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Invited Review

Carbosilane Dendrimers – Synthesis, Functionalization, Application

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Summary. This micro-review summarizes historical and recent developments in synthesis, functionalization, and characterization of carbosilane dendrimers. These compounds are the most important among the heteroatom-based dendrimers at present due to the flexibility of the synthetic route and to their chemical stability which allows versatile further functionalization. Synthesis as well as application potential of carbosilane dendrimers for catalysis, host-guest chemistry, liquid crystals, and novel polymer topologies is discussed.

Keywords. Carbosilane; Dendrimer; Catalysis; Liquid crystals; Hyperbranched.

Carbosilandendrimere – Synthese, Funktionalisierung und Anwendung

Zusammenfassung. Der vorliegende Mikroreview faßt historische und aktuelle Entwicklungen bezüglich Synthese, Funktionalisierung und Charakterisierung von Carbosilandendrimeren zusammen. Wegen der Variabilität der Syntheseroute und ihrer chemischen Stabilität, die weitere Funktionalisierung erlaubt, zählen diese Verbindungen zu den wichtigsten unter den Heteroatomdendrimeren. Synthese und Potential der Carbosilandendrimere auf den Gebieten der Katalyse, Wirt-Gast-Chemie, Flüssigkristalle und neuer Polymertopologien werden diskutiert.

1. Introduction

Dendrimers are three-dimensional, highly branched, monodisperse (in the ideal case) macromolecules with perfectly defined branching structure. Together with the hyperbranched polymers they represent the class of the cascade molecules. However, in contrast to the randomly branched hyperbranched polymers, dendrimers possess defined branches emanating from a central core (Fig. 1).

The dendrimer scaffold can be subdivided into three regions: (*i*) the core from which the branching units emanate, (*ii*) the region of the inner repeat units, and (*iii*) the outer region with the end groups. The individual layers around the core are designated "generations". Dendrimers are built up by iterative stepwise reaction

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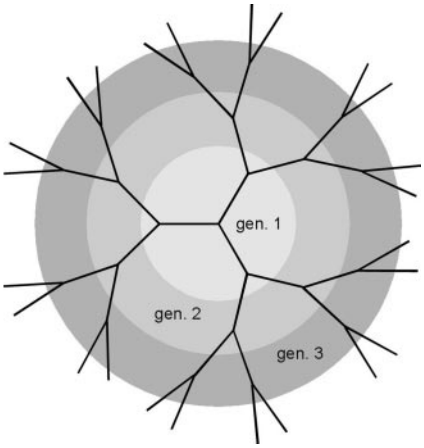


Fig. 1. Schematic representation of the dendrimer structure

sequences, either in the convergent [1, 2] or divergent [3] approach. In the divergent strategy, dendrimers are built from the central core outwards to the periphery. The convergent approach constructs the dendrimer from the periphery towards the central core.

Some of the developments in the area of the heteroatom-based dendrimers have been summarized in recent reviews [4, 5]. Silicon chemistry offers several quantitative reactions suitable for the construction of perfect dendrimers, such as transformation of chlorosilanes with organometallic reagents, *e.g. Grignard* reagents, as well as Pt-catalyzed hydrosilylation. To date carbosilane, carbosiloxane, and small silane dendrimers have been described. At present, carbosilane dendrimers represent the most important class of Si-based dendrimers. They are kinetically as well as thermodynamically very stable molecules owing to the dissociation energy of the Si–C bond (306 kJ/mol), which is comparable to that of C–C bonds (345 kJ/mol), and the low polarity of the Si–C bond. This is an important prerequisite for further functionalization. This micro-review aims at a summary of the developments in the synthesis, functionalization, and characterization of carbosilane dendrimers as well as some of their potential applications.

