

Functionalization of hyperbranched polycarbosilanes – block copolymers and electrochemistry

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1 Introduction

Silicon, the second most abundant element in earth's crust, is characterized by its strong affinity towards oxygen and is usually found in the form of silicon dioxide and silicates. The high stability and inertness of these structures account for the difficulties to isolate the pure element. Around 1800 first experiments were performed that probably resulted in the isolation of silicon, but it was not until 1823 when J. Berzelius recognized the elemental nature of silicon when he reduced silicon dioxide by elemental potassium.

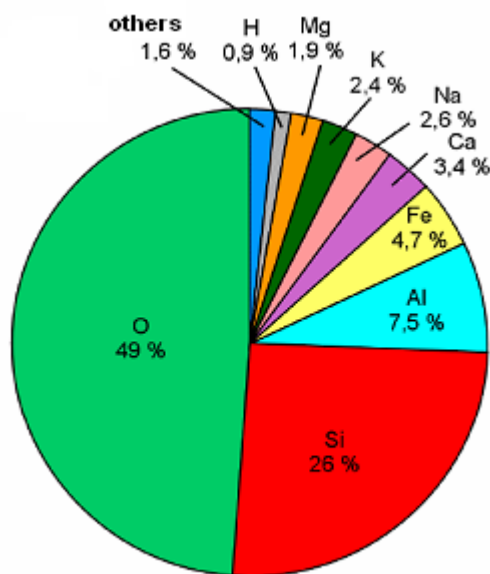


Fig. 1.1 Abundance of elements in earth's crust.

While silicon in its oxygen compounds is a principle component in glass and concrete, the rising need of elemental and purified silicon is a consequence of its use in the manufacturing of electronic circuits, photovoltaic devices and as principal component in most semiconductors. Elemental silicon is obtained by reduction of silicon oxide with reducing agents like magnesium or carbon.

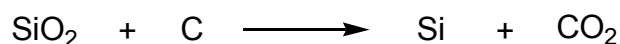


Fig. 1.2 Reduction of silica with carbon.

The produced silicon is subjected to further purification steps to achieve the purity necessary for the application in micro-chip assembly. Here, physical methods like

zone refining are nowadays substituted by converting silicon into a silicon compound that can be purified more easily than silicon itself. In the Siemens process¹ silicon is converted into trichlorosilane and the purified gas is converted back into silicon by exposure to silicon rods at high temperatures, resulting in material of extremely high purity.

Regarding silicon chemistry, the interface between organic and inorganic chemistry is constituted by silicones, poly(organosiloxane) polymers according to correct IUPAC terminology. These compounds may be viewed to represent an organically modified quartz, where some oxygen atoms are substituted by organic groups. The breakthrough for these materials was marked by the development of the industrial synthesis of chloromethylsilanes by Müller² and Rochow^{3, 4} in the early 1940ies. In the so-called “Direct Process”⁵, silicon-carbon bonds are formed by the oxidative addition of alkylhalides to silicon, catalyzed by several transition metals, mostly copper. This represents the fundamental industrial process to create Si-C bonds and yields a mixture of different silicon alkyl halides, preferably mainly Me_2SiCl_2 .

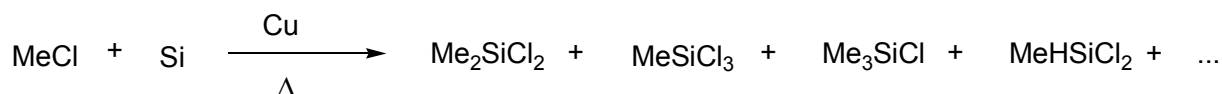


Fig. 1.3 Direct process (or Müller-Rochow process) for the production of Me_2SiCl_2 .

Hydrolysis of chloromethylsilanes results in cyclic, linear and crosslinked siloxane polymers that can be tailored in their properties for a large range of applications. Silicones are speciality plastics that are nowadays used in every part of daily life. Their unique properties comprise resistance against chemicals, temperature and UV-light, water repellence and electrical insulation, allowing their application as sealants, engine oil and coatings to mention only a few. Due to their non-toxicity and inertness they also find application in the field of medical technology and cosmetics.



Fig. 1.4 Example for the structure of polydimethylsiloxane (silicone) and polycarbosilane.

Further substitution of oxygen leads to polycarbosilanes, where Si-C bonds form the polymer backbone (Fig. 1.4). These inorganic-organic hybrid materials are used as precursors in the synthesis of SiC_x-ceramics and fibers⁶. Carbosilanes and carbosiloxanes, which contain Si-O-Si as well as Si-(CH₂)_n-Si groups, are characterized by high flexibility and good thermal and chemical stability. The unique properties and several high yielding reactions offered by silicon chemistry have lead to intense research interest in silicon-based dendrimers⁷⁻⁹, turning them into one of the best studied materials in the field of dendrimers. Besides for the structurally perfect dendrimers the same reactions have been used for the synthesis of hyperbranched structures. In the next chapter the synthesis of hyperbranched silicon containing polymers via hydrosilylation polymerization is described in detail.

1.1 Silicon-containing hyperbranched polymers¹

Silicon chemistry offers a variety of quantitative, high yielding reactions, i.e., hydrosilylation, Grignard reactions and controlled condensation of silanols that are suitable for the synthesis of organic-inorganic hybrid materials. Thus, silicon-based chemistry played a prominent role in the evolution of dendrimer chemistry⁸⁻¹¹. Consequently, it did not take long until the first examples of silicon-containing hyperbranched polymers were reported. Hyperbranched polymers are generally prepared by one-pot polymerization of AB_x (x≥2) monomers and are characterized by polydispersity as well as a randomly branched structure due to the multifunctional polycondensation or polyaddition process. The statistical treatment of such polyfunctional polycondensations was achieved in the early 1950s by Flory, who calculated both molecular weights as well as polydispersity in such systems, as will be discussed in section 1.3^{12, 13}. The properties of hyperbranched polymers are significantly different from the linear analogs and are characterized by good solubility, low viscosity and a large number of end groups that can be used for further functionalization. Despite the imperfection in branching and structure of hyperbranched polymers compared to the monodisperse dendrimers these

¹ The following chapters are an excerpt taken from: H. Schüle, H. Frey, Hyperbranched polycarbosilanes and polycarbosiloxanes via hydrosilylation polymerization. In *Silicon-Containing Dendritic Polymers*, Dvornic, P. R., Owen, M. J. (Eds), Springer: Guildford, UK, in press.

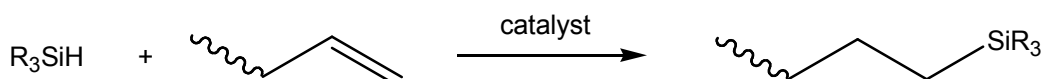
properties render them easily accessible competitors for dendrimers, particularly in applications where structural perfection is not a mandatory prerequisite.

As for dendrimers, the research interest for Si-containing hyperbranched polymers has focused on the preparation of carbosilanes, carbosiloxanes and siloxanes. These structures are generally highly flexible materials with low glass transition temperatures and are characterized by good thermal and chemical stability. The majority of Si-containing hyperbranched polymers was synthesized by polymerization of suitable AB_x monomers either via hydrosilylation, via nucleophilic substitution or condensation. However, the preparation of hyperbranched polymers based on A_2/B_3 approaches, i.e., by copolymerization of multifunctional monomers, is also known. To date the development of silicon-containing hyperbranched polymers has only been summarized as a subchapter in otherwise dendrimer-oriented reviews^{7, 14}. This chapter exclusively covers the field of hyperbranched carbosilane polymers prepared via hydrosilylation polymerization of AB_x monomers. Independent of the basic structure, monomers suitable for the preparation of hyperbranched silicon-containing polymers via hydrosilylation have to comprise a Si-H bond as well as a π -bond as polymerizable units. Here, either the Si-H or the π -bond may represent the A-unit. The resulting structures are characterized by a large number of functional end groups, i.e. silanes or alkenes, respectively, that can be used for further functionalization. At first the basic principles and reaction mechanism of transition metal-catalyzed hydrosilylations are summarized in a brief manner.

1.2 Hydrosilylation

Catalytic hydrosilylation is one of the most important industrial techniques for the formation of Si-C bonds, only outdone by the Direct Process, the transition metal catalyzed oxidative addition of alkylhalides to silicon. However, hydrosilylation is more generally applicable especially in laboratory setups and can generally be used for the introduction of functional silanes into organic molecules in high yield. The reaction leads to the formation of Si-C bonds by addition of the relatively weak Si-H across π -bonds, normally alkenes and alkynes (Scheme 1.1). Regarding the synthesis of hyperbranched structures, hydrosilylation can be used in a polyaddition-type polymerization to produce polymeric materials. Hence, a mechanistic analysis is of

crucial importance for the understanding of the polymerization pathway and of possible side-reactions that can have a significant influence on the molecular weight and molecular weight distributions of the polymers. The reaction can be performed under free-radical conditions (i.e. initiated with ultraviolet light or peroxides)¹⁵⁻¹⁷, but metal-assisted hydrosilylation is presently more popular and has been proven to be more efficient¹⁸.



Scheme 1.1 The hydrosilylation reaction

Several transition metals show catalytic activity in hydrosilylation reactions, however platinum complexes like Speier's catalyst ($H_2PtCl_6 \cdot iPrOH$)¹⁹ or Karstedt's catalyst^{20,21} are most commonly employed. Solid-supported catalysts like Pt/C are less reactive, however they can be removed by filtration after completion of the reaction, increasing the shelf life of the materials. Platinum catalysts tolerate a variety of polar functional groups (e.g. halogenes, NO_2 , CN, COOR, amines), as long as those are poor ligands. Strongly coordinating groups can compete with the alkene to be hydrosilylated for the platinum center, inhibiting the hydrosilylation. The most commonly accepted mechanism for platinum-catalyzed hydrosilylation has been proposed by Chalk and Harrod and is illustrated in Figure 1.5²² in its classical^{23, 24} and modified²⁵⁻²⁷ form. The first step involves the oxidative addition of the silane to the platinum-alkene complex I and subsequent formation of the platinum-alkene silyl hydride complex II. This is followed by migratory insertion of alkene into either the [Pt]-hydride (classical Chalk-Harrod) or [Pt]-silyl bond (modified Chalk-Harrod) of complex II to give the resulting complexes III or IV, respectively. The product V is obtained after Si-C or C-H reductive elimination and the metal-alkene complex is regenerated in excess of alkene. Despite the general acceptance of the Chalk-Harrod mechanism, further approaches have been made to explain some phenomena observed in experiments. Colloidal platinum, which is responsible for the yellow to brown color of hydrosilylation reactions, was first proposed to be the catalytically active species by Lewis and coworkers²⁸. However, they reported later that colloidal platinum is only an unreactive end product and instead a mononuclear two-coordinate platinum complex is the active species formed during the induction

period in a series of ligand exchanges²⁹. For platinum complexes in higher oxidation states, e.g. Speier's catalyst, the induction period was assigned to the initial reduction of platinum. They also stated that reaction of the silane with platinum precedes the coordination of the olefin. For several reaction systems small amounts of oxygen are necessary for the hydrosilylation to occur. According to the Lewis mechanism oxygen impedes the formation of catalytically inactive multinuclear platinum species by coordination to platinum.

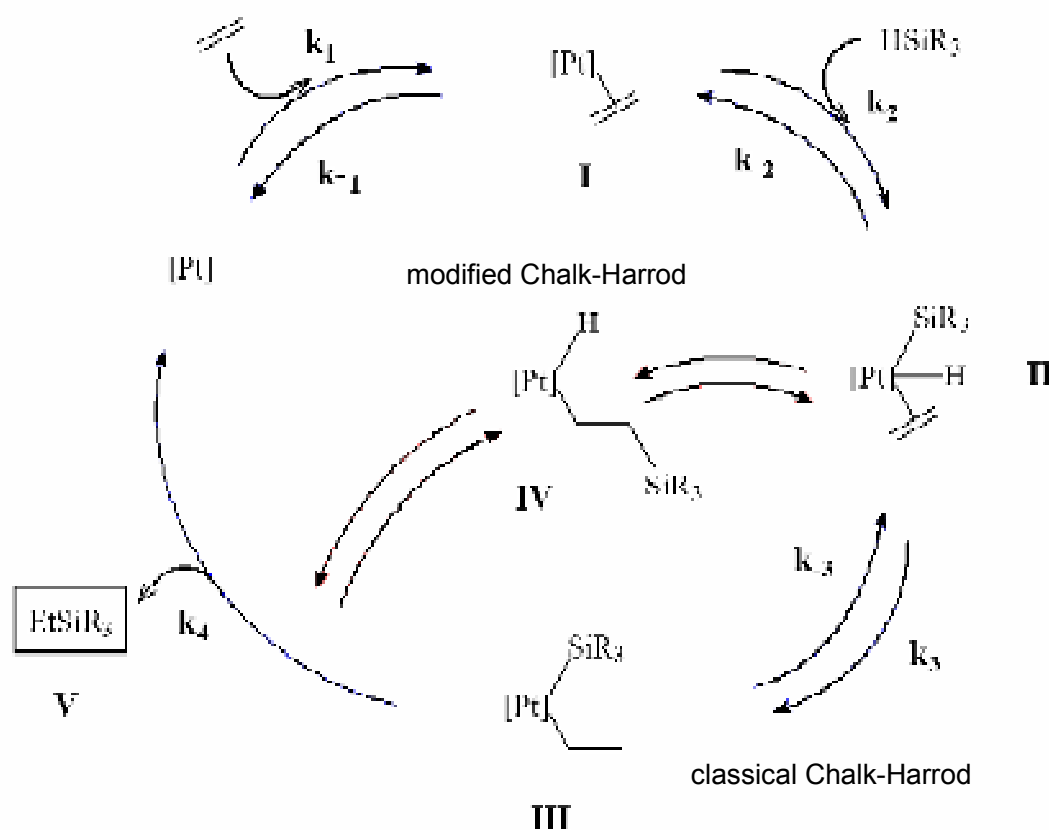


Fig. 1.5 Catalytic cycle for the hydrosilylation of olefins according to the classical and modified Chalk-Harrod mechanism²².

Electron withdrawing substituents on the silane and electron donating groups on the olefin generally accelerate the addition, resulting in higher reaction rates for monomers with $-OR$ or $-OSiR_3$ substituents compared to mere alkyl groups^{28, 30, 31}. However, steric effects are also of great importance in hydrosilylation and may eventually counteract this influence. Two possibilities exist for the addition of a silane R_3SiH to a substituted alkene: namely, Markovnikov or anti-Markovnikov addition, which results in the formation of branched (α -adduct) or linear (β -adduct) products,

respectively. The distribution of both products depends on the catalyst used as well as on the nature of the substituents on both the alkene and the silane¹⁸. Generally the β -adduct tends to predominate, since the silane favors the addition to the terminal position to minimize steric interactions. The formation of side-products can have a significant influence on the outcome of a polymerization. Thus, in the following possible side-reactions known for platinum catalysts are briefly summarized (Figure 1.6). Alkene isomerization of terminal double bonds leads to the formation of internal double bonds^{23, 24, 31-33}. Those are unreactive in hydrosilylations and thus limit the number of functionalities for growth of the polymer. The same holds true for hydrogenated double bonds resulting from platinum-catalyzed addition of hydrogen, which can be evolved in minor amounts during side-reactions²⁸. Dyotropic rearrangements at silicon comprise simultaneous exchange of substituents between two silanes. During the synthesis of hyperbranched polymers the exchange of functional groups of AB_2 monomers can lead to the formation of B_3 and A_2B monomers with B_3 representing a possible crosslinker, which can cause undesired gelation. If the metal complex is able to coordinate more than one alkene, the possibility of alkene coupling arises, resulting in dimerized products³⁴.

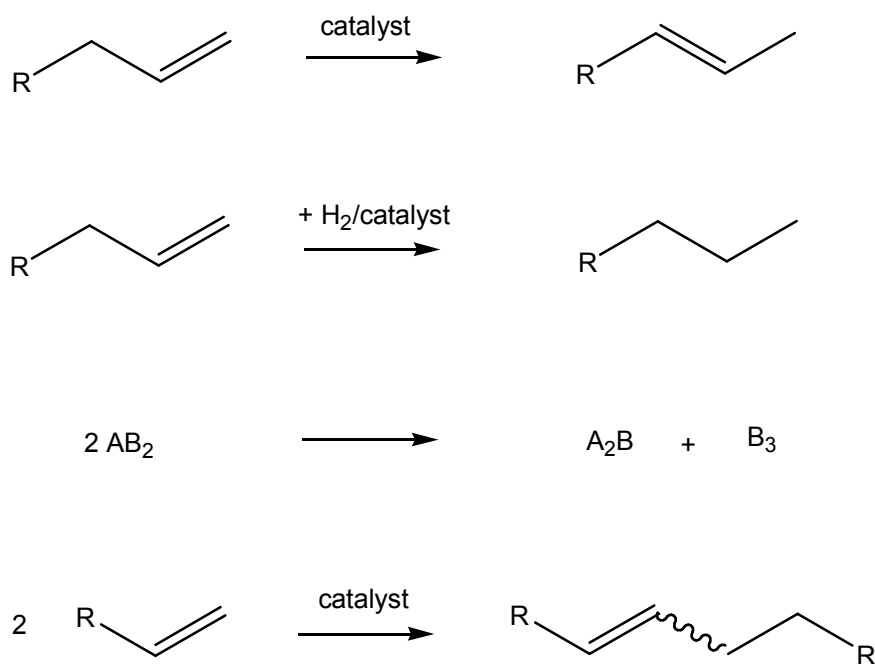


Fig.1.6 Possible side-reactions during hydrosilylation: alkene isomerization, hydrogenation, dyotropic rearrangement and alkene dimerization.

Additionally, dry reaction conditions are necessary during hydrosilylation since water present in the reaction mixture can hydrolyze silanes to give silanols and hydrogen. The aforementioned side-reactions are normally present only in minor amounts, however they can be the reason for limited molecular weights and gelation observed for certain systems. In summary, hydrosilylation is a high yielding reaction working best for activated silanes containing electron withdrawing groups like halogenes or alkoxy groups and electron-rich alkenes. Further details on catalytic hydrosilylation may be found in reviews on the subject³⁵⁻³⁸.

1.3 Synthesis and characterization

It is sometimes overlooked that the synthesis of hyperbranched polymers is based on an old concept, already described in basic work of Flory in the early 1950s. Flory provided the theoretical foundation as well as experimental evidence for the existence of branched macromolecules obtained via polycondensation of AB_n-type monomers^{12, 13}. In this case, the A and B functional groups of these monomers can react with each other to form new linkages leading to randomly branched structures as the polymerization progresses. The most important expressions derived by Flory for the number average degree of polymerization (DP) and polydispersity (PDI) of an AB_n monomer are given below (Equations 1.1 and 1.2, with p = conversion):

$$DP = \frac{1}{1-p} \quad (\text{Equation 1.1})$$

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} = \frac{1 - \frac{p^2}{n}}{1-p} \approx \overline{DP}_n / 2 \quad (\text{Equation 1.2})$$

The deduction of these equations is based on the assumption that all functional groups of a given type (A or B) show equal reactivity at any stage of the reaction. Additionally, the occurrence of intramolecular cyclization is intentionally neglected. In essence, these equations demonstrate that the conversion p of the reaction of A- and B-groups is the key parameter to obtain high molecular weights, i.e. only high-yielding transformations are suitable for the preparation of extended hyperbranched structures. On the other hand, the expressions show that the resulting structures will

always exhibit broad molecular weight distributions, characterized by large polydispersities. For instance, for a conversion of 99% (0.99) a degree of polymerization of 100 and a polydispersity M_w/M_n of 51 would be expected, which is of course dramatically large. On the other hand, cyclization of the single, “focal” A-group of the macromolecules with one of the multiple B-groups limits molecular weights, but also keeps polydispersity lower than the values calculated according to Eq. 1.2. As a consequence of the interesting properties found for dendrimers, the synthesis of hyperbranched polymers promised to represent an alternative leading to materials with similar properties, but facile preparation. The simple one-pot polymerization of AB_n ($n \geq 2$) monomers results in branched structures that are less defined than dendrimers, but display similar physical and structural properties, like low viscosity and a large number of end groups. As a result of the synthetic pathway, hyperbranched polymers possess a lower degree of branching (DB) than the monodisperse dendrimers. If side-reactions are excluded, the AB_n stoichiometry in these reactions does not permit gelation, unless an unlikely 100% intermolecular reaction of A-groups is achieved.

In the last decade, theoretical concepts have been developed for the control of molecular weight, degree of branching and polydispersity of hyperbranched polymers⁴⁰⁻⁴³. Copolymerization with core molecules of the B_f -type as well as slow monomer addition techniques can be employed to reduce polydispersity and to enhance control in the polymerization. These approaches permit the synthesis of rather well-defined hyperbranched structures with moderate, sometimes low polydispersity. For instance, a highly reactive monomer can be added slowly to the growing hyperbranched structure to avoid homopolymerization and favor attachment to the growing species. In the case of such an ideal slow monomer addition polymerization of an AB_2 monomer with a B_f -core it was found that the polydispersity can be lowered to $PDI = 1 + 1/f$, emphasizing the need for a high number of core functionalities f ⁴¹. An example for this strategy will be shown in part 1.4.3 of this review. Hyperbranched Si-containing structures usually exhibit excellent solubility and are thus well characterizable. Theoretical considerations for the description of the DB of hyperbranched polymers and its relationship with the number of end groups enabled the determination of this key parameter by NMR-spectroscopy. This is especially interesting for silicon chemistry, since well separated signals can generally be observed for the different branching units in ²⁹Si-NMR spectra.

Commonly, the analysis is based on low molecular weight model compounds possessing structures analogous to the respective branching units. The DB for AB₂ and AB₃ systems, as derived by Höltér and Frey is given in equations 1.3 and 1.4, respectively (with D = dendritic units, sD = semidendritic units, L = linear units)³⁹:

$$DB(AB_2) = \frac{2D}{2D + L} \quad (\text{Equation 1.3})$$

$$DB(AB_3) = \frac{2D + sD}{\frac{2}{3}(3D + 2sD + L)} \quad (\text{Equation 1.4})$$

In a random polycondensation the maximum value for DB is 0.5 for AB₂ monomers and 0.44 for AB₃ monomers. IR-spectroscopy can be a helpful tool to monitor the conversion during polymerization. Particularly, for monomers with a Si-H functionality as the A-group the disappearance of the Si-H stretching mode around $\tilde{\nu} = 2,100 \text{ cm}^{-1}$ is a significant indication for the course of the reaction. Finally, it has to be mentioned that characterization of hyperbranched polymers via SEC based on linear polystyrene standards is difficult and molecular weights are often significantly underestimated due to the more compact nature of hyperbranched structures. Thus, unless molecular weights determined by absolute methods are given, the results can only be taken as an indication of the actual degree of polymerization.

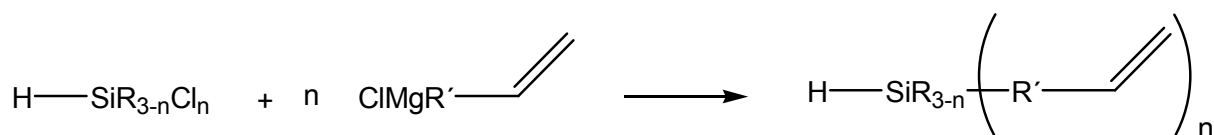
Among the various Si-based hyperbranched polymers, polycarbosilane and polycarbosiloxane structures have received the strongest attention to date. Polycarbosilanes are kinetically and thermodynamically very stable compounds, resulting from the low polarity of the Si-C bond and a dissociation energy of 306 kJ mol^{-1} , roughly comparable to that of C-C bonds (345 kJ mol^{-1}). Polycarbosiloxanes contain Si-(CH₂)_x-Si as well as Si-O-Si units in their polymer backbone. The Si-O bond in siloxanes is also characterized by excellent chemical resistance and a dissociation energy of 465 kJ mol^{-1} . Additionally, this structural element leads to further flexibility of the polymer. In contrast, under mildly acidic conditions alkoxy silane linkages of the Si-O-CH₂-type can undergo hydrolysis, which makes them suitable for the synthesis of degradable polymers. The synthesis of hyperbranched polymers via hydrosilylation results in materials that bear a large number of either π -bonds or Si-H groups, which are interesting for further

functionalization. In the case of Si-H end groups a transformation of the silanes is generally necessary in order to obtain air- and moisture-stable structures, since these moieties are easily hydrolyzed by water.

1.4 Polycarbosilanes

1.4.1 General synthetic strategy

The preparation of suitable monomers for the synthesis of hyperbranched polycarbosilanes (*hb*-PCS) via hydrosilylation is generally based on the nucleophilic substitution of halides in commercially available silanes, e.g. trichlorosilane or dichloromethylsilane, by metal alkyls (Scheme 1.2). To this end, Grignard and alkyl lithium reagents are used, which can conveniently be prepared by the reaction of alkyl halides with the respective metal. The branching multiplicity can be varied by using either di- or trihalide silanes. Additionally, the choice of the organometallic compound determines the chemical structure of the polymer backbone and the spacer length between the functionalities, which can be rather important for the polymerization result.



Scheme 1.2 Reaction scheme for the preparation of carbosilane monomers via Grignard reaction.

The first hyperbranched polycarbosilanes were reported in 1993 by Muzafarov et al. who polymerized methylvinylsilane, methyldiallylsilane, triallylsilane and methyldivinylsilane using platinum catalysis⁴⁴. Some examples of carbosilane monomer structures are given in Figure 1.7. Molecular weights of the resulting polymers depended on the polymerization conditions and decreased upon decrease of the monomer concentration as well as on increase of the catalyst concentration. Interestingly, upon addition of new monomer to the system no increase in molecular weight of the polymers could be observed. On the contrary, the reaction of the polymers with dichloromethylsilane proceeded quantitatively, which ruled out steric hindrance as the cause for this behavior. The authors explained the limited growth by kinetic factors. However, in agreement with more recent studies this limitation is most

likely due to competing cyclization that renders further polyaddition of the A-group impossible. The hyperbranched polymers of this study were used as effective modifiers of siloxane rubber blends to increase the tensile strength as well as tear strength of the blend. Modification of the double bonds allowed to adjust the compatibility with the polymer matrix. However, no detailed experimental data were presented in this work.

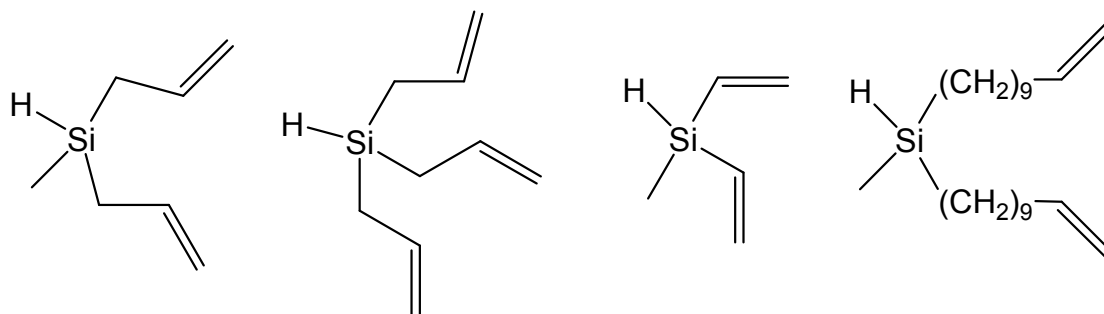


Fig. 1.7 Aliphatic carbosilane monomers with different spacer length (Muzafarov et al.).

An elaborated investigation of the branching structure of hyperbranched polycarbosilanes was reported by Frey et al., who determined the degree of branching of polytriallylsilane by ^{29}Si -NMR spectroscopy⁴⁵. A degree of branching of 0.48 was found for the polymerization of this AB_3 monomer which is in good agreement with the value of 0.44 expected for a random polymerization. Copolymerization of triallylsilane with the B_1 -core 2-(10-decen-1-yl)-1,3-oxazoline resulted in the first example of hyperbranched polycarbosilane macromonomers with an oxazoline group at the focal point (Figure 1.8). As expected, SEC measurements revealed a decrease of molecular weight and polydispersity with increasing amounts of the core molecule added. In subsequent work by Drohmann, Muzafarov and Möller the investigation was extended to study 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^{46, 47}. A strong influence of the reaction conditions and the spacer length on the polymerization result was found. Besides the decrease of the molecular weight of the resulting polymers upon dilution of the monomer, in some cases multimodal distributions and eventually crosslinking was observed. Monomodal molar mass distributions could be obtained by keeping the reaction temperature and the catalyst concentration low. The occurrence of multimodal

distributions was assigned to rearrangement reactions at elevated temperatures for the vinyl and allyl monomers.

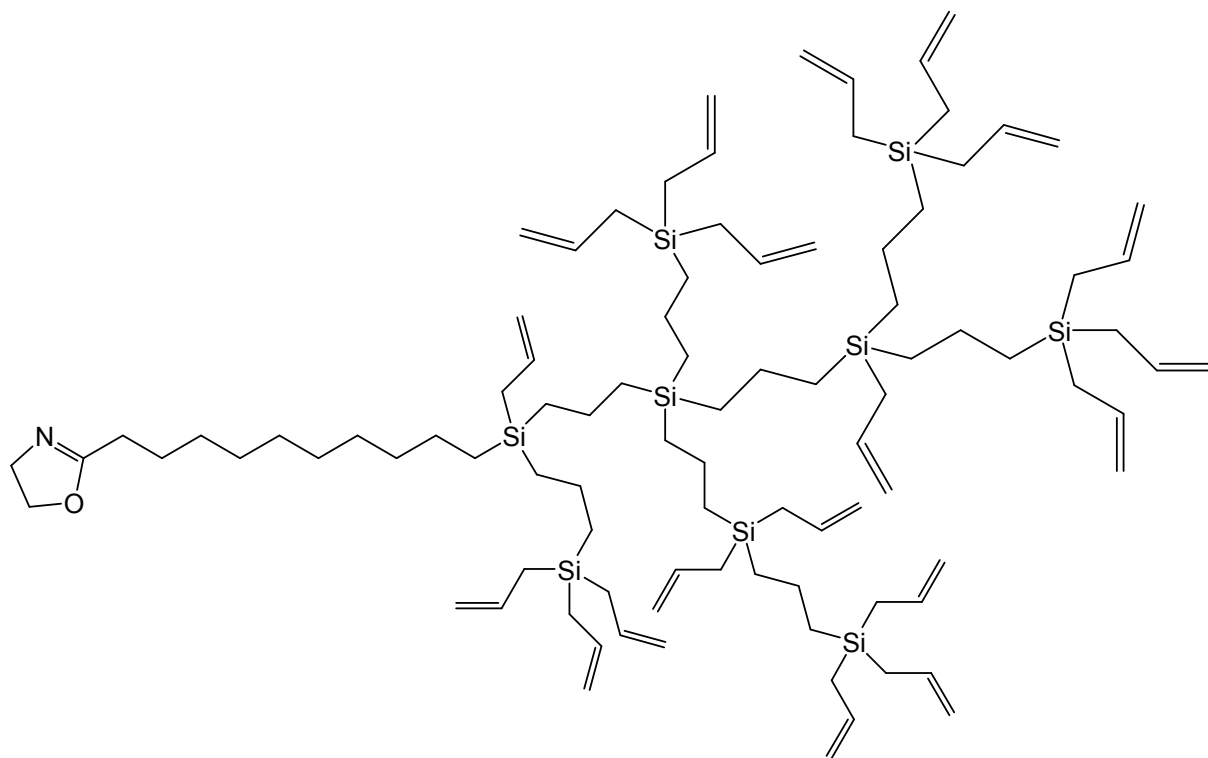


Fig. 1.8 Hyperbranched polytriallylsilane macromonomer possessing a focal oxazoline group (Lach et.al.).

It was confirmed that for the monomers diallylmethylsilane and methyldivinylsilane subsequent addition of monomer did not increase the molecular weight. In contrast, for methyldiundecenylsilane a gradual increase in molecular weight could be observed upon further monomer addition. According to the authors the formation of less sterically crowded polymers in the case of monomers with longer alkenyl spacer might be the reason for this finding, in comparison to a high structural density for the polymers based on monomers with short alkenyl spacers. However, intramolecular cyclization consuming Si-H functionalities is most likely the reason for the limited molecular weights when employing short alkenyl-substituents, as derived in work by Fréchet et al.⁴⁸ and Frey et al.⁴⁹. For large monomers cyclization is kinetically disfavored, enabling further growth of the polymer. These observations represent the first step towards molecular weight control of hyperbranched polycarbosilanes.

Son and Yoon reported the first examples of polycarbosilanes containing aromatic moieties^{50, 51}. A series of AB₃ carbosilarylene monomers was synthesized from dibromobenzenes using lithium-halogen exchange and subsequent treatment with chlorosilanes (Fig. 1.9). The polymer obtained from 1-dimethylsilyl-4-trivinylsilyl-

benzene exhibited improved thermal stability and better solubility than its linear analog. Despite the rigid aromatic moieties in the backbone the polymer shows a relatively low T_g (12°C) due to the hyperbranched structure.

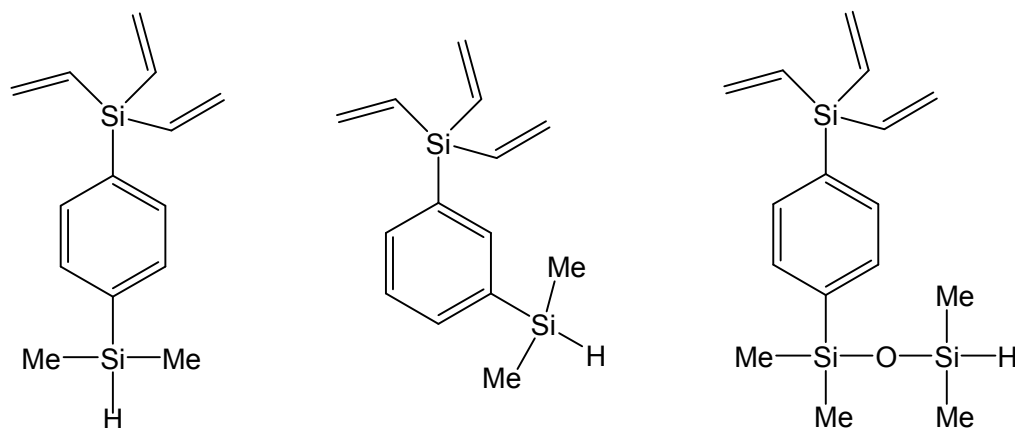


Fig. 1.9 AB₃ carbosilarylene monomers employed by Son et al.

