrons to interpenetrate increases greatly, eventually forming a dense molecular surface in higher generations. This is in agreement with the Monte Carlo model reported by Mansfield and Klushin [119]. Structural analyses of carbosilane dendrimers possessing different branching multiplicities and therefore cavities of different sizes have also been performed using molecular dynamics modeling techniques [120]. A simple equation for the calculation of the maximum possible dendrimer generation was derived.

Further insight into the carbosilane dendrimer structure has been gained from fluorescence spectra and the excimer formation of pyrenyl-labeled dendrimers [121–123]. The investigated dendrimers possessed a pyrenyl group, i.e., a fluorescent probe, at the central silicon atom. It was found that excimer formation did not occur with mere carbosilane dendrimers, whereas carbosiloxane dendrimers showed the formation of excimers, evidenced by time-correlated single-photon counting techniques and steady-state fluorescence spectroscopy. These results yielded information on the conformational mobility and steric hindrance of the investigated dendrimers. This may permit one to tailor new carbosilane dendrimers for the selective inclusion of guest molecules.

Only recently Krska and Seyferth reported the synthesis of water-soluble carbosilane dendrimers [88]. Nucleophilic reactions between mercapto-substituted amphiphiles and carbosilane dendrimers bearing (chloromethyl)silyl groups on their terminal branches yielded amphiphilic dendrimers with hydrophobic carbosilane cores and alcohol, dimethylamino, or sodium sulfonate amphiphilic groups at the periphery. To render the dimethylamino-terminated dendrimers water-soluble, they have been reacted with methyl iodide, providing quaternary ammonium iodide salts. The structure based on the first generation is exemplified in Fig. 15.

A detailed study of these dendrimers using MALDI-TOF mass spectrometry has been reported by Wu and Biemann [124]. Dendrimers terminated with tertiary amino groups have been detected as their $[M + H]^+$ ions. Dendrimers with chloroalkyl end groups required the addition of silver trifluoroacetate to produce $[M + Ag]^+$ ions. Interestingly, for the first and second generation with quaternary ammonium groups, complexes with three or seven matrix anions have been observed. This investigation once more confirms the importance of

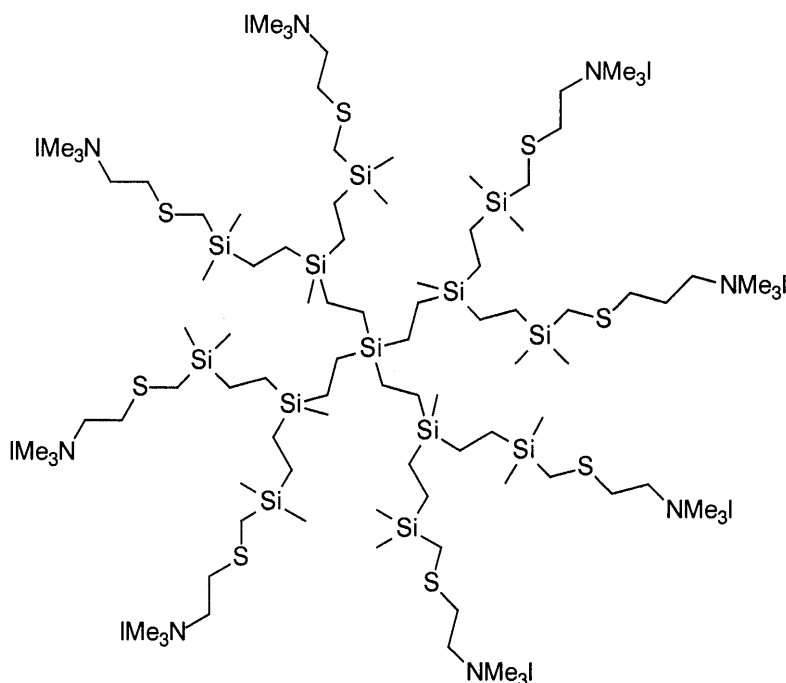


Fig. 15. Water soluble, dimethylamino-terminated dendrimers, reacted with methyl iodide lead to dendrimers with quaternary ammonium iodide salt end groups (Seyferth et al.)

MALDI-TOF mass spectrometry for the characterization of dendrimers. Both the negatively charged sulfonate terminated dendrimers as well as the positively charged ammonium terminated dendrimers were soluble in water. Preliminary studies demonstrated that the sulfonate terminated dendrimers were able to solubilize lipophilic alkyl-substituted benzene derivatives in aqueous solution in a micelle-like fashion. However, since aggregation was observed for the ammonium-terminated dendrimers, the formation of aggregates is also likely for the sulfonate-terminated dendrimers, leading to a solubility enhancement of the benzene derivatives. Detailed studies of our group revealed that aggregation was partly responsible for the solubilization of guest molecules by carbosilane dendrimers with modified surfaces [125]. Furthermore it was found that modified hyperbranched polytrialkylsilanes (Sect. 6.1) behaved very similar with respect to their solubilization behavior.

Crystalline dendritic arylalkylsilane/tetrahydrofuran inclusion complexes have been reported by Friedmann and co-workers [126, 127]. They obtained dendrimers with 12 and 36 phenyl groups at the periphery by means of the hydrosilylation/vinylation approach. The structure of the dendrimer carrying 36 phenyl group is sketched in Fig. 16.

The first generation (12 phenyl groups) gave rise to an inclusion compound when recrystallized in suitable solvents such as THF. Comparative X-ray structural analysis showed that the host dendrimer's conformation is nearly identical

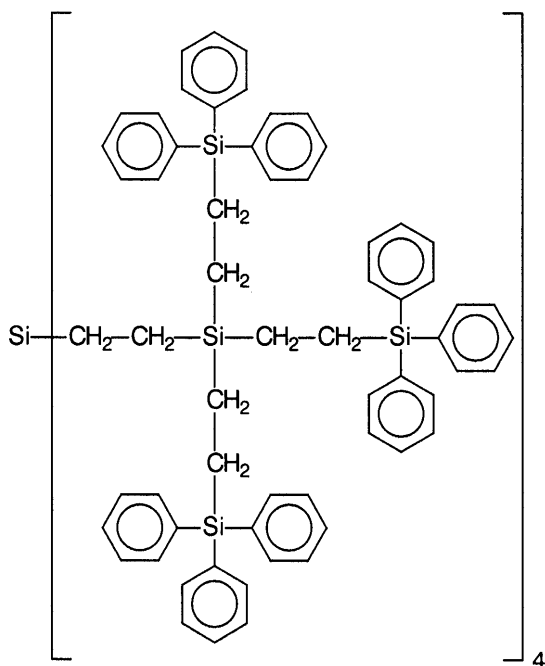


Fig. 16. Carbosilane dendrimer carrying 36 phenyl groups at the periphery (Friedmann et al.)

in the pure dendrimer and in the inclusion complex. Furthermore it revealed that the guest molecules are located in cavities created by paired host molecules. The authors conclude that the tetrahydrofuran molecules are deeply buried and probably firmly locked in these cavities. Inclusion complexes have also been found for organosilicon dendrimers composed of 16 thiophene rings [47].

2.2.5

Polymer Architectures Based on Carbosilane Dendrimers

2.2.5.1

Star Polymers

Because of their precisely defined topology and large number of end groups, dendrimers have been used as core molecules for star polymers with unusually large numbers of arms ("multiarm star polymers"). Particularly carbosilane dendrimers are suitable cores, owing to their chemical stability which allows a variety of reactions without degradation of the dendrimer scaffold. Two different approaches to star-shaped polymers based on carbosilane dendrimers have been reported so far: the first approach, relying on the *arm-first* strategy, involves the attachment of living polymer chains to a carbosilane dendrimer possessing reactive end groups. In pioneering work, Roovers et al. obtained star polymers with 32, 64, and 128 arms, respectively, by coupling silyl chloride

terminated dendrimers (G3 to G5) with living polybutadienyllithium chains [22, 128, 129]. The arm molecular weight was varied between 6400 and 72,000 g/mol. The obtained star polymers were investigated in detail with respect to their dilute-solution properties, employing osmometry, viscosimetry, and light scattering. It was found that the isolated stars behave like hard spheres. Investigations on semi-dilute solutions of star polymers in good solvents and beyond the overlap concentration revealed a gel-like characteristic [130]. The formation of a macrocrystalline ordered phase with spacings of the order of 100–500 Å (SANS) was also observed. In this respect, such materials may be considered to resemble colloidal crystals. Allgaier et al. published an investigation on the structural perfection of such unusual multichain polymers, concerning arm number and polydispersity [17]. For this study, polybutadiene shortarm star polymers structurally very similar to those obtained by Roovers et al. [129] were studied by MALDI-TOF mass spectrometry. The mass spectra revealed that up to a functionality of 16, the quality of the linking agent as well as the star polymer itself is almost ideal with respect to functionality and polydispersity. If higher generations are employed as linker for the chains, the structures appear to be less perfect, which is both due to imperfections of the dendritic linking agent and the incomplete coupling reaction of the living polymer chains as well as silyl chloride groups of the dendrimers. This incomplete reaction is explained by increasing surface congestion with increasing generation number.

A very interesting structure has been obtained by Möller and co-workers [131]. They prepared a star-shaped 12-arm poly(styrene-*block*-isoprene) block copolymer by the reaction of polystyryllithium and polyisopropenyllithium with a carbosilane dendrimer possessing silyl chloride end groups. The carbosilane dendrimer used was synthesized from triallylphenylsilane, employing repeated hydrosilylations with dichloromethylsilane and alkenylation with allylmagnesium bromide. Subsequently, the allyl groups of the second generation were converted to chlorodimethylsilylpropyl groups via hydrosilylation with dimethylchlorosilane prior to subsequent coupling with the different living polymer chains. SEC evidenced a narrow molecular weight distribution. As to be expected, the block copolymer exhibits two glass transition temperatures. TEM and AFM studies of the resulting block copolymers showed that these molecules form regularly organized micelles in solution.

The second approach, relying on the *core-first* strategy, involves the polymerization of monomers, such as styrene or ethylene oxide, from a carbosilane dendrimer serving as multifunctional initiator. Roovers et al. used a dendritic polyol [89] as initiator for the anionic polymerization of ethylene oxide [132, 133]. The resulting star polymers with 4, 8, and 16 arms, respectively, exhibit narrow molecular weight distributions. Characterization of the star polymers and comparison of the properties with those of linear poly(ethylene oxide) indicated that the core material has a minimal effect on the conformation of the stars in methanol.