2. Synthesis and Characterization

2.1. General Synthetic Strategy

To date, all reported carbosilane dendrimers have been synthesized *via* the divergent approach (Fig. 2). *Fetters et al.* reported the use of a G1 carbosilane dendrimer with 12 end groups for the synthesis of a star polymer as early as 1978 [6]. However, *van der Made et al.* [7, 8], *Roovers et al.* [9, 10], and *Muzafarov et al.* [11] independently reported the first syntheses aiming at carbosilane dendrimers of various generations. Starting from the central core (*G0*) possessing *f* alkenyl groups, the dendrimer is constructed using repeating sequences of alternating hydrosilylations with chlorosilanes and ω-alkenylations with *Grignard* reagents. *Van der Made et al.* used tetraallylsilane as core, $HSiCl_3$ as hydrosilylation reagent,

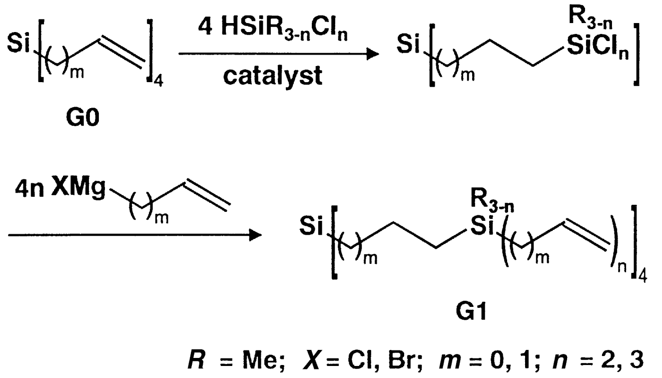


Fig. 2. Divergent synthesis of a typical carbosilane dendrimer

and allylmagnesium bromide as ω-alkenylation reagent to obtain dendrimers up to the fifth generation. However, it should be emphasized that the molecular weight and the structural perfection of these dendrimers were not substantiated by appropriate analytical methods. *Roovers et al.* started from a tetravinylsilane core and used $HMeSiCl_2$ and vinylmagnesium bromide to obtain dendrimers possessing a somewhat open structure. Dendrimers with an even more open structure were obtained by *Muzafarov* and coworkers who chose $HMeSiCl_2$ as hydrosilylation reagent, allylmagnesium chloride as ω-alkenylation reagent, and triallylmethylsilane as a core.

Obviously, the synthetic route to carbosilane dendrimers offers high flexibility and versatility. Not only the hydrosilylation reagent and the ω-alkenylation reagent (to some extent) but also the core molecule can be varied without drastic changes in the reaction conditions. Table 1 summarizes the carbosilane dendrimers reported to date (core molecules, segment length, and branching multiplicity).

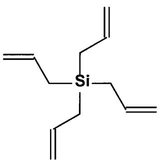
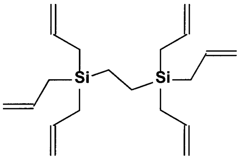
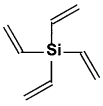
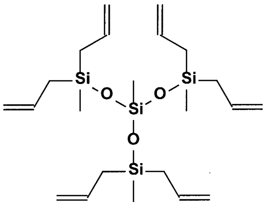
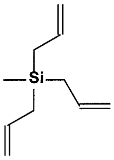
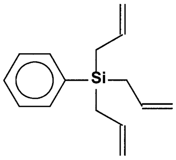
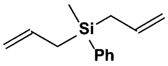
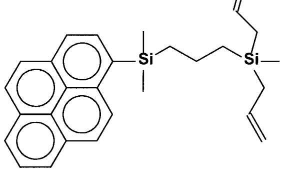
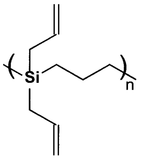
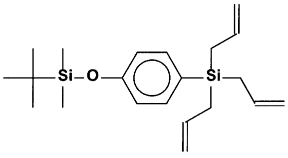
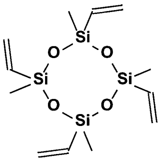
The most popular core molecules are tetraallylsilane and tetravinylsilane, which lead to dendrimers of spherosymmetrical topology. To date, the branching multiplicity has been varied from two to three and the length of the alkyl spacer from two to three methylene units (cf. Table 1). The use of a long alkylmagnesium bromide as *Grignard* reagent has been reported in one case [8]. However, reaction between long alkylmagnesium bromide and tetrahedral silicon is problematic [12].