The influence of meta-bending and the incorporation of siloxane linkages into the monomers was studied. Polymerization of a mixture of the monomers allowed to tailor the materials properties. The degree of branching was determined to be 0.42 by ²⁹Si-NMR, close to the expected value, indicating similar reactivity for all B-groups. The authors suggested the application of these materials in advanced elastomers, using the unreacted vinyl groups for crosslinking. In continuing work the same group reported the introduction of furan and thiophene moieties into a series of different AB₂ and AB₃ monomers (Fig. 1.10)^{52, 53}. The presence of oxygen and sulfur in the polymers was meant to enable their application in host-guest or metal-stabilization chemistry. The functional groups can be easily incorporated into the monomers via substitution of chlorosilanes with the respective organometallic compounds. The resulting polymers are air-stable, highly soluble and exhibit low glass transition temperatures between -61°C and -7°C. Molecular weights of the polymers were rather low between 1,400-3,200 g/mol as determined by vapor pressure osmometry. The branched structure was confirmed using ²⁹Si-NMR. McGill et al. reported on the synthesis of naphthalin-containing polycarbosilanes⁵⁴. The concept was to functionalize the free vinyl groups as well as the naphthyl moieties with hexafluoroacetone. Thus, hydrogen bonding imparts a response to nitroaromatics and organophosphonates, permitting the application as chemical sensor. First results

revealed a rapid response time for the polymer-coated sensors, however no further experimental data were given.

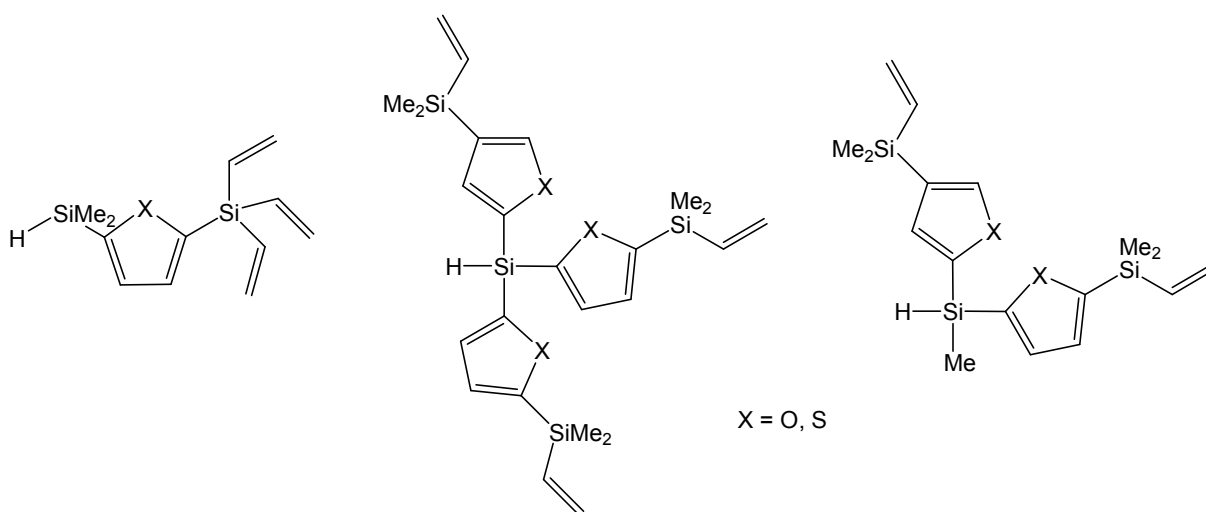


Fig. 1.10 Furan- and thiophene-containing monomers (Rim and Son).

Hydrosilylation addition of Si-H is not only applicable to alkenes, but also to alkynes. The polymerization of ethynyl-containing monomers leads to polymers with particular properties, since unsaturations are incorporated into the resulting polymer backbone. In the first example Son and coworkers polymerized methyldiethynylsilane using Karstedt's catalyst (Fig.1.11)⁵⁵. As expected, no additional hydrosilylation was observed for the internal double bonds formed in the reaction due to their low reactivity. The resulting polymer is air- and moisture-stable and exhibited excellent thermal stability in nitrogen with only 13% mass loss on heating to 1,300°C. The remaining ethynylgroups in the polymers can be used for crosslinking and as attachment sites for transition metals. An interesting study targeting the simple preparation of σ - π -conjugated polymers has been reported by Masuda et al.^{56, 57}. They polymerized the new AB₂ monomers bis(4-ethynylphenyl)methylsilane and *m*-bis(dimethylsilyl)phenylacetylene using Rh-catalyzed hydrosilylation (Fig. 1.12). Performing the polymerization at elevated temperatures, i.e. 80°C, directed the stereoselectivity towards *trans*-rich polymers. The soluble polymers could be obtained by polymerization in dilute solution or subsequent conversion of the Si-H groups with phenylacetylene, respectively. The branched, *trans*-vinylene structure was confirmed by ¹H-NMR.

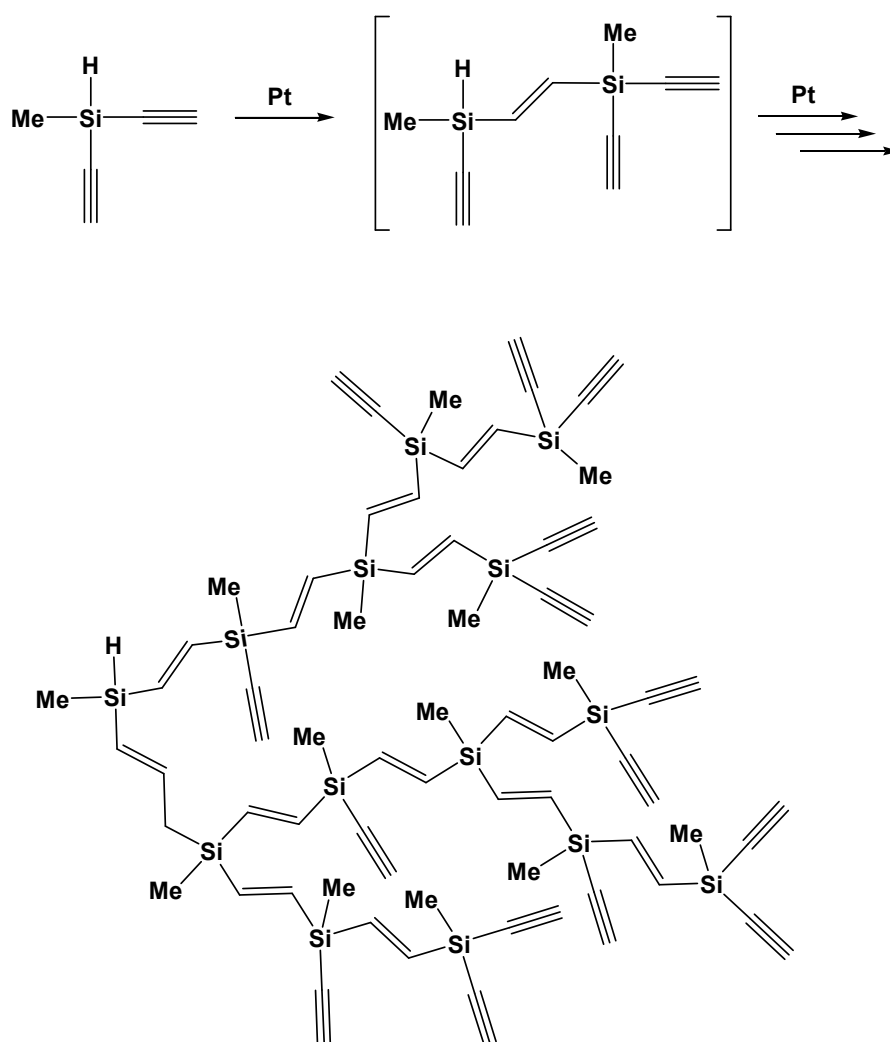


Fig. 1.11 Polymerization of methyldiethynylsilane (Son et al.).

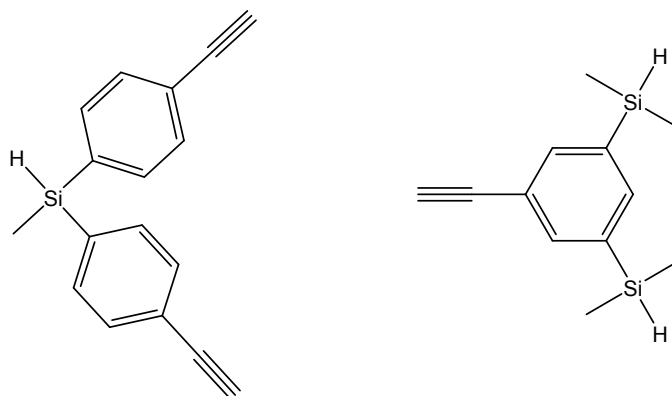


Fig. 1.12 Bis(4-ethynylphenyl)methylsilane and m -bis(dimethylsilyl)phenylacetylene (Masuda et al.).

Optical properties of the ethynyl-functional polymer were analyzed and compared to the linear analog. A weak absorption around 330 nm, hardly seen in the linear

polymer, was assigned to σ -to- π charge-transfer⁵⁷. The authors concluded that this is a result of the more compact structure of the hyperbranched polymer in solution, facilitating the required through-space interactions. The excess of Si-H groups in the polymer based on *m*-bis(dimethylsilyl)phenylacetylene can be used for the aerial oxidation or hydrolysis to give a crosslinked transparent film with siloxane linkages (Fig.1.13).

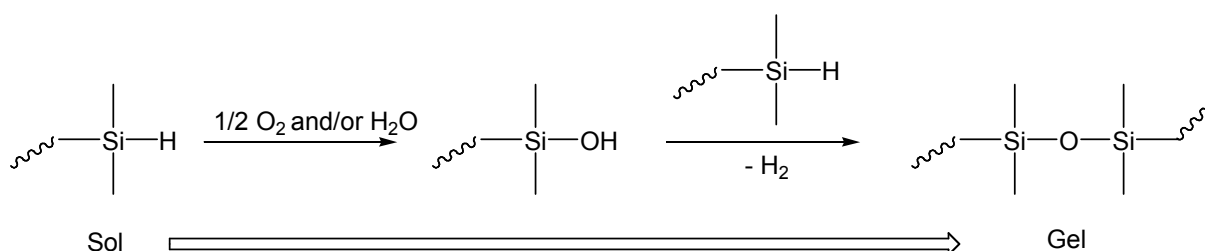


Fig. 1.13 Crosslinking reaction for Si-H terminated polymers⁵⁶.

The homogeneity of the surface as well as the uniform distribution of the siloxane linkages in the film was proven using SEM and EDX-spectroscopy. The charge-transfer phenomenon is accountable for the emission of an intense blue light, when the film is excited at the charge transfer absorption wavelength ($>300\text{nm}$). The excellent solvent resistance of the film was confirmed in extraction experiments⁵⁶.

1.4.2 Functionalization

The robustness and inertness of polycarbosilane structures towards most reaction conditions provides the basis for a variety of modification reactions. Several of the approaches described for carbosilane dendrimers have been adopted for the functionalization of the analogous hyperbranched polymers. Surprisingly, some of the most promising research areas for dendrimers, such as their application as supports for metal complexes and catalysts or as liquid crystalline materials have so far only been rarely studied. Frey et al. have shown that the combination of concepts known from dendrimer chemistry, namely the hydrosilylation of terminal double bonds with chlorosilanes and subsequent substitution with Grignard reagents can be applied for the enhancement of the degree of branching for hyperbranched polymers⁵⁸. The strategy of postsynthetic conversion of the double bonds of a hyperbranched polytriallylsilane leads to a structure without linear units that exhibit a formal degree of branching close to 1. The conversion of linear and semidendritic units to dendritic units was clearly confirmed by the decrease of the respective signals in the ^{29}Si -

NMR, as shown in Figure 1.14. This approach is generally applicable for hyperbranched polymers, however the resulting structures do not possess the symmetry and regularity known for dendrimers regardless of the high degree of branching.

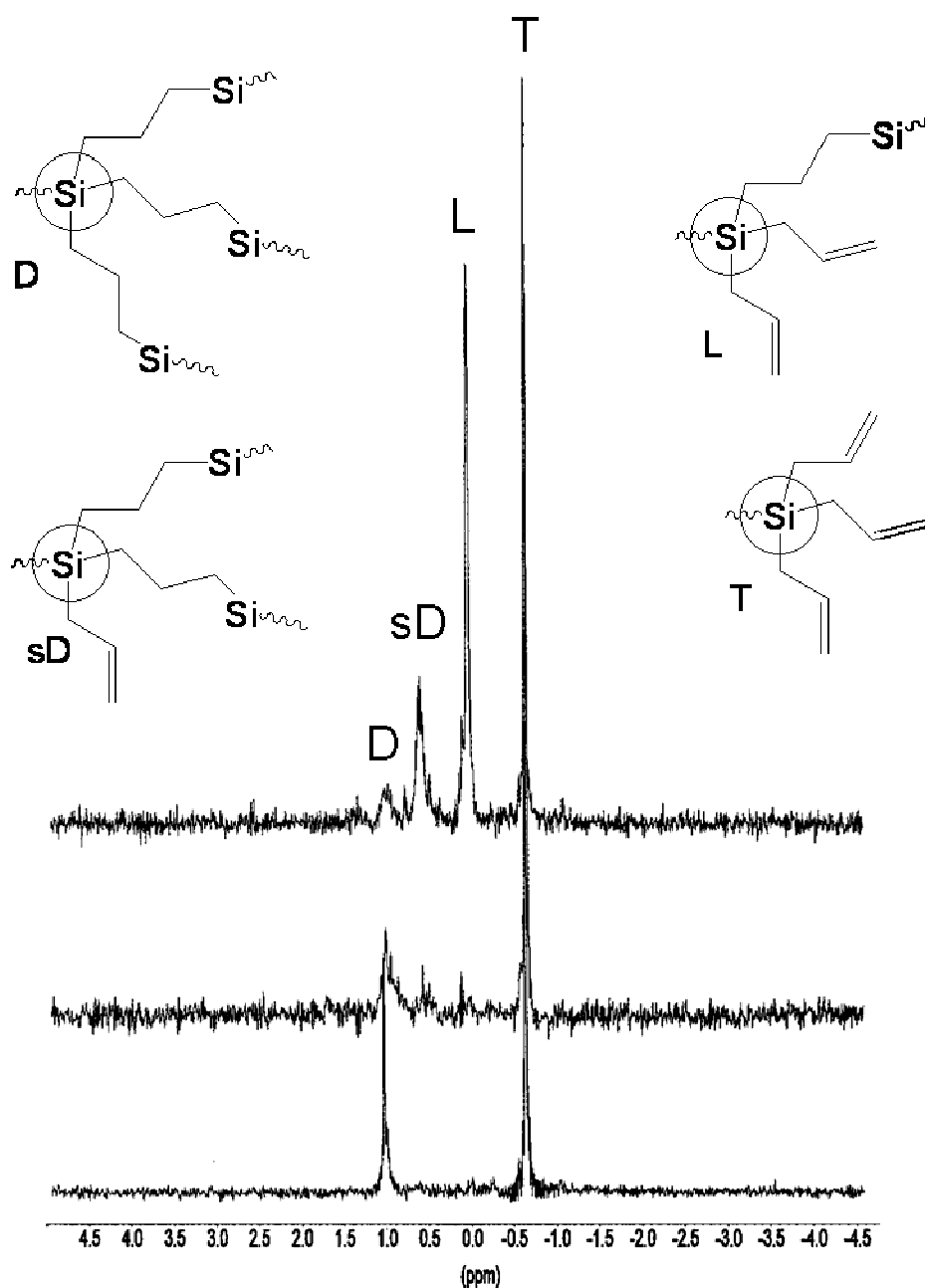


Fig. 1.14 Comparison of ^{29}Si -NMR spectra for hyperbranched polymer, hyperbranched polymer after modification and dendrimer (from top to bottom)⁵⁸.

First work on the supramolecular properties of hyperbranched polymers was published by Frey et al. in 1997. Oxazoline-functional polycarbosilanes were homopolymerized cationically as well as copolymerized with phenyloxazoline to give side chain hyperbranched polymers. Coupling of the oxazoline functionality with

trimesic acid resulted in trimers of the hyperbranched fragments. Interestingly, the trimers formed relatively well-defined aggregates in solution, despite the randomly branched structure of the building blocks. Aggregation into columnar structures was studied by WAXS, dynamic and static light scattering as well as AFM measurements and explained by hydrogen bonding between the polar cores, which form the centers of the stacks surrounded by an apolar, disordered corona^{59, 60}.

Carbosilane dendrimers are also studied for their application as scaffolds for catalytically active metal complexes. The soluble complexes permit good access to the reactive sites, in addition the catalyst system can be removed using ultracentrifugation or ultrafiltration and reused in analogy to a heterogenous catalyst. The only example where this approach has been transferred to hyperbranched carbosilanes was reported by Schlenk et al.^{61, 62}. Here, polytriallylsilane was used as soluble macromolecular support for homogeneous catalysis. Dimethylaminoaryl palladium(II) “pincer” complexes were introduced at the free double bonds as catalytically active sites in a sequence of lithiation/transmetalation procedures (Fig. 1.15).

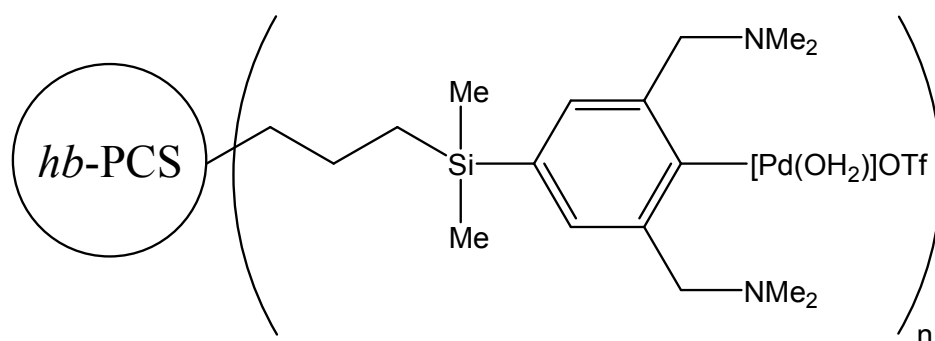


Fig. 1.15 Structure of the catalytically active site of polymer bound catalyst for aldol condensations (Schlenk et.al.).

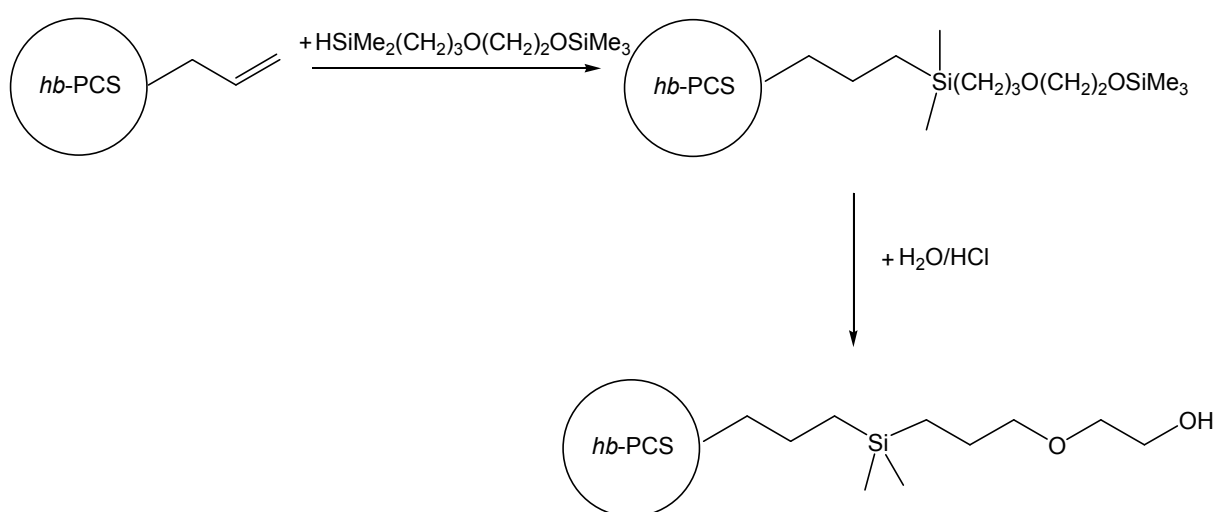
The soluble catalyst was employed for the aldol condensation of benzaldehyde and methyl isocyanoacetate and showed similar reactivities and conversion as the molecular catalyst (Table 1.1). The supported catalyst is impermeable for dialysis membranes, which permits its application in continuous membrane reactors.

Table 1.1 Aldol condensation catalysis using benzaldehyde and methyl isocyanoacetate as substrates.

catalyst	mol%	Yield [%]	TOF ^a	TTN/Pd site ^b
-	-	<5	-	-
molecular	0.99	99	37	100
polymer supported	0.79	>99	19	78

a) Turnover frequency per Pd center per hour; during the first hour b) After 24h obtained by specific signal integration using ¹H-NMR and mesitylene as internal standard (duplo experiment); TTN=total turnover number.

Kim and Kim gave further examples for possible modifications of the terminal double bonds of polytrialkylsilane and polydiallylmethylsilane⁶³. After hydrosilylation addition of dichloromethylsilane or chlorodimethylsilane the chlorides were substituted with allyl magnesium bromide, lithium amide, cholesterol, lithium bis(trimethylsilyl)amide or lithium phenylacetylenide to give the functional polymers. The polymers were characterized using NMR and MALDI-ToF, however no examination of the resulting properties or possible applications was reported. Hydrophilization of polyallylsilanes with hydroxyl end groups was reported by Getmanova et al.⁶⁴. They synthesized 1-(3-dimethylsilyl)propyloxy-2-trimethylsilyloxyethane and coupled it to the polymer double bonds. Hydrolysis of the trimethylsiloxy end groups afforded the desired hydroxyl derivative (Fig. 1.16). The formation of a hydrogen bond network was studied using IR spectroscopy and revealed high sensitivity towards temperature and dilution.

**Fig. 1.16** Synthesis of hyperbranched carbosilane based polyols (Getmanova et.al.).

An interesting approach to create nanometer-size cavities in a polymer matrix was reported by Möller, Muzafarov and coworkers⁶⁵. They modified polydiallylmethylsilane with methacrylate end groups via a degradable Si-O linkage (Fig.1.17). The resulting structures were copolymerized with different amounts of methacrylate monomers to form homogeneous copolymer networks. The sensitivity of Si-O linkages towards alcoholysis was utilized for degradation, resulting in small functional pores within the polymer matrix.

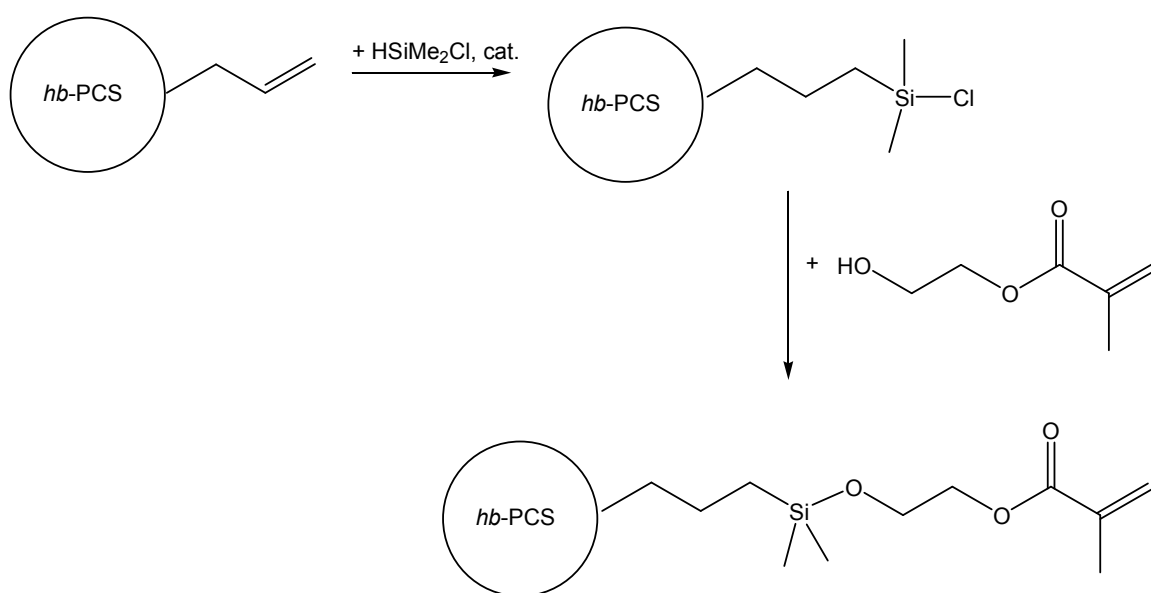


Fig. 1.17 Methacrylate-functionalized polycarbosilane (Möller et.al.).

Bystrova et al. prepared ethoxysilyl derivatives of polydiallylmethylsilane and studied the network formation by hydrolysis with acetic acid⁶⁶. The formation of siloxane bonds is accompanied by the evolution of ethyl acetate, alcohol and water, which allows the determination of the conversion of ethoxysilyl groups (70%). After extraction of the soluble part the network yield was >90%. The networks were stable in a wide temperature range. Unfortunately, no analysis of the mechanical properties of the materials was given. The spatial structure of polydiallylmethylsilane was studied by Ozerin and coworkers using X-ray scattering and molecular modelling^{67, 68}. The primary finding was that the hyperbranched structure was less dense than a dendrimer of the same molecular weight, but considerably more dense than a Gaussian coil of similar weight. A further detailed structural analysis of polydiallylmethylsilane was performed by Muzafarov et al., who studied fractionated samples using absolute molecular weight detection⁶⁹. As expected, it was found that

1.4.3 Block copolymers

[illegible]

The short polybutadiene block represents a multifunctional core due to the number of double bonds that are capable of reaction with carbosilane monomers. The slow monomer addition technique permits control of the size of the hyperbranched polycarbosilane block, while keeping the molecular weight distributions extremely narrow ($PDI < 1.1$). Morphological studies by TEM, AFM and SAXS on these systems demonstrated that various microdomain structures were obtained, despite the additional structural isomerism of the branched block adding to the polydispersity

regarding molecular weight. Manipulation of the composition of the materials allowed morphological control analogous to that in linear diblock copolymers with the observation of similar microphase-separated states. However, the branched structure appears to contribute a topological factor to the incompatibility and the resulting order, i.e. cylindrical structures were observed for the block copolymer $\text{PS}_{520}\text{-}b\text{-}[\text{PB}_{47}\text{-}hb\text{-}\text{PCSi}_{142}]$ with 49 wt% of the hyperbranched component (Fig. 1.19).

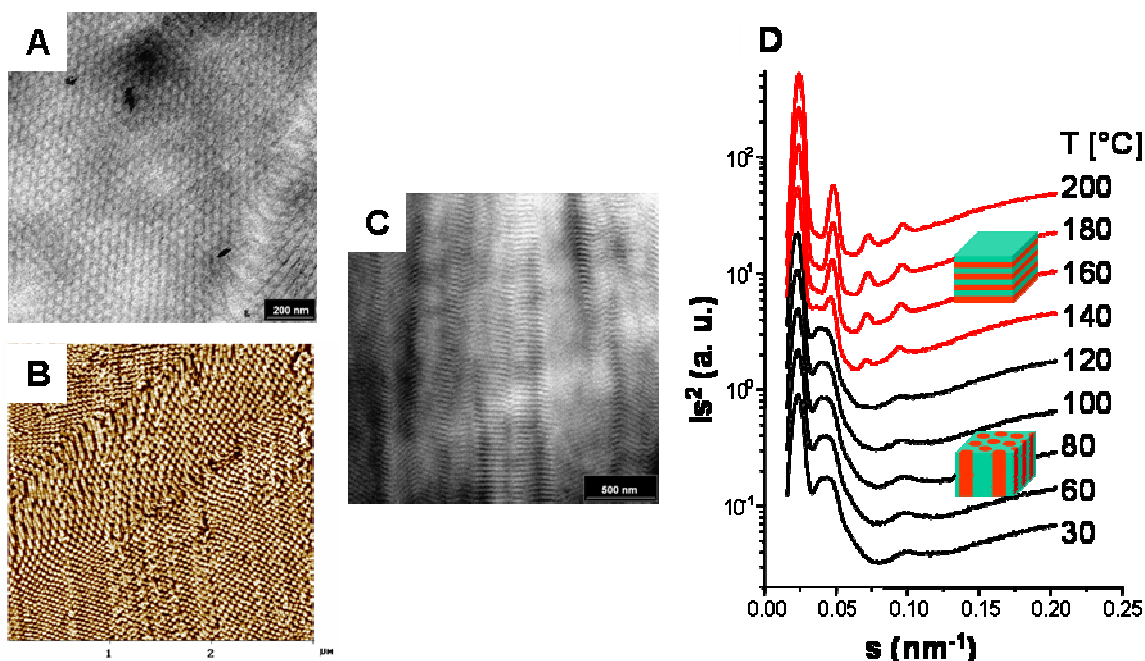


Fig. 1.19 Morphology of sample $\text{PS}_{520}\text{-}b\text{-}[\text{PB}_{47}\text{-}hb\text{-}\text{PCSi}_{142}]$: (A) and (B) unstained TEM and AFM phase image at room temperature from the melt-pressed sample, (C) TEM at room temperature of the solution-cast sample, (D) temperature-dependent one-dimensional SAXS pattern.

Since an irreversible transformation to the expected lamellar phase took place after annealing, the authors suggested the cylindrical morphology to represent a kinetically controlled or metastable state and not an equilibrium morphology. All of the block copolymers with hyperbranched polycarbosilane-block showed extremely rapid phase segregation due to the strong incompatibility of the linear polystyrene block and the hyperbranched polycarbosilane structure.

1.5 Summary and Perspectives

Although numerous basic synthetic pathways have been established for the preparation of hyperbranched materials based on hydrosilylation chemistry, it appears that the field is by no means fully exploited or mature. To date, the research

reported has only little capitalized on facile combination with sol-gel chemistry based on alkoxyasilanes. This may be promising in order to create toughened ceramics as well as unusual hybrid materials. Furthermore, the flexibility of carbosilanes may be used to create liquid crystalline architectures in analogy to perfectly branched LC-dendrimers. Finally, structure formation in linear-hyperbranched block copolymers can be studied in a systematic manner using carbosilane blocks. In summary, the area of hyperbranched polycarbosilanes and related structures offers interesting challenges for the future.

1.6 References

1. Sirtl, E.; Schmidt, O. *German Patent No. 1123300* **1962**.
2. Müller, R. *German Patent No. C57411* **1942**.
3. Rochow, E. G. *U.S. Patent No. 2,380,995 (to General Electric)* **1941**.
4. Rochow, E. G. *Journal of the American Chemical Society* **1945**, 67, 963.
5. Voorhoeve, R. J. H., *Organosilanes, Precursors to Silicones* Elsevier: Amsterdam: 1967.
6. Interrante, L. V.; Rushkin, I.; Shen, Q. *Applied Organometallic Chemistry* **1998**, 12, 695.
7. Frey, H.; Schlenk, C., Silicon-based dendrimers. In *Top Curr Chem*, Springer Berlin Heidelberg, 2000; Vol. 210, pp 69.
8. Majoral, J. P.; Caminade, A. M. *Chem Rev* **1999**, 99, (3), 845.
9. Mathias, L. J.; Carothers, T. W., In *Advances in dendritic macromolecules*, CAI Greenwich, 1995; p 101.
10. Frey, H.; Lach, C.; Lorenz, K. *Adv Mat* **1998**, 10, (4), 279.
11. van der Made, A. W.; van Leuwen, P. W. N. M. *J Chem Soc Chem Comm* **1992**, 1400.
12. Flory, P. J. *J Am Chem Soc* **1952**, 74, 2718.
13. Flory, P. J., *Principles of polymer chemistry*. University Ithaca, 1953.
14. Son, D. Y., Silicon-based dendrimers and hyperbranched polymers. In *The chemistry of silicon compounds*, Rappoport, Z.; Apeloig, Y., Eds. Wiley 2001; Vol. 3, pp 745.
15. Chatgililoglu, C. *Acc Chem Res* **1992**, 25, 188.
16. Kopping, B.; Chatgililoglu, C.; Zehnder, M.; Giese, B. *J Org Chem* **1992**, 57, 3994.
17. Sommer, L. H.; Pietrusza, E. W.; Whitmore, F. C. *J Am Chem Soc* **1947**, 69, 188.
18. Speier, J. L. *Adv Organomet Chem* **1979**, 17, 407.
19. Speier, J. L.; Webster, J. A.; Barnes, G. H. *J Am Chem Soc* **1956**, 79, 974.
20. Ashby, B. A.; Modic, F. J. *US Patent 4,288,345* **1981**.
21. Karstedt, B. D. *US Patent 3,715,334* **1973**.
22. Marciniak, B.; Maciejewski, H.; Duczmal, W.; Fiedorow, R.; Kitynski, D. *Appl Organomet Chem* **2003**, 17, (2), 127.
23. Harrod, J. F.; Chalk, A. J. *J Am Chem Soc* **1965**, 87, 16.
24. Harrod, J. F.; Chalk, A. J., In *Organic Synthesis via Metal Carbonyls*, Wender, I.; Pino, P., Eds. Wiley: New York, 1977; p 673.
25. Randolph, C. L.; Wrighton, M. S. *J Am Chem Soc* **1986**, 108, 3366.
26. Reichel, C. L.; Wrighton, M. S. *Inorg Chem* **1980**, 19, 3858.
27. Schroeder, M. A.; Wrighton, M. S. *J Organomet Chem* **1977**, (128), 345.
28. Lewis, L. N. *J Am Chem Soc* **1990**, 112, 5998.
29. Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J Am Chem Soc* **1999**, 121, 3693.
30. Stein, J.; Lewis, L. N.; Smith, K. A.; Lettko, K. X. *J Inorg Organomet Polym* **1991**, 1, 325.
31. Uriarte, R. J.; Lewis, L. N. *Organomet* **1990**, 9, 621.
32. Chalk, A. J.; Harrod, J. F. *J Am Chem Soc* **1964**, 86, 1776.
33. Haszeldine, R. N.; Parish, R. V.; Taylor, R. J. *J Chem Soc A* **1974**, 2311.
34. Hill, A. F., *Organotransition Metal Chemistry*. Royal Society of Chemistry: Cambridge, 2002.
35. Hiyama, T.; Kusumoto, T., Hydrosilylation of C=C and C C. In *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I., Eds. Pergamon: Oxford, 1991; Vol. 8, p 763.