An elegant work, using the second approach has been reported by Muzafarov and co-workers [134–136]. They synthesized polyolithium derivatives of carbosilane dendrimers, which they used as initiators for the anionic polymerization

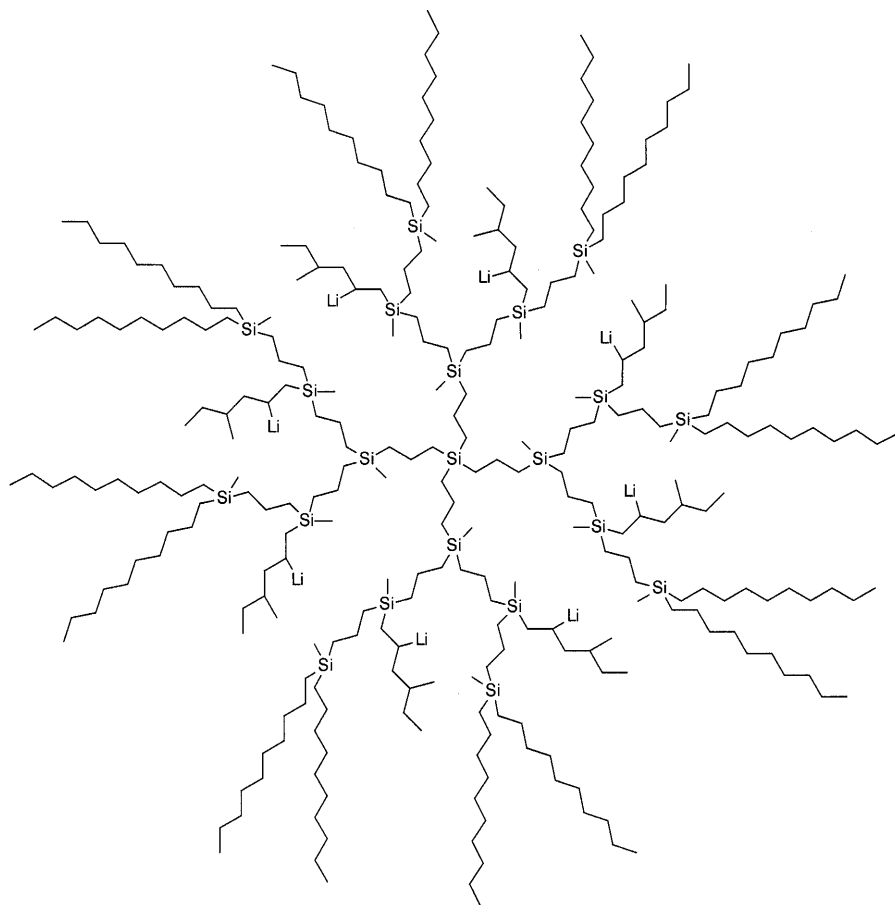


Fig. 17. Polyolithium derivative of a carbosilane dendrimer, obtained by reaction of inner allyl groups with *sec*-BuLi. Such dendrimers can be employed as polyfunctional initiators for the anionic polymerization of cyclic siloxanes, ethylene oxide, and styrene (Möller, Muzafarov et al.)

of different monomers, such as styrene, hexamethylcyclotrisiloxane, and ethylene oxide. The polyolithium derivatives were obtained by hydrosilylation of allyl-terminated dendrimers with the sterically demanding bisdecylmethylsilane. This led to the reaction of only one-half of the end groups, leaving allyl groups unreacted in the interior of the dendrimer. The reaction of these allyl groups with *sec*-butyllithium afforded the desired polyolithium derivative of the carbosilane dendrimer. One of the obtained polyanions is shown in Fig. 17. The important feature of this approach lies in the fact that, due to the location of the lithium atoms in the inner area of the dendrimers, a main problem of polyolithium compounds, i.e., their high tendency of aggregation, was avoided. The polyolithium compounds prepared were employed as polyfunctional initiators for the anionic polymerization of hexamethylcyclotrisiloxane, ethylene oxide,

and styrene. In all cases the polymerization afforded star polymers with a monomodal, narrow molecular weight distribution.

2.2.5.2

Dendronized Polymers

In recent years there has been a surge of interest in “dendronized polymers,” i.e., linear chain polymers with sterically demanding, “wedge-shaped” dendron side chains [137, 138]. This leads to strong stiffening and stretching of the chains, controlled by the shape of the dendritic substituents. The first example of a “dendronized” Si-based polymer was reported by Kim et al. [139]. Kim and co-workers treated poly(diphenylsilylenepropylene) $(\text{Ph}_2\text{SiCH}_2\text{CH}_2\text{CH}_2)_n$ with triflic acid, leading to the corresponding silyltriflate derivative of the polymer after cleavage of the Ph-Si bonds. The reaction with allylmagnesium bromide gave $(\text{allyl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2)_n$, which was used as core molecule for the synthesis of dendritic carbosilane wedges attached to a carbosilane polymer backbone. According to the authors dendrimeric wedges up to the third generation are accessible.

Dendronized polymers with polysiloxane backbone and carbosilane dendritic wedges (G1 and G2, branching multiplicity 3) have been mentioned by Skoulios and co-workers recently. Small angle neutron scattering was employed to characterize these macromolecules. A pronounced increase of the persistence length as well as the Mark-Houwink parameter α from 0.53 (G0) to 0.94 (G2) indicated strong stretching of the chains to a rodlike conformation [140]. However, according to the authors preparation of G3-dendronized polymers failed and formation of insoluble products was observed, which is most probably due to the extremely high functional group density in the dendrons with a branching multiplicity of 3.

2.2.5.3

Applications

Due to their high functionality, dendrimers are considered to be interesting precursors for the preparation of nano-structured polymer networks, which are of interest in various fields. Having said this, one should remark critically that only very special properties will justify the use of such tediously prepared, discrete molecules in a crosslinking reaction, particularly if higher generations are considered. For instance, one may envisage peculiar template effects permitting an extremely precise control of the nanoporosity of novel hybrid materials.

In the first approach developed in this area by Michalczyk and Sharp, inorganic/organic hybrid networks were obtained via sol-gel chemistry, using dendritic alkoxyxilanes as precursors [141, 142]. Coupling trialkoxysilyl groups to small carbosilane dendrimers afforded the desired precursors. Incorporation of organic branching points into the glassy network markedly reduces brittleness and enhances toughness, which is explained by the high flexibility of the carbosilane precursor. Furthermore, gelation rates of star gel precursors were found to be considerably higher than those of conventional tetraalkoxyxilanes. A comprehen-

sive review concerning the perspectives of this approach for specialty glasses was published recently [143].

Carbosilane dendrimers have also been used as precursors for xerogels. Corriu and co-workers prepared carbosilane dendrimers up to the second generation by standard procedures [144], using triallylphenylsilane or triallyloctadecylsilane to introduce bulky units. Reactive functionalization for the gelation process was achieved by transformation of the trichlorosilyl end groups into trimethoxysilyl groups by methanolysis. Polycondensation of these molecules in a sol-gel procedure yielded the targeted xerogels. Porosity measurements revealed that the symmetrical dendrimers gave porous material while the unsymmetrical dendrimers formed porous and nonporous material depending on structure and gelation conditions. However, removal of the organic fraction by thermal oxidation was found to be critical and the porosity of the resulting silica network could not be controlled by varying the size of the precursors.

Recently Kriesel and Tilley also used carbosilane dendrimers as building blocks for xerogels [145]. Dendrimers with end groups suitable for the sol-gel process were obtained by hydrosilylation of the triallylsilyl terminated dendrimers (G2 and G3) with triethoxysilane. Hydrolysis of these compounds was carried out under acidic conditions. Solvent processing afforded xerogels, which were characterized using IR spectroscopy and nitrogen adsorption porosimetry, showing that there was an increase in the total surface area and pore volume with generation number. This unexpected result was tentatively explained by the authors with the compressibility of the dendritic precursors and the assumption that G2 might be more deformable than G3 because of the less congested surface.

The use of allyl-substituted dendrimers of the first generation in hardenable substances for dental use was patented by Zech and Lechner [146]. Carbosilane dendrimers containing no reactive groups have been patented by Mager et al. for the use as calibration materials in analytical processes and as fillers in plastics [147]. Oligoethyleneoxide-terminated carbosilane dendrimers have been used in a study comparing the hematotoxicity and in vitro cytotoxicity of various dendrimers [148]. The dendrimers used in this study were obtained by radical addition of mercapto-substituted derivatives of hydroxy terminated oligoethylene oxide. These dendrimers showed no toxicity towards various cell lines when incubated. However, the lowest generation was cytotoxic towards B16F10 cell lines at higher concentrations. With increasing branching, the toxicity diminished.

3 Siloxane and Carbosiloxane Dendrimers

3.1 Siloxane Dendrimers

Silicones (IUPAC: polysiloxanes) are by far the most important class of Si-based polymers, finding use as oils, elastomers, and silicone resins. Considering the widespread use of this class of polymers in specialty applications, e.g., in

medicine and highly water repellent coatings, the literature on dendritic siloxane structures is surprisingly scarce. In a recent review, the state of the art of branched polysiloxane architectures has been summarized by Bischoff and Cray [149]. Only very few dendrimers exclusively based on siloxane groups are known at present. The first work describing the synthesis of dendritic silsesquioxane molecules was reported by Muzafarov et al. in 1989 [150]. Muzafarov et al. obtained the dendrimers up to the third generation by repeated treatment of trichloromethylsilane or the intermediate product with sodium diethoxymethylsilanolate and subsequently with thionyl chloride. The ideal structure of the molecules prepared contains 48 ethoxy or chloride functionalities in the case of the third generation. However, a detailed characterization of the structural perfection was not given.