Numerous reports on the synthesis of carbosilane dendrimers with allyl end groups have been published by *Kim et al.* [42–44, 46] who used various core molecules (2,4,6,8-tetramethyl-2,4,6,8-tetravinyltetrasiloxane, diallylphenylmethylsilane, and triallylmethylsilane) and constructed the dendrimers with allylmagnesium bromide as *Grignard* reagent and either $HSiCl_3$ or $HMeSiCl_2$ as hydrosilylation reagent. In further publications, these authors report the synthesis of carbosilane dendrimers terminated by phenylethynyl and *p*-bromophenoxy and biphenyl groups, respectively [47, 48]. In one case, the obtained products were characterized by MALDI-TOF mass spectrometry [48].

The synthesis of carbosilane dendrimers bearing 12 or 36 phenyl rings at the periphery has been reported by *Friedmann* and coworkers [37]. The obtained dendrimers were characterized by X-ray diffraction analysis and NMR spectroscopy. NMR showed the retention of solvent with the second generation.

Gossage et al. described the synthesis and characterization of a carbosilane dendrimer with a functionalizable core [52, 53]: 4-triallylsilylphenol, whose phenolic hydroxy group was protected by a *tert*-butyldimethylsilyl group while constructing the dendrimer scaffold. After deprotection, this core permits facile attachment of transition metal complexes or molecular probes.

Table 1. Carbosilane dendrimers reported to date: core molecules, segment structure, and branching multiplicity (b.m.)

Core (*G0*)	Spacer	b.m.	Ref.	Core (*G0*)	Spacer	b.m.	Ref.
	C3	3 2	[7, 8, 13–23} [24–34]		C3	2	[48]
	C2	3 2	[35–37] [9, 10, 38–41]		C3	2	[49]
	C3	2	[11, 42]		C3	2	[50]
	C3	3 2	[43] [44]		C3	2	[51]
	C3	3	[45]		C3	3	[52]
	C3	3/2 [2]	[46] [47]				

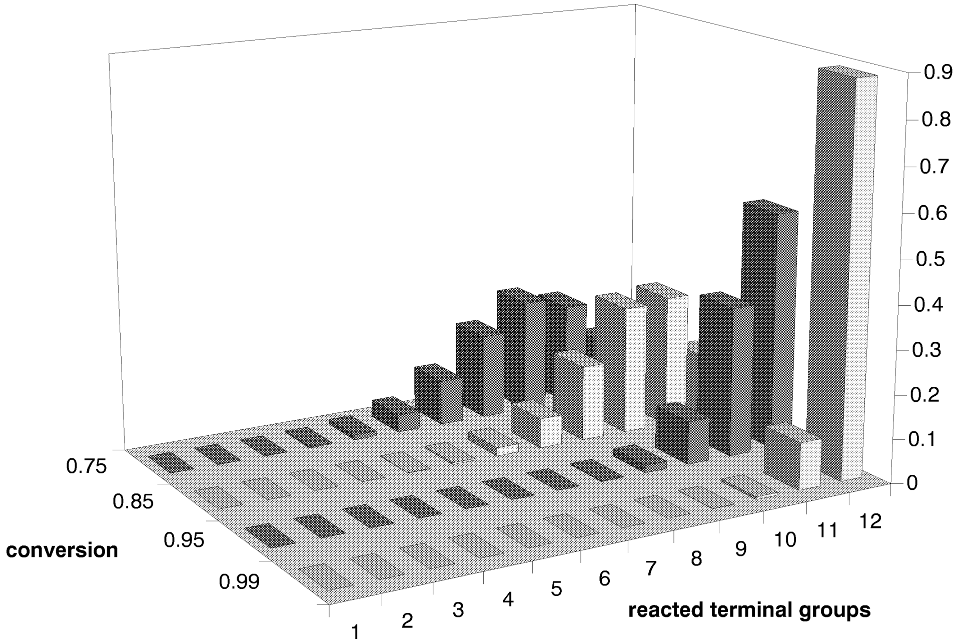


Fig. 3. Relative abundance of dendrimer molecules *vs.* conversion and number of reacted terminal groups, demonstrating the importance of full conversion in dendrimer synthesis

2.2. Other Systems

Besides the carbosilane dendrimers whose synthesis is based on the repeating sequences of alternating hydrosilylations with chlorosilanes and ω-alkenylations with *Grignard* reagents, only a few other systems have been developed: *Nakayama* and *Lin* synthesized the first generation of an organosilicon dendrimer composed of thiophene rings [54]. Tetralithiation of tetra-2-thienylsilane followed by reaction with methoxy-tri-2-thienylsilane gave the desired first generation, 5,5′,5″,5‴-*tetrakis*(tri-2-thienylsilyl(tetra-2-thienyl))silane, which forms inclusion complexes with CCl_4, CH_2Cl_2, benzene, and acetone when crystallized from these solvents or mixtures of these solvents and hexane. *Kim et al.* started from *tetrakis*(phenylethynyl)silane and obtained a carbosilane dendrimer of the third generation *via* a repeated sequence of alternating hydrosilylations with dichloromethylsilane and ω-alkynylations with lithium phenylacetylide. Figure 4 shows generation 2 of this interesting new class of carbosilane dendrimers.