-
36. Ojima, I., The Hydrosilylation Reaction. In *The Chemistry of Organic Silicon Compounds*, Rappoport, Z.; Apeloig, Y., Eds. Wiley: Chichester, UK, 1989; Vol. 1, p 1479.
 37. Ojima, I.; Zi, Z.; Zhu, J., Recent Advantages in the Hydrosilylation and Related Reactions. In *The Chemistry of Organic Silicon Compounds*, Rappoport, Z.; Apeloig, Y., Eds. Wiley: Chichester, UK, 1998; Vol. 2, p 1687.
 38. Brook, M. A., *Silicon in Organic, Organometallic and Polymer Chemistry*. Wiley: Canada, 2000.
 39. Hölter, D.; Burgath, A.; Frey, H. *Acta Polymer* **1997**, 48, 30.
 40. Burgath, A.; Sunder, A.; Frey, H. *Macromol Chem Physics* **2000**, 201, 782.
 41. Hanselmann, R.; Hölter, D.; Frey, H. *Macromolecules* **1998**, 31, (12), 3790.
 42. Hölter, D.; Frey, H. *Acta Polymer* **1997**, 48, (8), 298.
 43. Radke, W.; Litvinenko, G.; Müller, A. H. E. *Macromolecules* **1998**, 31, (2), 239.
 44. Muzafarov, A. M.; Gorbacevich, O. B.; Rebrov, E. A.; Ignat'eva, G. M.; Chenskaya, T. B.; Myakushev, V. D.; Bulkin, A. F.; Papkov, V. S. *Polym Sci* **1993**, 35, (11), 1575.
 45. Lach, C.; Müller, P.; Frey, H.; Mülhaupt, R. *Macromol Rapid Commun* **1997**, 18, (3), 253.
 46. Drohmann, C.; Gorbatshevich, O. B.; Muzafarov, A. M.; Möller, M. *Polym Prepr Am Chem Soc* **1998**, 39, (1), 471.
 47. Drohmann, C.; Möller, M.; Gorbatshevich, O. B.; Muzafarov, A. M. *J Polym Sci Pol Chem* **2000**, 38, (4), 741.
 48. Gong, C. G.; Miravet, J.; Fréchet, J. M. J. *J Polym Sci Polym Chem* **1999**, 37, (16), 3193.
 49. Burgath, A.; Sunder, A.; Frey, H. *Macromol Chem Physic* **2000**, 201, (7), 782.
 50. Yoon, K.; Son, D. Y. *Macromolecules* **1999**, 32, (16), 5210.
 51. Son, D. Y.; Yoon, K. *Polym Mater Sci Eng* **1999**, 80, 200.
 52. Rim, C.; Son, D. Y. *Macromolecules* **2003**, 36, (15), 5580.
 53. Son, D. Y.; Rim, C. *Polym Prepr Am Chem Soc* **2002**, 43, (2), 1180.
 54. Simonson, D. L.; Houser, E. J.; Stepnowski, J. L.; Pu, L.; McGill, R. A. *Polym Mater Sci Eng* **2003**, 89, 866.
 55. Wong, R. A.; Xiao, Y.; Son, D. Y. *Polym Prepr Am Chem Soc* **2000**, 41, (1), 608.
 56. Kwak, G.; Takagi, A.; Fujiki, M.; Masuda, T. *Chem Mat* **2004**, 16, (5), 781.
 57. Kwak, G.; Masuda, T. *Macromol Rapid Commun* **2002**, 23, 68.
 58. Lach, C.; Frey, H. *Macromolecules* **1998**, 31, (7), 2381.
 59. Lach, C.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromol Rapid Commun* **1998**, 19, (9), 461.
 60. Frey, H.; Schlenk, C.; Pusel, T.; Lach, C. *Polym Prepr Am Chem Soc* **2000**, 41, (1), 568.
 61. Schlenk, C.; Kleij, A. W.; Frey, H.; van Koten, G. *Angew Chem Int Edit* **2000**, 39, (19), 3445.
 62. Schlenk, C.; Kleij, A. W.; Frey, H.; van Koten, G. *Angew Chem Int Edit* **2000**, 39, (21), 3736.
 63. Kim, C.; Kim, H. *J Polym Sci Pol Chem* **2001**, 39, (19), 3287.
 64. Getmanova, E. V.; Chenskaya, T. B.; Gorbatshevich, O. B.; Rebrov, E. A.; Vasilenko, N. G.; Muzafarov, A. M. *React Funct Polym* **1997**, 33, (2-3), 289.
 65. Muzafarov, A. M.; Rebrov, E. A.; Gorbacevich, O. B.; Golly, M.; Gankema, H.; Moller, M. *Macromol Symp* **1996**, 102, 35.
 66. Bystrova, A. V.; Tatarinova, E. A.; Buzin, M. I.; Muzafarov, A. M. *Polym Sci Ser A* **2005**, 47, (8), 820.
 67. Fadeev, M. A.; Rebrov, A. V.; Ozerina, L. A.; Gorbatshevich, O. B.; Ozerin, A. N. *Polym Sci Ser A* **1999**, 41, (2), 189.
 68. Ozerin, A. *Macromol Symp* **2001**, 174, 93.
 69. Tarabukina, E. B.; Shpyrkov, A. A.; Potapova, D. V.; Filippov, A. P.; Shumilkina, N. A.; Muzafarov, A. M. *Polym Sci Ser A* **2006**, 48, (9), 974.
 70. G. Marcos, A.; Pusel, T. M.; Thomann, R.; Pakula, T.; Okrasa, L.; Geppert, S.; Gronski, W.; Frey, H. *Macromolecules* **2006**, 39, (3), 971.
 71. Frey, H.; Marcos, A. G.; Pusel, T.; de Castro, B. D.; Geppert, S.; Thomann, R.; Gronski, W. *Polym Prepr Am Chem Soc* **2003**, 44, (1), 534.
 72. Lang, H.; Lühmann, B. *Adv Mat* **2001**, 13, (20), 1523.
 73. Mathias, L. J.; Carothers, T. W. *Polym Prepr Am Chem Soc* **1991**, 32, (3), 633.
 74. Mathias, L. J.; Carothers, T. W. *J Am Chem Soc* **1991**, 113, 4043.
 75. Mathias, L. J.; Carothers, T. W.; Bozen, R. M. *Polym Prepr Am Chem Soc* **1991**, 32, (1), 82.
 76. Carothers, T. W.; Mathias, L. J. *Polym Prepr Am Chem Soc* **1993**, 34, (2), 538.
 77. Carothers, T. W.; Mathias, L. J. *Polym Prepr Am Chem Soc* **1993**, 34, (1), 503.
 78. Rubinsztajn, S. *J Inorg Organometal Polym* **1994**, 4, (1), 61.
 79. Rubinsztajn, S.; Stein, J. *J Inorg Organometal Polym* **1995**, 5, (1), 43.
 80. Miravet, J. F.; Fréchet, J. M. J. *Polym Mater Sci Eng* **1997**, 77, 141.

-
81. Miravet, J. F.; Fréchet, J. M. J. *Macromolecules* **1998**, 31, (11), 3461.
 82. Herzig, C.; Deubzer, B. *Polym Prepr Am Chem Soc* **1998**, 39, (1), 477.
 83. Vasilenko, N. G.; Rebrov, E. A.; Myakushev, V. D.; Muzafarov, A. M. *Polym Prepr Am Chem Soc* **1998**, 39, (1), 603.
 84. Oishi, M.; Minakawa, M.; Imae, I.; Kawakami, Y. *Macromolecules* **2002**, 35, (13), 4938.
 85. Ishida, Y.; Yokomachi, K.; Seino, M.; Hayakawa, T.; Kakimoto, M. *Macromol Res* **2007**, 15, (2), 147.
 86. Gong, C.; Fréchet, J. M. J. *J Polym Sci Polym Chem* **2000**, 38, 2970.
 87. Si, Q. F.; Wang, X.; Fan, X.-D.; Wang, S. J. *J Polym Sci Pol Chem* **2005**, 43, 1883.
 88. Si, Q. F.; Fan, X. D.; Liu, Y. Y.; Kong, J.; Wang, S. J.; Qiao, W. Q. *J Polym Sci Pol Chem* **2006**, 44, (10), 3261.
 89. Seino, M.; Hayakawa, T.; Ishida, Y.; Kakimoto, M. A. *Macromolecules* **2006**, 39, (26), 8892.
 90. Nogami, K.; Kakimoto, M.; Hayakawa, T.; Yokomachi, K.; Seino, M.; Sakamoto, K. *Chem Lett* **2006**, 35, (1), 134.
 91. Nogami, K.; Sakamoto, K.; Hayakawa, T.; Kakimoto, M. *J Power Sources* **2007**, 166, 584.
 92. Seino, M.; Yokomachi, K.; Hayakawa, T.; Kikuchi, R.; Kakimoto, M.; Horiuchi, S. *Polymer* **2006**, 47, (6), 1946.
 93. Ding, L. J.; Hayakawa, T.; Kakimoto, M. A. *Polym J* **2007**, 39, (6), 551.
 94. Muzafarov, A. M.; Golly, M.; Möller, M. *Macromolecules* **1995**, 28, (24), 8444.
 95. Xiao, Y. X.; Son, D. Y. *J Polym Sci Pol Chem* **2001**, 39, (19), 3383.
 96. Kim, C.; Kim, H. *C R Chimie* **2004**, 7, 503.
 97. Kong, J.; Fan, X. D.; Si, Q. F.; Zhang, G. B.; Wang, S. J.; Wang, X. *J Polym Sci Pol Chem* **2006**, 44, (12), 3930.
 98. Yoon, K.; Son, D. Y. *Org Lett* **1999**, 1, (3), 423.
 99. Zhang, G. B.; Fan, X. D.; Kong, J.; Liu, Y. Y.; Wang, M. C.; Qi, Z. C. *Macromol Chem Phys* **2007**, 208, (5), 541.

2 Objective

2.1 Ferrocenyl-functionalized polycarbosilanes

In the preceding chapter the research efforts concerning hyperbranched polycarbosilanes have been comprehensively summarized. The characteristic properties of these materials like high flexibility and thermodynamic and chemical inertness have already resulted in a variety of functional polymers. However, one of the most self-evident applications resulting from their inertness, the incorporation of redox-active metal complexes has been neglected to date.

The first part of this work is motivated by the interesting results obtained by Cuadrado and Casado et al. for the application of ferrocene-functionalized carbosilane dendrimers in electrode modification and as redox sensors^{1, 2}. Therefore, the preparation of hyperbranched polycarbosilanes with electrochemical properties has been targeted in this thesis. Pursuing this approach, redox-active units based on ferrocene will be synthesized, which can be used for the functionalization of polycarbosilanes (Figure 2.1 left, middle). Different strategies for the synthesis of ferrocenyl-functionalized polycarbosilanes are compared: a) synthesis of hyperbranched polycarbosilane and subsequent functionalization, b) one-pot synthesis by copolymerization of carbosilane monomer and ferrocenyl unit. The resulting polymers will be analyzed regarding their electrochemical properties using cyclic voltammetry. Additionally, their possible application in the modification of electrodes has been studied.

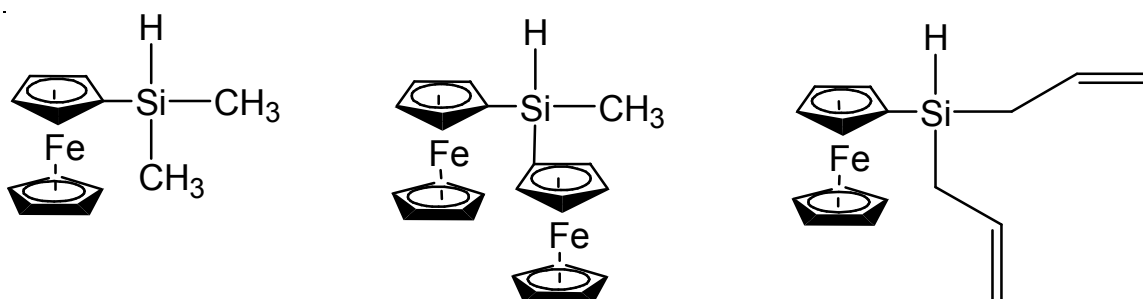


Fig. 2.1 Ferrocenylsilanes for functionalization of hyperbranched polycarbosilanes and ferrocenyl-containing monomer.

Functionalization of hyperbranched polymers is in most cases achieved by reaction of the end groups with functional compounds. However, complete functionalization is often not realizable, since the groups close to the focal unit are shielded and thus difficult to convert. In addition, the low molecular weight functional molecules as well as other compounds used for reaction have to be removed afterwards. Silicon chemistry offers the opportunity to attach four (different) substituents to a silicon atom. Thus, the synthesis of an AB₂ carbosilane monomer that carries an additional functional ferrocenyl group at silicon will be developed (Figure 2.2 right). Polymerization of this monomer yielding functional hyperbranched structures and an electrochemical characterization will be performed.

2.2 Core-functional polycarbosilanes

Hyperbranched polycarbosilanes are usually synthesized in a simple bulk polymerization of AB₂ monomers. However, this allows no controlled polymerizations. In order to enhance the control of molecular weight and molecular weight distribution the synthesis of multifunctional core molecules will be presented (Fig. 2.2).

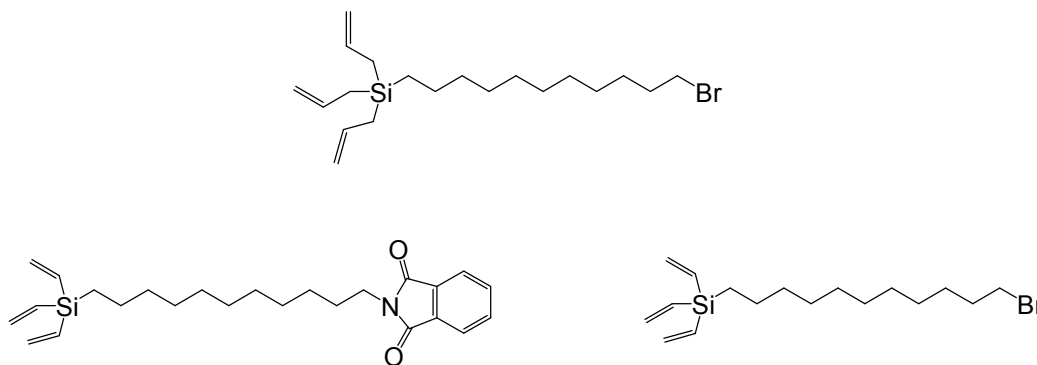


Fig. 2.2 Functional core molecules for synthesis of hyperbranched polycarbosilanes.

Subsequently, the influence of the number of functionalities and reactivity of these core molecules in copolymerization with AB₂ carbosilane monomers will be tested using different polymerization techniques.

The resulting core-functional polycarbosilanes will be chemically modified to alter the polymer properties. Reactions can take place at the core as well as at the unsaturations of the carbosilane part. The functional core renders these polymers possible building blocks for hyperbranched block copolymers. In these context, the application as macroinitiator in the ring opening polymerization of glycidol resulting in amphiphilic hyperbranched-hyperbranched block copolymers will be presented. The targeted structure is shown in Figure 2.3. 1,3-Dipolar cycloaddition of azide-functional polycarbosilanes will be employed to obtain linear-hyperbranched block copolymers.

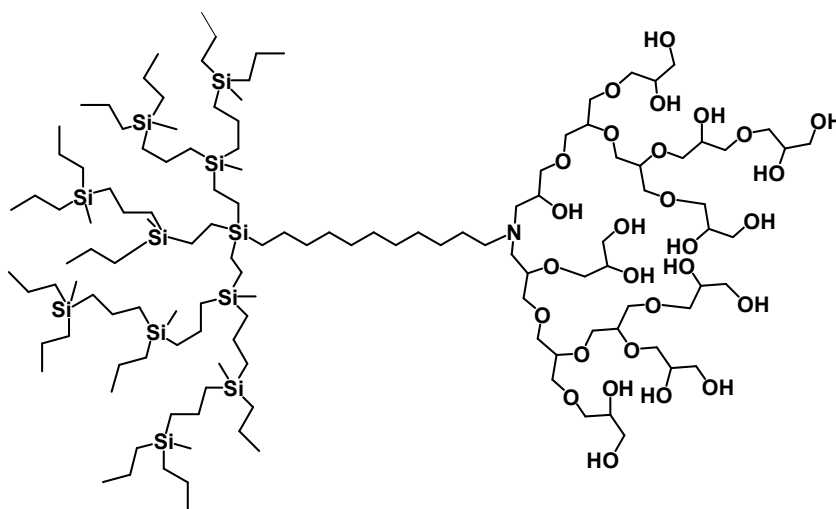


Fig. 2.3 Hyperbranched-hyperbranched block copolymer.

2.3 References

1. Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; García, B.; González, B.; Losada, J. *Coordination Chemistry Reviews* **1999**, 185-186, 53.
2. Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F., Organometallic Dendritic Macromolecules: Organosilicon and Organometallic Entities as Cores or Building Block. In *Advances in Dendritic Macromolecules*, JAI Press: 1996; Vol. 3, pp 151.

3 Ferrocenyl-functionalized hyperbranched polycarbosilanes

3.1 Introduction

Ferrocene, bis(η^5 -cyclopentadienyl)iron, was discovered in the early 1950s and has since been one of the most extensively studied compounds in organometallic chemistry^{1, 2}. The high thermal and photochemical stability and the unique redox properties provide a basis for possible applications in fields such as electrochemistry, materials science, organic synthesis and catalysis^{3, 4}. In this context, the incorporation of ferrocene into polymers as a pendant group or as integral part of the polymer backbone has been reported. Such ferrocenyl-functional polymers are of interest in the chemical modification of electrodes, as electrode mediators, electrochemical sensors, as materials for the construction of liquid crystals, electronic devices, non-linear optical systems and as chiral ligands for asymmetric catalysis⁵⁻⁹. One of the most prominent examples in this field are polyferrocenylsilanes, prepared via ring-opening polymerization (ROP) of sila[1]ferrocenophanes (Figure 3.1)^{10, 11}. The capability to prepare multiblock structures continues to raise interest in these polymers with respect to nanostructured materials¹².

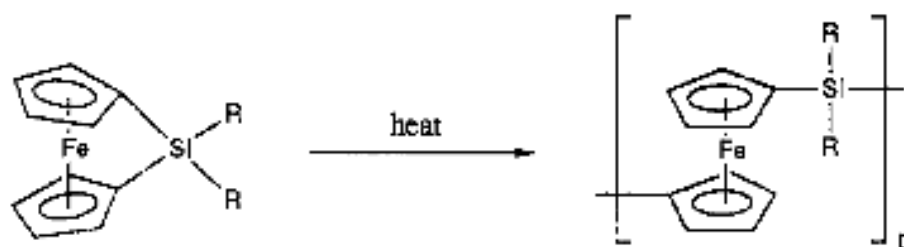


Fig. 3.1 Thermal ROP of sila[1]ferrocenophanes.

The facile and reversible oxidation and reduction of ferrocene allows its application as mediator in electrochemical recognition. A mediator works as intermediate between a substrate, e.g., glucose oxidase and the electrode. Due to kinetic effects the direct reaction between electrode and substrate can be hindered, so that a transfer through an interconnecting redox cycle is favored. However, ferrocene, or more precisely the oxidized form ferrocinium, is generally not stable on electrodes and is removed when placing the electrode in solvents. As a consequence ferrocene has to be attached to a polymer support, which sticks firmly to the electrode

independent of the oxidation state of ferrocene. To this end, one of the most promising developments was the synthesis of ferrocenyl-functionalized dendrimers reported by the groups of Cuadrado and Casado et al.^{13, 14} They modified carbosilane and siloxanes dendrimer scaffolds with electronically isolated¹⁵ and communicating ferrocene moieties^{16, 17}. These dendrimer types are particularly suitable due to their highly flexible structure, electrochemical stability and good accessibility of the redox centers and which are inert under the redox conditions. According to the respective dendrimer generation an increasing and defined number of redox active units can be attached per molecule (Figure 3.2). This precise value allows a calculation of the amount of redox centers that are active in each redox cycle. The feasibility of modifying electrode surfaces with such redox-active metallo-dendrimers by oxidative precipitation was proven¹⁸. Modified electrodes have been applied as electron mediators in amperometric biosensors¹⁹ and in the electrochemical recognition of anions²⁰, while terminal ferrocene moieties can be used for inclusion complexation with cyclodextrins. For applications where the exact number of electrons transferred is not essential, ferrocenyl-functionalized hyperbranched carbosilane polymers can represent an attractive substitute. They can be synthesized in one-pot procedures, but still possess the high flexibility and stability of the carbosilane dendrimers.

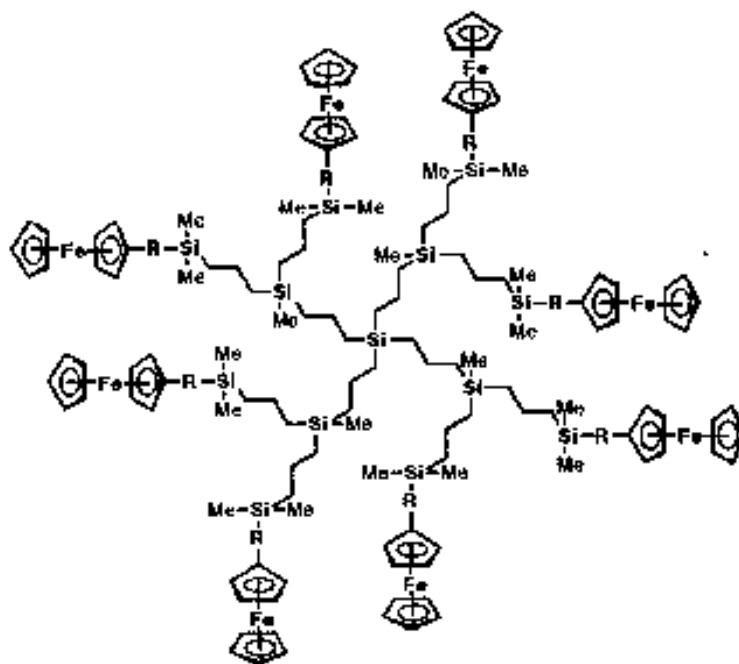


Fig. 3.2 Ferrocenyl-functionalized carbosilane dendrimer.

To date, only some rare examples of the incorporation of ferrocenes into hyperbranched structures have been reported. Deffieux et al. modified polystyrene combs and dendrigrafts bearing di(hydroxymethyl) group termini at each branch end with ferrocenyl moieties²¹. Cyclic voltammetry revealed that only a small fraction of ferrocenyl groups is electrochemically active in combs and linear polystyrene. In contrast, in dendrigrafts all ferrocenyl groups participate in the oxidation-reduction cycles due to the better accessibility in the branched structure.

Tang et al. reported the synthesis of a series of hyperbranched poly(1,1'-ferrocenylenesilyne) (Fig. 3.3). Pyrolysis of the polymers yielded mesoporous, conductive and magnetic ceramics. The hyperbranched structures are superior to their linear counterparts in terms of pyrolytic conversion to inorganic networks and retention of elemental iron in the ceramic products^{22, 23}. Besides these main chain ferrocene-containing polymers the same group reported the synthesis of hyperbranched polymers with ferrocenes as pendant groups. Polymerization was achieved by cyclotrimerization of 1,8-nonadiyne and ferrocene-functionalized phenylacetylene²⁴.

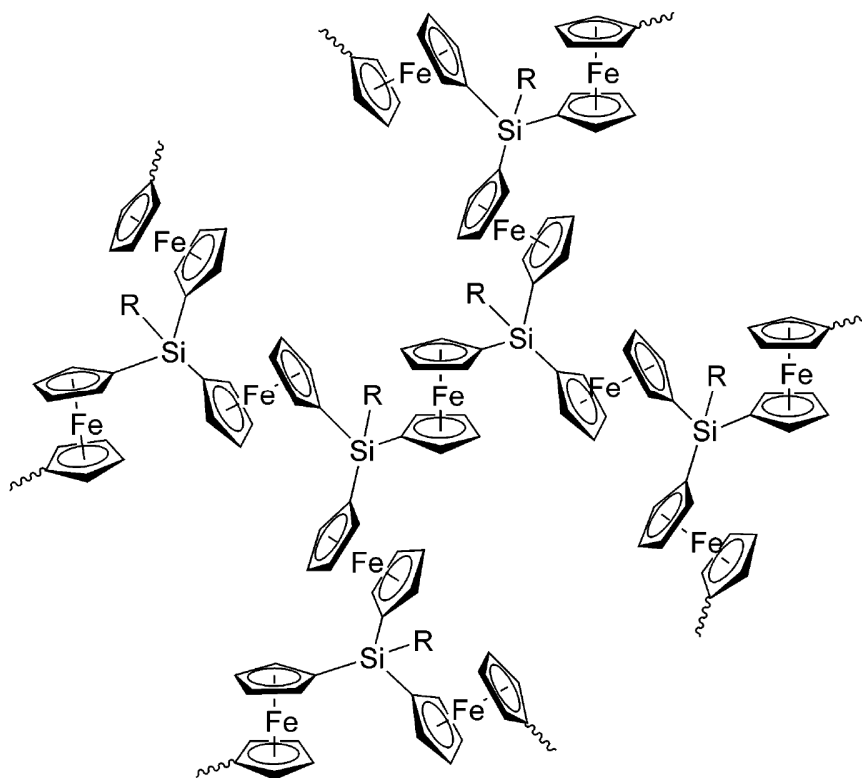


Fig 3.3 Hyperbranched polyferrocenylenesilyne prepared by Tang et al.

In the following chapter the synthesis of hyperbranched polycarbosilanes and their modification with redox-active ferrocene units is described. Hyperbranched polycarbosilanes are readily synthesized by polymerization of AB₂-alkenyl monomers. In order to vary the structure and thus the flexibility of the polymer, monomers with allyl as well as undecenyl groups have been used. Two different redox-active silane units were prepared, bearing either one or two ferrocene molecules at silicon. These moieties can be attached to the polycarbosilane scaffold via hydrosilylation. The synthesis of the ferrocenyl-functionalized polymers is presented and the resulting polymers are analyzed regarding their electrochemical properties.

3.2 Synthesis of hyperbranched polycarbosilanes

AB₂-type carbosilane monomers were synthesized according to a slightly modified procedure reported by Drohmann et al.²⁵ and García-Marcos et al.²⁶ via a Grignard-type reaction. Alkenyl-magnesium bromide reagents were prepared from allyl bromide or 11-bromoundec-10-en by reaction with magnesium turnings. The resulting Grignard reagents were reacted with dichloromethylsilane to give the AB₂ monomers with varied spacer length (Figure 3.4).

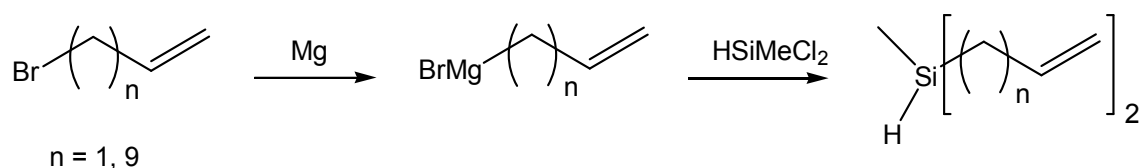


Fig. 3.4 Synthesis of AB₂-alkenylsilane monomers.

The reactions were performed in dry ether in an inert atmosphere, using an excess of magnesium (3 to 6 fold) to suppress the undesired Wurtz-coupling reaction, which results in dimers of the respective alkenes. The monomers, diallylmethylsilane and methyldiundec-10-enylsilane (Figure. 3.5), were purified by distillation and obtained in 57% and 75% yield, respectively.

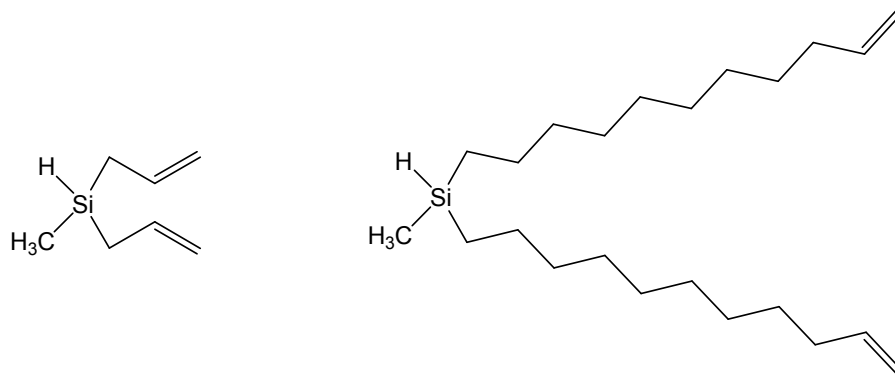


Fig. 3.5 Diallylmethylsilane and methyldiundec-10-enylsilane.

Several catalysts have been reported for the synthesis of hyperbranched polycarbosilanes. Their influence on molecular weight and molecular weight distribution at different temperatures and concentrations was intensely studied. In this context Karstedt catalyst (Figure 3.6), Pt(0)-bis(divinyltetramethyldisiloxane), has been proven to give the best results for the systems studied here. Because of its high reactivity it can also be applied for the functionalization reaction with sterically demanding ferrocenyl compounds.

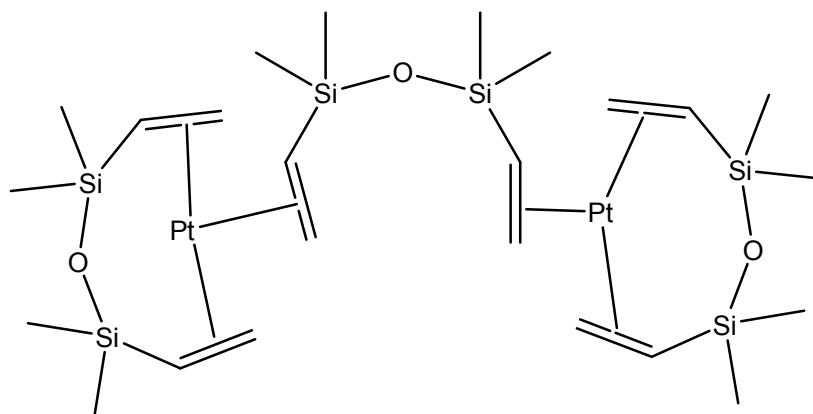


Fig. 3.6 Structure of Karstedt catalyst Pt(0)-bis(divinyltetramethyldisiloxane).

The polymerizations were performed at room temperature in order to minimize side reactions. The low viscosity of the polymers allowed the polymerization in bulk which generally results in higher molecular weights compared to diluted reaction conditions. The polymers, polydiallylmethylsilane (PDAMS) and polymethyldiundecenylsilane (PMDUS), were purified by precipitation into methanol and isolated as viscous,

slightly brownish liquids in yields between 70-90%. The polymerization results are summarized in Table 3.1.

Table 3.1 Polymerization results for *hb*-polycarbosilanes

	GPC(CHCl_3)		% isom. ¹
	M_n	PDI	
PDAMS	3780	2.73	<5
PMDUS	5560	2.16	36

¹ % of isomerized double bonds determined by NMR.

In order to functionalize the polymers a large number of end-groups is desirable. However, it is well known for these systems that isomerization of the external double bonds can occur (see Fig. 1.6). As a consequence unreactive internal double bonds are formed that are no longer capable of functionalization. In the case of PDAMS isomerization is minor and was kept below 5% (Fig. 3.9). In contrast, for PMDUS about one third of the end groups are isomerized (Fig. 3.8). This differs from the findings of Drohmann et al.²⁵, who reported only 3% of isomerization. However, this was not verified by NMR characterization and recent results in our group confirm a degree of isomerization between 33%-65% depending on the reaction conditions²⁶.

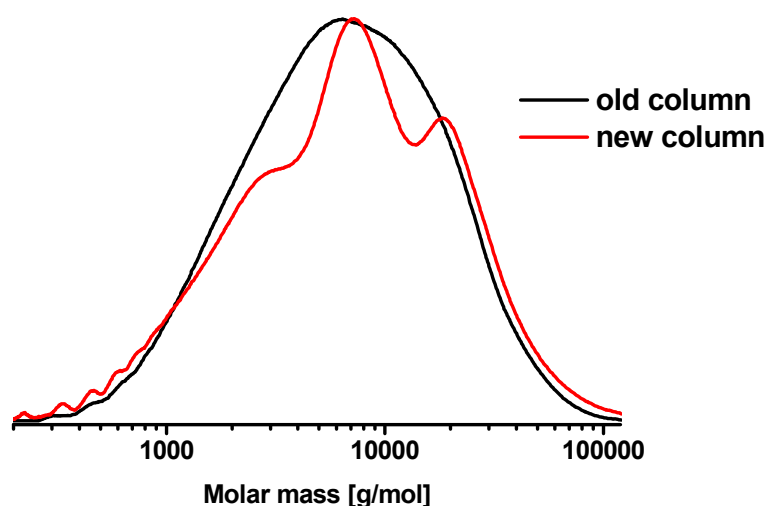


Fig. 3.7 GPC curves in CHCl_3 (RI-signal) for PDAMS using different columns.

A surprising result was obtained for some polymers when they were analyzed by GPC at varying measurement conditions. In Figure 3.7 the GPC results for

polydiallylmethylsilane polymerized in bulk are shown, using two different sets of columns. The molecular weight measured in both cases is the same with $M_n = 3700$ g/mol and also the molecular weight range obtained on both columns is comparable. However, due to the better resolution of the new column it is clearly revealed that the polymer actually shows a trimodal distribution. The higher peak maxima can be assigned to coupled products with a two- or threefold molecular weight. Although such a multimodal distribution has not been reported for this polymer so far, it is assumed that this is a fundamental characteristic of the system, since molecular weight distribution or polydispersity is comparable to the literature values. The occurrence of side reactions that can lead to crosslinking has been reported before and was shown to be more pronounced the longer the reaction time^{25, 26}. However, here it becomes obvious that also polymers that are not crosslinked consist of an overlap of different molecular weight distributions which significantly increase the polydispersity. For this reason it has to be assumed that side reactions are present from the beginning of the polymerization resulting in coupling of macromolecules. Thus, in early stages of the reaction dimers and trimers are formed, while after increased reaction times high molecular weight shoulders or eventually crosslinked material is obtained.

3.3 Spectroscopic characterization

The spectroscopic characterization of hyperbranched polydiallylmethylsilane (PDAMS) and polymethyldiundec-10-enylsilane (PMDUS) was performed in detail in a recent thesis²⁶. Therefore, here only a summary of the results is reported, which are necessary for the characterization of the functionalized polymers. Particularly, the ^1H - and ^{29}Si -NMR spectra are considered in the following. Additionally, the degree of branching (DB) for PDAMS was determined by integration of the ^1H -NMR spectrum. In order to assign the respective signals in the proton spectrum a correlated HSQC spectrum for the coupling between silicon and adjacent protons was recorded.