In 1990 Uchida and co-workers introduced silicone dendrimers with terminal silicon hydrides, which could be used for further modification [151–153]. Figure 18 shows one of the obtained dendrimers. The dendrimers were constructed by the coupling of $(^{\text{H}}\text{OMD}_3)_3\text{T}$ [154] and $(^{\text{H}}\text{MD}_3)_2\text{D}^{\text{Cl}}$. Repeated conversion of the hydrides into hydroxy groups followed by further treatment with $(^{\text{H}}\text{MD}_3)_2\text{D}^{\text{Cl}}$ led to higher generations. The dendrimers were characterized by NMR spectroscopy, SEC, as well as mass spectrometry. The presence of functional groups on the periphery renders these dendrimers suitable for further modification. Shortly after Uchida et al., Kakimoto and his co-workers presented a polysiloxane dendrimer bearing functionalizable groups at the periphery [155]. As core tris[(dimethylphenylsiloxy)dimethylsiloxy] methylsilane was used, as building block [bis(dimethylphenylsiloxy)methylsiloxy]dimethylsilanol. Treatment of the core molecule with bromine followed by diethylamine afforded the (*N,N*-diethylamino)silyl substituted siloxane, which was reacted with the building block to obtain G1. Repeating twice the series of bromination, amination, and reaction with the building block resulted in the synthesis of G2 and G3. After purification by preparative SEC the polysiloxane dendrimers were characterized by NMR spectroscopy. Furthermore, intrinsic viscosities were measured. The Mark-Houwink coefficient was found to be 0.21, indicating a spherical structure of the obtained dendrimers.

Cholesterol groups have been attached to siloxane dendrimers in the work of Shibaev and co-workers [156]. In this approach towards dendritic liquid crystalline polymers the authors first prepared a G1 dendrimer containing six Si-Cl groups according to the above-mentioned work of the same group [150]. The cholesterol containing mesogenic groups, whose synthesis is described below, were grafted to the chlorosiloxane dendrimer by heterofunctional condensation. Acetylation of cholesterol with the acyl chloride of 10-undecenoic acid followed by hydrosilylation of the terminal double bond with chlorodimethylsilane and hydrolysis in the presence of ammonia led to the mesogenic groups mentioned above. Due to this route the cholesterol groups are separated from the siloxane scaffold by a spacer consisting of ten methylene groups, which enhances the flexibility of the system. Polarizing optical microscopy revealed birefringence and formation of a fan texture typical for smectic liquid crystals.

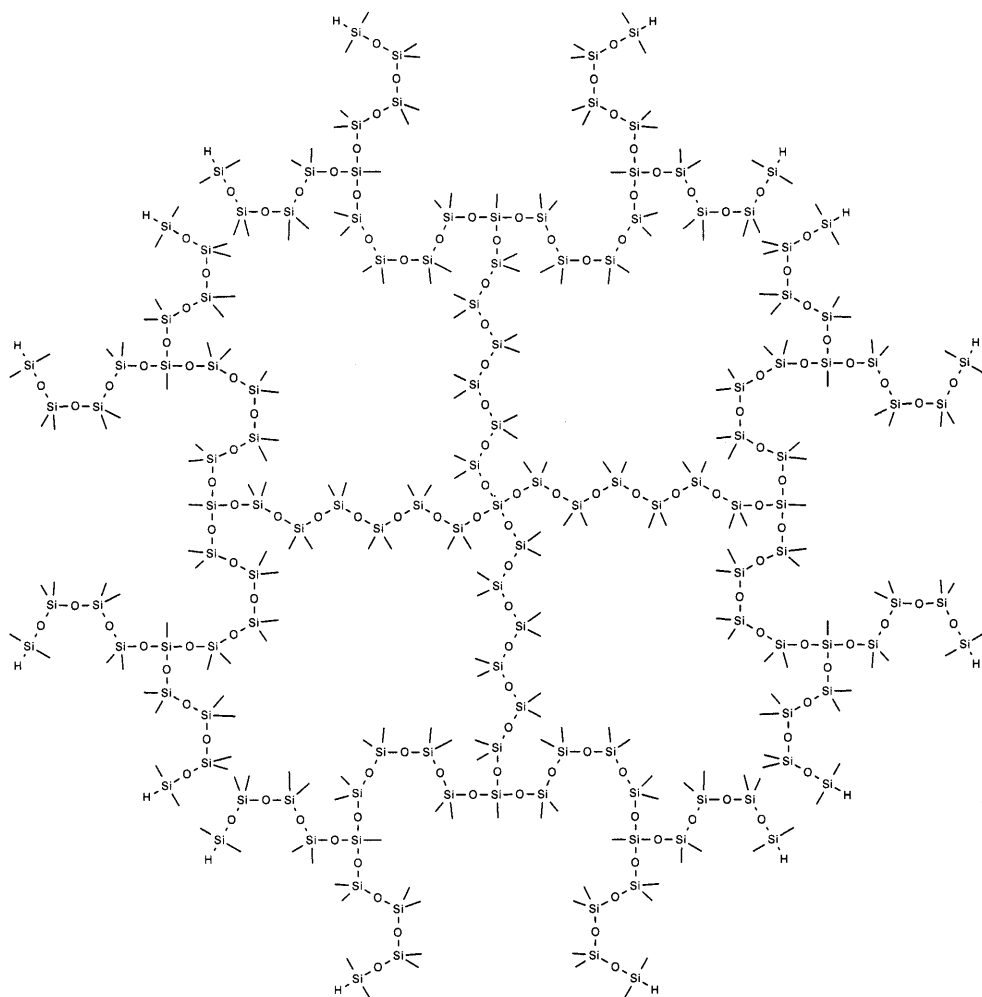


Fig. 18. G2 polysiloxane dendrimer (Masamune et al.)

3.2

Carbosiloxane Dendrimers

In general, carbosiloxane dendrimers are prepared by hydrosilylation of a terminal double bond with a chlorosilane to form an electrophilic silicon species, which is then reacted with a silanol. Thus, carbosiloxane dendrimers contain Si-O-Si groups as well as Si-(CH₂)_n-Si units. An interesting structure has been reported by Kakimoto et al. [157]. Applying the convergent strategy, Kakimoto and co-workers started with the hydrosilylation of allyl cyanide with chlorodimethylsilane. Subsequent amination with diethylamine followed by reaction

with the building block, allylbis[4-(hydroxydimethylsilyl)phenyl]methylsilane, afforded the first generation dendron. By repeating the procedure of hydrosilylation of the allyl group with chlorodimethylsilane, amination, and reaction with the building block, the dendrons G2, G3, and G4 possessing 4, 8, and 16 cyano groups, respectively, were obtained. By coupling the G3 dendrons to tris [4-(hydroxydimethylsilyl)phenyl]methylsilane, a dendrimer with 24 cyano end groups could be prepared. The molecules were characterized by NMR spectroscopy and SEC. The glass transition temperatures were around -50°C , reflecting the high flexibility of these compounds. It has been found that the glass transition temperatures increase with increasing generation number, which is in agreement with the theoretical work of Stutz [158].

Based on their previous work [24, 159], Muzafarov and co-workers introduced a scheme for the synthesis of large organosilicon dendrimers in 1997 [160]. This strategy, called “universal scheme” by the authors, combines the divergent and the convergent synthetic approach. First the authors prepared a carbosilane dendrimer of the first generation possessing eight allyl groups in the common divergent approach. Via a convergent approach Muzafarov et al. synthesized a G2 carbosiloxane monodendron possessing one Si-H group at the focal point. After coupling of core and monodendrons, the resulting carbosiloxane dendrimer (cf. Fig. 19) contains 93 silicon atoms and has a molecular weight of 7513 g mol^{-1} .

MALDI-TOF mass spectra, showing good agreement with the calculated molecular weight, have been published in a work of Sheiko et al. [161] concerning the solid-like states of the obtained dendrimer. Sheiko et al. studied the aggregation and film formation behavior of these molecules (Fig. 20) by SFM on samples which were prepared by casting dilute solutions on flat substrates, i.e., mica, pyrolytic graphite, and glass plates. The slow aggregation process of the dendrimers starts from single molecules, which coagulate to clusters and the latter to fluid droplets, eventually followed by the formation of a complete layer on the solid substrate. From dilute solutions cast on glass plates the authors were able to obtain images of single molecules or couples of them. The size of the molecules was found to be around 2.5 nm, which is consistent with the size estimated from the structure. Although being liquid at room temperature, the dendrimers exhibited rather low compliance when probed by the oscillating tip of the microscope and retained their mechanical integrity. In order to obtain corresponding macroscopic information, the dynamic shear compliance was measured. The resulting master curve showed a low plateau for the storage compliance in the range of the tapping frequency, which explains why the liquid dendrimer droplets could be observed by tapping force microscopy. In another study of Sheiko and co-workers the spreading of the carbosiloxane dendrimer discussed above on the air/water interface was dealt with [85, 86]. In contrast to the carbosilane dendrimer also studied (described in the carbosilane section of this review), the carbosiloxane dendrimer, obtained using the “universal scheme,” did not spread to form a monolayer, but retracted into a thicker film which did not affect the surface pressure until a molecular area considerably lower than the hard-disk area of a hypothetical sphere with the molecular mass and density of the investigated dendrimer was reached. This behavior is attributed to lower surface tension of the carbosiloxane dendrimer possessing