2.3. Molecular Characterization

In the early days of dendrimer chemistry, molecular characterization was carried out in most cases by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy as well as size exclusion chromatography (SEC). However, in higher generations the differences between the relative intensities of the signals of the perfect structure and those of the imperfect structure are too marginal to be detected. Thus, NMR spectra can only be

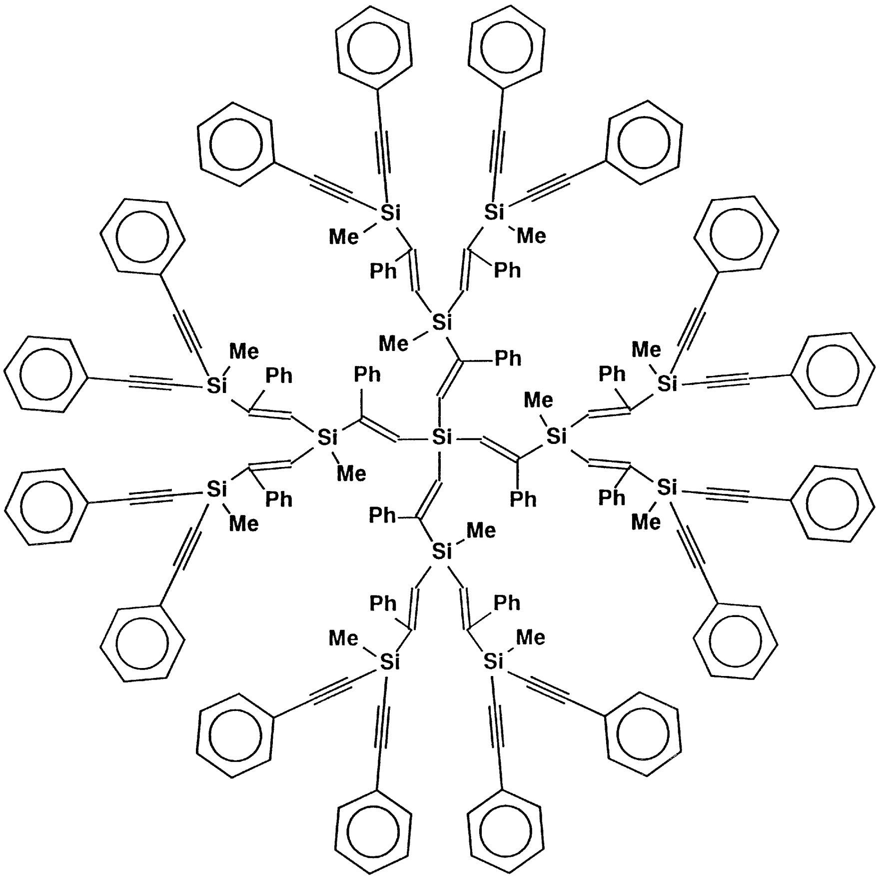


Fig. 4. Generation 2 of carbosilane dendrimers based on phenylethynyl segments

taken as an indication of the perfection of the dendrimer structure. The usefulness of SEC to determine molecular weights or molecular weight distribution of dendrimers is also limited, because dendrimers do not fit the calibration curves based on linear standards. Generally, one observes an overestimation of the molecular weight for dendrimers of lower generations and an underestimation for dendrimers of higher generations. Owing to the broadening of the SEC traces by diffusion, correct molecular weight distributions are not obtained.

With the introduction of MALDI-TOF mass spectrometry (matrix assisted laser desorption ionization and time of flight detection) in dendrimer chemistry, it became possible to determine not only molecular weights but also the molecular weight distribution of dendrimers, as in the MALDI-TOF mass spectrometry fragmentation of the molecular ions does not occur [15, 17, 26, 48, 55].