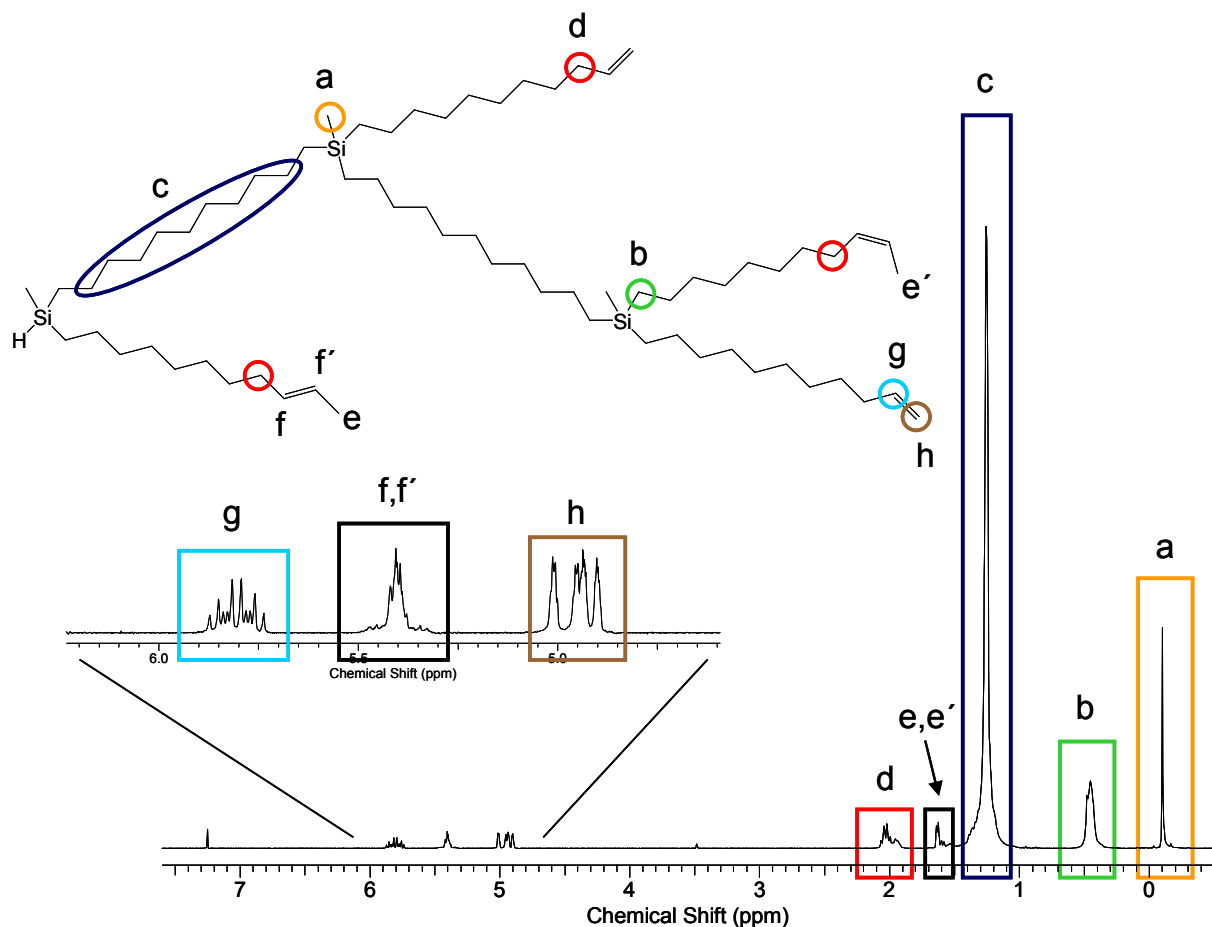


Fig. 3.8 ^1H -NMR spectrum in CDCl_3 for PMDUS.

The ^1H -NMR spectrum of *hb*-PMDUS is presented in Figure 3.8. At -0.10 ppm and 0.45 ppm the signals for Si-CH₃ (a) and Si-CH₂ (b) appear as sharp peaks in a ratio of 3:6, in agreement with the depicted polymer structure. The absence of other signals in this region gives evidence for the regioselective β -addition in the hydrosilylation reaction. Between 1.45 and 1.10 ppm a broad resonance is representative of the different -CH₂- protons (c) of the polymer backbone. The terminal double bonds are represented by signals at 2.00 ppm, 4.95 ppm and 4.80 ppm belonging to the allylic protons adjacent to the double bonds (d) and to the methylene (h) and methine protons (g) of the double bond. The peak at 5.41 ppm is assigned to the isomerized double bonds (f,f'), which emerge as side products in the hydrosilylation reaction. The -CH₃ group (e,e') originating from the *cis*- and *trans*-isomerization of the double bond into the 2-position appears between 1.5 and 1.65 ppm. Further isomerization (i. e. to the 3-position and onward) can be ruled out due to the absence of methyl protons between 0.9 and 1.0 ppm. The long alkyl spacer between the silicon atoms prevents discrimination between the different silicon

branching points in the polymer. Thus, in the ^{29}Si -NMR spectrum a single peak at 3.02 ppm can be observed which gives no information concerning the degree of branching.

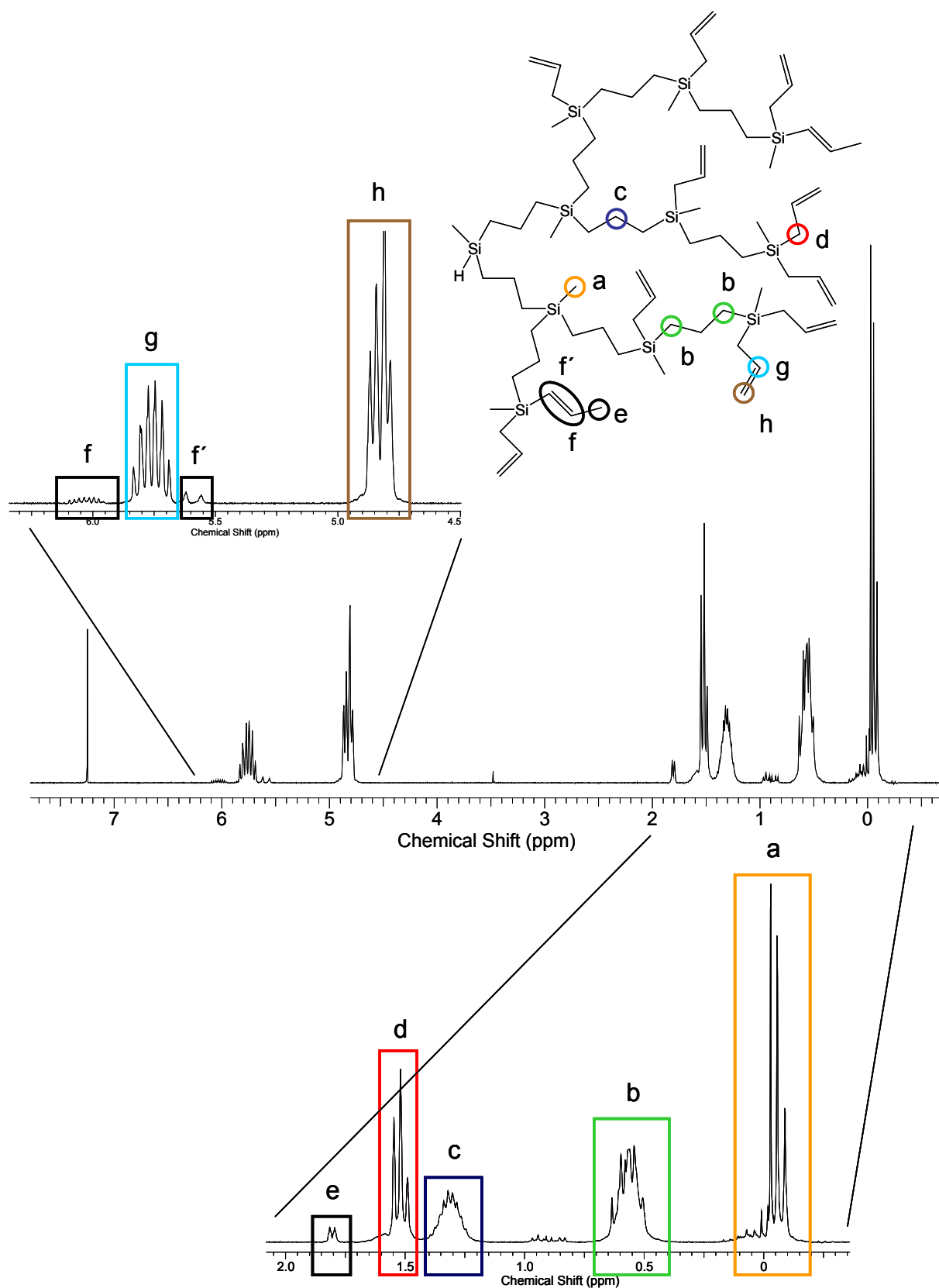


Fig. 3.9 ^1H -NMR spectrum in CDCl_3 for PDAMS.

The ^1H -NMR spectrum for PDAMS is presented in Figure 3.9. The signals for the methine (g) and methylene (h) protons of the terminal double bonds can be observed at 5.77 ppm and 4.84 ppm, with the associated allylic protons (d) as a triplet at 1.53 ppm. The small amount of isomerized double bonds (<5%) accounts for the peaks at 6.02 ppm and 5.58 ppm (f, f'). In addition, the methyl group attached to this structural element gives rise to a signal at 1.81 ppm (e). Two broad signals, centered at 1.32 ppm and 0.58 ppm, appear at a 1:2 ratio and can be assigned to the methylene protons (c) and (b) of the alkyl spacer. In the range between 0.05 ppm and -0.10 ppm an overlap of singlets results from the methyl groups bound to silicon. The separation of the peaks reflects the different chemical environments of the adjacent silicon. Here, four to five peaks can be distinguished corresponding to dendritic (D), linear (L) and terminal units (T). Separated peak are also observed in ^{13}C -NMR for the olefinic and Si-CH₃ carbons attached to different branching units, confirming the branched structure of the polymer.

The degree of branching (DB) is one of the key parameters for the characterization of hyperbranched polymers²⁷⁻²⁹. According to the equation derived by Höltter et al. the DB can be calculated, if the relative amounts of linear (L) and dendritic (D) units are known (Equation 3.1).

$$DB = \frac{2D}{2D + L} \quad (\text{Equation 3.1})$$

Lach et al. have calculated the degree of branching for polytriallylsilane using quantitative ^{29}Si -NMR³⁰ (see Fig. 1.14). This approach has been adapted for PDAMS, however this procedure is tedious and due to the strong baseline noise errors are rather large. Additionally, the low natural occurrence of the ^{29}Si isotope causes a rather poor signal to noise ratio in the resulting spectra. Therefore, errors in quantification by signal integration are rather large. Since for *hb*-PMDAS separated signals can be observed for the protons of the Si-CH₃ group in the ^1H -NMR, those peaks have been assigned to the branching units and the integral values were used for the calculation of the DB. Despite of imprecisions due to the overlap of the signals, this allows an estimation of the degree of branching by a standard technique. In Figure 3.10 the different branching units that can be distinguished in the NMR spectra are presented. Besides the expected linear, dendritic and terminal units,

further signals at -7.33 and -8.29 ppm can be assigned to groups, at which one of the pendant allyl group is isomerized. These have been assigned previously to terminal groups carrying one or two isomerized allyl groups (T_1 , T_2)²⁶. However, because of the low amount of isomerized double bonds it is rather unlikely from a statistical point of view that two isomerized groups are present at the same branching point. It is more probable that the second signal at -7.33 ppm belongs to a linear group with an isomerized double bond (L_1).

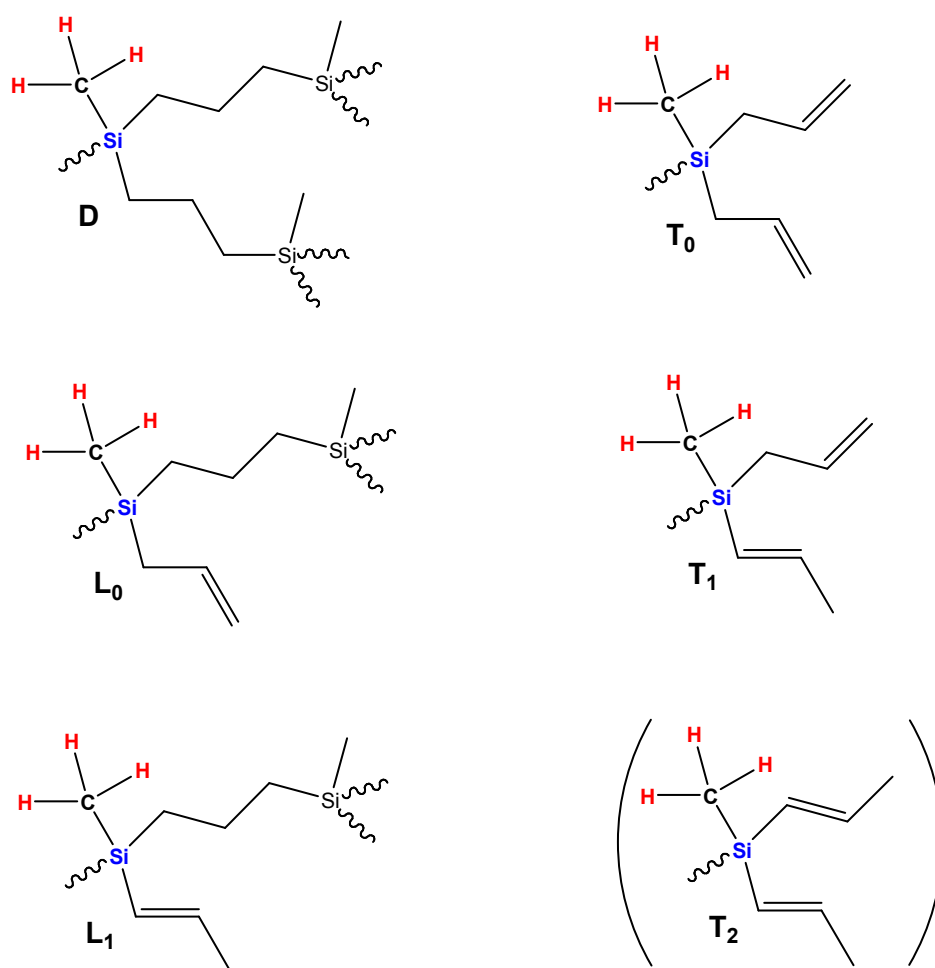


Fig. 3.10 Different branching units for *hb*-PMDAS.

In Figure 3.11 the HSQC spectrum for the correlation between silicon- and proton-nuclei is given. This allows to transfer the assignments for the silicon shifts of the different branching points, already known, to the respective signals of the Si-CH₃ protons. As expected, strong coupling can be observed between the three main peaks for dendritic (D), linear (L_0) and terminal (T_0) units in the silicon spectrum with the main signals for the methyl groups. Additionally, for L_0 and T_0 coupling with the methylen protons adjacent to the double bond is observed. The two signals shifted

up-field in the ^{29}Si -NMR (L_1, T_1), belonging to branching points with isomerized groups, can be correlated with small signals in the proton spectrum. In Table 3.2 the relative amounts of the different branching units are given and compared to the results obtained by integration of quantitative silicon NMR for a similar polymer.

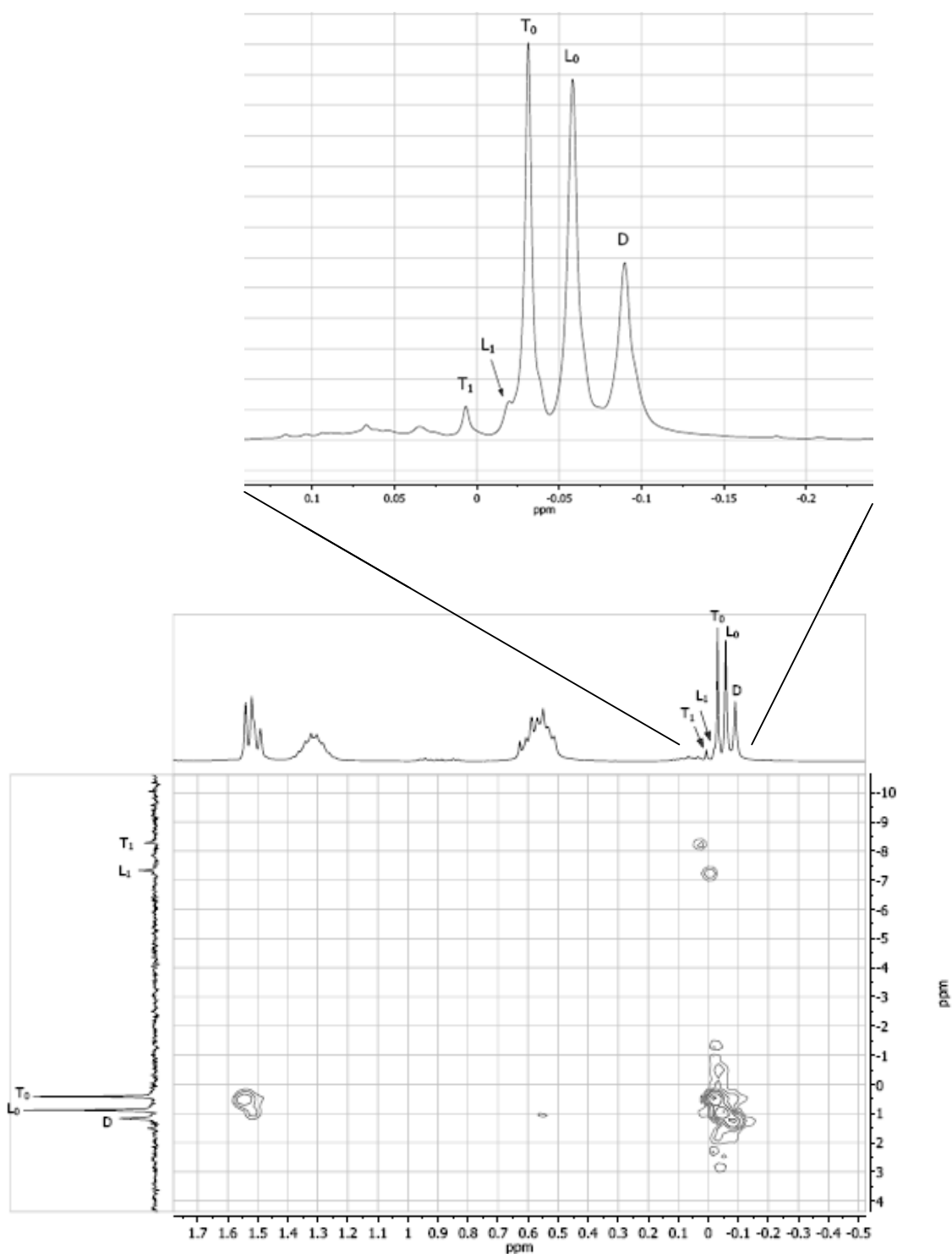


Fig. 3.11 HSQC spectrum in CDCl_3 for the Si-H correlation.

According to Equation 3.1 a DB of 0.55 is obtained from ^1H -NMR, which is slightly lower than the value obtained from ^{29}Si -NMR (0.62). However, the result is close to the theoretical value of 0.50 for random reaction of all double bonds.

Table 3.2 Relative amounts of the different branching units in ^{29}Si - and ^1H -NMR and calculated DB.

nucleus	Relative abundances					DB
	T	T ₁	L	L ₁	D	
^1H	30	3,5	37,5	3,5	25,5	0,55
$^{29}\text{Si}^{\text{a}}$	31	2,5	37	2,5	32	0,62

^aadopted from reference 26.

3.4 Synthesis of communicating and non-communicating ferrocenylsilanes

Hydrosilylation is not only applicable for the polymerization of carbosilane monomers but can also be a powerful tool for the functionalization of polymers. Therefore, suitable ferrocenylsilanes were synthesized that can be added to the free double bonds of the polycarbosilane. It is well known that interactions between ferrocene units, e.g., via a bridging silicon, can lead to significant changes in the redox behaviour of such a compound compared to isolated ferrocene units^{17, 31, 32}. Hence, two different ferrocenylsilanes were synthesized bearing one or two ferrocene units at silicon. These compounds were prepared by reaction of ferrocenyllithium with chlorodimethylsilane or dichloromethylsilane, respectively (Fig. 3.12).

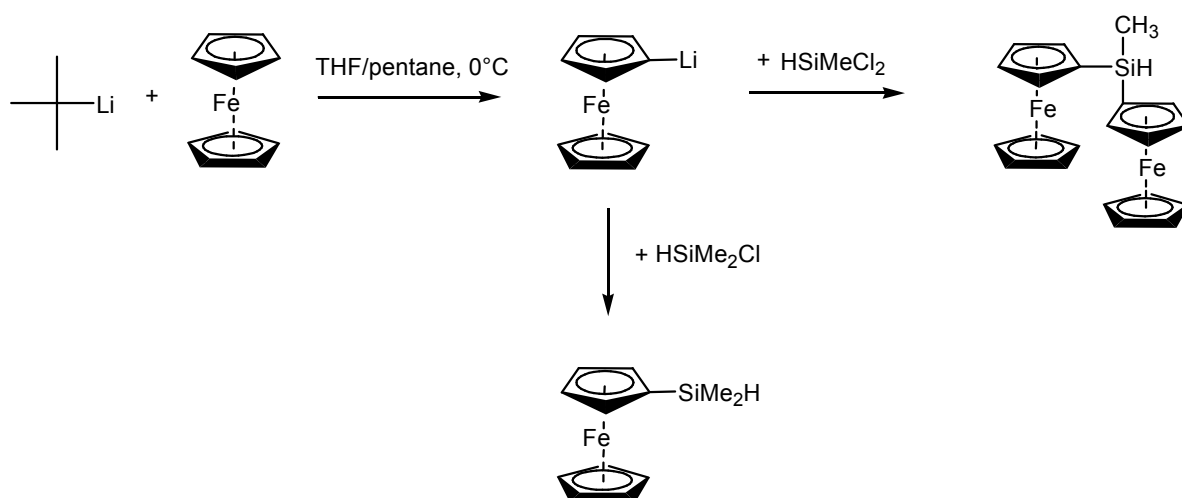


Fig. 3.12 Synthesis of ferrocenylsilanes.

Direct preparation of ferrocenyllithium generally results in a mixture of products, including unreacted ferrocene and 1,1'-dilithioferrocene. In order to minimize these side products an optimized procedure reported by Kagan et al. was applied³³. The ferrocenylsilanes were purified by column chromatography in hexanes/chloroform and characterized using ^1H -, ^{13}C - and ^{29}Si -NMR spectroscopy. The ^1H -NMR spectrum for diferrocenylmethylsilane is shown in Figure 3.13. Coupling between the methyl protons and the Si-H proton gives rise to a quartet at 4.93ppm for Si-H (a) and a duplett for the methyl protons at 0.58ppm (e). Protons of the unsubstituted cyclopentadienyl ring of ferrocene are chemically equal and appear at 4.14ppm. Protons of the substituted ring result in signals at 4.38 and 4.20ppm.

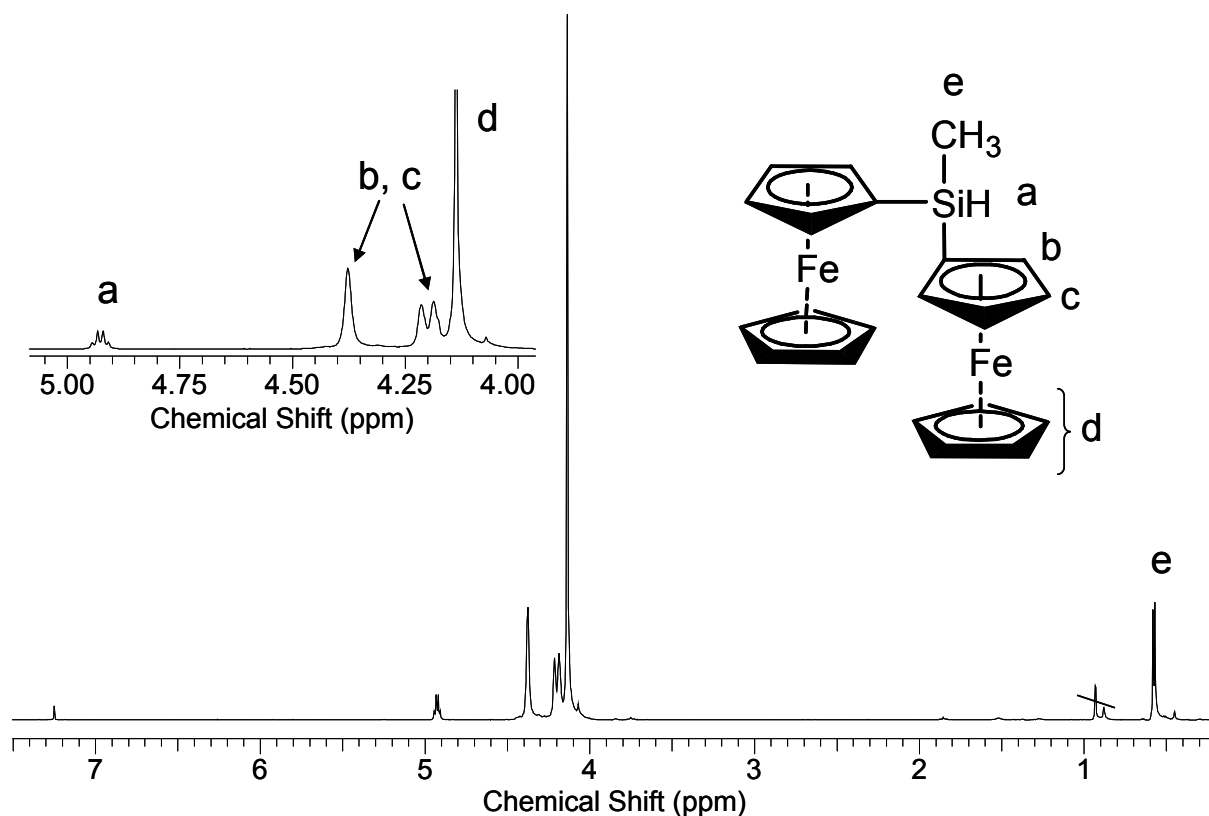


Fig. 3.13 ^1H -NMR spectrum in CDCl_3 for diferrocenylmethylsilane.

3.5 Modification of hyperbranched polycarbosilanes

At first, functionalized polymers (Fig 3.14) were synthesized by addition of ferrocenylsilanes to the preformed polymers. The reactions were performed in pentane or chlorobenzene solution at room temperature or 60°C using Karstedt

catalyst. In combination with a change of the stoichiometry between polymer and ferrocenylsilane, polymers with varying degree of functionalization and thus varying ferrocene content were obtained. All polymers were purified by dialysis (molecular weight cut-off (MWCO)=1000 g/mol) to remove unreacted ferrocene units which could have an influence on the redox chemistry. In the following polymers functionalized with diferrocenylmethylsilane or ferrocenyldimethylsilane are denoted X-Fc₂ or X-Fc, respectively.

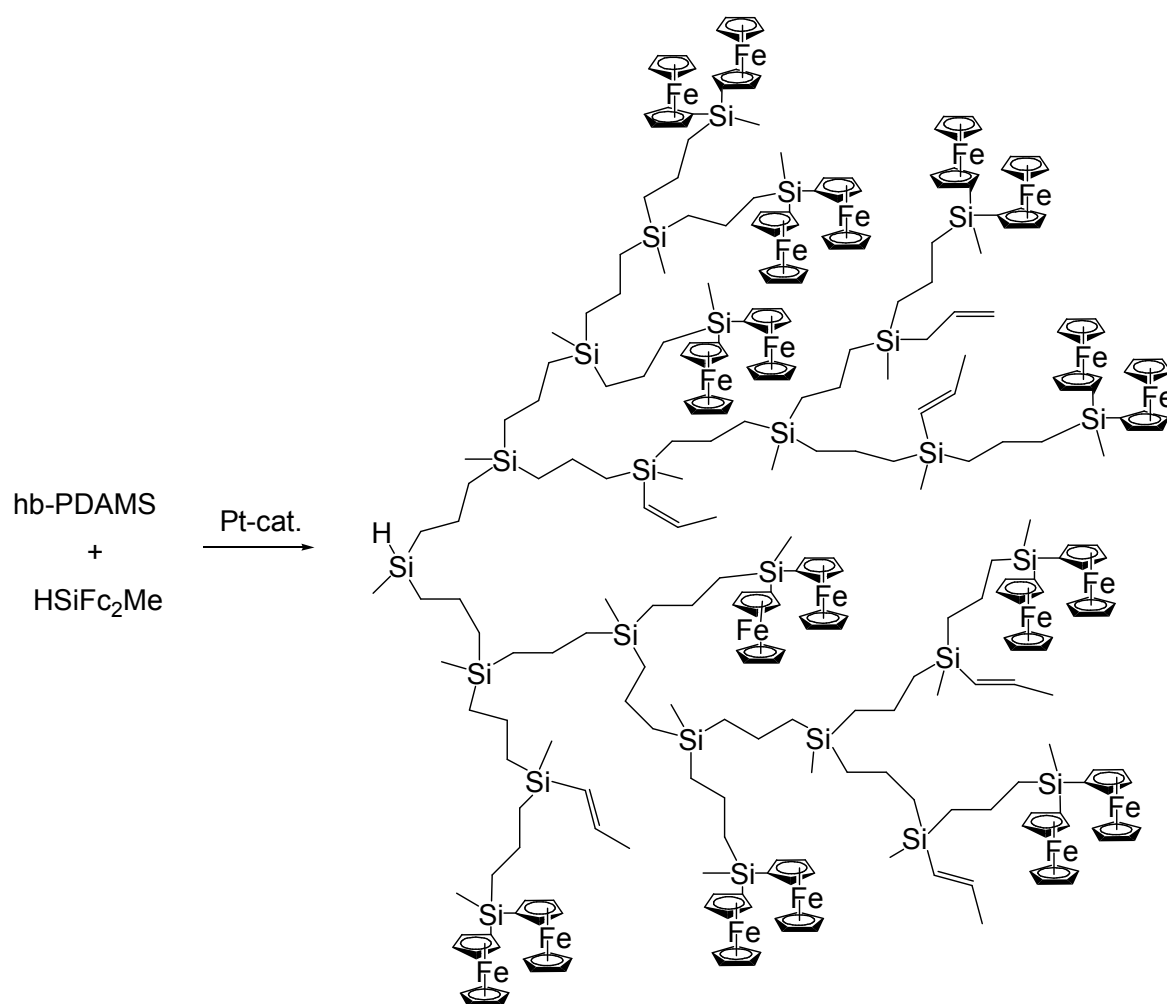


Fig. 3.14 Functionalization of polydiallylmethylsilane with diferrocenylmethylsilane.

3.5.1 Ferrocenyl-modified polydiallylmethylsilane

The results for the functionalization of polydiallylmethylsilane are summarized in Table 3.3. Nearly quantitative functionalization was achieved with diferrocenylmethylsilane and ferrocenylmethylsilane using a slight excess of silane

and elevated temperatures. In pentane solution at room temperature addition of ferrocenylsilane is slow and isomerization becomes a significant side reaction. Diferrocenylsilane-functionalized polymers with a degree of functionalization of 90%, 48% and 19%, respectively were obtained. The materials are highly viscous with an orange to red color. In Figure 3.15 GPC results for polydiallylsilane before and after functionalization are compared confirming the molecular weight increase after addition of ferrocenylsilane units.

Table 3.3 Results for functionalization of polydiallylsilane

sample	structure	reaction condition	ratio ^a	NMR		GPC(CHCl ₃)	
				funct.	isom.	M _n	PDI
1	PDAMS	-	-	-	<5	3800	2.7
2a	PDAMS-Fc ₂	chlorobenzene, 60°C	1:1,2	90	10	8900 ^b	5.7
2b	PDAMS-Fc ₂	pentane, RT	1:1	48	45	6500	3.7
2c	PDAMS-Fc ₂	pentane, RT	2:1	19	56	6200	2.8
3	PDAMS-Fc	chlorobenzene, 60°C	1:1,2	97	3	6700 ^b	3.2

a) molar ratio double bonds:silane, b) GPC in THF

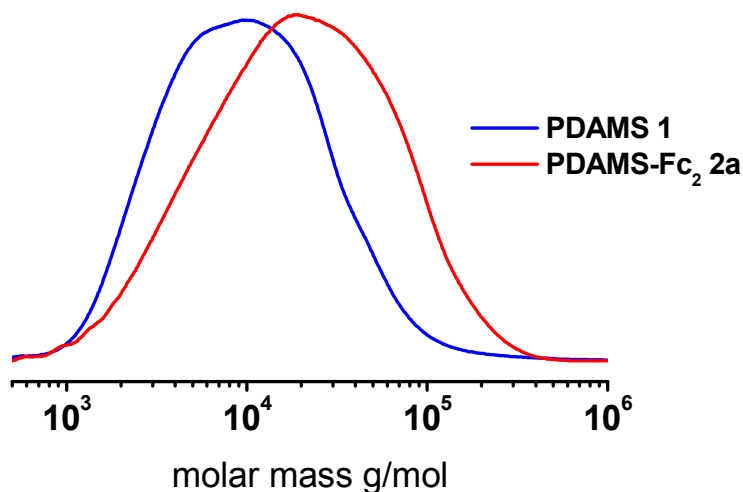


Fig. 3.15 GPC traces in CHCl₃ for polydiallylsilane before and after functionalization.

In Figure 3.16 the ¹H-NMR spectra for PDAMS **1** and PDAMS-Fc₂ **2a** are compared. Almost quantitative addition of the ferrocenylsilane is confirmed by disappearance of the signals between 6-4.8 ppm which can be assigned to the alkenyl groups. Ferrocene protons are visible at 4.45-4.25 and 4.20-3.95 ppm. The methyl group bound to SiFc₂ gives rise to a sharp signal at 0.49ppm clearly distinguishable from the Si-CH₃ groups of the polymer scaffold. The calculation of the degree of

functionalization is based on the ratio of the integrals for Si-CH₃ between -0.15 to -0.20ppm (representing the amount of AB₂ monomers) and ferrocene moieties.