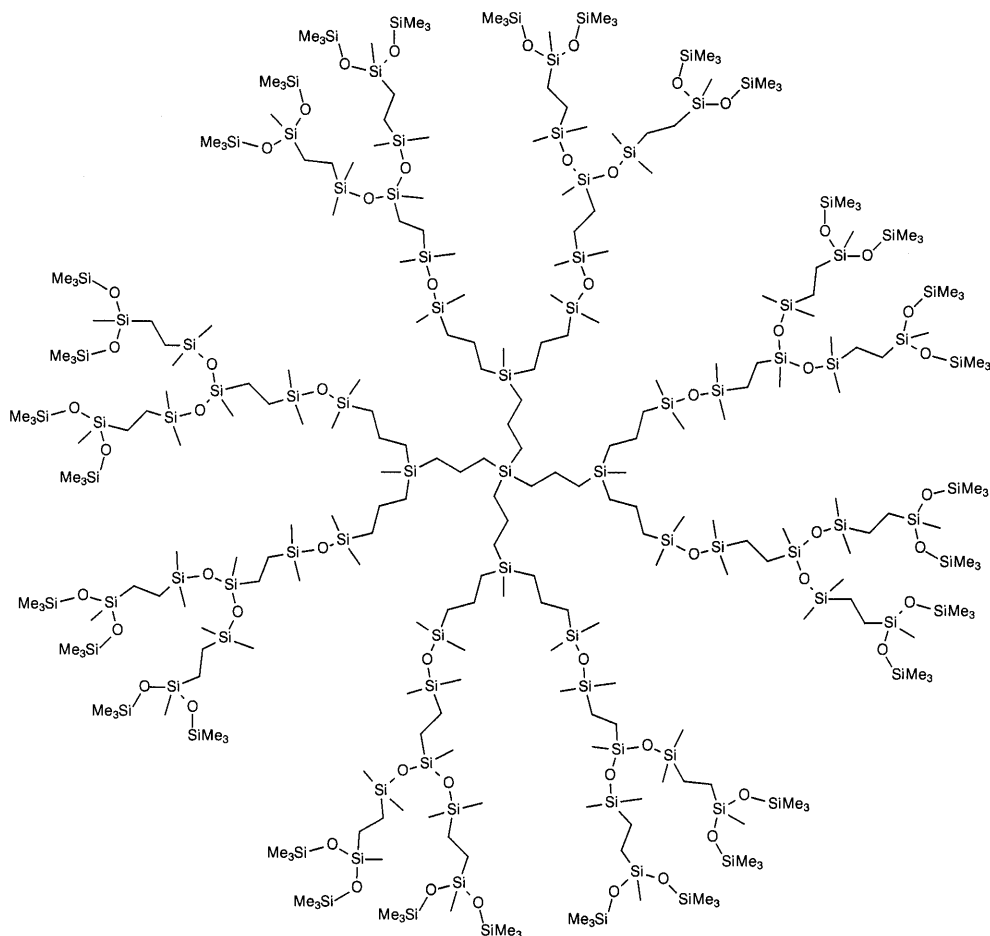


Fig. 19. G2 carbosiloxane dendrimer containing 93 silicon atoms (Muzafarov et al.)

trimethylsilyl end groups compared to the carbosilane dendrimer with hydroxyl end groups.

Fluorescently labeled carbosiloxane dendrimers have been reported by Muzafarov et al. [162]. Using similar reactions as in their previous work introducing the “universal scheme” [160] but starting from 1-(trialkylsilyl)-3-(dimethylpyrenylsilyl)propane as core, the authors obtained a carbosiloxane dendrimer carrying a pyrenyl group attached to the central silicon atom. An interesting result was obtained in a study of the concentration dependence of the spectra. Analysis evidenced excimer formation in concentrated solutions of both compounds indicating mutual accessibility of the pyrenyl groups in the core molecule and in the dendrimer. This result is especially remarkable, since no excimers were found in a solution of a pyrenyl group containing carbosilane

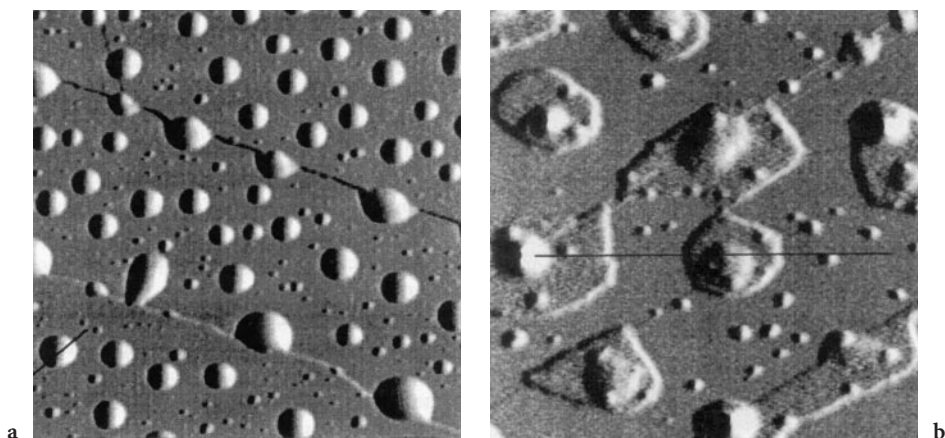


Fig. 20a, b. Ordering of G2 carbosiloxane dendrimers on mica surface: **a** directly after deposition on the mica-substrate (fluid nanodroplets); **b** after 1 month under ambient conditions; an ordered crystal-like state of the droplets is observed (Sheiko et al.)

dendrimer [121]. This behavior is attributed by the authors to a higher mobility of the trimethylsiloxy end groups of the carbosiloxane dendrimer producing a lower shielding effect in the course of excimer formation compared to the mobility of the allyl end groups of the carbosilane dendrimer. Excimer formation of the carbosiloxane dendrimer reviewed above and of a similar, somewhat larger, dendrimer has been examined in more detail in [123]. The fluorescence anisotropy decay of a pyrenyl group attached to the dendrimers has also been measured. It was found that the decay for the pyrenyl group attached to a small dendrimer deviates from that for a large dendrimer only at early times but both differ entirely from pure pyrene.

Transport properties of siloxane dendrimers at ambient and low temperatures have been studied by Bakeev et al. [163]. Bakeev and co-workers used carbosiloxane and carbosilane dendrimers with triethylsiloxy end groups, which were synthesized by Muzafarov et al. [159]. The gas permeability of supported liquid membranes filled with the dendrimers as well as with a linear oligodimethylsiloxane has been measured. It was found that the permeability of the dendritic fillers was five to ten times lower than that of the linear siloxane.

3.3

Alkoxy silane Dendrimers

Although alkoxy silane dendrimers contain no Si-O-Si groups, these materials are reviewed in this section since they are based on T-siloxane units [154] as branch points. Kim and co-workers reported alkoxy silane dendrimers with either 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane or 1,2-bis(triallyloxysilyl)ethane as core and branching multiplicities varying from 2 to 3 [164, 165]. The molecules were built up using the reaction sequence of alternating hydrosilylations with chlorosilanes and alcoholysis with allyl-alcohol. Hydro-

silylations were carried out with dichloromethylsilane or trichlorosilane, depending on the desired branching multiplicity. The alcoholysis was carried out in a mixture of TMEDA and toluene. Starting from cyclotetrasiloxane and using trichlorosilane as hydrosilylation reagent, (branching multiplicity 3), dendrimers up to G2 were accessible only, whereas in the case of dichloromethylsilane (branching multiplicity 2), dendrimers up to G5 could be obtained. Dendrimers with 1,2-bis(trialkylsiloxy)ethane as core and a branching multiplicity of 2 were reported up to the third generation. A dendrimer with a branching multiplicity of 3 could not be obtained using this core, most probably because of surface congestion.

Only recently Brüning and Lang reported the synthesis of similar allyloxy-silane dendrimers with different branching patterns, prepared under slightly different reaction conditions [166]. The use of tetraallyloxysilane as core, dichloromethylsilane as hydrosilylation reagent, and allyl alcohol for the alcoholysis afforded dendrimers of the first and second generation. Elemental analysis and NMR spectroscopy were used for structure determination. To show the suitability of these dendrimers for further functionalization with organometallic building blocks via hydrosilylation reactions, the conversion of the obtained second generation with the metallocene ($\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{H}$)($\eta^5\text{-C}_5\text{H}_5$)TiCl₂ is mentioned. However, no experimental data or characterization have been given. Lang and co-workers used this approach to obtain alkoxysilane dendrimers with propargyloxy end groups [77]. These end groups were reacted with Co₂(CO)₈ to give the acetylenedicobalt hexacarbonyl terminated dendrimer. In addition to IR and NMR spectroscopy, SEC was used to characterize the compounds prepared.

4

Silane Dendrimers

Polysilanes are unusual polymers due to their photo- and semiconductivity, thermochromism as well as nonlinear optical properties caused by the catena Si-structure [167]. However, potential applications are limited by the relatively low stability of the Si-Si bond (dissociation energy 207 kJ mol⁻¹). Dendrimers based on oligosilane segments are extremely compact molecules, because each Si atom has to be completely saturated by methyl groups, since Si-H groups are highly reactive. The consideration that a dendritic structure might increase the inertness of such molecules by restricting or prohibiting the access of reagents to the inner bonds led to the synthesis of the first polysilane dendrimer by Lambert et al. in 1995 [168], who reported a G1 polysilane dendrimer. The synthesis is based on the commercially available tris(trimethylsilyl)silane, which is converted into methyltris(trimethylsilyl)silane via successive reaction with CHCl₃ and methyllithium. The reaction of methyltris(trimethylsilyl)silane with chlorotrimethylsilane and aluminum chloride gave methyl[tris(chlorodimethylsilyl)]silane. The conversion of this trichlorinated silane with tris(trimethylsilyl)silyllithium led to 2,2,6,6-tetrakis(trimethylsilyl)-[2',2'-bis(trimethylsilyl)-1',1',3',3',3'-pentamethyltrisilyl]undecamethylheptasilane, the desired polysilane dendrimer of the first generation (cf. Fig. 21).

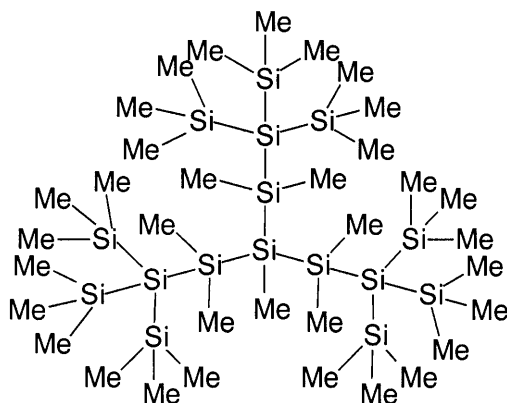


Fig. 21. Polysilane dendrimer of the first generation (Lambert et al.)