3. Properties and Application Potential

3.1. Metal Complexes and Catalysis

One of the most promising applications of carbosilane dendrimers is the use as scaffolds for catalytically active metal complexes. Dendrimer-bound catalysts combine the advantages of heterogenous and homogenous catalysis; they allow the accurate control of the number and structure of the active sites, as homogenous catalysts do, and they are easily removed from a product containing solution using ultrafiltration as known from heterogenous catalysts. The first example of a homogenous catalyst based on a dendritic carbosilane scaffold was reported by *van Koten et al.* [13]. They connected 4-amino substituted 2,6-*bis*((dimethylamino)-methyl)-1-bromobenzene, a precursor entity for the organometallic site, to the periphery of generation 0 with 4 end groups and generation 1 with 12 end groups, respectively, by a 1,4-butanediol linker. The obtained dendritic precursor was then reacted with an excess of the zerovalent nickel complex $Ni(PPh_3)_4$ to produce the desired nickel complex containing dendrimers. The prepared dendrimers were successfully employed as homogenous catalysts for the *Kharasch* addition reaction.

A carbosilane dendrimer with 12 peripheral iodoarene groups was prepared from polyol precursors by *Hoare et al.* [21]. The iodoarene groups were attached to the polyols by esterification with 4-iodobenzoyl chloride. The obtained compound was reacted with Pd(dibenzylideneacetone)$_2$ in presence of N,N,N′,N′-tetramethylethylenediamine to yield periphery-palladated complexes. The prepared dendrimer represented the first example of an exclusively σ-bonded completely periphery-palladated dendrimer (Fig. 5).

The strategies developed to introduce metals at the peripheral sites of carbosilane dendrimers were summarized recently by *van Koten* and *Jastrzebski* [14]. In further elegant work the incorporation of reactive Ru(II) *PCP′* complexes into carbosilane dendrimers was described [56].

Alonso et al. reported the first carbosilane dendrimers bearing a controlled number of redox active centres, *i.e.* ferrocenyl units [24]. They attached the corresponding ferrocenyl containing organometallic units to *G0* and *G1 via* two different synthetic routes: the first included the reaction between ferrocenyllithium with chlorosilane terminated dendrimers, the second used also the Si–Cl bonds of the chlorosilane terminated dendrimers, but converted them into Si–N bonds by reaction with β-aminoethylferrocene. The dendrimers were isolated as red-orange materials. The CVs of these compounds exhibited a single reversible oxidation wave. The number of electrons exchanged was found to correspond directly to the number of ferrocenyl units. In addition, differential pulse voltammetry measurements showed only one wave. Thus, the metal centres act independently in redox processes, although they are coupled by the dendrimer scaffold. Such materials have been used to modify redox electrodes [57].

Carbosilane dendrimers have been used furthermore as scaffolds for chromium tricarbonyl moieties [25]. *Lobete* and coworkers prepared a carbosilane dendrimer functionalized with phenyl rings on the periphery by termination of the dendrimer synthesis with a hydrosilylation step with dimethylphenylsilane. The π-coordinating ability of these surface-located arene rings has been utilized to attach the chromium tricarbonyl moieties. It was found that the $Cr(CO)_3$ moieties are bonded by η^6-coordination at the phenyl ring. Cyclopentadienyl functionalized dendrimers used to coordinate $Co(CO)_2$ as well as carbosilane dendrimers containing Si–Co and Si–Fe σ-bonds have also been reported [58]. However, it has to be mentioned that in this case only *G0* dendrimers were used.