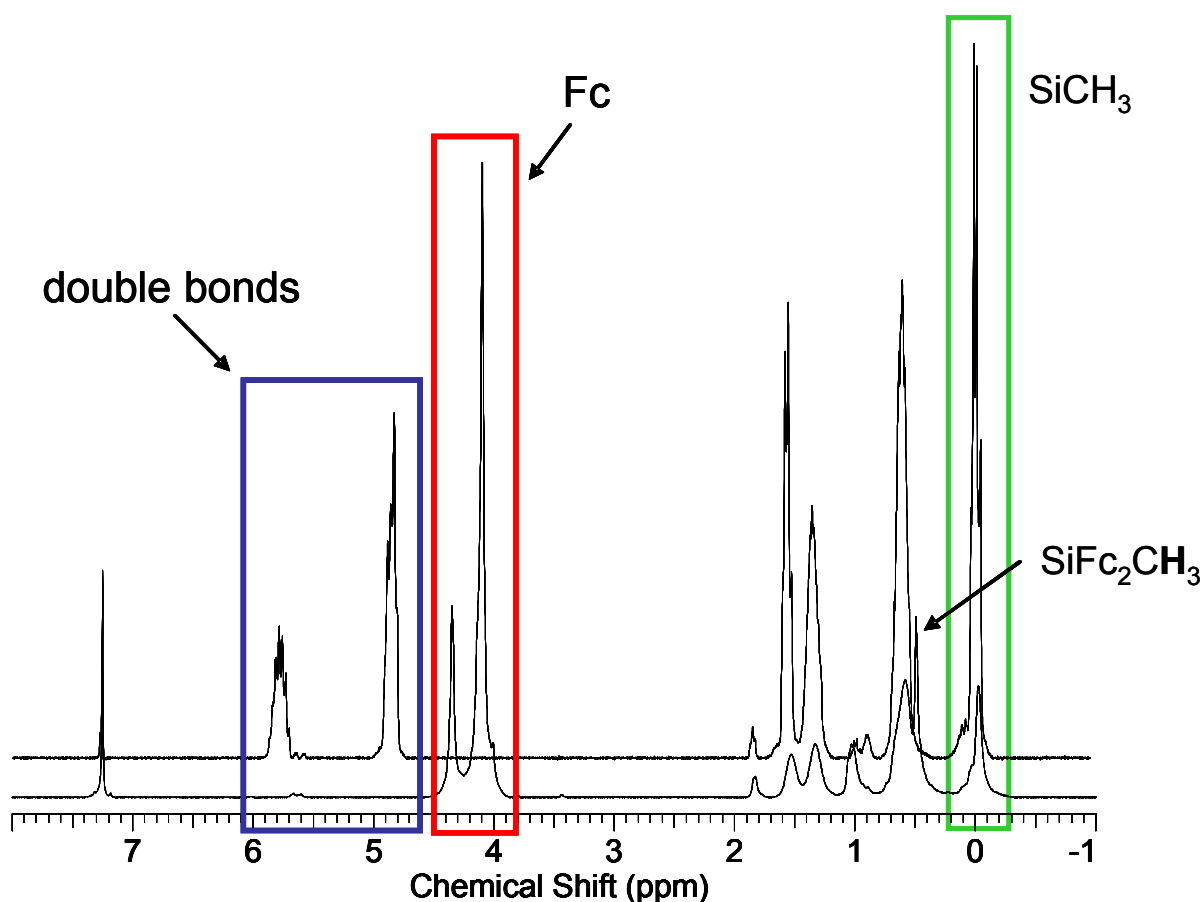


Fig. 3.16 ¹H-NMR spectrum for polydiallylsilane 1 (top) and functionalized polymer 2a (bottom).

Table 3.4 Degree of functionalization and glass transition temperature for PDAMS-Fc₂.

sample	Functionalization NMR	UV-vis	w%Fc	DSC T _g [°C]
1	-	-	-	-85
2a	90	90	67	3
2b	48	59	55	-19
2c	19	18	34	-52

In order to confirm the ferrocene content in the polymer the degree of functionalization was additionally determined by UV-vis spectroscopy. The ferrocene content was calculated by comparison with a calibration curve recorded for a dilution series of ferrocene in chloroform, using the absorption band at 445nm. The results are summarized in Table 3.4 and are in good accordance with the results obtained by NMR. Likewise, the glass transition temperature (T_g) was recorded for the polymers

and found to be in correlation with the ferrocene content. T_g increases from -85°C for polydiallylmethylsilane to 3°C for the polymer with 90% functionalization.

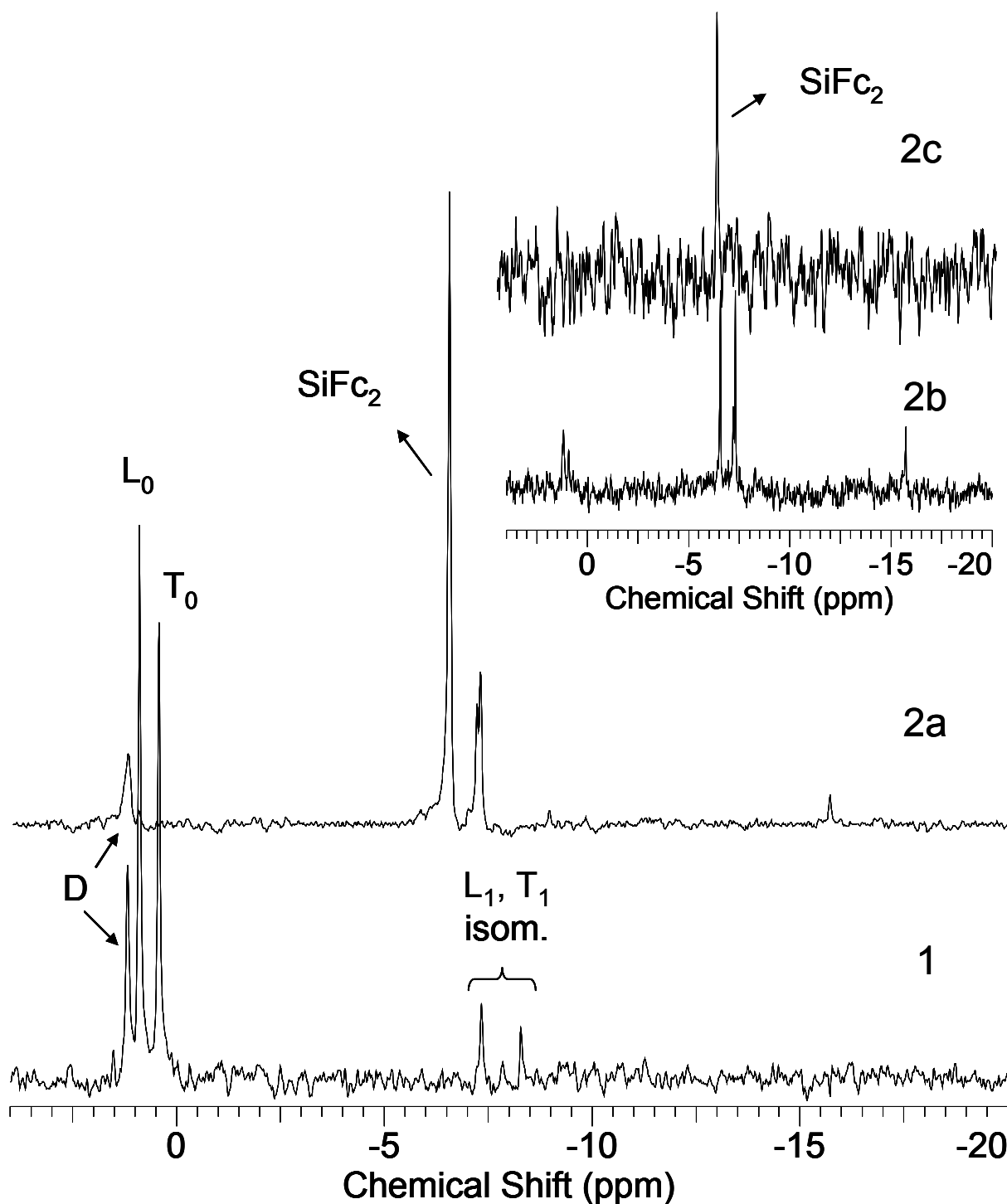


Fig. 3.17 ^{29}Si -NMR of polydiallylmethylsilane **1** and PDAMS- Fc_2 **2c**, **2b**, **2a** (from bottom to top).

In Figure 3.17 the ^{29}Si -NMR spectra for polydiallylmethylsilane (Chapter 3.3) and ferrocene-containing polymers are compared. After functionalization with diferrocenylmethylsilane a new signal at -6.54 ppm is present which can be assigned

to the added silane. Linear and terminal units, L_0 and T_0 , with allyl groups completely disappear after the reaction. They are either transformed into dendritic units after addition of ferrocenylsilane or they are shifted up-field due to isomerization (e.g. signal at -7.29 ppm). For polymer **2a** with a degree of branching of 90% only one signal at -6.54 ppm for $-\text{SiFc}_2\text{Me}$ is detected. Silicon branching units of the polymer structure are probably shielded by the ferrocene units at the periphery.

3.5.2 Ferrocene-modified polymethyldiundecenylsilane

Limiting factor in the functionalization of PDUMS is the significant amount of isomerized internal double bonds present in the polymer, which are unreactive in the functionalization by hydrosilylation. In Table 3.5 the functionalization results are presented. Despite the addition of a threefold excess of silane only 49% of the double bonds were accessible for reaction with diferrocenylsilane. A higher degree of substitution was achieved with ferrocenyldimethylsilane probably due to the lower steric hindrance.

Table 3.5 Results for functionalization of polymethyldiundecenylsilane.

sample	structure	reaction condition	ratio ^a	NMR		GPC(CHCl_3)	
				funct.	isom.	M_n	PDI
4	PMDUS	-	-	64	36	5600	2.2
5a	PMDUS- Fc_2	chlorobenzene, 60°C	1:3	49	51	5400	2.7
5b	PMDUS- Fc_2	pentane, RT	1:1	24	76	5900	2.7
6	PMDUS-Fc	chlorobenzene, 60°C	1:1,2	71	29	7000 ^b	2.1

As an example the ^1H -NMR for PDUMS-Fc **6** is shown in Fig 3.18. The polymer scaffold is represented by signals for the isomerized double bonds (blue), the methylene groups of the polymer backbone between 1.45-1.05 ppm and the Si-CH_3 signal at -0.09 ppm. The methylene and methyl group next to ferrocene are shifted down-field resulting in signals at 0.75-0.58 ppm and 0.20 ppm, respectively. All functionalized polymers based on PDUMS exhibit two signals in ^{29}Si -NMR. The silicon atoms of the polymer backbone result in a signal at 3.02 ppm, unchanged from the starting polymer. Depending on the ferrocenyl compound signals at -2.31

ppm or -5.91 ppm are observed for the added ferrocenyldimethylsilane or differrocenylmethylsilane.

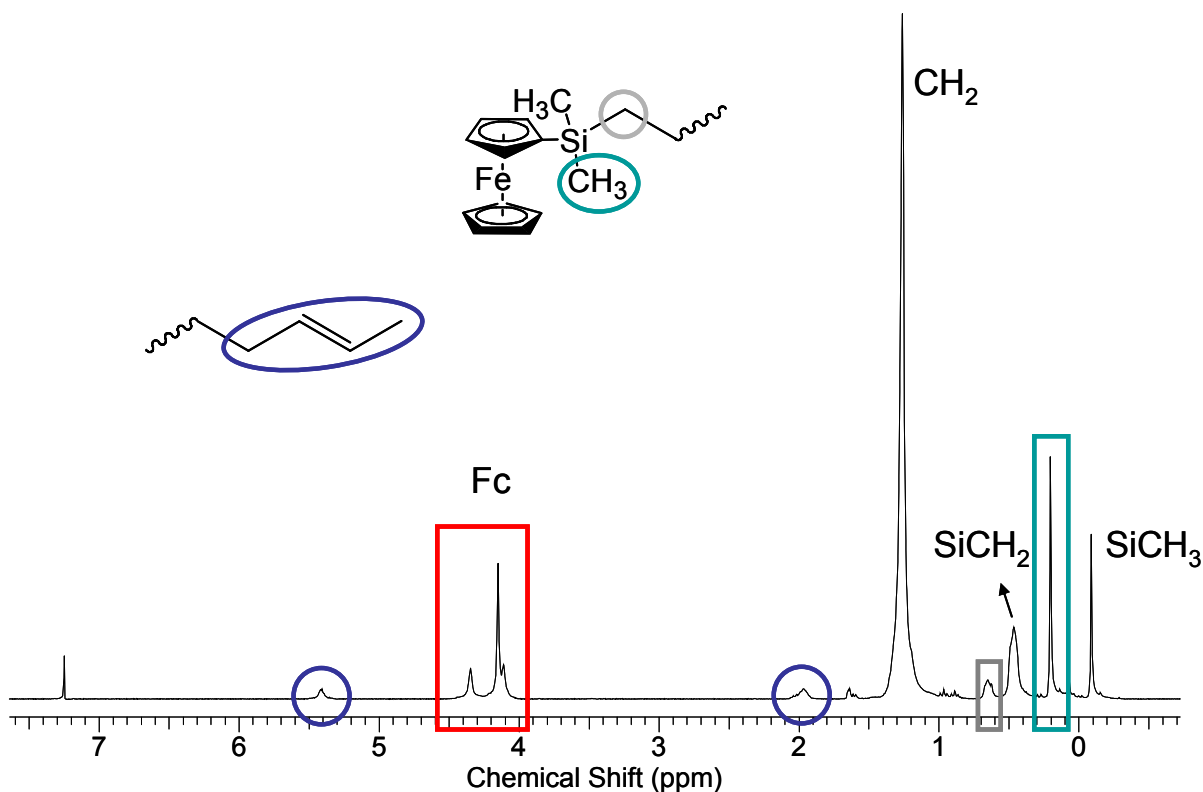


Fig. 3.18 ^1H -NMR spectrum for PDUMS-Fc **6**.

3.6 Copolymerization of AB₂-monomers and HSiFc₂Me

Despite the two step approach consisting of a polymerization and a subsequent functionalization step, ferrocenyl-containing polymers can also be obtained by copolymerization of AB_2 monomers with functional AX monomers (Fig 3.19). Here, the AX monomer ferrocenylsilane acts as a monofunctional end-capper. The degree of functionalization is governed by the molar ratio of the monomers.

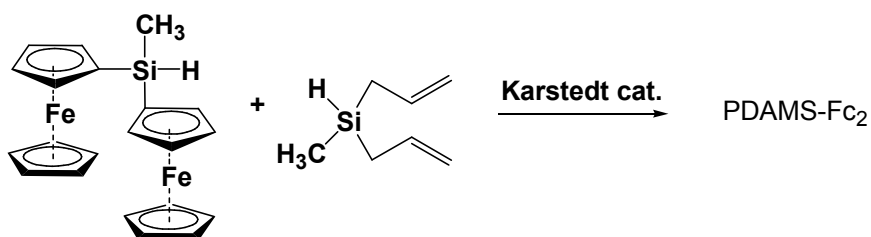


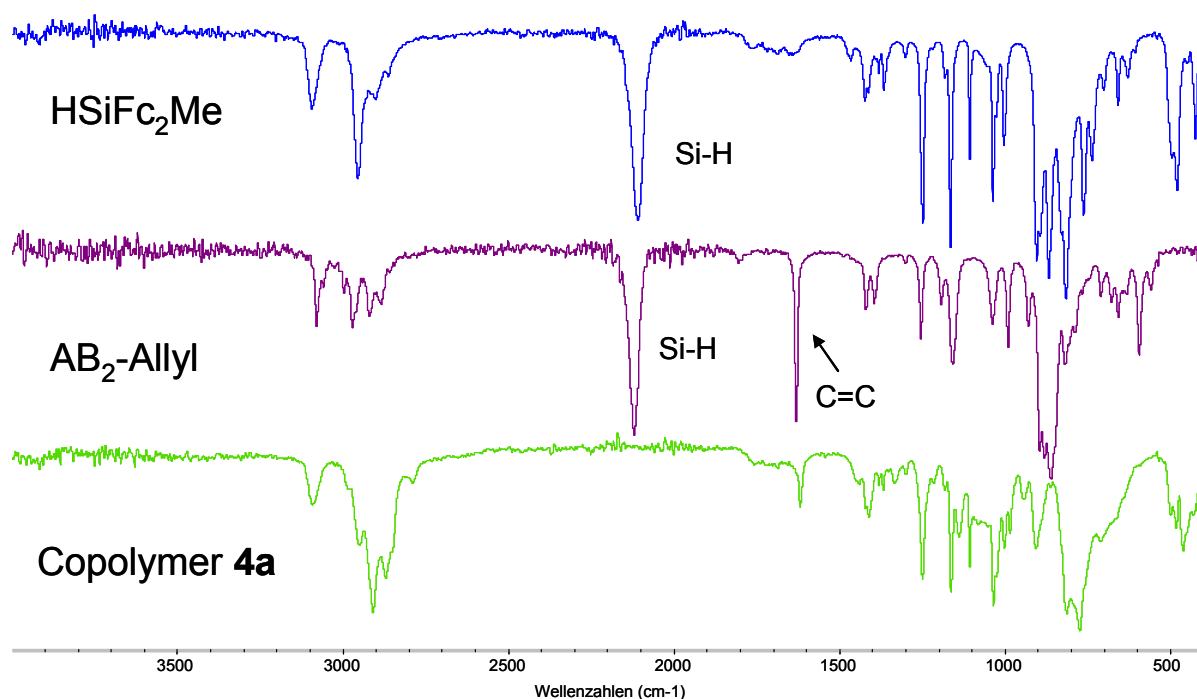
Fig. 3.19 Copolymerization of AB₂ monomer with functional AX monomer.

Table 3.6 Results for copolymerization of AB₂ monomers with HSiFc₂Me.

sample	structure	ratio ^a	Functionalization			w%Fc	DSC T _g [°C]	GPC(CHCl ₃)	
			theor.	NMR	UV-vis			M _n	PDI
7a	PDAMS-Fc ₂	1:1	100	59	56	59	-11	3100	2.0
7b	PDAMS-Fc ₂	2:1	50	50	61	56	-17	2500	2.5
7c	PDAMS-Fc ₂	3:1	33	35	39	48	-32	2800	2.7
8a	PMDUS-Fc ₂	1:1	100	73	75	42	-58	2400	2.4
8b	PMDUS-Fc ₂	2:1	50	31	39	24	-73	3200	2.5
8c	PMDUS-Fc ₂	3:1	33	23	29	19	-74	4400	3.3

a) molar ratio AB₂/AX

In Table 3.6 the polymerization results for different stoichiometric ratios of the monomers are combined. As expected larger amounts of the AX monomer result in higher degrees of functionalization. Changing the molar ratio allows for a control of the ferrocene content, although the theoretically predicted values are not always achieved. In Fig. 3.20 the IR spectra for HSiFc₂Me, AB₂-allyl and a polymer mixture after complete conversion of monomers are compared. Completion of the reaction is clearly indicated by the disappearance of the Si-H vibration at ~2100cm⁻¹ in FT-IR spectra. NMR characterization is identical to the previously described signal assignment and analysis.

**Fig. 3.20** Copolymerization followed by FT-IR spectroscopy : HSiFc₂Me (top), AB₂-allyl (middle) and polymerization mixture after complete conversion of Si-H (bottom).

Thus, copolymerization offers a simple one-step approach to functionalized polycarbosilanes with varying degree of substitution. However, molecular weights are limited due to the terminating effect of the monofunctional monomer. Additionally, yields are superior when the two-step approach is applied.

3.7 Electrochemical characterization

3.7.1 Cyclic voltammetry

Cyclic voltammetry (CV) is a versatile analytical technique for measuring redox events. Electrochemical behaviour can be studied for species diffusing to an electrode, interfacial phenomena at an electrode surface and bulk properties of materials in or on electrodes^{34, 35}. Typically, three-electrode set-ups are used for the measurement consisting of reference electrode, working electrode and counter or auxiliary electrode (Fig 3.21 A). Cyclic voltammetry is a dynamic electrochemical method in which the potential applied to an electrochemical cell is ramped linearly versus time (Fig. 3.21.B).

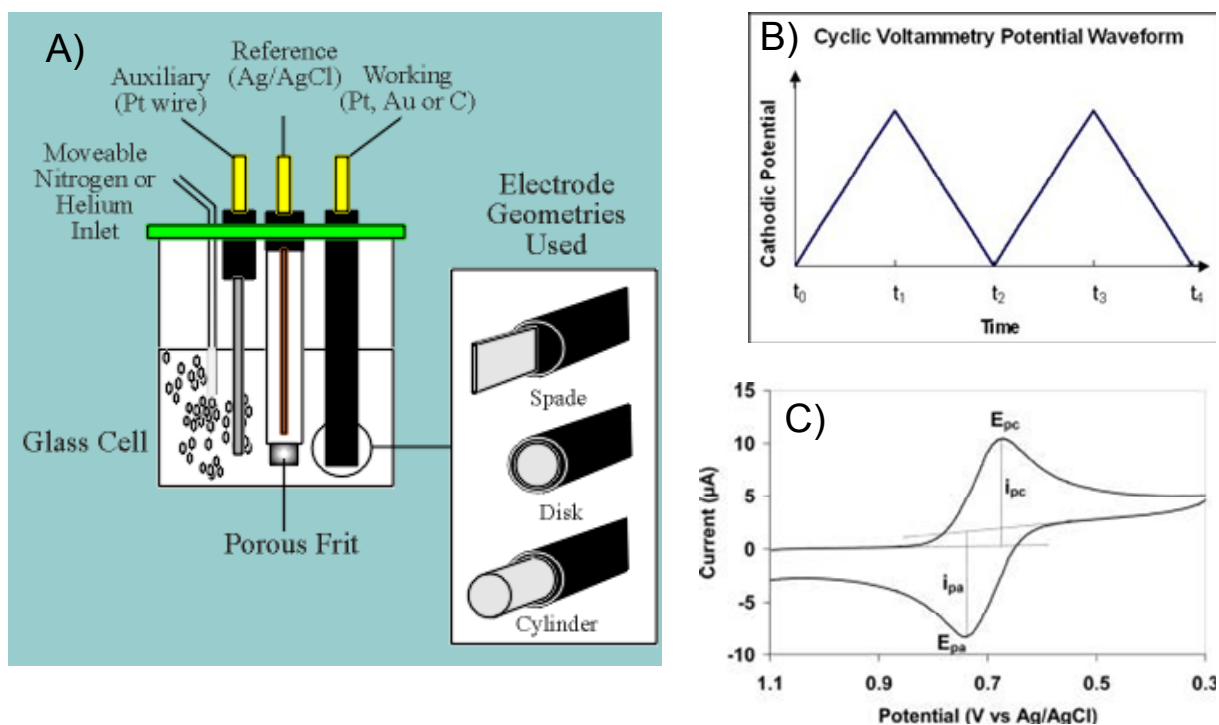


Fig. 3.21 A) Three-electrode cell with reference electrode, working electrode and auxiliary or counter electrode B) Plot of potential versus time in cyclic voltammetry experiment C) Example for cyclic voltammogram.

The ramping is known as the scan rate ν (V/s). The potential of the working electrode is controlled versus a reference electrode (in the following experiments this is a saturated calomel electrode (SCE)). The result of cyclic voltammetry is a plot of the current I_p flowing between working electrode and the counter electrode versus the applied potential V (Fig 3.21 C). During the forward scan a current peak is observed for any analyte that is oxidized throughout the examined potential range. The current increases as the potential approaches the oxidation potential of the analyte, but then declines as the analyte is depleted close to the electrode surface. For reversible redox processes in the reverse scan the oxidized species formed at the electrode are reduced and a current flow of reversed polarity is observed. The key parameters of a cyclic voltammogram are the magnitudes of the anodic (I_{pa}) and cathodic peak current (I_{pc}) and the anodic (E_{pa}) and cathodic peak potential (E_{pc}) as labelled in Fig. 3.21 C). When the electron transfer between analyte and electrode is fast, the current is limited by the diffusion of analyte to the electrode surface. In this case of a diffusion-controlled process the current I_p is proportional to the square root of the scan rate ν , as described by the Randles-Sevcik equation:

$$I_p = (2,69 \times 10^5) n^{3/2} A D^{1/2} c \nu^{1/2} \quad (\text{Equation 3.1})$$

with n number of electrons transferred, A electrode area (cm^2), D diffusion coefficient (cm^2/s) and c concentration (mol/cm^3). In an ideally reversible redox system the difference between the oxidation (E_{pa}) and the reduction potential (E_{pc}) is 59mV for a one electron process and the ratio for the maximum peak current I_{pa}/I_{pc} is near unity (Fig 3.21 C)). The formal reduction potential $E_{1/2}$ of the analyte is defined as $E_{1/2} = (E_{pa} + E_{pc})/2$. Deposition of thin films of redox-active material on electrode surfaces alters the result of a cyclic voltammogram. At very low scan rates these coated electrodes are characterized by a symmetric cyclic voltammetric peak shape ($E_{pa} - E_{pc} \sim 0$). Peak currents I_p in this case are directly proportional to the scan rate ν :

$$I_p = \frac{F^2}{4RT} A \Gamma_s \nu \quad (\text{Equation 3.2})$$

$$\text{and } \Gamma_s = \frac{Q}{FA} \quad (\text{Equation 3.3})$$

with F Faraday's constant, R gas constant, T temperature in K, Γ_s moles of analyte per cm^2 of electrode surface and Q charge. In some cases square wave voltammetry was utilized as an additional tool to characterize the redox behavior. This method is a highly sensitive pulse technique in which a waveform composed of a symmetrical wave, superimposed on a base staircase potential is applied. The current is sampled twice during each square-wave cycle detecting forward current as well as the reverse current. A plot of the net current is symmetrical about the half-wave potential and the peak current is proportional to concentration.

3.7.2 Characterization in solution

An important aspect of this chapter was to the evaluation of the redox properties of the prepared ferrocenyl-functionalized hyperbranched polymers in view of sensor applications. Thus, electrochemical behaviour of the synthesized compounds was studied by cyclic voltammetry in CH_2Cl_2 solutions containing 0.1M Bu_4NPF_6 as supporting electrolyte at platinum electrodes. The influence of the architecture on the electrochemical response of the ferrocenyl units was analyzed. Depending on the distance of the metal centers in the structure the ferrocenyl groups can either behave as isolated species or exhibit mutual interaction. Electrochemical data for selected polymers are presented in Table 3.7.

Table 3.7 Cyclic voltammetric data for ferrocenyl-functionalized polymers in 1mM solution in CH_2Cl_2 .

sample	structure	wt%Fc	$E'_{1/2}$ [V]	$E''_{1/2}$ [V]	ΔE [mV] ^c
2a	PDMAS- Fc_2	67	0,40 ^b	0,55	150
2b	PDMAS- Fc_2	55	0,40 ^a	0,55	150
7a	PDMAS- Fc_2	59	0,40 ^a	0,56	160
3	PDMAS-Fc	50	0,43 ^b	-	-
5a	PDMUS- Fc_2	33	0,38	0,55	170
8a	PDMUS- Fc_2	42	0,41	0,59	180
6	PDMUS-Fc	25	0,41	-	-

a) after addition of acetonitrile b) 0.1mM solution c) $\Delta E = E''_{1/2} - E'_{1/2}$

As expected, a single reversible oxidation wave is observed for the polymers functionalized with HSiMe_2Fc **3** and **6** at $E_{1/2} = 0.43$ and 0.41V, respectively. These

values resemble those observed for perfectly branched carbosilane dendrimers functionalized with isolated ferrocene units ($E_{1/2}=0.40\text{--}0.44\text{V}^{15}$) in the periphery. Square wave voltammetry showed only one wave, confirming that the oxidation of all ferrocenyl units occurs at the same potential. Therefore, in these compounds the ferrocenyl moieties are essentially non-interacting redox centers. Apparently, the hyperbranched structure of the polymer scaffold has no peculiar influence on the redox potential. In Figure 3.22 the cyclic voltammogram for polymer **3** is shown at different scan rates. The plot of peak current versus square root of scan rate confirms a linear relationship indicating a diffusion controlled process. This means that electron transfer is fast and diffusion of the polymer to the electrode surface is the rate-limiting process.

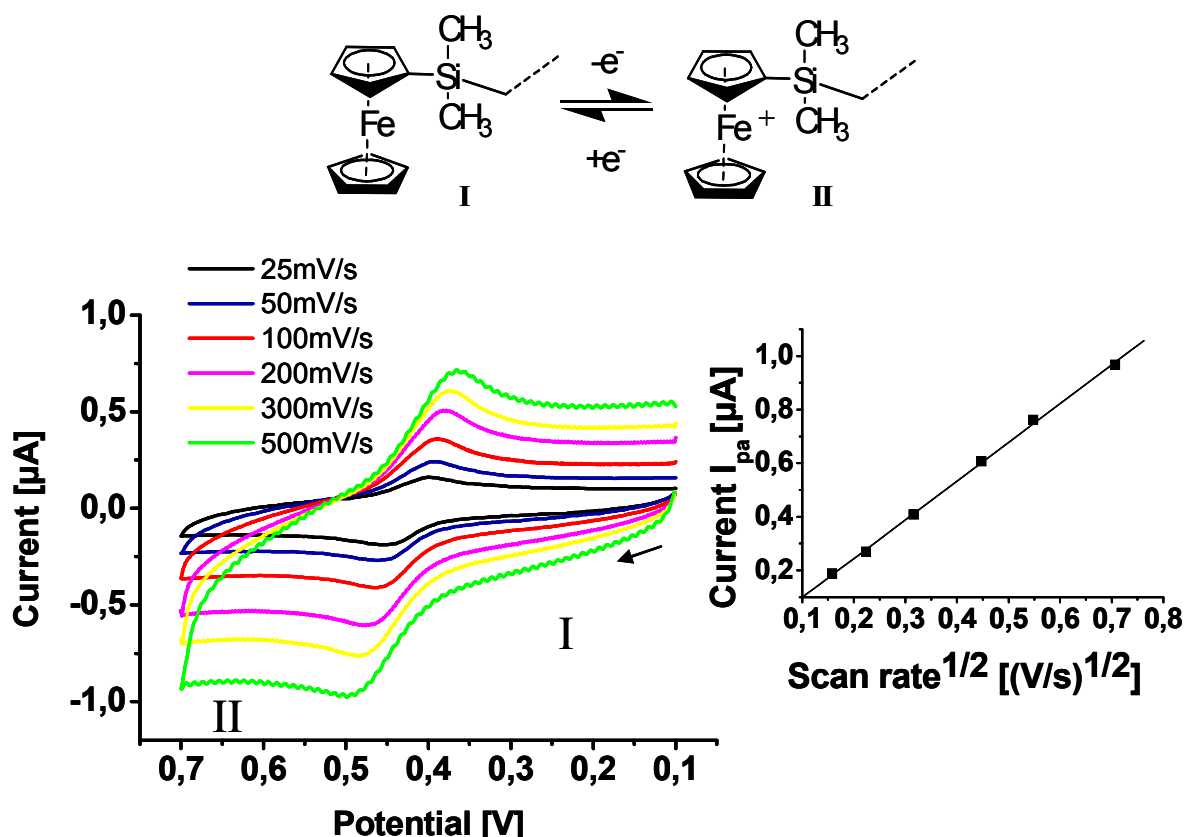


Fig. 3.22 Top: oxidation process in functionalized polymer; bottom: Cyclic voltammogram at a platinum disk electrode and different scan rates in CH_2Cl_2 (left) and plot of peak current versus scan rate^{1/2} (right).

The cyclic voltammogram for polymers functionalized with HSiMeFc_2 is characterized by two well-separated oxidation waves, consistent with the existence of appreciable interaction between the two iron centers bridged by silicon. As an example, the cyclic voltammogram of polymer **2b** is shown in Fig. 3.23. The potential scan starts at 0.1V,

where no electrolysis occurs. At about 0.3V the oxidation of ferrocene units starts, reaching the maximum current at ~0.40V. Subsequently the current decreases until a second maximum is reached at ~0.55V. In Figure 3.23 (top) the different stages of the redox process are presented. Oxidation of the first of the silicon-bridged ferrocenes results in a shift of the oxidation potential for the second one, i.e., the charge in close proximity hampers oxidation of the second ferrocene.

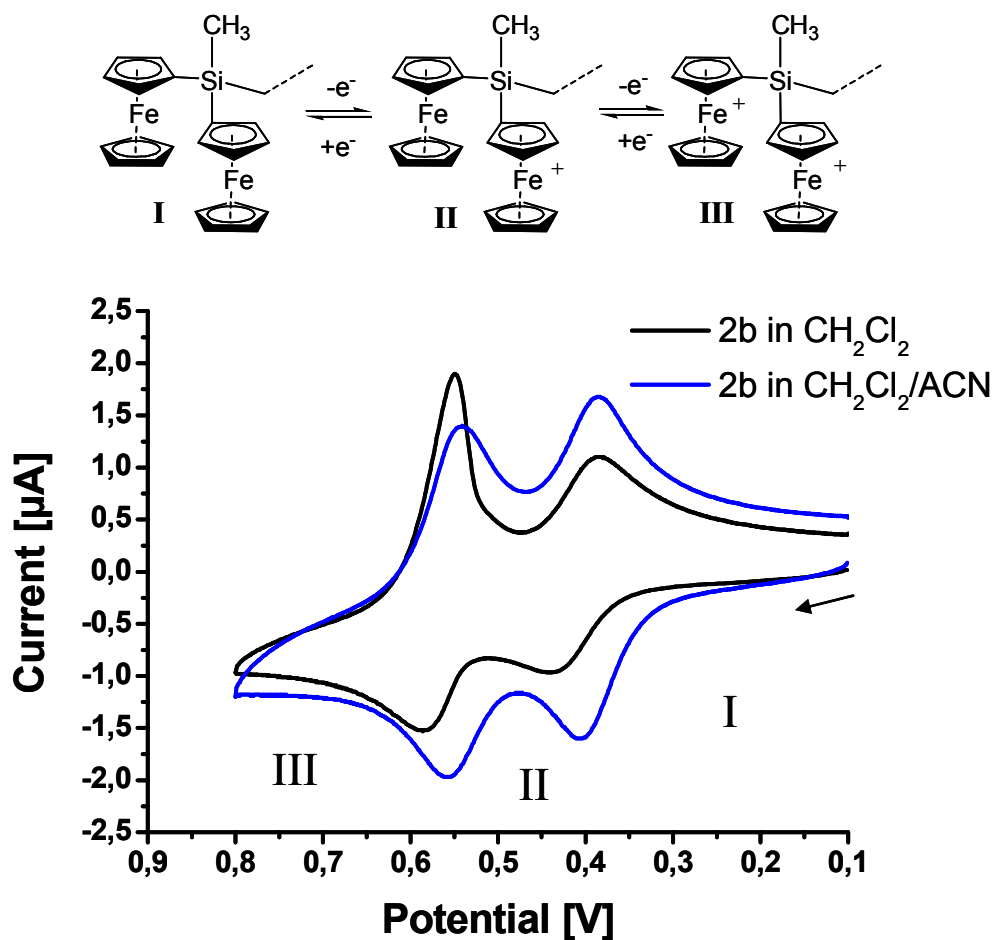


Fig. 3.23 Top: oxidation process in functionalized polymer; bottom: Cyclic voltammogram at a platinum disk electrode and scan rate of 100mV/s for 1mM solutions of **2b** in CH_2Cl_2 and CH_2Cl_2 /acetonitril.