The structure of the obtained dendrimer was characterized by mass spectrometry, ^{29}Si NMR spectroscopy and further supported by X-ray diffraction. UV measurements revealed an absorption maximum of 272 nm, which lies in the range of linear silanes with similar chain length due to the longest polysilane chain of the dendrimer. However, the extinction coefficient was found to be one order of magnitude higher than that of corresponding linear silanes. The explanation given by Lambert and co-workers for this enormous increase is the high redundancy of the branched structure: in contrast to linear polysilanes, the longest polysilane chain can be found several times in the dendritic structure. The same type of dendrimer also has been obtained by Suzuki et al. [169] and Sekiguchi et al. [170]. Starting from trichlorosilane, Suzuki and co-workers obtained methyl[tris(dimethylsilyl)]silane in a Wurtz-type reaction with chlorodimethylsilane and lithium. This silane was chlorinated with CCl_4 to afford methyl[tris(chlorodimethylsilyl)]silane, which was converted into the targeted dendrimer by reaction with tris(trimethylsilyl)silyllithium. The UV spectrum was found to be almost identical to that of the linear heptasilane, which was explained with the similar length of the longest chain of the dendrimer. However, the fluorescence spectrum was strikingly different from that of linear polysilanes, exhibiting two very weak and broad emission maxima at 320 nm and 400 nm, respectively. The strong emission usually observed for linear polysilanes was not present. This behavior may be due to the high dimensionality of the silicon backbone structure in the dendrimer. Sekiguchi and co-workers employed a different, very elegant route to polysilane dendrimers. Using 2-lithio-1,3-diphenylpentamethyltrisilane as a key intermediate, they obtained dendrimers up to G2. The key intermediate was prepared by reaction of bis(1,3-diphenylpentamethyltrisilanyl)mercury with lithium. In the first step it was reacted with chlorodimethylphenylsilane to yield methyl[tris(dimethylphenylsilyl)]silane. By treatment with trifluoromethanesulfonic acid the phenyl groups were replaced by the better leaving group trifluoromethanesulfonate. The resulting precursor was reacted either with 2-lithioheptamethyltrisilane to give the permethyl-substituted first generation or with the key intermediate to

yield G1 with phenylsilyl groups. By repeating the treatment with trifluoromethanesulfonic acid followed by reaction with 2-lithioheptamethyltrisilane, the permethyl-substituted second generation was obtained. The dendrimers were characterized by NMR spectroscopy, mass spectrometry, as well as UV spectroscopy, showing a considerably larger extinction coefficient for the G2 compared to G1. Crystal structures have been obtained both for G1 of the phenyl-substituted and the permethyl-substituted polysilane dendrimers recently [171].

In 1996 Lambert et al. reported on the synthesis and characterization of a variety of polysilane dendrimers (G1) [172]. Structures varying in core multiplicity, number of spacer atoms between branch points, and branching multiplicity have been obtained. Synthetic strategies were analogous to the previous work [168]. Polysilane dendrimers with a tetrafunctional core and without spacers could not be isolated because of steric constraints. In another case, steric congestion was relieved by fragmentation into a smaller dendrimer or by angle distortion as seen from the crystal structures. X-ray diffraction confirmed the importance of orthogonal arrangements in polysilanes. Despite the absence of all-anti pathways, the dendrimers show UV absorption maxima at long wavelengths. As for linear polysilanes an increase is seen in λ_{\max} with increasing length of the longest polysilane chain in the dendrimers. The extinction coefficients were found to range from slightly to significantly higher than in the linear counterparts, presumably as a result of the numerous pathways. Unexpectedly, absorption maxima and intensities are insensitive to the conformations of the dendrimers.

As mentioned above, one dendrimer, 2,6-bis(trimethylsilyl)-4-[2'-(trimethylsilyl)-1',1',2',3',3',3'-hexamethyltrisilyl]tridecamethylheptasilane, failed to crystallize. The structure of this dendrimer was determined by a new NMR technique, the 2D $\text{Si}^{29}\text{-Si}^{29}$ INADEQUATE experiment [173]. This experiment provided the connectivity for each of the three Si-Si bonds in the molecule and therefore allowed, in combination with the 1D ^{29}Si NMR spectra, the determination of the molecular structure. Since this 2D INADEQUATE method does not require crystalline or solid materials, it is a useful addition to X-ray diffraction. Another ^{29}Si NMR study was carried out by Thomas and co-workers [174]. Polysilane dendrimers (G1) with various substitution patterns were prepared and characterized by ^{29}Si NMR spectroscopy.

The polysilane dendrimer with the longest polysilane chain reported so far has been described by Lambert and Wu in 1998 [175]. The dendrimer, tris[2,2,5,5-tetrakis(trimethylsilyl)hexasilyl]methylsilane, with 13 silicons in the longest chain, was obtained by reaction of tris(chlorodimethylsilyl)methylsilane with 1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3,5,5,5-heptamethylpentasylolithium. The structure was confirmed by NMR, mass spectrometry, UV spectroscopy, and X-ray diffraction. The molecule exhibits two UV maxima comparable to that known for linear polysilanes of similar length. Yet the extinction coefficients of the dendrimer are an order of magnitude higher. This is again attributed to the presence of multiple linear pathways in the structure. The authors state that polysilane dendrimers with their expected more robust properties should be superior to linear systems in the field of conductive and nonlinear optical applications.

based on dendrimers as templates, e. g., to create nanoporous materials. The first polycarbosilazane dendrimers have been reported by Hu and Son in 1998 [177, 178]. Starting from tris(dimethylvinylsilyl)amine as core molecule they obtained carbosilazane dendrimers up to G2 by repeated hydrosilylation with chloro-dimethylsilane and nucleophilic substitution with lithiumbis(dimethylvinylsilyl)amide (cf. Fig. 23).

G3 could not be realized because the reaction of the chlorosilyl-terminated intermediate with the lithium amide failed to be complete. Steric congestion mentioned by the authors does not seem to be a likely reason for this problem due to the fact that the spacers between the branch points are long and only a branching multiplicity of 2 was employed. The dendrimers have been characterized by IR and NMR spectroscopy, elemental analysis, as well as vapor pressure osmometry. Preliminary MALDI-TOF-MS data confirming the perfect structures were mentioned. Although carbosilazane dendrimers are stable to air,

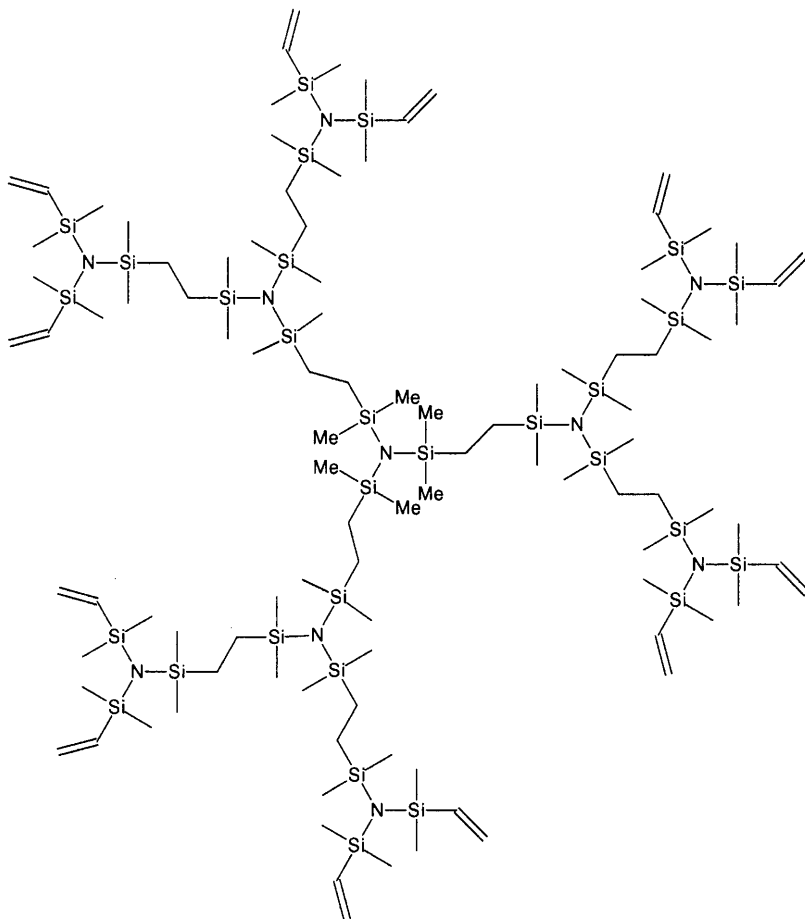


Fig. 23. Polycarbosilazane G1 dendrimer structure (Hu and Son)

water, and anhydrous hydrogen chloride solutions, they degrade rapidly and exothermically in aqueous hydrochloric acid solutions. A notable result is the observed interaction of anhydrous HCl with these dendrimers. IR spectroscopy suggests that H-N interactions exist.

Only recently, similar polycarbosilazane dendrimers have been reported by Veith et al. [179]. Using an analogous, although considerably improved, synthetic protocol [177, 178], dendrimers up to G4 have been obtained. Showing that the limiting generation lies beyond G2, this result is in contrast to the work of Hu and Son. Veith and co-workers characterized the dendritic molecules by elemental analysis, NMR spectroscopy and MALDI-TOF mass spectrometry, in which the protonated molecular ions of all compounds but the dendrimer of the fourth generation were observed. According to the authors the spectra show no impurities and no signals due to imperfectly branched dendrimers, originating from incomplete reactions in the course of the divergent synthesis. Surprisingly, single crystals of the methyl-substituted derivatives of the dendrimers of the first and second generation could be grown, but X-ray diffraction structure determination has failed so far.

5.2

Silatrane Dendrimers

An unusual class of Si-based dendrimers are the silatranes. Silatranes, in this case derivatives of 2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane, are of interest because of their biological activity. Applications in agricultural chemistry have shown significant potential, e.g., for insecticides and crop yield enhancement. To provide novel biological properties, silatrane dendrons have been developed as an entirely new class of silatrane-containing materials by Kemmitt and Henderson in 1997 [180]. The structure of one of the obtained dendritic silatrane wedges is illustrated in Fig. 24. This structure has been prepared in a convergent approach. Reaction of trimethoxy(glycidoxypropyl)silane with triisopropanolamine led to 1-glycidoxypropyl-3,7,10-trimethylsilatrane. The pendant glycidoxy groups of two such molecules have been reacted with ethanolamine to give a tri-alkanolamine, which can form a silatrane upon reaction with a trimethoxysilane. Thus, sequential addition of trimethoxy(glycidoxypropyl)silane and ethanolamine, respectively, allowed the construction of the desired dendritic silatrane wedges. By use of ammonia or diethanolamine instead of ethanolamine, the branching multiplicity could be controlled conveniently. Characterization was achieved by means of NMR spectroscopy. Electrospray mass spectrometry was used to confirm the structures. Mass spectra supported the purity of the obtained compounds.