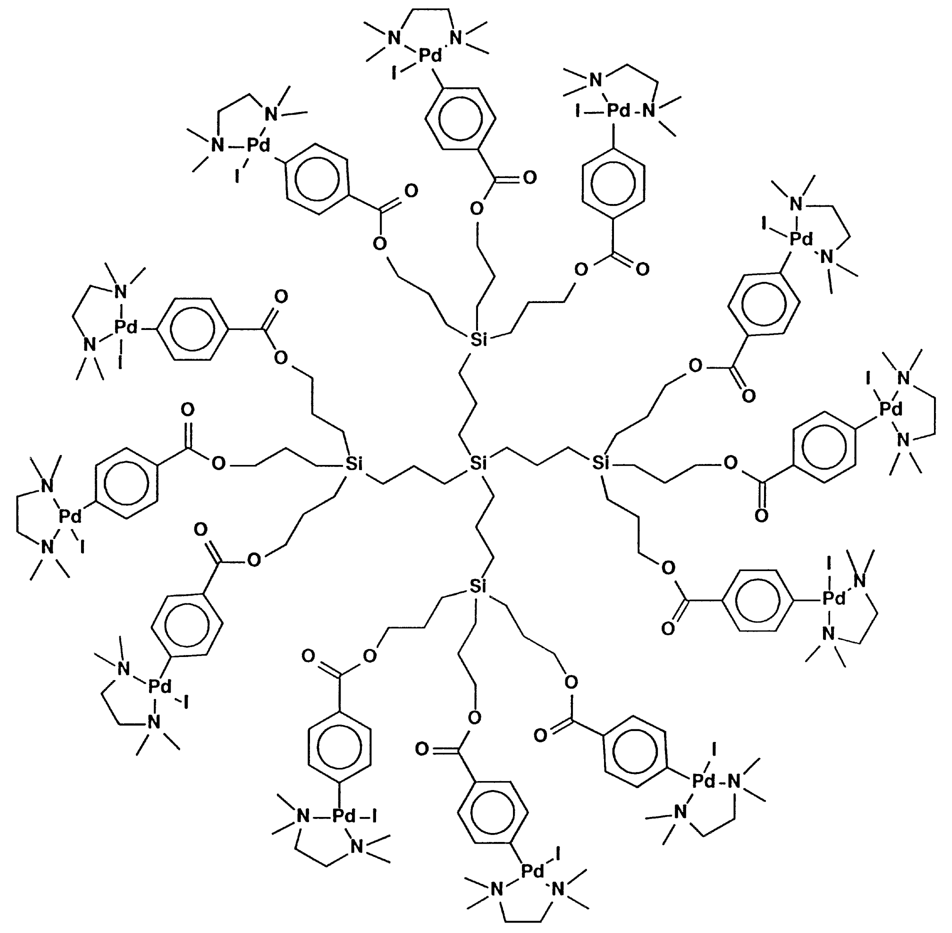


Fig. 5. Organopalladium functionalized carbosilane dendrimer [21]

Carbosilane dendrimers bearing peripheral acetylene-dicobalt hexacarbonyl substituents have been reported by *Seyferth et al.* [36] who prepared dendrimers of the first and second generation that contain peripheral ethynyl groups. These compounds were reacted with dicobalt octacarbonyl to give the desired complexes on the surface of the dendrimers.

3.2. Host-Guest-Chemistry

Due to their inner cavities and the fixed spherical topology, dendrimers with an amphiphilic structure may be regarded as unimolecular analogs of micelles. The first dendrimer that acts like a micelle of common tensides was synthesized by *Newkome et al.* [59] who prepared a carboxylate terminated hydrocarbon dendrimer which – in contrast to usual amphiphiles – shows no critical micelle concentration.

Carbosilane chemistry permits to control the size of the inner cavities. This has been shown by *Lach et al.* in a molecular force field study concerning the host properties of carbosilane dendrimers [60]. *Lach et al.* found that the dimensions of the inner cavities can be varied from 5–15 Å through variation of branching multiplicity and/or spacer length.

Only recently, *Krska* and *Seyferth* reported the synthesis of water soluble carbosilane dendrimers [41]. Nucleophilic reactions between mercapto substituted amphiphiles and carbosilane dendrimers bearing (chloromethyl)silyl groups on their terminal branches led to amphiphilic dendrimers with hydrophobic carbosilane cores and hydroxyl, dimethylamino, or sodium sulfonate amphiphilic groups at the periphery.