Likewise, square wave voltammetry reveals two separate oxidation waves with the same integral intensity (Fig 3.24), indicating that an equal number of electrons are transferred in both redox processes. The cyclic voltammogram of **2b** in dichloromethane displays a sharp peak with enhanced intensity when the potential is scanned back. This so-called precipitation or stripping peak is a result of a change in solubility of the polymer accompanied by a change in oxidation state. The complete

oxidation of the polymer results in precipitation of the polymer on the electrode surface. Thus, on the reverse scan the deposited polymer film is reduced and (partly) redissolved.

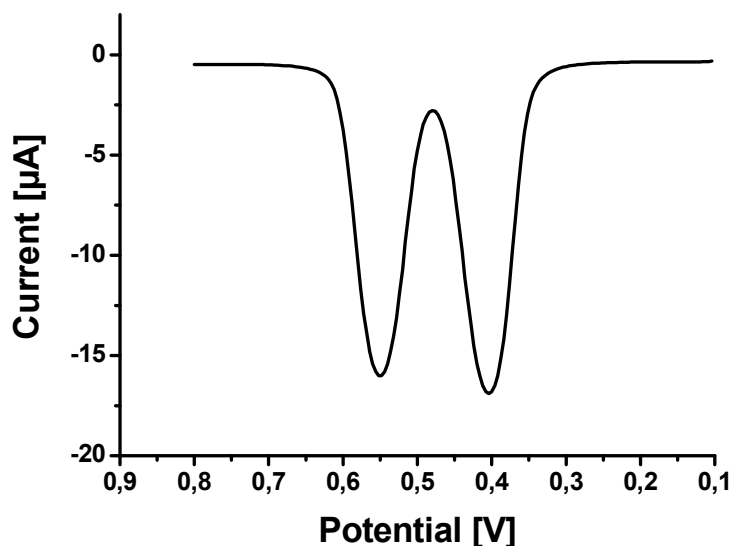


Fig. 3.24 Square wave voltammogram for **2b**.

In addition, upon continuous scanning in the range between 0 and +1 V versus SCE an increase in the peak current with each successive scan can be observed. This indicates the formation of an electroactive film on the electrode surface. The amount of polymer adsorbed to the electrode can be controlled by the number of scans. Additionally, the electrode can be modified by electrodeposition at a fixed potential higher than the oxidation potential of ferrocene. Here, the amount of polymer deposited to the surface can be tuned by the time the potential is applied. The result of the electrode modification will be presented in the next section. If a small amount of acetonitrile (ACN) is added to the CH_2Cl_2 electrolyte solution, the cathodic stripping peak disappears and two reversible oxidation peaks of the same height are observed due to the improved solubility of the oxidized polymer (Fig. 3.23 blue). It is known that in linked metallocenes the difference in the redox potential ΔE observed for the two waves is a measure of the degree of electronic interaction between the two metal sites³⁶. A comparison of the ΔE values for PDAMS- Fc_2 (150-160 mV) and PMDUS- Fc_2 (170-180 mV) indicates that surprisingly the magnitude of the interaction between the neighboring iron sites in PMDUS is slightly larger than for PDAMS.

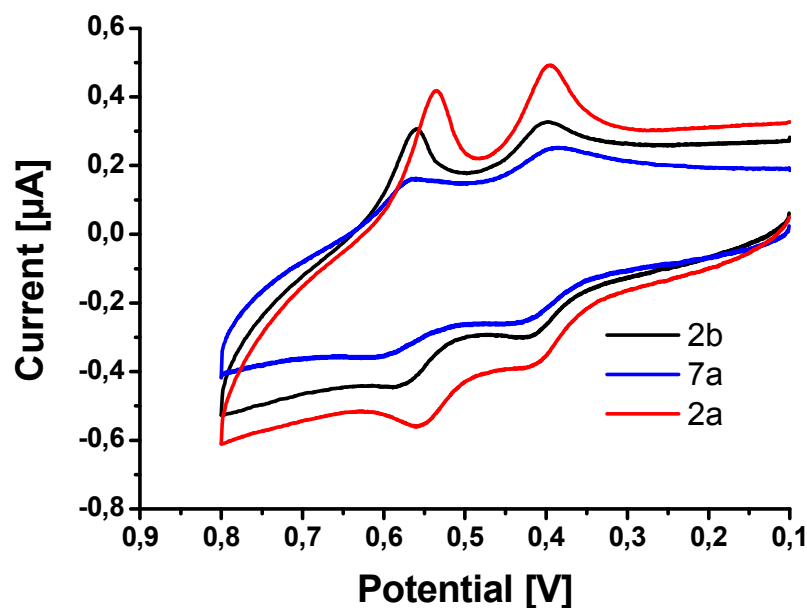


Fig. 3.25 Cyclic voltammogram at a platinum disk electrode and scan rate of 100mV/s in CH_2Cl_2 for 0.1mM solutions of PDMS- Fc_2 **2a**, **2b** and **7a**.

In Figure 3.25 polymers of the structure PDMS- Fc_2 are compared. Polymers **2b** and **7a** possess essentially the same degree of functionalization. However, molecular weights are different with 6500g/mol and 3100g/mol, respectively. Upon oxidation polymer **2b** turns insoluble and a precipitation peak is observed on the reverse scan. This polymer bears a higher number of ferrocene groups per molecule compared to the lower molecular weight compound, resulting in a higher average charge upon oxidation. The precipitation peak is even more distinct for the polymer **2a** with the highest degree of functionalization and molecular weight. The lower ferrocene content for the polymers based on polymethyldiundecenylsilane keeps the polymers soluble upon oxidation, consequently no precipitation is observed for these polymers.

3.7.3 Modification of electrodes

A remarkable feature of the redox behavior of hyperbranched ferrocenyl-functionalized polymers is their ability to modify electrode surfaces. The polymers can be deposited on electrode surfaces either by repeated cycling of the potential between 0 and 1V or by controlled potential electrolysis at a fixed potential of 0.7V. Therefore, the amount of electroactive material deposited can be controlled with the electrolysis time or the number of scans. Applying these methods modification of electrodes with all hyperbranched ferrocenyl-containing polymers was successful.

The stability of the modified electrodes can be tested by cyclic voltammetry in fresh solutions containing only electrolyte. Repeated cycling in acetonitrile results in a loss of electroactive material on the surface and degradation of the modified electrode due to the solubility of the oxidized species in this solvent. In contrast, electrodes exhibit a reproducible and persistent response in dichloromethane or even water. In Table 3.8 voltammetric data for modified electrodes are summarized.

Table 3.8 Cyclic voltammetric data for electrodes modified by electrodeposition in 0.1mM polymer solutions in CH₂Cl₂.

sample	structure	wt%Fc	$E'_{1/2}$ [V]	$E''_{1/2}$ [V]	ΔE [mV] ^c
2a	PDMAS-Fc ₂	67	0,39 ^a	0,52	130
2b	PDMAS-Fc ₂	55	0,41 ^b	0,55	150
7a	PDMAS-Fc ₂	59	0,41	0,55	140
3	PDMAS-Fc	50	0,41 ^a	-	-
5a	PDMUS-Fc ₂	33	0,40 ^b	0,53	130
8a	PDMUS-Fc ₂	42	0,42 ^{a,b}	0,55	140
6	PDMUS-Fc	25	0,40 ^b	-	-

a) prepared by 50 redox cycles in polymer solution; b) prepared in 1mM solution

The voltammetric response of an electrodeposited film of **3** in dichloromethane is shown in Fig 3.27. A well-defined symmetrical oxidation–reduction wave is observed, characteristic of a surface confined redox couple, with the expected linear relationship of peak current to potential scan rate (Fig 3.27 right). Repeated scanning does not alter the voltammograms, demonstrating that films are stable to electrochemical cycling. A formal potential value of $E_{1/2}=0.41$ was found for films of **3**, which is nearly identical to the formal potential of the polymer in solution. The surface coverage of electroactive ferrocenyl sites in the film Γ_s was determined from the integrated charge of the cyclic voltammetric wave and was found to be $\Gamma_s=3.3 \times 10^{-10}$ mol ferrocene units/cm² for the example shown in Fig. 3.27. The modified electrode can also be utilized in aqueous solution as shown in Fig. 3.28. Here, the peak shape is slightly sharper with a smaller full width at half-maximum, indicating attractive interactions between the ferrocene moieties. However, the polymer-coated electrodes are stable upon repeated cycling and show the expected linear dependence between peak current and scan rate. Modified electrodes that can

be applied in water are especially interesting when applications in biosensors are targeted, e.g., as mediators in amperometric glucose sensors.

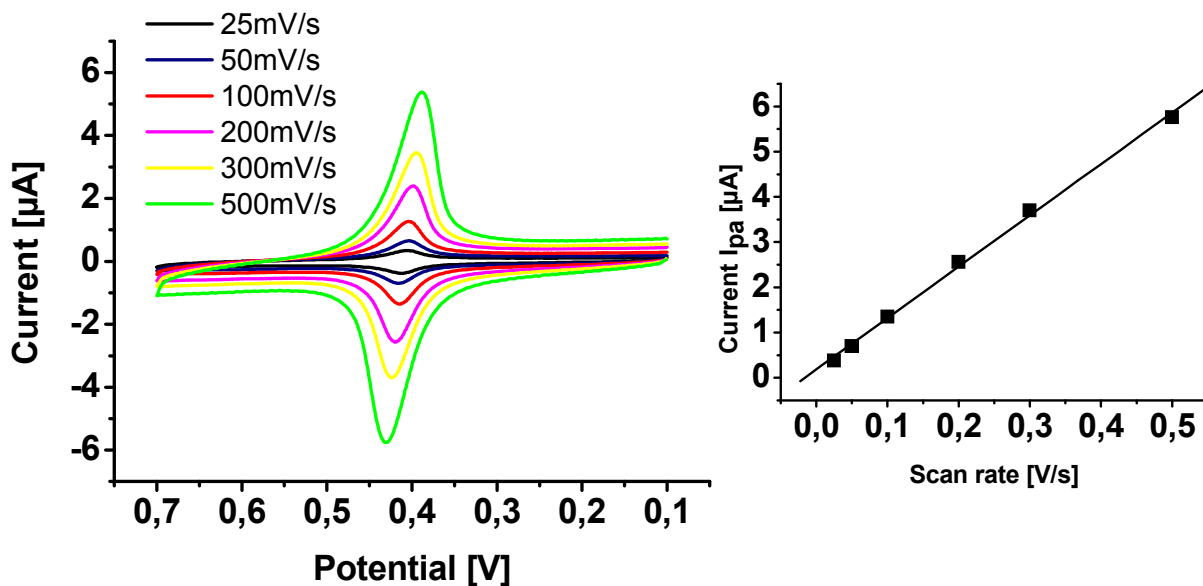


Fig. 3.26 Voltammetric response of a platinum electrode modified with polymer **3** measured in $\text{CH}_2\text{Cl}_2/0.1\text{M NBu}_4\text{PF}_6$ (left); Scan rate dependence of the peak current (right).

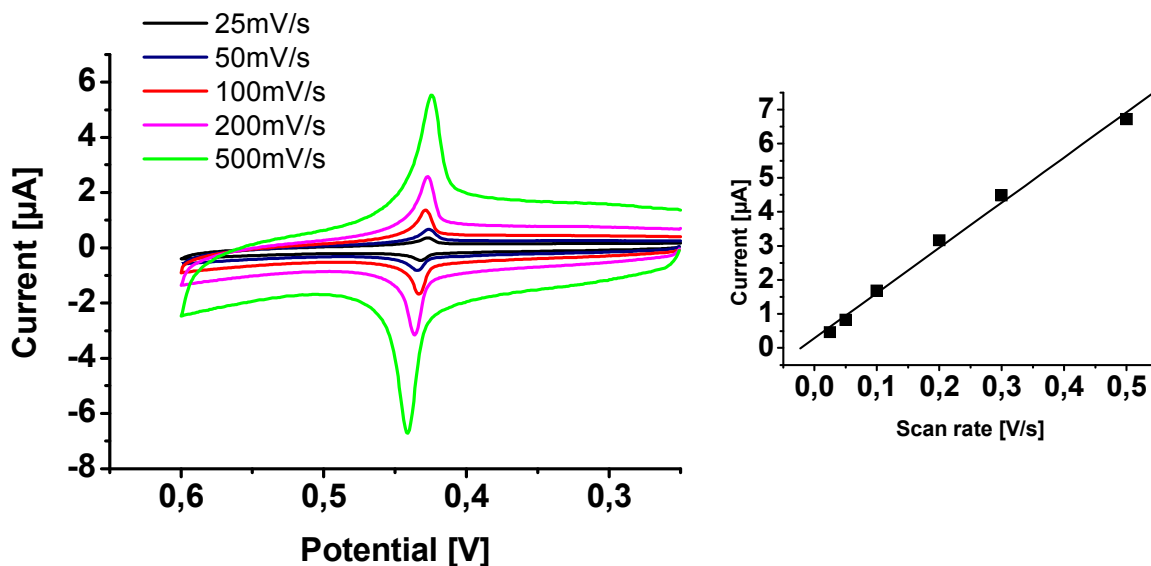


Fig. 3.27 Voltammetric response of a platinum electrode modified with polymer **3** measured in $\text{H}_2\text{O}/0.1\text{M LiClO}_4$ (left); Scan rate dependence of the peak current (right).

As a representative example for differrocenylsilane modified polymers the response of an electrode coated with polymer **2a** is shown in Fig. 3.28 in CH_2Cl_2 (left) and

water (right). Two well-defined oxidation-reduction waves are observed in dichloromethane with formal potential values of $E'_{1/2}=0.39\text{V}$ and $E''_{1/2}=0.52\text{V}$ with a linear relationship between peak current and scan rate. The surface coverage of electroactive ferrocenyl sites in the film was found to be $\Gamma_S=8.0\times 10^{-10}\text{mol ferrocene cm}^2$. The peak splitting between positive and negative scans is $<10\text{mV}$ for scan rates up to 100mV/s , which indicates that the rate of electron transfer is rapid on the time scale.

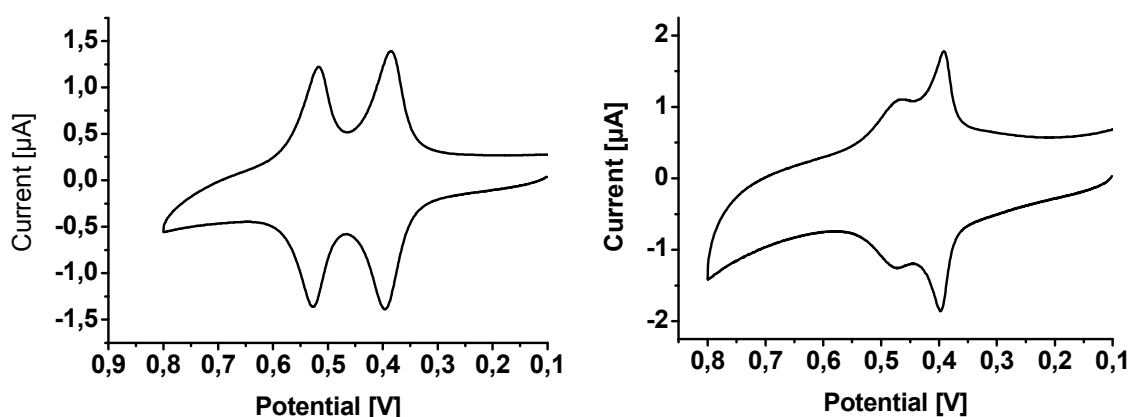


Fig. 3.28 Voltammetric response of a platinum electrode modified with polymer **2a** measured in $\text{CH}_2\text{Cl}_2/0.1\text{M NBu}_4\text{PF}_6$ (left) and $\text{H}_2\text{O}/0.1\text{M LiClO}_4$ (right).

The voltammetric data presented clearly indicates the surface-confined nature of the electroactive polymer film. Cycling of the electrode in water/electrolyte solution gives a stable voltammetric response, as well (Fig. 3.28). However, the shape of the oxidation-reduction wave is no longer symmetrical. After oxidation the initially non polar polymer film turns more polar due to the positive charge. It is assumed that this significantly influences the interaction with the polar solvent.

3.8 Conclusion

In the preceding chapter the synthesis of hyperbranched polycarbosilanes was described. $^1\text{H-NMR}$ spectroscopy was applied as a standard technique for an estimation of the degree of branching of polydiallylmethylsilane. Suitable ferrocenylsilanes were synthesized in order to functionalize polycarbosilanes via hydrosilylation. The ferrocenyl-functionalized polymers were prepared by modification of the preformed polymers and by copolymerization of AB_2 carbosilane monomers

with the ferrocene compounds (Fig. 3.29). The degree of functionalization for the addition to preformed polycarbosilane can be >90%, if an excess of ferrocenylsilane and suitable reaction conditions are applied. The degree of functionalization obtained by copolymerization can be tuned by the ratio of carbosilane monomer to ferrocenylsilane, however it does not exceed 70%. In conclusion, both approaches are feasible for the synthesis of ferrocenyl functionalized polymers. Copolymerization of AB₂ carbosilane and AX ferrocenylsilane monomers represents a facile pathway towards this class of polymers. However, modification of preformed polymers may be advantageous in cases where higher molecular weights, degrees of functionalization and yields are desired.

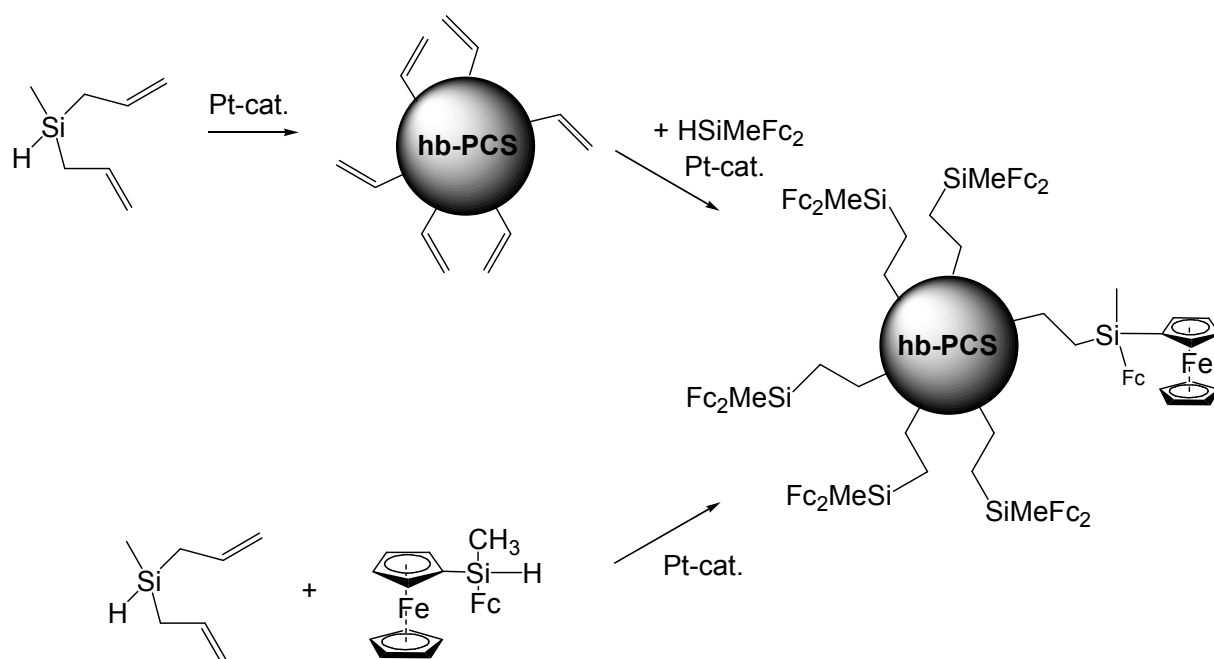


Fig. 3.29 Synthesis of ferrocenyl-functionalized polycarbosilanes by functionalization and copolymerization.

The ferrocene-functionalized polycarbosilanes were characterized by cyclic voltammetry in solution and confined on electrodes. The possibility to modify electrode surfaces with organometallic hyperbranched polymers has been demonstrated. The resulting electrodes are stable even after repeated cycling in suitable organic solvents or aqueous solution. In conclusion, hyperbranched polymers with isolated and electronically communicating organometallic units were prepared that can be used for the preparation of persistent modified electrodes. The presented work has proven that ferrocenyl-functionalized hyperbranched polymers

exhibit similar electrochemical properties as the analogous dendrimers. Thus, they represent a readily available alternative in cases where a precisely defined number of redox centers is not necessary.

3.9 Experimental

3.9.1 Materials

Allylbromide, 11-bromoundec-1-en, dichloromethylsilane, chlorodimethylsilane, ferrocene were used as received. Pentane and diethyl ether were dried by refluxing them over sodium/benzophenone and were distilled prior to use. Platinum-divinyltetramethyldisiloxane complex (Karstedt catalyst) in xylene with 2.1-2.4% platinum concentration was purchased from Gelest.

Methyldiundec-10-enylsilane. The monomer was synthesized according to literature procedures^{25, 37} using 50g (21.4mmol) 11-bromoundec-1-en, 26.1g (1,1mol) magnesium and 8.21g (7,1mmol) dichloromethylsilane. Yield: 17,4g (75%); bp 144-149°C, 0,2mbar.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 5.83 (m, 2H, -CH=CH₂); 4.97 (dd, 4H, -CH=CH₂); 3.77 (m, 1H, Si-H); 2.05 (m, 4H, -CH₂-CH=CH₂); 1.47-1.14 (m, 28H, CH₂); 0.58 (m, 4H, Si-CH₂); 0.05 (d, J=3.68Hz, 3H, Si-CH₃).

Diallylmethylsilane. The monomer was synthesized according to literature procedures^{25, 37} using 68.96g (0.57mol) allylbromide, 69.28g (2.85mol) magnesium and 21.86g (0.19mol) dichloromethylsilane. Yield: 13.82g (57%); bp 123°C.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 5.78 (m, 2H, -CH=CH₂); 4.95-4.83 (m, 4H, -CH=CH₂); 3.79 (m, 1H, Si-H); 1.68-1.52 (m, 4H, -CH₂-CH=CH₂); 0.09 (d, J=3.67Hz, 3H, Si-CH₃).

hb-PMDUS. Under nitrogen atmosphere 10μl (0.001 mmol Pt) Karstedt catalyst solution were added to 0.5g (1.4mmol) methyldiundec-10-enylsilane in 2.5ml pentane and stirred for 24h. The polymer was precipitated in methanol and further purified by dialysis (MWCO 1000g/mol). Yield: 0.37g (74%).

^1H -NMR (300 MHz, CDCl_3) δ [ppm]: 5.81 (m, $-\text{CH}=\text{CH}_2$); 5.44-5.37 (m, $-\text{CH}=\text{CH}-$); 5.03-4.88 (m, $-\text{CH}=\text{CH}_2$); 2.03 (m, $-\text{CH}_2-\text{CH}=\text{CH}_2$); 1.98-1.90 (m, $-\text{CH}=\text{CH}-\text{CH}_2-$); 1.66-1.56 (m, $-\text{CH}=\text{CH}-\text{CH}_3$); 1.45-1.07 (m, CH_2 polymer backbone); 0.55-0.32 (m, $\text{Si}-\text{CH}_2$); -0.10 (s, $\text{Si}-\text{CH}_3$). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: 139.25 ($-\text{CH}=\text{CH}_2$); 131.71, 130.92, 124.49, 123.57 ($-\text{CH}=\text{CH}-$); 114.08 ($-\text{CH}=\text{CH}_2$); 33.83 ($-\text{CH}_2-\text{CH}=\text{CH}_2$); 32.64 ($\text{CH}_2-\text{CH}=\text{CH}-$); 29.72, 29.58, 29.43, 29.36, 29.19, 28.98, 26.87, 23.93 (CH_2 polymer backbone); 17.94 ($-\text{CH}=\text{CH}-\text{CH}_3$); 13.90 ($\text{Si}-\text{CH}_2$); -5.12 ($\text{Si}-\text{CH}_3$). ^{29}Si -NMR (60 MHz, CDCl_3) δ [ppm]: 3.02.

hb-PDAMS. Under nitrogen atmosphere 100 μl (0.01 mmol Pt) Karstedt catalyst solution were added to 3.0 g (23.8 mmol) diallylmethylsilane and stirred for 24 h. The polymer was dissolved in 5 ml pentane and purified by precipitation in methanol. Yield: 2.6 g (87%).

^1H -NMR (300 MHz, CDCl_3) δ [ppm]: 6.03 (m, $-\text{CH}=\text{CH}-\text{CH}_3$); 5.75 (m, $-\text{CH}=\text{CH}_2$); 5.59 (d, $J=18.75\text{ Hz}$, $-\text{CH}=\text{CH}-\text{CH}_3$); 4.83 (m, $-\text{CH}=\text{CH}_2$); 1.81 (d, $J=6.25\text{ Hz}$, $-\text{CH}=\text{CH}-\text{CH}_3$); 1.52 (t, $J=8.39$, $-\text{CH}_2-\text{CH}=\text{CH}_2$); 1.42-1.20 (m, CH_2); 0.70-0.44 (m, $\text{Si}-\text{CH}_2$); 0.01 (T_1), -0.02 (L_1), -0.03 (T_0), -0.06 (L_0), -0.09 (D) (s, $\text{Si}-\text{CH}_3$). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: 143.36, 142.61 ($-\text{CH}=\text{CH}-\text{CH}_3$); 135.30 ($-\text{CH}=\text{CH}_2$, T), 134.81 ($-\text{CH}=\text{CH}_2$, L); 129.53, 128.57 ($-\text{CH}=\text{CH}-\text{CH}_3$); 113.04 ($-\text{CH}=\text{CH}_2$, L); 112.61 ($-\text{CH}=\text{CH}_2$, T); 22.75 ($-\text{CH}=\text{CH}-\text{CH}_3$); 22.01, 21.47 ($-\text{CH}_2-\text{CH}=\text{CH}_2$); 19.50-17.20 (CH_2); -4.85, -5.01, -5.34, -5.73 ($\text{Si}-\text{CH}_3$). ^{29}Si -NMR (60 MHz, CDCl_3) δ [ppm]: 1.18 (D); 0.89 (L_0); 0.43 (T_0); -7.33 (L_1), -8.29 (T_1).

Ferrocenyldimethylsilane (FcMe_2SiH). In a dried flask 4.65 g (25 mmol) ferrocene were suspended in 25 ml pentane/THF (1:1) under nitrogen atmosphere and cooled to 0°C . A 1.5 M solution of *t*-butyllithium in pentane (16.5 ml, 25 mmol) was slowly added and stirred for 30 min. The formation of ferrocenyllithium is indicated by the dark-red color of the suspension. During the dropwise addition of 4.2 ml (38 mmol) chlorodimethylsilane at 0°C color change to light orange occurred. After 90 min the mixture was hydrolyzed by adding 10 ml H_2O . The water layer was separated and washed with hexanes. The combined organic layers were washed with water and dried with MgSO_4 . Unreacted ferrocene (2.76 g, 14.8 mmol) was removed by crystallization from hexanes. The purified product was obtained as dark-red oil by column chromatography in PE/ CHCl_3 20:1 ($R_f=0.68$). Yield: 3.4 g (56%).

^1H -NMR (300 MHz, CDCl_3) δ [ppm]: 4.43 (sept, $J = 3.68$ Hz, 1H, Si-H); 4.38 (m, 2H, $\text{Cp}_{\text{subst.}}$ -H); 4.20 (m, 2H, $\text{Cp}_{\text{subst.}}$ -H); 4.17 (s, 5H, Cp-H); 0.33 (d, $J = 3.31$ Hz, 6H, Si- CH_3). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: 73.41, 71.10 ($\text{Cp}_{\text{subst.}}$ -C); 68.39 (Cp); 68.15 (Cp-C); -3.15 (Si- CH_3). ^{29}Si -NMR (60 MHz, CDCl_3) δ [ppm]: -18.57.

Diferrocenylmethylsilane (Fc_2MeSiH). The product was prepared analogously to ferrocenyldimethylsilane using 4.65g (25mmol) ferrocene, 16.5ml (1.5M in pentane; 25mmol) *t*-butyllithium and 1.44g (12.5mmol) dichloromethylsilane. The purified product was obtained as dark-red crystals by column chromatography in PE/CHCl_3 20:1 ($R_f=0.37$). Yield: 2.1g (40%).

^1H -NMR (300 MHz, CDCl_3) δ [ppm]: 4.93 (q, $J = 3.68$ Hz, 1H, Si-H); 4.38 (m, 4H, $\text{Cp}_{\text{subst.}}$ -H); 4.20 (m, 4H, $\text{Cp}_{\text{subst.}}$ -H); 4.14 (s, 10H, Cp-H); 0.58 (d, $J = 3.68$ Hz, 3H, Si- CH_3). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: 73.81, 70.99 ($\text{Cp}_{\text{subst.}}$ -C); 68.40 (Cp); 67.14 (Cp-C); 4.31 (Si- CH_3). ^{29}Si -NMR (60 MHz, CDCl_3) δ [ppm]: -20.51.

Ferrocenyl-functionalized polymers

Functionalization. The polymers (200mg) and the respective amount of ferrocenylsilane were dissolved in 12ml pentane or 3ml chlorobenzene under nitrogen atmosphere. Karstedt catalyst was added and the solution stirred at room temperature or 60°C for 1-2 days. The polymer was precipitated from methanol and further purified by dialysis ($\text{MWCO}=1000\text{g/mol}$). Yield: 70-90%.

Copolymerization. Diallylmethylsilane or methyldiundecenylsilane and the respective amount of diferrocenylmethylsilane were dissolved in toluene under nitrogen atmosphere. Karstedt catalyst was added and the solution was stirred until complete conversion was confirmed by IR spectroscopy. The polymers were precipitated from methanol and purified by dialysis. Yield: 50-70%.

All polymers are highly viscous materials with an orange to red color.

hb-PMDUS-Fc. ^1H -NMR (300 MHz, CDCl_3) δ [ppm]: -0.09 (s, 3H, Si- CH_3); 0.20 (s, 6H, $-\text{SiFc}(\text{CH}_3)_2$); 0.35-0.55 (m, 6H, Si- CH_2); 0.58-0.75 (m, 2H, $-\text{CH}_2\text{SiMe}_2\text{Fc}$); 1.10-1.45 (m, 28H, CH_2); 1.55-1.70 (m, $-\text{CH}=\text{CH}-\text{CH}_3$); 1.90-2.10 (m, $-\text{CH}=\text{CH}-\text{CH}_2-$); 4.05-4.20 (m, 7H, Fc); 4.30-4.40 (m, 2H, Fc); 5.35-5.45 (m, $-\text{CH}=\text{CH}-$). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: -5.12 (Si- CH_3); -2.22 ($-\text{SiFc}(\text{CH}_3)_2$); 13.87 (Si- CH_2); 17.93 ($-\text{CH}=\text{CH}-\text{CH}_3$); 23.92 (CH_2 polymer backbone); 24.05 ($\text{FcMe}_2\text{SiCH}_2\text{CH}_2$); 26.84 ($-\text{CH}=\text{CH}-$).

CH₂CH₃); 29.10-30.20 (CH₂); 32.61 (CH₂-CH=CH-); 33.68 (CH₂-CH=CH-); 33.85 (CH₂-CH=CH); 68.57 (Cp); 71.04 (Cp_{subst}); 73.44(Cp_{subst}); 123.54, 124.46, 130.58, 131.80 (-CH=CH-). ²⁹Si-NMR (60 MHz, CDCl₃) δ [ppm]: 3.02 ; -2.31 (SiFc).

hb-PMDUS-Fc₂. ¹H-NMR (300 MHz, CDCl₃) δ [ppm]: -0.10 (s, 3H, Si-CH₃); 0.04-0.55 (m, 6H, Si-CH₂); 1.15-1.45 (m, 28H, CH₂); 1.56-1.66 (m, -CH=CH-CH₃); 1.90-1.97? (m, -CH=CH-CH₂-); 2.03 (q, J = 6.99 Hz, 2H, -CH₂-CH₂=CH₂); 4.88-5.05 (m, 2H, -CH=CH₂); 5.35-5.45 (m, -CH=CH-); 5.73-5.88 (m, 1H, -CH=CH₂). ²⁹Si-NMR (60 MHz, CDCl₃) δ [ppm]: 3.02 ; -5.91 (SiFc₂).

hb-PDAMS-Fc. ¹H-NMR (300 MHz, CDCl₃) δ [ppm]: -0.20 – 0.15 (m, 3H, Si-CH₃); 0.49 (m, 3H, -SiFc₂CH₃); 0.40-0.75 (m, 6H, Si-CH₂); 0.90-1.15 (m, 2H, -CH₂SiMeFc₂); 1.20-1.65 (m, 2H, CH₂); 1.83? (m, -CH=CH-CH₃); 3.95-4.25 (m, 7H, Fc); 4.25-4.45 (m, 2H, Fc). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm]: -4.95 - -4.45 (Si-CH₃); -2.46 (-SiFc₂CH₃); 18.40-19.60 (CH₂); 20.98 (CH₂); 68.33, 70.68, 73.41 (Fc-Cp). ²⁹Si-NMR (60 MHz, CDCl₃) δ [ppm]: 1.18 (D); -2.96 (SiFc).

hb-PDAMS-Fc₂. ¹H-NMR (300 MHz, CDCl₃) δ [ppm]: -0.20 – 0.15 (m, Si-CH₃); 0.49 (m, -SiFc₂CH₃); 0.40-0.75 (m, Si-CH₂); 0.90-1.15 (m, -CH₂SiMeFc₂); 1.20-1.65 (m, CH₂); 1.83 (m, -CH=CH-CH₃); 3.95-4.25 (m, Fc); 4.25-4.45 (m, Fc); 5.50-5.70 (-CH=CH-CH₃); 5.90-6.25 (-CH=CH-CH₃). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm]: (-4.95) – (-4.45) (Si-CH₃); -2.46 (-SiFc₂CH₃); 18.40-19.60 (CH₂); 20.98 (CH₂); 68.33, 70.68, 73.41 (Fc-Cp). ²⁹Si-NMR (60 MHz, CDCl₃) δ [ppm]: 1.26 (D); 0.94 (L₀); -6.54 (SiFc₂), -7.30 (L₁); -15.73 (?).