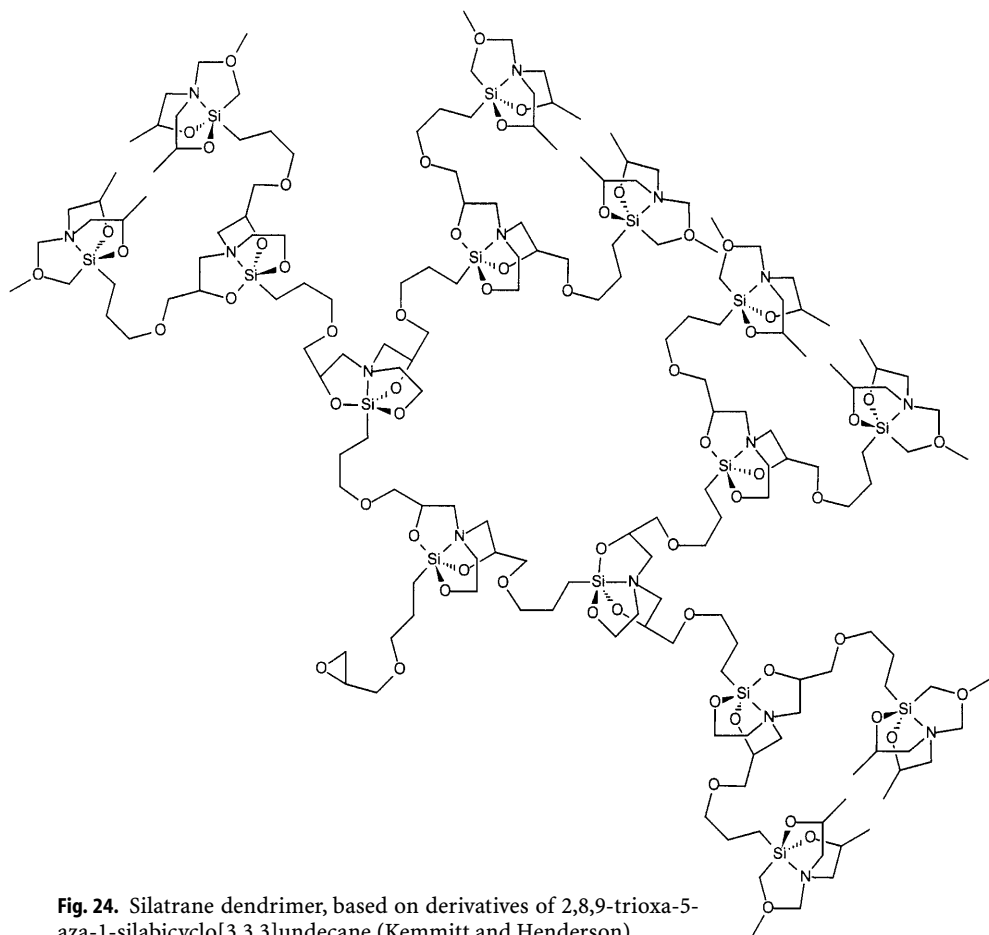


Fig. 24. Silatrane dendrimer, based on derivatives of 2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (Kemmitt and Henderson)

6 Silicon-Based Hyperbranched Polymers

Although silicon-based dendrimers are the central topic of this review, this would not be a comprehensive summary without a discussion of recent advances in the field of silicon-based hyperbranched polymers. As already discussed in the introduction, hyperbranched polymers are the randomly branched analogues of dendrimers, obtained in a one step synthesis by polycondensation or polyaddition of AB_m monomers, m being ≥ 2 . Due to the dendrimer hype in recent years, it has sometimes been overlooked that the branch-on-branch structure principle typical for cascade-type macromolecules has in fact been known for almost 50 years. In the early 1950s, Flory published theoretical and experimental evidence for the existence of branched “three-dimensional” macromolecules obtained via polycondensation of AB_m -type monomers

[181, 182]. Flory designated these polymers “AB_m-random polycondensates”. Although such polymers show no entanglements like conventional linear chain polymers, they are not very tough materials and were thus considered to be of little interest as polymeric materials. The field remained dormant until Kim and Webster coined the term “hyperbranched” for this class of materials in 1987 [183]. In recent years, in the tailwind of dendrimers, hyperbranched polymers have also seen a surge of interest [184]. As already shown by Flory almost 50 years ago, the fundamental dilemma of hyperbranched polymers lies in the fact that the high conversions required to achieve reasonable molecular weights in a random polycondensation reaction of AB_m monomers inevitably lead to extremely broad molecular weight distributions, often exceeding $M_w/M_n = 5$, and in many cases polydispersities exceeding 10 are obtained. A second dilemma, which was mentioned (but intentionally neglected) by Flory, lies in the reaction of the one focal A group of the macromolecules with one of the B-endgroups (“intramolecular cyclization”), which severely limits molecular weights achievable [185]. Furthermore, in contrast to the perfectly branched dendrimers, hyperbranched polymers are characterized by a randomly branched structure that is described by the “degree of branching” (DB). Theoretical foundations for the description and control of the DB as well as its relationship with the number of end groups and degree of polymerization have only been laid in recent years [186–188]. Commonly, the DB is determined by NMR-spectroscopy on the basis of low molecular weight model compounds possessing structures analogous to the perfectly branched (i.e., dendritic) and imperfectly branched units and end groups (i.e., terminal units) in the respective hyperbranched polymer.

At present, hyperbranched polymers are often regarded as the “poor cousins” of dendrimers, being considerably less defined; however, in the long run they are likely to present a cheap alternative to dendrimers for applications that necessitate high functionality, but do not require the high structural precision of a dendrimer. In recent years, theoretical concepts for the control of the key parameters molecular weight and polydispersity of hyperbranched polymers have also been developed. For instance, it has been shown that copolymerization of a core molecule B_f can be employed to reduce polydispersities [189]; slow monomer addition techniques in combination with a polyfunctional initiator can lower the polydispersity further [190]. The improved theoretical understanding is likely to permit the preparation of hyperbranched polymers that may eventually rival dendrimers [191].

Although hyperbranched analogs have been prepared for various Si-based dendrimers, the corresponding hyperbranched polymers have not been reported for all of them; for instance hyperbranched polysilazanes have not yet been prepared. In the next section we will briefly summarize the works on hyperbranched polycarbosilanes, polycarbosiloxanes, and polyalkoxysilanes published so far. It should be emphasized that the characterization of hyperbranched polymers is difficult and molecular weights determined by SEC based on linear polystyrene standards may in some cases be overestimated by an order of magnitude. Thus, unless molecular weights given were determined by absolute methods, they can only be taken as an indication of the actual degree of polymerization.

6.1

Hyperbranched Polycarbosilanes

A number of suitable AB_m -monomers for the preparation of hyperbranched polycarbosilanes have been reported in recent years. Some typical monomer structures are shown in Fig. 25.

The first hyperbranched carbosilane polymer was prepared by Interrante and co-workers in 1991 [192, 193]. Their approach to hyperbranched polymers involved the condensation of (chloromethyl)trichlorosilane via a Grignard reaction, in which the Grignard-reagent formed in situ after addition of Mg represents the AB_3 monomer. In order to obtain hydrolytically stable polymers, the intermediate hyperbranched polychlorocarbosilane was reduced with $LiAlH_4$ to obtain a carbosilane polymer possessing the formal structure $(SiCH_4)_n$. The structure of this material is schematically shown in Fig. 26.

The molecular weight was found to be in the range of 600 g mol^{-1} , corresponding to a degree of polymerization DP_n of 13. Taking advantage of the chemical stability of the backbone Si-C bonds and the high reactivity of the Si-X ($X=H, Br$) bond, Interrante and co-workers modified the end groups of the obtained hyperbranched polycarbosilane via bromination followed by alkylation using Li or Mg organometallic compounds [194]. Carrying out the alkylation

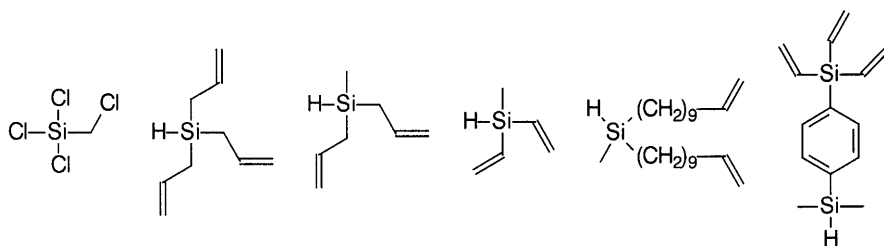


Fig. 25. Typical AB_2 and AB_3 monomers for the preparation of hyperbranched polycarbosilanes

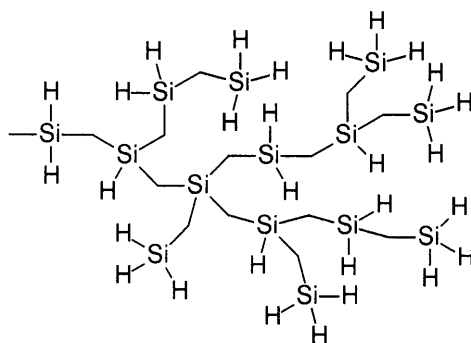


Fig. 26. Hyperbranched polycarbosilane prepared by condensation of (chloromethyl)trichlorosilane via a Grignard reaction. The intermediate hyperbranched polychlorocarbosilane was reduced with $LiAlH_4$ (Whitmarsh and Interrante)

tion with allylmagnesium bromide afforded an allyl-substituted hyperbranched polycarbosilane, which could be functionalized further by applying hydrosilylation with various silanes, e.g., dimethylphenylsilane or chlorodimethylsilane. Characterization by NMR and IR spectroscopy and SEC revealed that a high degree of substitution was achieved in the modification and that in most cases no decomposition respectively cross-linking reactions occurred during functionalization. The native hyperbranched polycarbosilane and the partially allyl-substituted derivative have proven useful as SiC matrix sources for SiC fibers and particulate-reinforced composites [195]. In further work, hyperbranched alkoxy-substituted polycarbosilanes based on the system described above were used to synthesize cross-linked polycarbosilanes/siloxane hybrid polymers by sol-gel processing [196]. The silicon oxycarbide ceramics formed by the pyrolysis of the obtained gels in high yields (~85%) have been found to exhibit relatively high surface areas and a microporous structure, which renders them interesting as catalyst supports or ceramic membranes for gas separation.