3.3. Dendritic Liquid Crystalline Polymers (DLCP)

Currently, there is growing research interest in the combination of branched structures and mesogenic units, motivated by the fact that a globular shape might reduce the bulk viscosity and hence the switching times of the materials. For example, hyperbranched topologies have been combined with mesogenic units by *Bauer et al.* [61] and *Percec et al.* [62]. Furthermore, *Percec et al.* reported on a perfect dendrimer with mesogenic branching units showing thermotropic liquid crystalline phases [63]. A more recent approach is concerned with the coupling of flexible, dendritic carbosilane scaffolds with rigid mesogenic units resulting in dendritic liquid crystalline polymers (DLCPs). 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. We have prepared carbosilane dendrimers with 12, 36, and 108 cholesteryl end groups *via* esterification of dendritic carbosilane polyols with cholesteryl chloroformiate [16, 17]. In further studies we have investigated the influence of *i*) generation, *ii*) spacer length, and *iii*) type of mesogen attached on the phase behaviour of the dendritic liquid crystalline polymers [19, 20, 23]. All obtained DLCPs have been fully characterized by polarizing microscopy, DSC, WAXS, and SAXS with respect to their phase behaviour in bulk. It was found that most of the DLCPs investigated develop layered (smectic) structures which are rationalized by separate ordering of the calamitic surface groups and the core which, however, leads to a deformation of the dendritic scaffolds. Reducing the spacer length and/or increasing the number of end groups (*i.e.* the generation number) complicates the formation of well-developped smectic phases.

Similar results were obtained by *Ponomarenko et al.* [27] and *Terunuma et al.* [50]. *Ponomarenko et al.* used cyanobiphenyl, methoxyphenyl benzoate, and cholesteryl groups as mesogenic units. These units were coupled to the carbosilane dendrimers bearing eight allyl groups by hydrosilylation. Smectic phases were also found for carbosilane dendrimers substituted with mesogenic units based on azobenzene at their surface [64].

Besides classical calamitic mesogens, perfluoralkyl groups ($-C_6F_{13}$) have been attached to carbosilane dendrimers [22]. 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 mercaptan, which affords the corresponding thioether functionalized end groups. Perfluorinated dendrimers of generation 0 to generation 3 with 4, 12, 36, and 108 perfluoralkyl end groups, respectively, have been obtained. The dendrimer periphery of these dendrimers is immiscible with the carbosilane interior. Such core-shell type dendrimers also exhibit generation dependent mesophase formation.

3.4. Polymer Architectures Based on Carbosilane Dendrimers

Due to their spherical topology and the large number of end groups, carbosilane dendrimers have been used as core molecules for star shaped polymers. Two elegant approaches have been reported to date. *Roovers et al.* obtained multiarm star polymers with 32, 64, and 128 arms, respectively, by coupling Si–Cl terminated dendrimers with living poly(butadienyl)lithium [9, 39, 65]. The arm molecular weight was varied between 6400 and 72000 g/mol.

Vasilenko et al. reported another way to star shaped polymers based on carbosilane dendrimers [31, 34] using polylithium derivatives of carbosilane dendrimers as initiators for the anionic polymerization of different monomers such as styrene, hexamethylcyclotrisiloxane, and ethylene oxide. The polylithium derivatives were obtained by hydrosilylation of allyl terminated dendrimers with the sterically demanding bidecylmethylsilane. 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 yielded the desired polylithium derivative of the carbosilane dendrimer. Due to the location of the lithium atoms in the inner space of the dendrimer, a main problem of polylithium compounds, *i.e.* the high tendency of aggregation, was solved.

4. Conclusions and Outlook

In this short review we have summarized historical and recent developments in the field of carbosilane dendrimers. Due to their chemical stability and the possibility to tailor branching multiplicity, segment length, and core molecule, these are useful scaffolds for supramolecular dendrimer chemistry in general. Their flexibility renders them an important synthetic platform for dendrimer based liquid crystalline polymers that show generation dependent liquid crystalline phases. The versatile construction strategy permits design of dendrimer structures with varying geometry, which is necessary to establish structure-property correlations valid for dendrimers in general. On the other hand, such dendrimers can be used to create novel polymer structures, *e.g.* multiarm star polymers.

Concerning the potential application of such materials, on the long run hyperbranched carbosilane polymers (not discussed in the current article) might become strong competitors for dendrimers, particularly in applications where perfection is not a necessary prerequisite. These polymers are prepared in a one-step procedure by polymerization of AB_2 or AB_3 monomers, *i.e.* dialkenyl-alkylsilanes or trialkenylsilanes, and possess a certain polydispersity and randomly branched structure as expected from the statistics of an AB_m polymerization [4, 66].

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