3.10 References

1. Kealy, T. J.; Pauson, P. L. *Nature* **1951**, 168, 1039.
2. Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632.
3. Author, A., *Metallocenes. Synthesis, reactivity, Applications*. Wiley/VCH: New York/Weinheim, 1998.
4. Togni, A.; Hayashi, T., *Ferrocenes. Homogenous Catalysis, Organic Synthesis, Materials Science*. VCH: Weinheim, 1995.
5. Nguyen, P.; Gómez-Elípe, P.; Manners, I. *Chem. Rev.* **1999**, 99, 1515.
6. Peckham, T. J.; Gómez-Elípe, P.; Manners, I., *Metallocenes. Synthesis, Reactivity, Applications*. Wiley/VCH: New York/Weinheim, 1998; p 732.

7. Gonsalves, K. E.; Chen, X., *Ferrocenes. Homogeneous Catalysis, Organic Synthesis, Materials Science*. VCH: Weinheim, 1995; p 497.
8. Sheats, J. E.; Carraher Jr., C. E.; Pittman Jr., C. U., *Metal-Containing Polymeric Systems*. Plenum Press: New York, 1985.
9. Sheats, J. E.; Carraher Jr., C. E.; Pittman Jr., C. U., *Inorganic and Metal-Containing Polymeric Materials* Plenum Press: New York, 1990.
10. Bellas, V.; Rehahn, M. *Angew. Chem. Int. Ed.* **2007**, 46, 5082.
11. Herbert, D. E.; Mayer, U. F. J.; Manners, I. *Angew. Chem. Int. Ed.* **2007**, 46, 5060.
12. Rulkens, R.; Ni, Y.; Manners, I. *J. Am. Chem. Soc.* **1994**, 116, 12121.
13. Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F., Organometallic Dendritic Macromolecules: Organosilicon and Organometallic Entities as Cores or Building Block. In *Advances in Dendritic Macromolecules*, JAI Press: 1996; Vol. 3, pp 151.
14. Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; García, B.; González, B.; Losada, J. *Coordination Chemistry Reviews* **1999**, 185-186, 53.
15. Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575.
16. Alonso, B.; González, B.; García, B.; Ramírez-Oliva, E.; Zamora, M.; Casado, C. M.; Cuadrado, I. *Journal of Organometallic Chemistry* **2001**, 637-639, 642.
17. Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, 119, 7613.
18. Alonso, B.; Morán, M.; Casado, C. M.; Lobete, F.; Losada, J.; Cuadrado, I. *Chem. Mater.* **1995**, 7, 1440.
19. Losada, J.; Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Barranco, M. *Analytica Chimica Acta* **1997**, 338, 191.
20. Casado, C. M.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. *Journal of Electroanalytical Chemistry* **1999**, 463, 87.
21. Bernard, J.; Schappacher, M.; Ammannati, E.; Kuhn, A.; Deffieux, A. *Macromolecules* **2002**, 35, (24), 8994.
22. Sun, Q.; Lam, J. W. Y.; Xu, K.; Xu, H.; Cha, J. A. K.; Wong, P. C. L.; Wen, G.; Zhang, X.; Jing, X.; Wang, F.; Tang, B. Z. *Chem. Mater.* **2000**, 12, 2617.
23. Sun, Q.; Xu, K.; Peng, H.; Zheng, R.; Häussler, M.; Tang, B. Z. *Macromolecules* **2003**, 36, 2309.
24. Li, Z.; Lam, J. W. Y.; Dong, Y.; Dong, Y.; Sung, H. H. Y.; Williams, I. D.; Tang, B. Z. *Macromolecules* **2006**, 39, 6458.
25. Drohmann, C.; Möller, M.; Gorbatshevich, O. B.; Muzafarov, A. M. *J Polym Sci Pol Chem* **2000**, 38, (4), 741.
26. García-Marcos, A. *Thesis University Mainz* **2006**.
27. Holter, D.; Frey, H. *Acta Polym* **1997**, 48, (8), 298.
28. Hölter, D.; Burgath, A.; Frey, H. *Acta Polym* **1997**, 48, 30.
29. Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *Journal of the American Chemical Society* **1991**, 113, 4583.
30. Lach, C.; Muller, P.; Frey, H.; Mulhaupt, R. *Macromol Rapid Comm* **1997**, 18, (3), 253.
31. Dement'ev, V. V.; Cervantes-Lee, F.; Parkanyi, L.; Sharma, H.; Pannell, K.; Nguyen, M. T.; Diaz, A. *Organometallics* **1993**, 12, 1983.
32. Foucher, D.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, 114, 6246.
33. Guilleaux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, 60, 2502.
34. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications*. Wiley: New York, 1980.
35. Rusling, J. F.; Suib, S. L. *Advances Materials* **1994**, 6, (12), 922.
36. Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, 97, 637.
37. G. Marcos, A. *Dissertation, University of Mainz* **2006**.

4 Synthesis and polymerization of ferrocenyl-containing monomers

4.1 Introduction

In the preceding chapter the synthesis of redox active polymers obtained by functionalization of hyperbranched polycarbosilanes with appropriate ferrocene units was studied. In a further approach the direct incorporation of ferrocene units into the polymerizable monomer was of interest. In this way ferrocene-containing polymers can be obtained in a single polymerization step. The previously described polymers were functionalized with the redox-active units in a post-polymerization step or by copolymerization with monofunctional ferrocene-containing monomers resulting in end-group modification. In this case an accumulation of ferrocene units at the periphery of the structure is expected due to the spatial arrangement and distribution of functional groups in the polymer. In contrast, if the active unit is incorporated into the monomer, a completely homogeneous distribution is achieved throughout the polymer. So far there have been few examples of branched monomers with functional units that can be used for the synthesis of hyperbranched polymers. In order to obtain hyperbranched polymers, AB_2 -monomers (or AB_x with $x > 2$) have to be polymerized. This implies that functional monomers have to include at least four functional groups: one A group, at least two B groups and the functional unit. Thus, synthesis of such molecules is commonly difficult to accomplish. However, silicon allows attachment of up to four substituents by nucleophilic substitution reaction. Since the preparation of AB_2 monomers with one unreactive methyl group is well established, the aim was to substitute the methyl group with a redox-active ferrocene group (Figure 4.1).

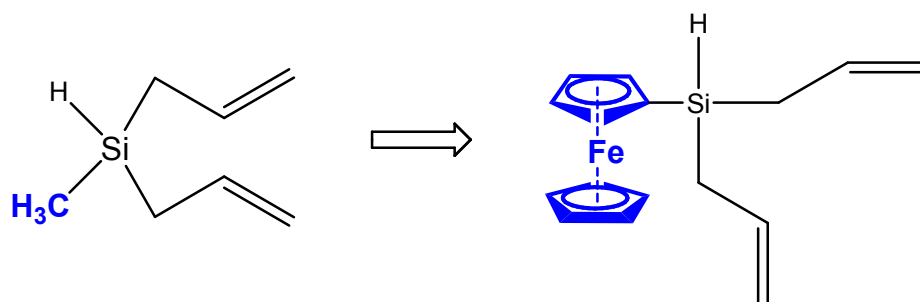


Fig. 4.1 AB_2 monomers with methyl and ferrocenyl substituents.

In this chapter the synthesis and polymerization of two ferrocenyl-containing monomers is described, which permit the synthesis of linear and hyperbranched redox active polymers.

4.2 Monomer synthesis

A modification of the procedure known for the synthesis of diallylmethylsilane was used for the preparation of ferrocenyl-functionalized monomers. The reaction sequence commences with trichlorosilane, which comprises three chlorides that can be substituted by nucleophiles. In the first step one of the chlorides ought to be exchanged with ferrocenyllithium. Here, of course, a substitution of more than one of the chlorides is possible. In order to minimize twofold substitution, an excess of trichlorosilane was added to a freshly prepared solution of monolithiated ferrocene at -78°C in THF/pentane. The solution was then slowly allowed to warm to room temperature. The formed dichloroferrocenylsilane was purified by distillation and obtained in 35% yield as red viscous liquid. In a Grignard reaction the remaining chlorides were exchanged by allyl magnesium bromide (Fig. 4.2). The monomer was purified by column chromatography and obtained as red oil in 74% yield.

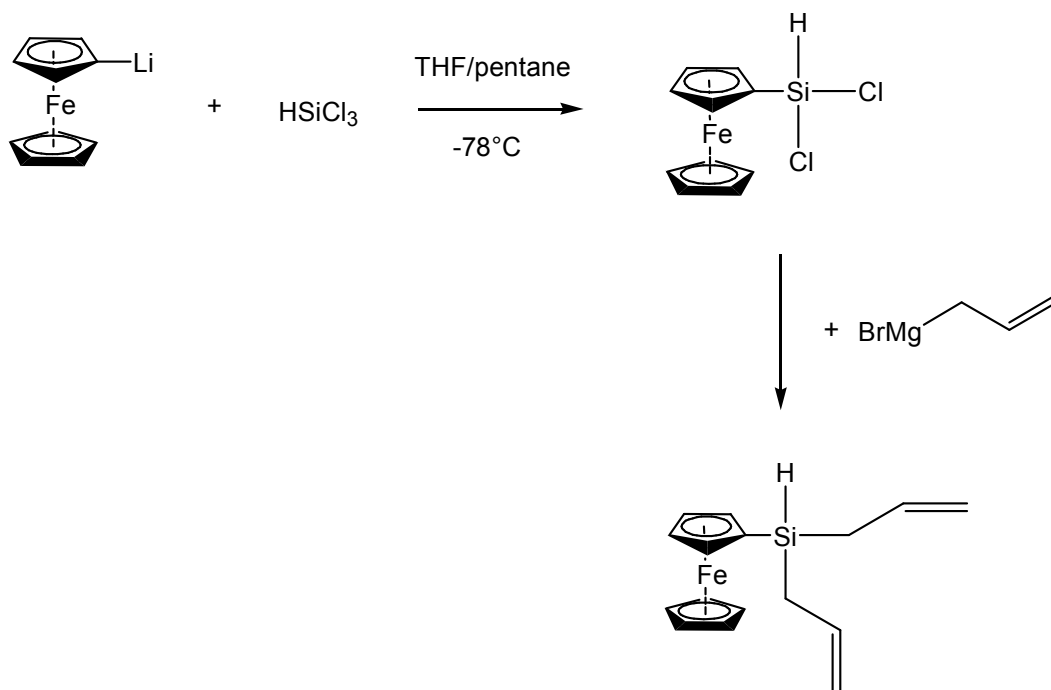


Fig. 4.2 Reaction sequence for the synthesis of diallylferrocenylsilane.

The purity of the product was confirmed using NMR-spectroscopy, FD-MS and elemental analysis. The ^1H -NMR spectrum of the substance is shown in Figure 4.3. The signals can be clearly assigned to the protons of the ferrocene group (blue), the allyl group (green) and the silane (red).

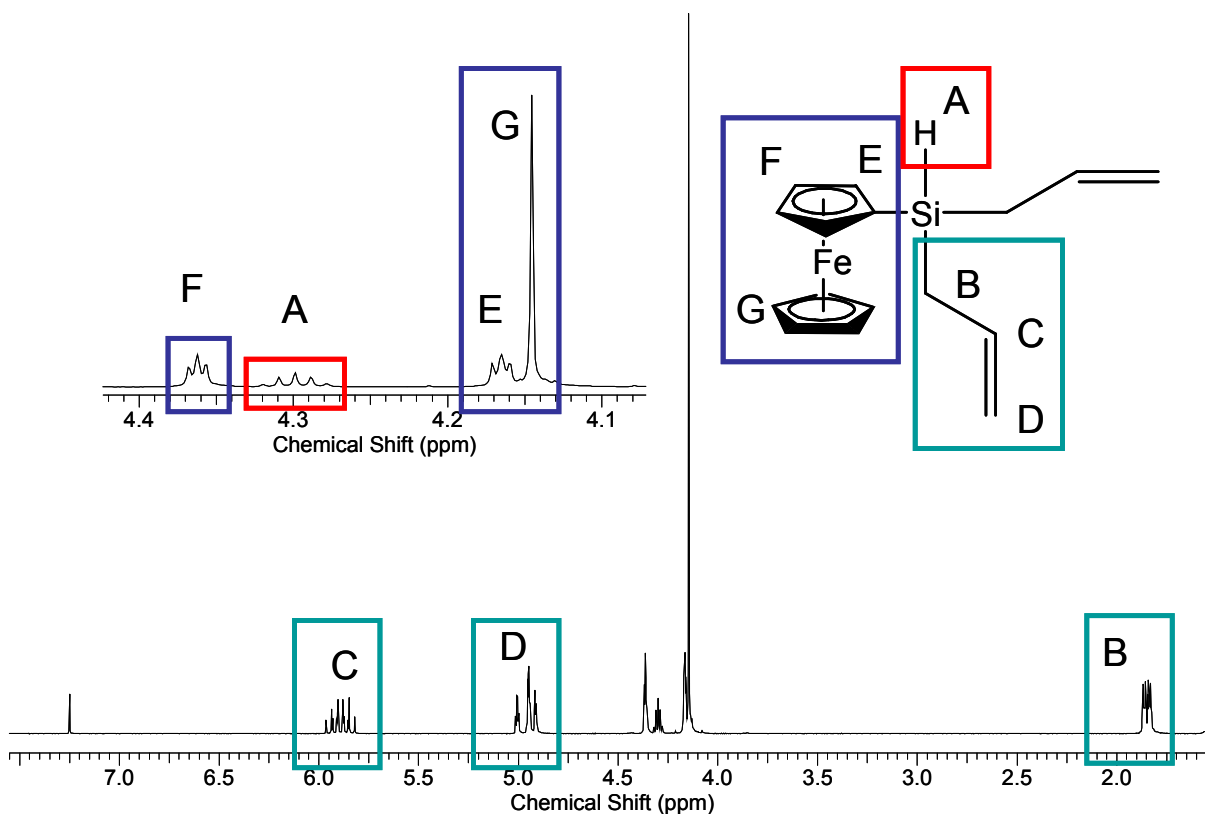


Fig. 4.3 ^1H -NMR spectrum of diallylferrocenylsilane in CDCl_3 .

During the synthesis of the dichloroferrocenylsilane, chlorodiferrocenylsilane was obtained as a side product. Substitution with allyl magnesium bromide can be used to obtain a diferrocenyl-functionalized AB-monomer (Figure 4.4).

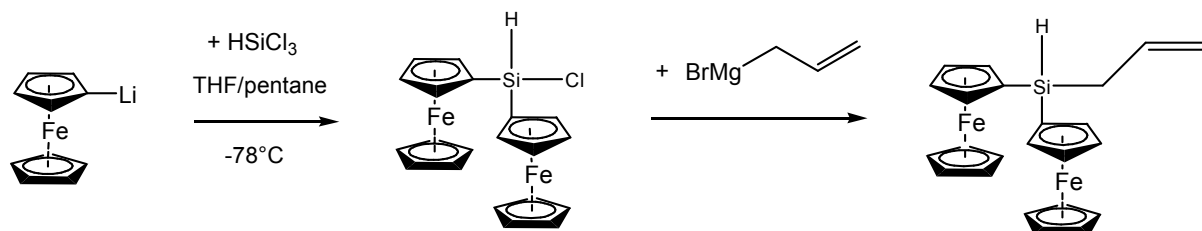


Fig. 4.4 Synthesis of allyldiferrocenylsilane.

Allyl diferrocenylsilane can be synthesized as the main product, in analogy to the synthesis described before by decreasing the amount of trichlorosilane added to the ferrocenyllithium solution. In this manner allyl diferrocenylsilane was obtained in an overall yield of 33% as red crystals. The product was identified using NMR spectroscopy, elemental analysis, IR spectroscopy and FD-mass spectrometry.

^{29}Si -NMR spectra for the ferrocenyl-functionalized monomers display a single peak. In Table 4.1 the ^{29}Si - and ^1H -(Si-H) chemical shifts are summarized and compared with the respective methyl substituted compounds.

Table 4.1 ^1H - and ^{29}Si -NMR shifts of AB_x allyl-type monomers.

monomer	δ_{Si} [ppm]	$\delta_{\text{H(Si-H)}}$ [ppm]
dimethylallylsilane	-12.17	3.89
diallylmethylsilane	-13.98	3.81
allyldiferrocenylsilane	-14.20	4.32
diferrocenylallylsilane	-17.94	4.89

4.3 Polymerization and characterization

Polymerization of the monomers can be performed by hydrosilylation addition. Polymerization of diallylferrocenylsilane was performed in bulk or chlorobenzene solution using Karstedt's catalyst. The course of the reaction is accompanied by an increase of viscosity of the mixture. Completion of the polymerization was determined by IR-spectroscopy following the decrease of the Si-H bond vibration at $\tilde{\nu} = 2117\text{cm}^{-1}$. The polymers were purified by precipitation into methanol in yields ranging from 70-80%. The results for different reaction conditions are summarized in Table 4.2. Conversion is very slow at room temperature, indicating a decreased reactivity of this monomer compared to diallylmethylsilane. In contrast, reasonable reaction times are achieved at 60°C . Molecular weights of the resulting polymers are moderate. A typical GPC curve for the polymers is presented in Figure 4.5 showing several oligomeric peaks. Comparison with the GPC curve for the monomer reveals that indeed all monomer is converted as indicated by IR-spectroscopy. However, dimer and trimers are present in the polymer. MALDI-ToF spectrometry confirmed the structure of the polymer (Figure 4.6). The distribution contains mainly oligomeric

species with a mass increment of 296g/mol representing the repeating unit of diallylferrocenylsilane.

Table 4.2 Polymerization and copolymerization of diallylferrocenylsilane.

sample	feed	reaction condition	reaction time ^a	GPC(CHCl ₃)		DSC T _g [°C]
				M _n	PDI	
9	HSiFcAlI ₂	0.5M, RT	4d	1300	1.90	-9
10	HSiFcAlI ₂	1M, 60°C	6h	1200	1.82	-11
11	HSiFcAlI ₂	bulk, 60°C	3h	1600	2.23	-5
12	HSiFcAlI ₂ /TAS	8:1, bulk, 60°C	3h	1400	1.84	-18
13	HSiFcAlI ₂ /HSiMeAlI ₂	1:1, 1M, 50°C	n.d.	1150	4.3	-42

a) determined by IR-spectroscopy

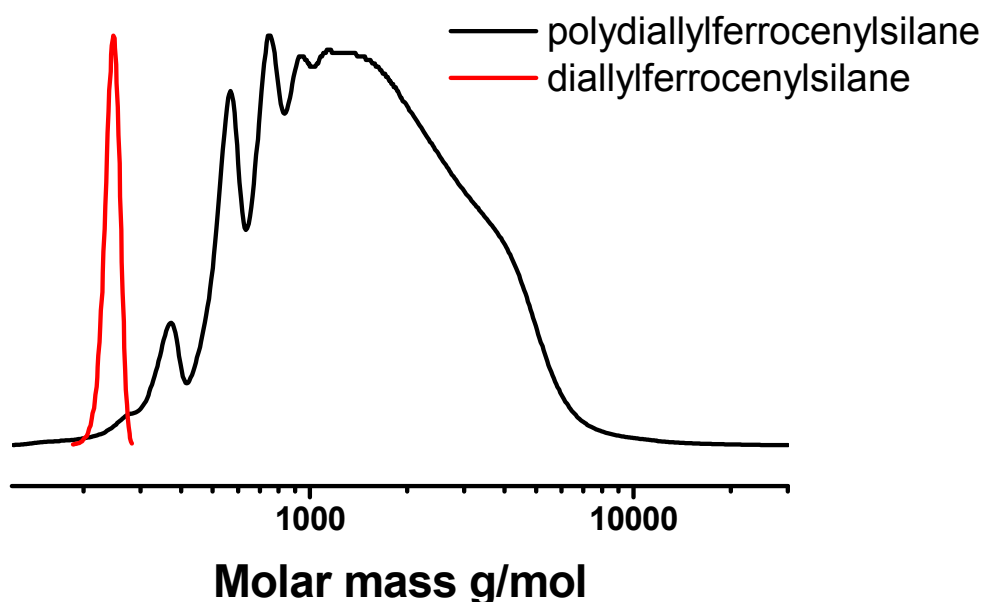


Fig. 4.5 GPC curve in CHCl₃ for diallylferrocenylsilane and polydiallylferrocenylsilane **11**.

In order to obtain absolute molecular weights and to exclude the influence of the branched structure on molecular weight detection, GPC triple detection with MALLS was applied to extend the molecular weight characterization. It is well known that GPC may give a useful estimate of the polydispersity and molecular weight distribution, but may grossly under- or overestimate the real molecular weights. In our case, for example for sample **11** molecular weight determined by MALLS was found to be 10.100g/mol ($dn/dc=0.165$). Light scattering clearly indicates that higher molecular weight polymer is present in the distribution; however the low molecular weight fraction is below the detection limit for MALLS and thus not represented in the

calculation. As expected, the glass transition temperature for polydiallylferrocenylsilane ($T_g = -5^\circ\text{C}$) is significantly higher than for polydiallylmethylsilane (-80°C).

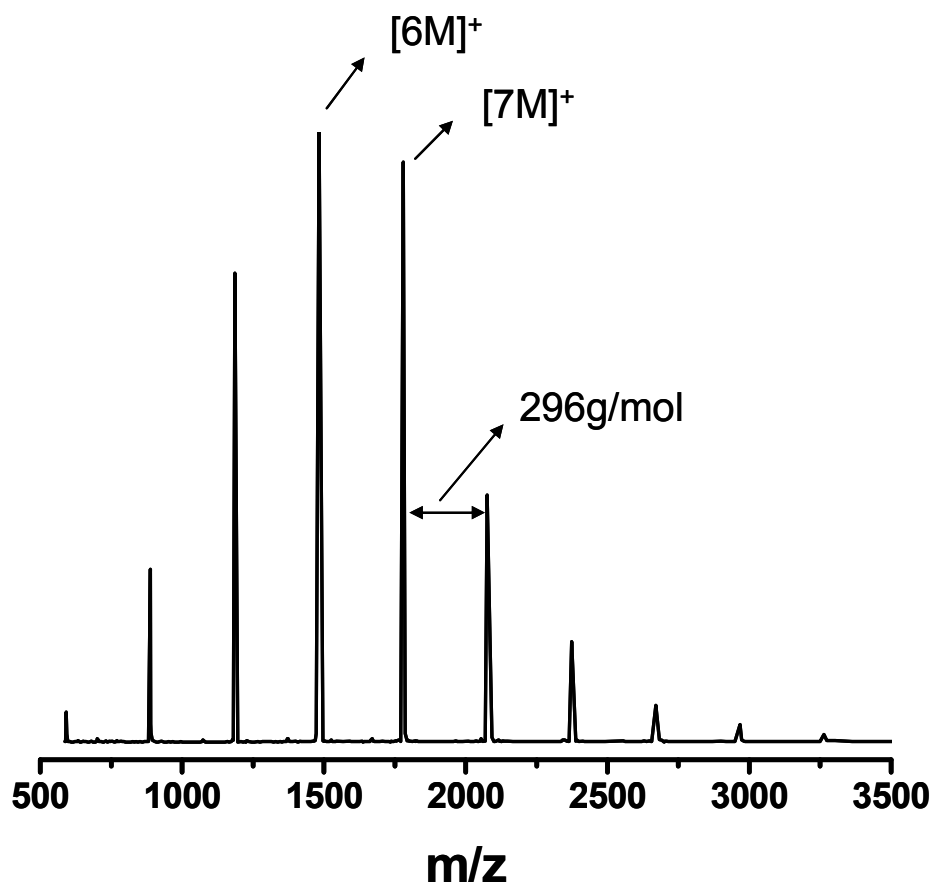


Fig. 4.6 MALDI-ToF spectrum for polydiallylferrocenylsilane 3.

Further efforts have been made to modify and control the polymer structure. In order to enhance the molecular weight control tetraallylsilane (TAS) was added as a core molecule. This results in a slight decrease of T_g indicating a more flexible structure (Table 4.2). However, MALDI-ToF spectrometry shows that the core is only partly incorporated into the polymer molecules (Figure 4.7). Copolymerization with diallylmethylsilane results in multimodal and broad molecular weight distributions caused by the differing reactivities of the monomers. However, $^1\text{H-NMR}$ shows that the feed composition is maintained in the polymer. Additionally, UV- and refractive index signal in GPC measurements are equal, indicating a uniform distribution of both monomers. Thermal analysis shows that T_g of the copolymer ($T_g = -42^\circ\text{C}$) is intermediate between those of the homopolymers polydiallylmethylsilane and polydiallylferrocenylsilane ($T_g = -80^\circ\text{C}$ and -5°C).

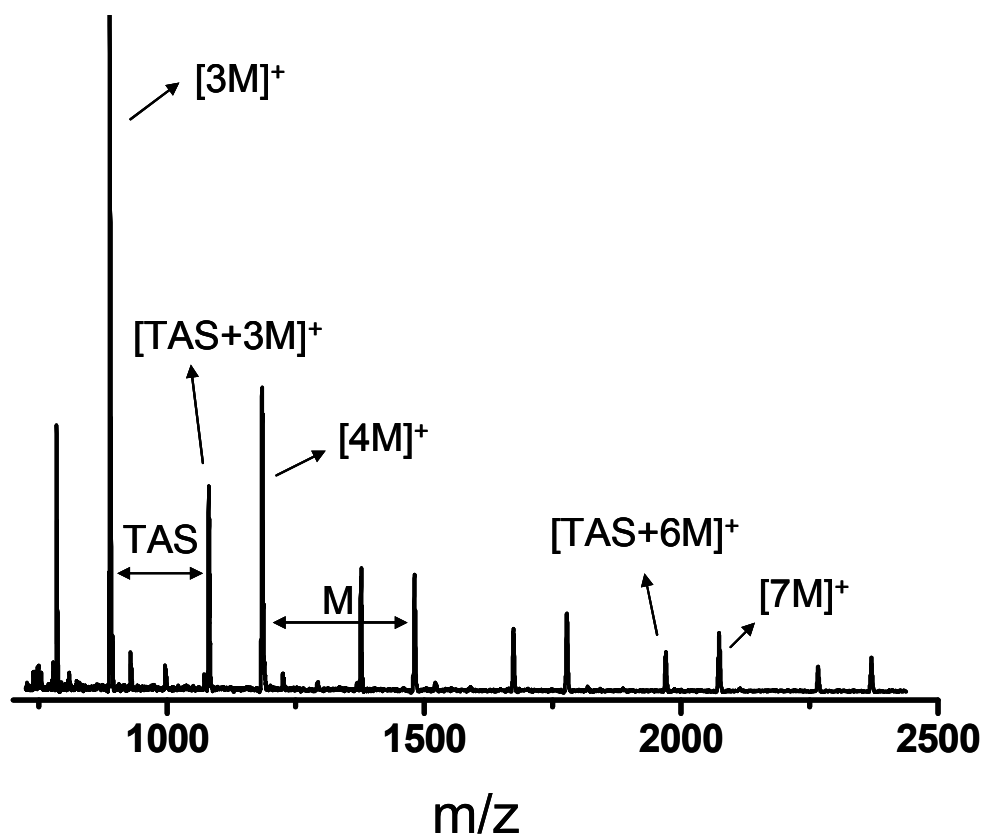


Fig. 4.7 MALDI-ToF spectrum for copolymer of tetraallylsilane and diallylferrocenylsilane **12**.

In order to analyze the structure of the polymers, both ^{13}C - as well as ^{29}Si -NMR spectroscopy have been employed. The ^{13}C -NMR spectrum for polydiallylferrocenylsilane is given in Figure 4.8. The signals can be readily assigned to the different structural elements. The splitting of the signals for the olefinic carbons is particularly worth mentioning. In analogy to the peak splitting observed for polydiallylsilane (Chapter 3.3), the different signals can be assigned to the double bonds attached to linear and terminal units confirming the branched character of the polymer.

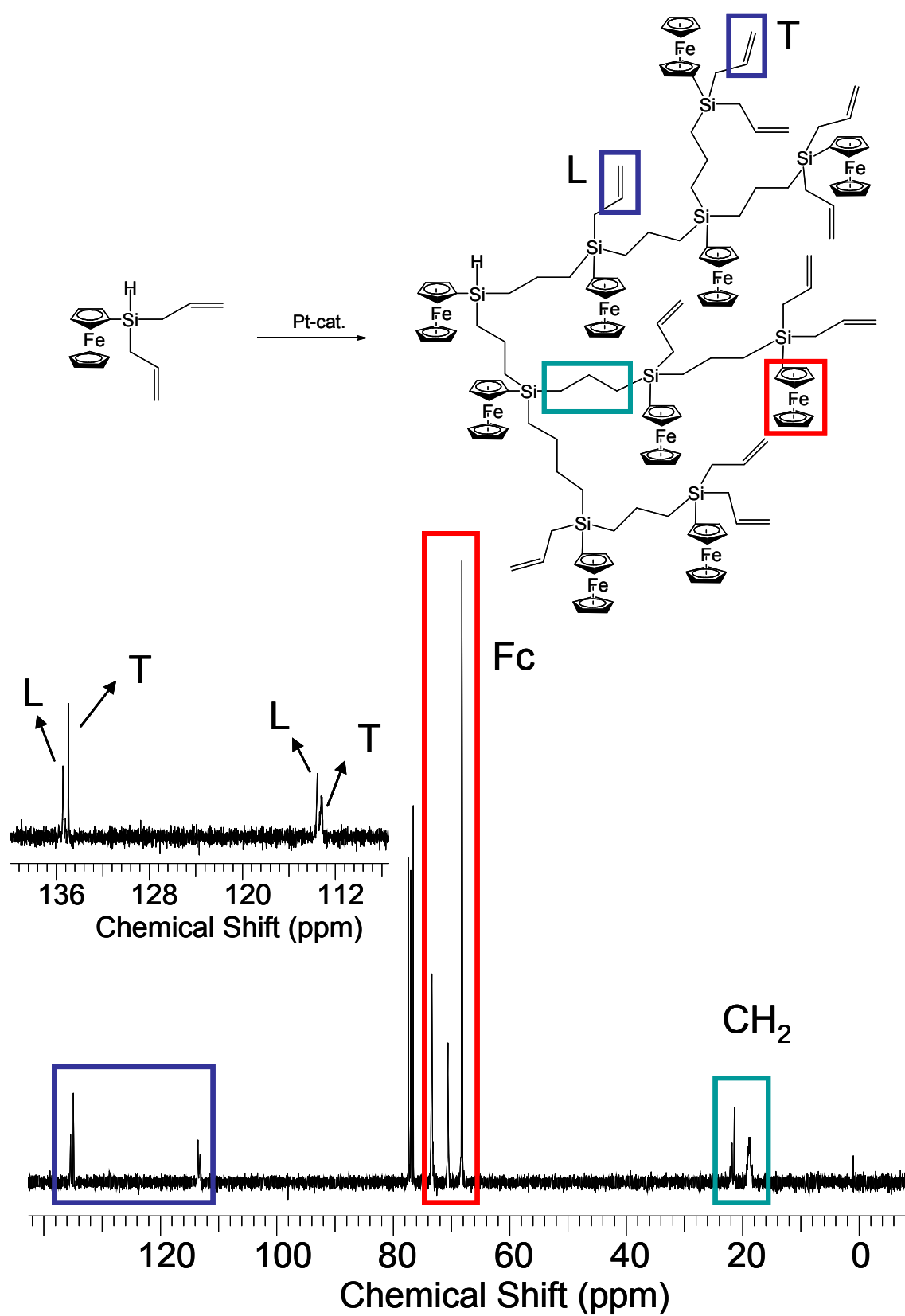


Fig. 4.8 ^{13}C -NMR in CDCl_3 for polydiallylferrocenylsilane.

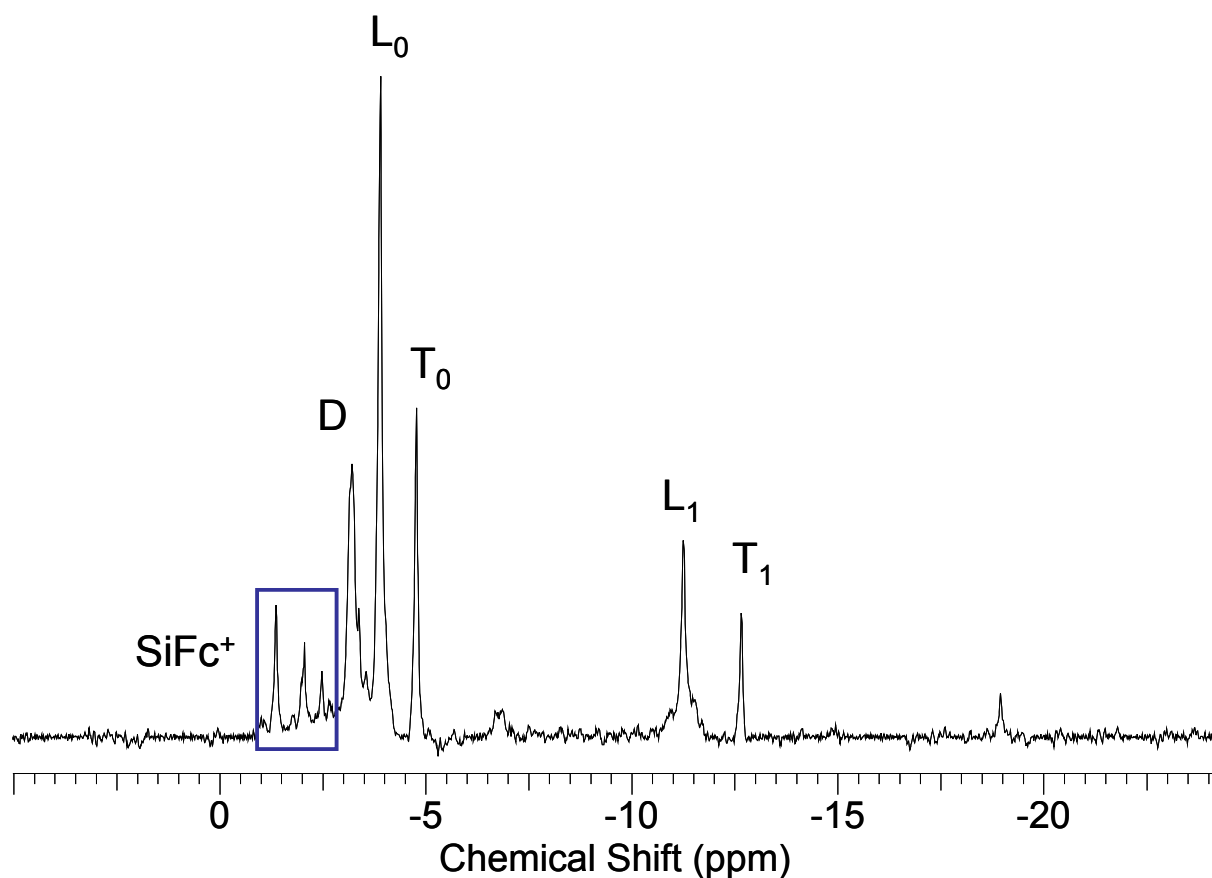


Fig. 4.9 ^{29}Si -NMR in CDCl_3 for polydiallylferrocenylsilane.