In 1998 Yao and Son reported on hyperbranched carbosilane oligomers also prepared by a "Grignard polymerization" [197]. Using (chloropropenyl)dichloromethylsilane as monomer they obtained a polymer possessing C-C double bonds. The product was characterized by NMR spectroscopy. An average DP_n of 8 was obtained [198]. Also based on a Grignard-coupling reaction, the same authors recently reported the preparation of hyperbranched poly(2,5-silylthiophenes) using the Grignard reagent derived from 2-bromo-5-(trimethoxysilyl)thiophene as AB_3 monomer. The polymers contain alternating silylene and thiophene groups along the branches, and are interesting in view of their σ - π -conjugation properties [199].

However, most hyperbranched polycarbosilanes prepared to date have been obtained by hydrosilylation of monomers containing C-C double bonds as well as Si-H groups. In 1993 Muzafarov et al. [24] reported on the synthesis of poly(methylvinylsilane). However, polymerization of the gaseous monomer proved to be difficult. For that reason the authors also considered the AB_m monomers diallylsilane, divinylsilane, and triallylsilane. An unexpected result was obtained upon addition of monomer to the hyperbranched polymer, which did not result in a significant effect on the molecular weight of the polymer. Since accessibility of all functional groups of the hyperbranched polymer could be proven by quantitative conversion with dichloromethylsilane, using analogous reaction conditions as for the polymerization, steric hindrance could be ruled out as the cause of this behavior. The authors explain the limited growth by kinetic factors; however, as shown below and in agreement with more recent studies, it is most likely due to cyclization. However, no detailed experimental data were presented in this work.

A detailed investigation of the degree of branching of hyperbranched polycarbosilanes obtained from the Pt-catalyzed polymerization of triallylsilane, based on ^{29}Si -NMR spectroscopy was reported by our group. The study showed that the polymerization of this AB_3 -monomer takes a random course, with all allyl groups possessing the same reactivity, manifested by the degree of branching of 0.42, which was in good agreement with the value of 0.44 expected for random polymerization of AB_3 monomers [186]. Copolymerizing

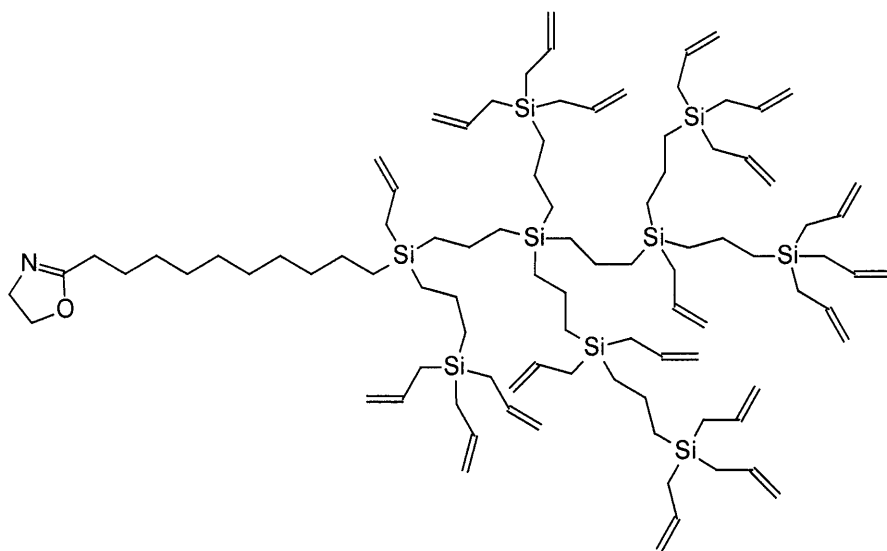


Fig. 27. Hyperbranched poly(triallylsilane) macromonomers possessing a focal oxazoline group (Frey et al.)

2-(10-decen-1-yl)-1,3-oxazoline as a B_1 -core molecule with triallylsilane prior to hydrosilylation, control over the degree of polymerization was achieved and poly(triallylsilane) possessing one oxazoline group was obtained (cf. Fig. 27) [200].

Since the oxazoline group can be polymerized, the obtained carbosilane represents the first example of a “hyperbranched macromonomer.” As expected, SEC measurements on several reactions employing different amounts of 2-(10-decen-1-yl)-1,3-oxazoline revealed a decrease of molecular weight and polydispersity with increasing amounts of the latter. In further work we reported polymerization of the oxazoline groups as well as attachment of the oxazoline-based hyperbranched macromonomers to a trifunctional core affording trimers of the hyperbranched fragments [201, 202]. Unexpectedly, the core-linked trimer was obtained as a transparent, rubber-like solid and strong, directed aggregation in solution was observed by various techniques. The results support formation of columnar structures by interaction of the polar cores of the trimers with their amide-ester bonds capable of forming hydrogen bonds. These polar centers of the stacks are surrounded by an apolar, disordered exterior [203].

In further work Getmanova and co-workers synthesized a hydroxyl end group-containing derivative of poly(diallylmethylsilane) [83]. 1-(3-Dimethylsilyl)propyloxy-2-trimethylsilyloxyethane was coupled with the hyperbranched polymer via hydrosilylation. Hydrolysis of the trimethylsiloxy group afforded the desired hydroxy derivative. IR spectroscopy provided evidence for the formation of a complicated hydrogen-bonded network in this compound. The structure of a hyperbranched polycarbosilane in solution has been investigated by Ozerin et al. [204]. Poly(diallylmethylsilane) was studied by small-angle X-ray scattering and molecular modeling.

Hybrid concepts, combining hyperbranched polymers with strategies from dendrimer chemistry, may also play a role in the future to improve structural control over hyperbranched polymers. Combining a reaction sequence well-known from carbosilane dendrimer synthesis, namely the hydrosilylation of terminal double bonds with trichlorosilane and subsequent displacement of the chloride groups by allylmagnesium bromide, with the synthesis of hyperbranched poly(triallylsilane) [24, 200] allows enhancement of the degree of branching postsynthetically [205]. An almost completely branched structure with a degree of branching close to 1 (“pseudodendrimer”) was generated in this manner. The introduced concept is universal and applicable not only to hyperbranched polycarbosilanes. However, it should be noted that the resulting polymers contain numerous short branches and do not possess the symmetry of a dendrimer despite the high degree of branching.

Investigations concerning the effect of a variation of the monomer structure on the kinetics of the addition reaction, the branching structure, and the occurrence of side reactions have been reported by Möller and co-workers [206]. It was confirmed that, in the case of diallylmethylsilane and methyldivinylsilane, subsequent addition of further monomer did not lead to an increase of the molecular weight. This was explained by a “self-regulation” process due to structural density. However, according to recent work by Fréchet et al. [219] as well as our group [207], this is probably due to cyclization consuming Si-H functionalities, thereby limiting the growth of polymer molecules. In the case of bis(undecenyl)methylsilane, the successive addition of new monomer yielded polymers with gradually increasing molecular weights. According to the authors this might be explained by the formation of sterically less crowded polymers in the case of monomers with long alkenyl groups. However, kinetically disfavored cyclization due to the large monomers appears to be a more likely explanation in this case.

Only recently Son and Yoon used 1-dimethylsilyl-4-trivinylsilylbenzene in an innovative approach as AB₃-monomer to obtain the first aromatic hyperbranched polycarbosilane by hydrosilylation [208]. Despite the presence of rigid aromatic moieties within the branching points, the glass transition temperature of the polymer is still relatively low ($T_g = 12^\circ\text{C}$) and general solubility is high. The hyperbranched poly(carbosilarylene)s based on AB₃-monomers were investigated in detail with respect to the formation of linear, semidendritic, and perfectly branched dendritic units [209]. The degree of branching was determined to be 0.42, close to the expected value of 0.44 for a random AB₃ polycondensation, indicating that all B-groups possessed the same reactivity. The authors suggest that such polymers could be used as components for advanced elastomers.

6.2

Hyperbranched Polycarbosiloxanes

Typical monomer structures employed for the preparation of hyperbranched polycarbosiloxanes are depicted in Fig. 28.

As early as 1991, Mathias and co-workers described the use of hydrosilylation to obtain highly branched carbosiloxane polymers [210, 211]. Hydrosilylation of

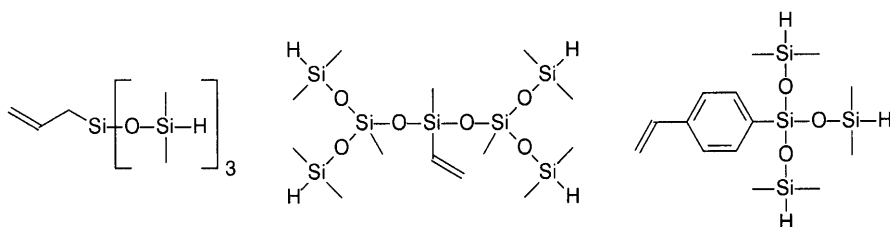


Fig. 28. Typical monomers (AB_3 , AB_4) for the preparation of hyperbranched polycarbosiloxanes

allyltris(dimethylsiloxy)silane afforded a hyperbranched polycarbosiloxane with a molecular weight of $19,000 \text{ g mol}^{-1}$ and an unexpectedly narrow molecular weight distribution. The structure of the obtained polymer is schematically shown in Fig. 29.

In order to convert the material into a less reactive derivative, the terminal Si-H groups containing hyperbranched polycarbosiloxane has been hydrosilylated with allyl phenyl ether. In further work, not only the reaction of the non-substituted hyperbranched polycarbosiloxane with allyl phenyl ether, but also with other allyl and vinyl groups containing molecules, e. g., acrylic acid and allyl terminated oligo(ethylene oxide), have been reported [212]. Reaction with oligo(ethylene oxide) remained incomplete. In subsequent work, the authors showed that intramolecular reaction of the monomer, allyltris(dimethylsiloxy)-

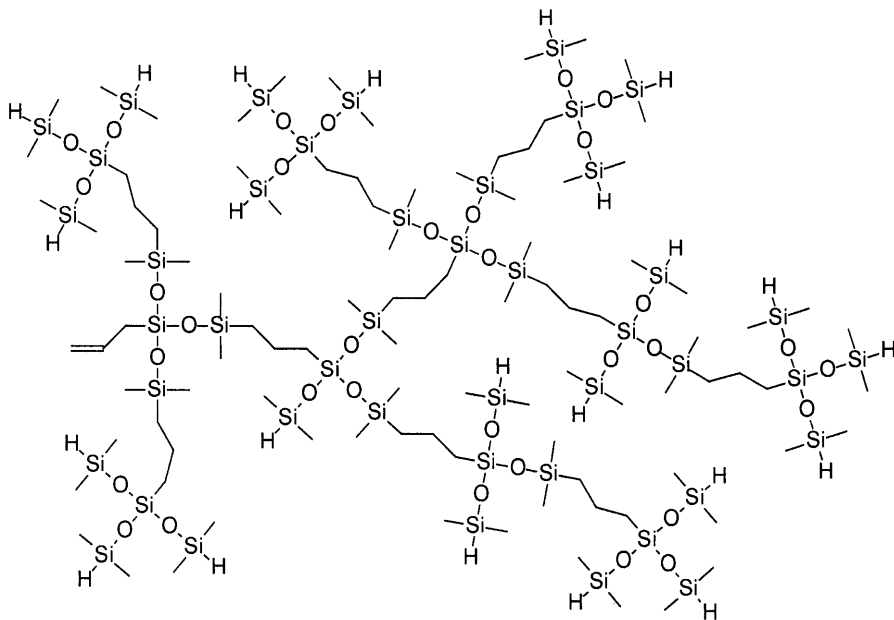


Fig. 29. Hyperbranched carbosiloxane polymer obtained by hydrosilylation of allyltris(dimethylsiloxy)silane (Mathias and Carothers)

silane, leading to a six-membered cycle, was prevalent in the system [213]. The cycle acts as a bifunctional (B_2) core during the polymerization, broadening the molecular weight distribution. To disfavor this undesired cyclization reaction entropically, Carothers and Mathias employed longer alkene-containing monomers such as 6-hex-1-enyltris(dimethylsiloxy)silane. However, the obtained polymers showed broad, multi-modal SEC traces with polystyrene equivalent molecular weights ranging from 12,000 to 21,000 g mol⁻¹.

Rubinsztajn also reported the synthesis of related polycarbosiloxanes [214]. He confirmed the formation of a significant amount of a six-membered cyclic product in the polymerization of allyltris(dimethylsiloxy)silane. To favor the intermolecular reaction leading to hyperbranched polymers, Rubinsztajn used vinyltris(dimethylsiloxy)silane and tris(dimethylvinylsiloxy)silane as monomers. The products of the intramolecular reaction of these monomers are five-membered cycles with high ring strain, which should diminish the yield of cyclic products. Polymerization of the novel monomers afforded the corresponding polymers in yields significantly higher compared to the monomer allyltris(dimethylsiloxy)silane. As expected, SEC analysis showed broad molecular weight distributions.

Vinyltris(dimethylsiloxy)silane has also been used as a monomer [215]. Herzig and Deubzer prepared hyperbranched polycarbosiloxanes by feeding the monomer to a multi(Si-H) functionalized core, e.g., propyltris(dimethylsiloxy)silane. Using this approach, the authors were able to control the viscosity of the products. However, cyclization of the monomers could also not be avoided. Up to 10 mol-% of the monomer cyclized during the polymerization. The authors also showed that the polymers obtained can be used as crosslinkers in addition cure formulations.

An interesting study of the effect of the branching multiplicity on the resulting polymers has been reported by Miravet and Fréchet [216, 217] using monomers with branching multiplicities of 2 (methylvinylbis(dimethylsiloxy)silane), 4 (methylvinylbis[methylbis(dimethylsiloxy)siloxy]silane) and 6 (vinyltris[methylbis(dimethylsiloxy)siloxy]silane), respectively. The polymerization of these monomers afforded hyperbranched polymers with terminal silicon hydride groups. In all cases, SEC traces showed the presence of multiple resolved peaks with elution volumes corresponding to low molecular weight compounds that were assigned to oligomers. Also a large peak with a retention volume essentially identical to that of the monomer was detected. Since spectroscopic analysis of the materials revealed no vinyl groups, this peak is most probably due to the product obtained by intramolecular cyclization of the monomers. Depending on the monomer employed, molecular weights up to 8900 g mol⁻¹ have been obtained after removal of the oligomers, the highest molecular weight being obtained from the monomer with a branching multiplicity of 4. Addition of extra monomer resulted in all cases in a very moderate increase of the molecular weight and afforded materials that, like the initial polymer, contained low molecular weight oligomers. All of the hyperbranched polycarbosiloxanes possess fully accessible terminal Si-H groups that have been modified with allyl or vinyl groups containing reagents such as allyl phenyl ether or allyl methyl triethylene glycol.

In order to overcome the molecular weight limitations and to obtain hyperbranched polycarbosiloxanes with higher molecular weights, Fréchet and co-workers applied the slow monomer addition method developed by our group as well as Müller et al. independently [189, 190] to the system discussed above [218, 219].

In this case, the resulting polymers were obtained in higher yields (72–79%) with higher molecular weights than in the analogous random polycondensation (8700–61,000 g mol⁻¹ after removal of the low molecular weight fractions). According to the authors, both the rate of addition of the monomer and the amount of monomer feed showed a predictable effect on molecular weight and polydispersity of the final polymer, affecting the cyclization probability.

An interesting structure was obtained by Muzafarov and co-workers polymerizing poly(dimethylsiloxane) macromonomers [220]. The macromonomers employed possess degrees of polymerization of 10, 50, and 100, respectively and contain one vinyl and two silicon-hydride end groups. Polymerization by hydrosilylation afforded long-chain hyperbranched polycarbosiloxanes bearing Si-H functionalities with molecular weights ranging from 15,000 g mol⁻¹ to 800,000 g mol⁻¹ depending on the macromonomer employed.

Another intriguing monomer was reported by Rubinsztajn and Stein [221]. They synthesized (4-vinylphenyl)tris(dimethylsiloxy)silane, which can be polymerized to give either hyperbranched polycarbosiloxanes or linear tris(dimethylsiloxy)silyl substituted polystyrenes. The hyperbranched polymer was prepared by hydrosilylation, and its molecular weight was found to be 9800 g mol⁻¹ (SEC). The polymer can easily be functionalized, as demonstrated by the authors by reaction with trimethylvinylsilane. Compared to the corresponding hyperbranched polymers based on the aliphatic monomer tris(dimethylsiloxy)vinylsilane, the new polymer showed a higher decomposition temperature.

6.3

Hyperbranched Polyalkoxysilanes

Hyperbranched poly(bis(undecenyloxy)methylsilane) was obtained by Möller and co-workers in 1995 [222]. The monomer structure used is shown in Fig. 30.

Choosing bis(undecenyloxy)methylsilane as monomer it was the authors' intention to synthesize a degradable polymer with a molecular surface defined by the topological arrangement of the end groups. This structure can be used as a template to create nanometer-size cavities in the matrix of another material. The authors showed that agglomerates of the hyperbranched molecules in a methacrylate resin could be removed from the latter by hydrolysis [223] leading to cavities in the matrix. This result clearly shows the feasibility of this approach.

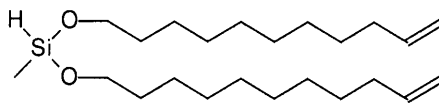


Fig. 30. Hyperbranched poly(bis(undecenyloxy)methylsilane) as an example for a hyperbranched poly(alkoxysilane) (Möller et al.)

An entirely inorganic hyperbranched structure has been reported by Muzafarov et al. in 1996 [224, 225]. Two different monomers, i.e., triethoxysilanol and triethoxysilyltri fluoroacetate, have been prepared starting from tetraethoxysilane. The heterofunctional condensation of each monomer led to hyperbranched ethyl silicates. The ethoxy end groups of these materials were converted into trimethylsilyl end groups rendering the polymer stable for the characterization. The obtained polymers were characterized by means of NMR spectroscopy and SEC. SEC revealed molecular weights up to hundreds of thousands depending on the reaction conditions during synthesis.

7

Summary and Outlook

Less than ten years after the first reports on Si-based dendrimer structures, a large variety of dendrimers based on a relatively small set of construction reactions has been developed, demonstrating the versatility silicon chemistry has to offer for both dendrimers and hyperbranched polymers. The basic synthetic routes towards branched Si-C-, Si-O-, Si-N-, and Si-Si based macromolecules are well-established by now. Despite this synthetic progress our knowledge concerning materials properties or effects that would systematically exploit the peculiar nature of the branched structures is still surprisingly limited.

With respect to the construction of unusual dendrimer topologies, combination of the different building principles known at present can easily be used to construct intriguing molecules in the future. One might envisage hybrid structures consisting of siloxanes and carbosilanes, radially layered dendrimer structures as well as novel macromolecular architectures, such as dendronized Si-based polymers.

With respect to macroscopic properties, the variability of the branching multiplicity of Si-based dendritic polymers represents a major advantage, which is valuable for the elucidation of fundamental structure-property relationships valid for dendrimers in general. This has for instance been demonstrated in the section on dendritic liquid crystalline structures that strongly depend on the branching multiplicity and consequently, the end group density. For instance, the high endgroup density attainable in relatively low generations of carbosilane dendrimers in the case of a branching multiplicity of 3 is an important peculiarity in order to get further insight into dendrimer-specific properties.

Turning to larger scale materials applications and considering the crucially important role silicone-based materials play in medicine, pharmaceutical applications, as well as specialty coatings and in many other areas, globular highly branched Si-based polymers hold great promise for the future. In addition, the combination of dendritic topologies with sol-gel chemistry as well as the exploitation of the peculiar rheological properties of this class of polymers offers attractive potential for the future. However, it is likely that for these types of applications, hyperbranched Si-based polymers will be the materials of choice, rather than the structurally perfect dendrimers. These, however, serve as valuable model compounds for the hyperbranched materials. In the long run, the combi-

nation of a branching monomer with conventional linear structures may reduce cost and still permit one to retain the peculiar properties of dendritic polymers [226]. Progress in this area may eventually lead to novel materials, particularly tough coatings, lubricants, adhesives, as well as fluids with unusual rheological properties. However, all of these applications will have to be based on improved understanding of structure formation and structure-property relationships [227].

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