Recording of ^{29}Si -NMR spectrum was affected by the presence of small amounts of oxidized ferrocene groups in the polymer, which can be formed by contact with air. The paramagnetic character of these groups results in significant peak broadening. Thus, an evaluable spectrum was only obtained with increased measuring times (Figure 4.9). The main peaks can be assigned in analogy to hyperbranched polydiallylsilane (Figure 3.3) to dendritic (D), linear (L_0), terminal (T_0), linear isomerized (L_1) and terminal isomerized (T_1) branching units. It is assumed that the small peaks between -1.35-1.50 ppm are due to branching units connected to oxidized ferrocene units.

Polymerization of allyl diferrocenylsilane affords linear structures with two ferrocene units linked by silicon (Figure 4.10). The reaction was performed in chlorobenzene solution and results in low molecular weight oligomers **14** ($M_n=1000$, PDI= 1.30). In this case, most probably the bulky structure of the two ferrocene groups inhibits high molecular weight formation.

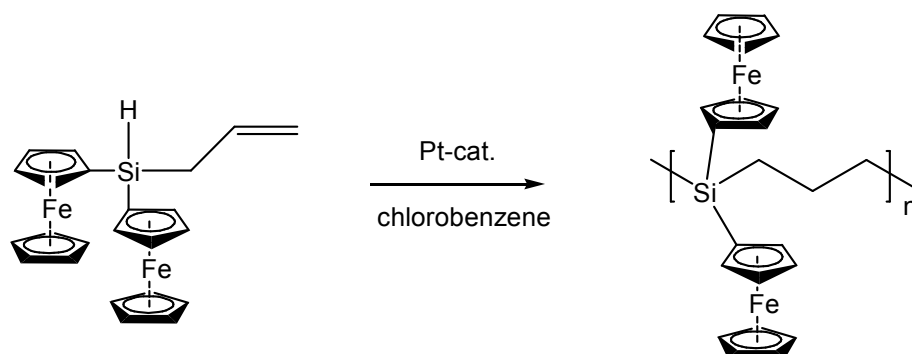


Fig. 4.10 Synthesis of linear poly(SiFc₂AlI) **14**.

4.4 Electrochemical characterization

Solution cyclic voltammetry (CV) was used to investigate the electrochemical properties of the newly synthesized monomers and polymers. The compounds were analyzed in CH₂Cl₂ using Bu₄NPF₆ as electrolyte. The results are summarized in Table 4.3.

Table 4.3 Cyclic voltammetric data

sample	wt%Fc	$E'_{1/2}$ [V] ^a	$E''_{1/2}$ [V] ^a	ΔE [mV] ^b
HSiAlI ₂ Fc	63	0,55	-	-
11	63	0,48	-	-
HSiAlIFc ₂	85	0,47	0,63	160
14	85	0,43	0,56	130

a) $E_{1/2} = (E_{pa} + E_{pc})/2$; b) $\Delta E = E'_{1/2} - E''_{1/2}$.

The results show that for diallylferrocenylsilane and the corresponding polymer a single reversible oxidation wave is observed (Figure 4.11 and 4.12). This indicates that all ferrocenyl units in the polymer possess the same redox potential independent of the structural environment in the hyperbranched structure, due to a lack of interaction between the metal centers. The peak current I_{pa} is linearly proportional to the square root of the scan rate ν confirming the diffusion control of the redox process (Figure 4.12 inset).

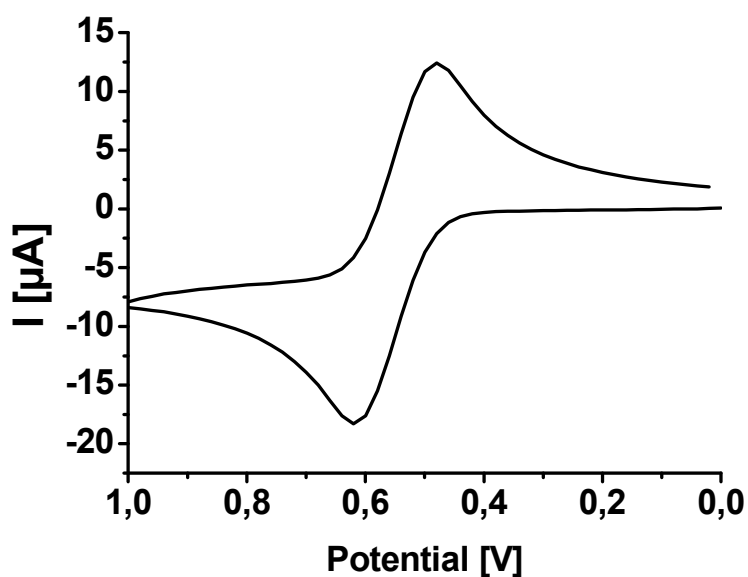


Fig. 4.11 Cyclic voltammogram at a Pt disc electrode and scan rate of 100mV/s of diallyl ferrocenylsilane in CH_2Cl_2 .

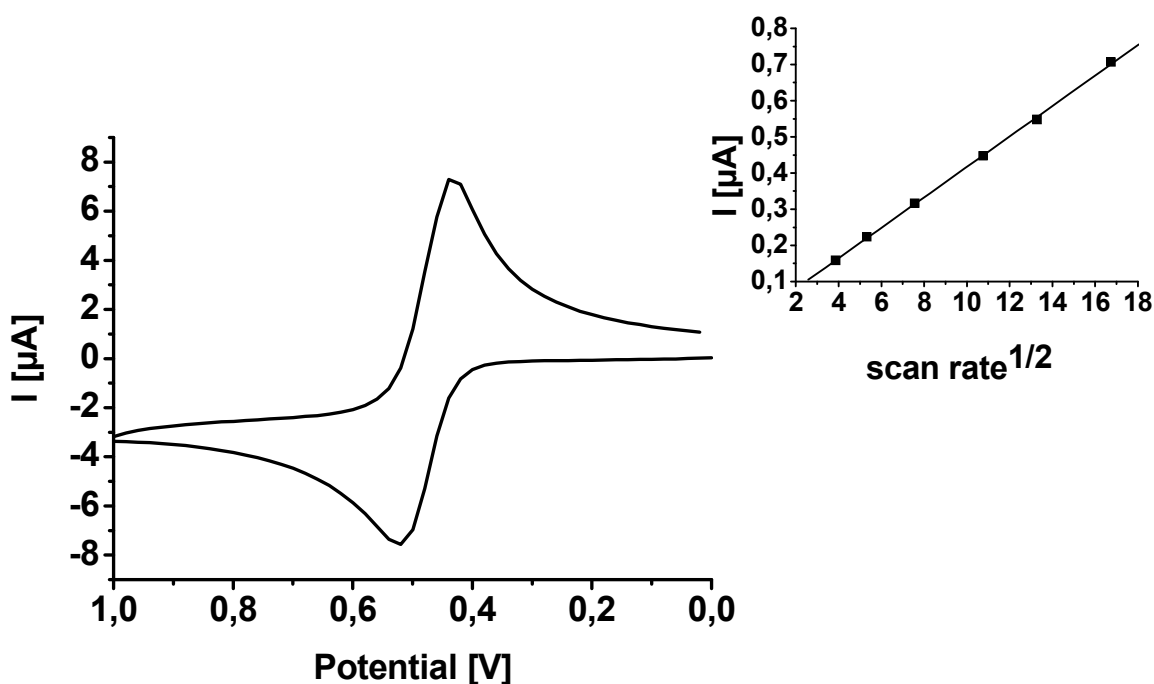


Fig. 4.12 Cyclic voltammogram at a Pt disc electrode and scan rate of 100mV/s of polydiallylferrocenylsilane **11** in CH_2Cl_2 .

The cyclic voltammogram for allyl diferrocenylsilane is characterized by two well separated and reversible oxidation waves of equal intensity at $E'_{1/2} = 0.47 \text{ V}$ and $E''_{1/2} = 0.63 \text{ V}$ (Fig. 4.13). For the corresponding polymer a similar response is observed with oxidation waves at $E'_{1/2} = 0.43 \text{ V}$ and $E''_{1/2} = 0.56 \text{ V}$ (Fig. 4.14). This is consistent with the existence of appreciable interaction between the two iron centers,

which are linked together by a bridging silicon atom. For poly(allyl diferrocenylsilane) a sharp signal, i.e., a cathodic stripping peak, of significantly increased intensity is observed for the first reduction peak. This indicates oxidative precipitation upon oxidation to the polycation yielding adsorbed films on the Pt surface. Thus, upon reduction the response is characterized by the adsorbed species, instead of soluble molecules diffusing to the electrode.

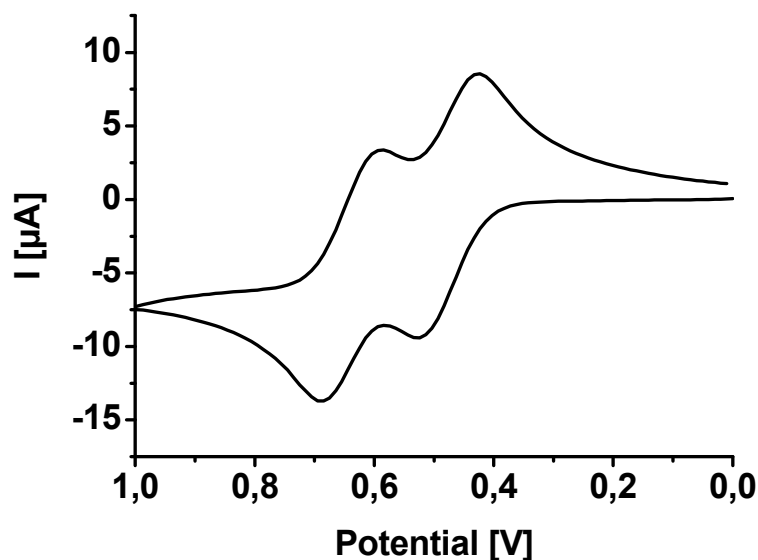


Fig. 4.13 Cyclic voltammogram at a Pt disc electrode and scan rate of 100mV/s of allyl diferrocenylsilane in CH_2Cl_2 .

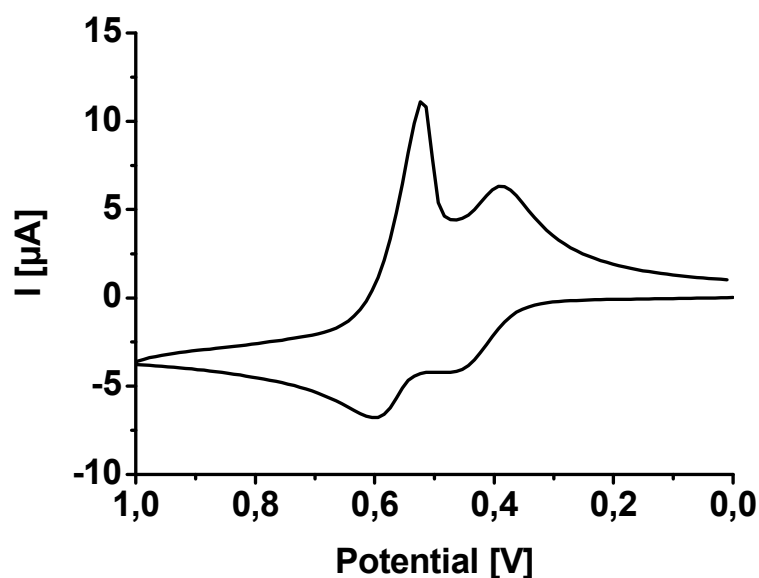


Fig. 4.14 Cyclic voltammogram at a Pt disc electrode and scan rate of 100mV/s of poly(allyl diferrocenylsilane) **14** in CH_2Cl_2 .

4.5 Conclusion

In this chapter the synthesis of ferrocenyl-functionalized monomers was described. Diallylferrocenylsilane and allyl diferrocenylsilane (Figure 4.15) were successfully synthesized by nucleophilic substitution reactions at silicon. Polymerization results in electroactive polymers, which were analyzed by cyclic voltammetry. Of special interest is the new monomer diallylferrocenylsilane allowing the one-pot synthesis of ferrocenyl-functionalized hyperbranched polymers.

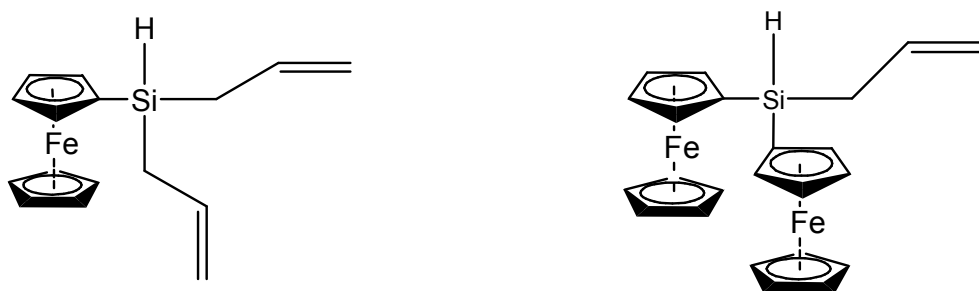


Fig 4.15 Diallylferrocenylsilane and allyl diferrocenylsilane.

4.6 Experimental

4.6.1 Materials

Ferrocene, trichlorosilane, t-butyllithium (1.5M in pentane) were used as received. Allyl magnesium bromide solutions in diethyl ether were prepared according to literature procedures using a threefold excess of magnesium. The solvents, pentane and tetrahydrofuran, were dried by refluxing them over sodium/benzophenone and were freshly distilled prior to use.

Dichloroferrocenylsilane. An amount of 13.02 g of ferrocene (70mmol) was suspended in 75ml freshly distilled pentane/THF (1:1) under N₂ atmosphere, cooled to 0°C and stirred for 15 min. A volume of 50ml of a 1.5M solution of t-butyllithium in pentane (75mmol) was added over 60 min. The mixture was stirred for an additional 30min at 0°C and was then cooled to -78°C. The mixture was treated with 11.38g HSiCl₃ (84mmol) via syringe. The mixture was allowed to warm to room temperature

and stirred over night. The precipitate was removed by filtration and the filtrate was concentrated by evaporation of the solvent. The residue was diluted with 30ml of pentane and filtered once again. Pentane was removed and the product was purified by vacuum distillation (bp. 77-80°C/4·10⁻³mbar). Yield: 6.14g (31%) of a viscous red oil.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 6.03 (s, 1H, Si-H); 4.56 (t, J = 1.47 Hz, 2H, η-C₅H₄); 4.39 (t, J = 1.47 Hz, 2H, η-C₅H₄); 4.28 (s, 5H, η-C₅H₅).

Diallylferrocenylsilane. A solution of 6.00g dichloroferrocenylsilane (21mmol) in 10ml dry diethyl ether was slowly added to 90 ml of a freshly prepared solution of allylmagnesiumbromid (0.9M; 81mmol) in diethyl ether. For completion of the reaction the mixture was stirred for 12h under reflux. At 0°C 10ml of a sat. solution of NH₄Cl were added, followed by 15ml H₂O. The organic layer was separated and washed twice with a sat. Na₂CO₃-solution. The diethyl ether layer was washed with water until neutral reaction of the aqueous layer. The organic layer was dried with MgSO₄ and 5,9g of the crude product were obtained by removal of the solvent. The product was purified by column chromatography (PE, R_f=0.22). Yield: 4,6g (74%) of a red oil.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 5.92 (m, 2H, -CH=CH₂); 5.09-4.85 (m, 4H, -CH=CH₂); 4.38 (m, 2H, η-C₅H₄); 4.32 (m, 1H, Si-H); 4.19 (m, 2H, η-C₅H₄); 4.17 (s, 5H, η-C₅H₅); 1.91-1.81 (m, 4H, CH₂). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm]: 134.56 (-CH=CH₂); 114.05 (-CH=CH₂); 73.75 (η-C₅H₄(CH)); 71.13 (η-C₅H₄(CH)); 68.51 (η-C₅H₅); 64.57 (η-C₅H₄(C)); 19.84 (CH₂). ²⁹Si-NMR (60 MHz, CDCl₃) δ [ppm]: -14.20. IR ν [cm⁻¹]: 3075 (stretching C-H); 2954, 2922, 2853 (stretching C-H), 2117 (stretching Si-H); 1630 (stretching C=C). FD-MS: 295.9 (calc. for C₁₆H₂₀FeSi: 296.3). Elemental Analysis: C, 64.85%; 6.80% (cal. for C₁₆H₂₀FeSi: C, 64.87%; H, 6.80%).

Allyl diferrocenylsilane. An amount of 13.02 g of ferrocene (70mmol) was suspended in 75ml freshly distilled pentane/THF (1:1) under N₂ atmosphere, cooled to 0°C and stirred for 15 min. A volume of 50ml of a 1.5M solution of t-butyllithium in pentane (75mmol) was added over 60 min. The mixture was stirred for an additional 30min at 0°C and was then cooled to -78°C. The mixture was treated with 3.79g HSiCl₃ (28mmol) via syringe. The mixture was allowed to warm to room temperature and was stirred over night. The precipitate was removed by filtration and the filtrate was concentrated by evaporation of the solvent. A solution of the crude product in dry

diethyl ether was slowly added to 75ml of a freshly prepared solution of allylmagnesiumbromide (0.1mol) in diethyl ether. To complete the reaction the mixture was stirred for 12h under reflux. At 0°C 10ml of a sat. solution of NH_4Cl were added, followed by 15ml H_2O . The organic layer was separated and washed twice with a sat. Na_2CO_3 -solution. The diethyl ether layer was washed with water until neutral reaction of the aqueous layer. The organic layer was dried with MgSO_4 and the crude product was obtained by removal of the solvent. The product was purified by column chromatography (PE: CHCl_3 20:1, $R_f=0.39$). Yield: 4.12g (33%) of red crystals. Mp. 73.7°C.

^1H -NMR (300 MHz, CDCl_3) δ [ppm]: 6.04 (m, 1H, $-\text{CH}=\text{CH}_2$); 5.13-4.95 (m, 2H, $-\text{CH}=\text{CH}_2$); 4.89 (t, 1H, Si-H); 4.40 (m, 4H, $\eta\text{-C}_5\text{H}_4$); 4.25 (m, 4H, $\eta\text{-C}_5\text{H}_4$); 4.15 (s, 5H, $\eta\text{-C}_5\text{H}_5$); 2.15-2.04 (m, 2H, CH_2). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: 135.16 ($-\text{CH}=\text{CH}_2$); 114.01 ($-\text{CH}=\text{CH}_2$); 74.05, 73.75 ($\eta\text{-C}_5\text{H}_4(\text{CH})$); 71.13, 71.04 ($\eta\text{-C}_5\text{H}_4(\text{CH})$); 68.57 ($\eta\text{-C}_5\text{H}_5$); 64.54 ($\eta\text{-C}_5\text{H}_4(\text{C})$); 21.51 (CH_2). ^{29}Si -NMR (60 MHz, CDCl_3) δ [ppm]: -17.94. IR ν [cm^{-1}]: 3091 (stretching C-H); 2969, 2920 (stretching C-H); 2109 (stretching Si-H); 1629 (stretching C=C). FD-MS: 439.7 (calc. for $\text{C}_{23}\text{H}_{24}\text{Fe}_2\text{Si}$: 440.2). Elemental Analysis: C, 62.78%; H, 5.69% (cal. for $\text{C}_{23}\text{H}_{24}\text{Fe}_2\text{Si}$: C, 62.75%; H, 5.50%).

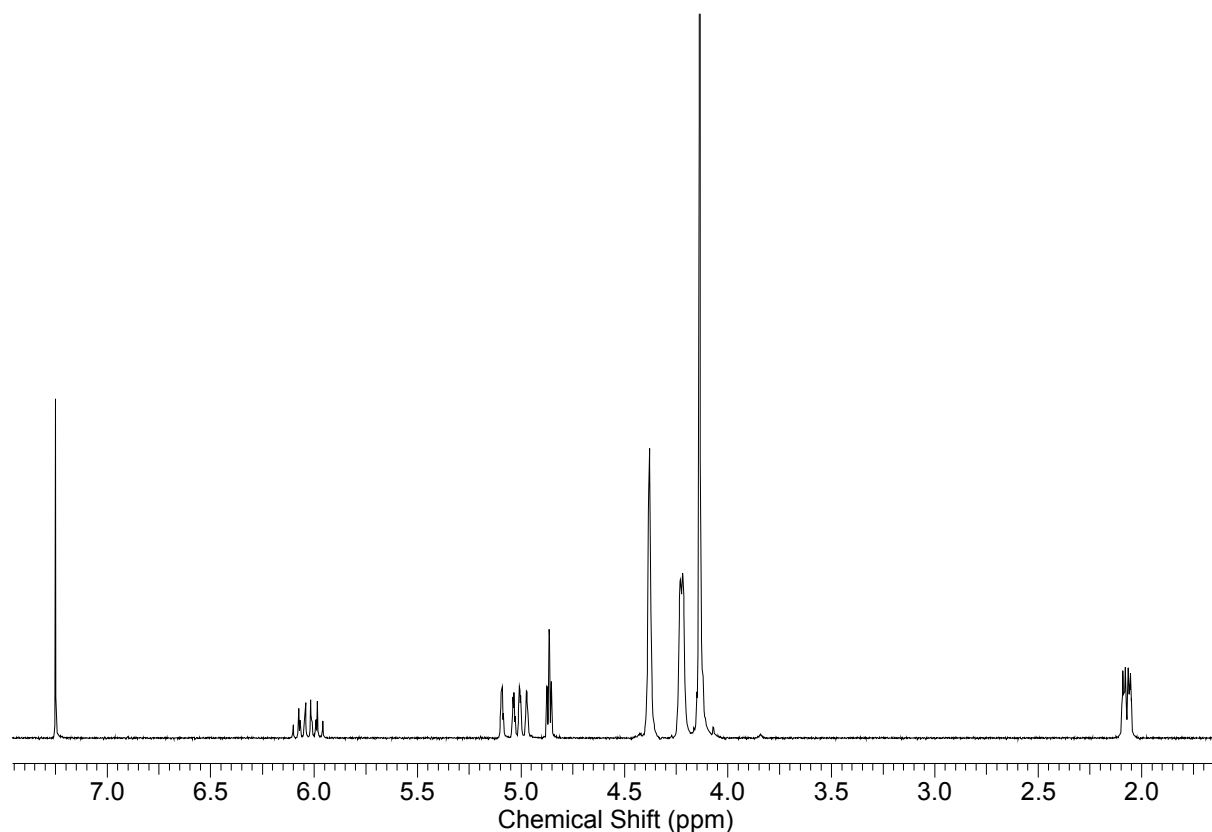


Fig. 4.15 ^1H -NMR spectrum of allyldiferrocenylsilane in CDCl_3 .

Polymerization

Polydiallylferrocenylsilane. Under nitrogen atmosphere 4 μ l Karstedt catalyst solution were added to 100mg (0.23mmol) diallylferrocenylsilane and 0.25ml chlorobenzene. The mixture was stirred at room temperature or 60°C until complete conversion was confirmed by IR spectroscopy. The polymer was purified by precipitation in methanol. Yield: 70-80%.

^1H -NMR (300 MHz, CDCl_3) δ [ppm]: 6.06-5.68 (-CH=CH₂); 5.08-4.73 (-CH=CH₂); 4.41-4.27 (η -C₅H₄); 4.19-3.97 (η -C₅H₄, η -C₅H₅); 1.99-1.72 (-CH₂-CH=CH₂); 1.68-1.36 (CH₂); 1.18-0.59 (Si-CH₂). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: 135.41 (-CH=CH₂, T), 134.95 (-CH=CH₂, L); 113.56 (-CH=CH₂, L); 113.14 (-CH=CH₂, T); 73.36 (η -C₅H₄); 70.63 (η -C₅H₄); 68.21 (η -C₅H₅); 22.00-21.40 (-CH₂-CH=CH₂); 19.50-17.20 (CH₂). ^{29}Si -NMR (60 MHz, CDCl_3) δ [ppm]: -1.36 (D_{ox}); -2.05 (L_{ox}); -2.47 (T_{ox}); -3.21 (D); -3.90 (L₀); -4.77 (T₀); -11.25 (L₁), -12.66 (T₁).

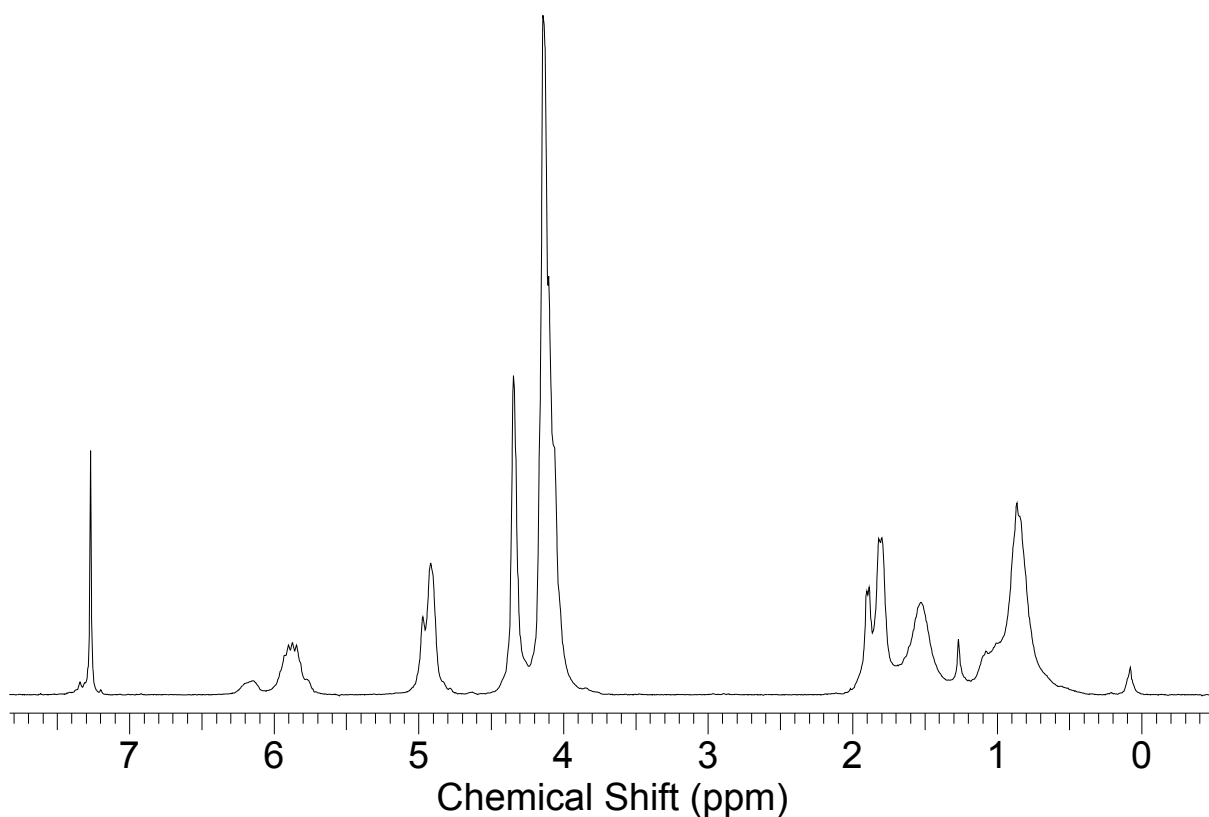


Fig. 4.16 ^1H -NMR spectrum of polyallyldiferrocenylsilane in CDCl_3 .

Poly(allyl diferrocenylsilane). Under nitrogen atmosphere 4 μ l Karstedt catalyst solution were added to 50mg (0.11mmol) allyl diferrocenylsilane and 0.11ml chlorobenzene. The mixture was stirred at 60°C until complete conversion was confirmed by IR spectroscopy. The polymer was purified by precipitation in methanol. Yield: 65%.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm]: 6.09-5.81 (-CH=CH₂); 5.16-4.71 (-CH=CH₂); 4.60-3.71 ($\eta\text{-C}_5\text{H}_4$, $\eta\text{-C}_5\text{H}_5$); 2.29-0.54 (-CH₂-CH=CH₂; CH₂; Si-CH₂).

5 Synthesis of core-functional polycarbosilanes

5.1 Introduction

Hyperbranched polymers are generally synthesized by a simple one-pot polymerization of AB_x ($x \geq 2$) monomers, which offers significant ease in the preparation of branched structures compared to dendrimer synthesis. This is of particular importance, since some of the unique properties of dendrimers like a large number of end groups, a globular structure and low viscosity can also be found for hyperbranched polymers. The drawback of course is that hyperbranched polymers are less defined with an irregular structure. The polymers show broad molecular weight distributions and a lack in molecular weight control. Intramolecular cyclization can be an additional feature that limits the molecular weight built up (Fig. 5.1 top).

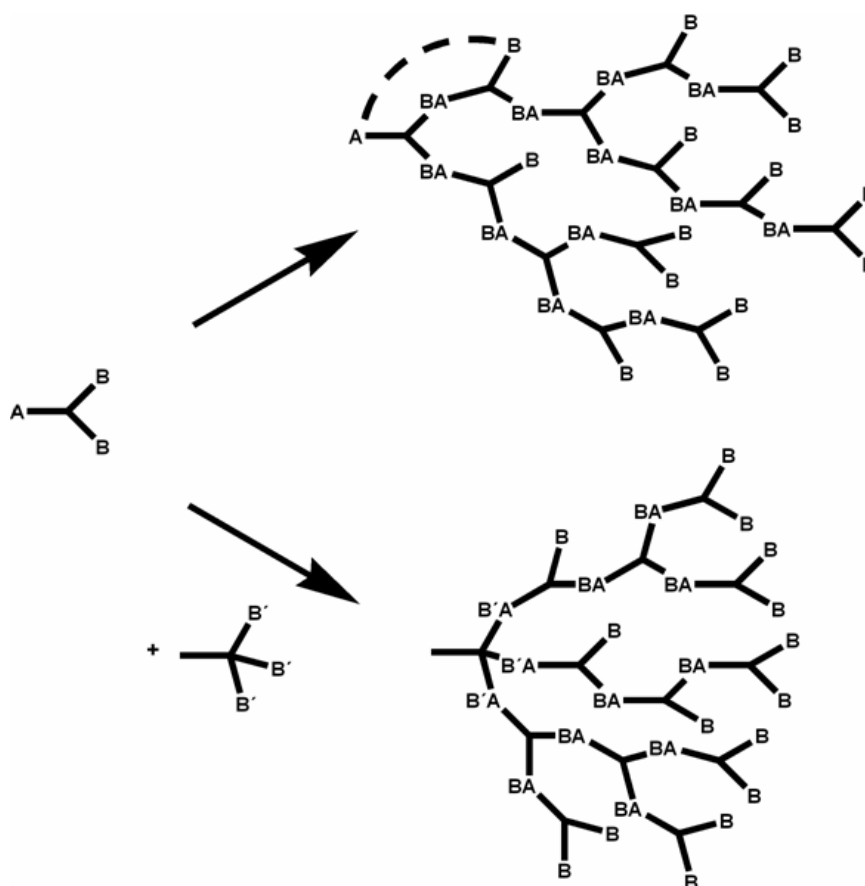


Fig. 5.1 Top: structure of hyperbranched polymer without core and possible intramolecular cyclization (dashed line). Bottom: structure of hyperbranched polymer with added core molecule B_3 .

Several concepts have been developed to improve the synthesis of hyperbranched polymers^{6, 8-15}. There are essentially two ways to gain control of the polymerization: a) usage of a core molecule B_f with a number of functionalities f and b) the slow addition of monomers. In the ideal case, the addition of one monomer after the other to a multifunctional core is desirable. Under these circumstances the reaction of monomers with each other is negligible and all monomers are attached to (macro)molecules containing core units. Computer simulation as well as theoretical calculations have been performed to predict the influence of core molecules and slow addition procedures on the polymerization result. Frey et al. have shown in computer simulation studies, that by slow addition of a dilute solution of AB_2 monomer to a core molecule in the ideal case the molecular weight of a hyperbranched polymer can be controlled by the core to monomer ratio. Additionally, a decrease in the polydispersity according to $PDI = 1 + 1/f$ can be observed depending on the number of functionalities f in the core B_f . The degree of branching (DB) can be enhanced from 0.5 for a random one-pot polymerization to 0.67 under the slow addition conditions^{1, 2}. Basically the same results have been obtained by Radke et al. from theoretical considerations³. Since those first studies of the topic, several articles have been published, in which kinetic models have been adapted to the practical virtualities. In a laboratory set-up monomers can only be added at a certain feed rate. Cheng examined the influence of the feed rate of monomer on the average degree of polymerization, polydispersity and the degree of branching for the addition of an AB_2 monomer to a C_3 core⁴. For low feed rates Φ (e.g. $\Phi = 0.1$) the polydispersity index reaches a value of ~ 1.4 , close to that of 1.33 obtained in the extreme case, when one monomer is added after the other. On the other hand, the evolution of the polydispersity with the degree of polymerization resembles that of a simple one-pot polymerization, when a high feed rate (e.g. $\Phi = 100$) is applied (Fig. 5.2). The group also showed that the polydispersity can be further decreased by using a reactive core molecule⁵. Here, the average degree of polymerization DP_n , and thus the number-average molecular weight, is not influenced by the reactivity of the core, only by the core to monomer ratio. In contrast, the core with higher reactivity yields a lower weight-average degree of polymerization DP_w . Thus, polydispersity drops when using core molecules of high reactivity (Fig. 5.3, $\beta=10$).

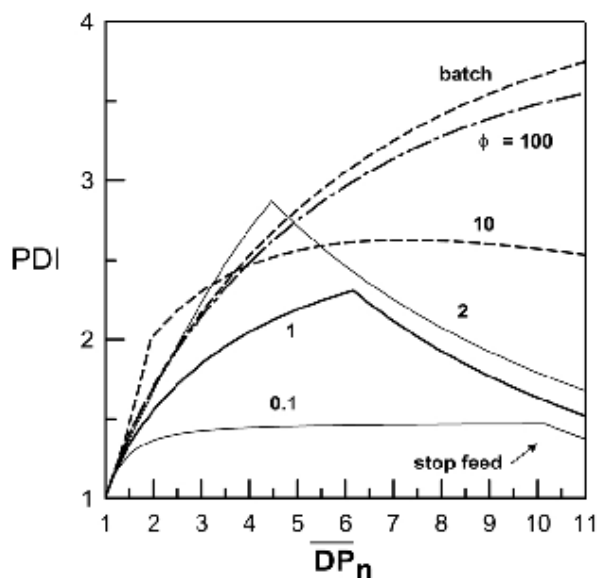


Fig. 5.2 Dependence of the polydispersity on the degree of polymerization at various feed rates (core/monomer ratio = 0.1)⁴.

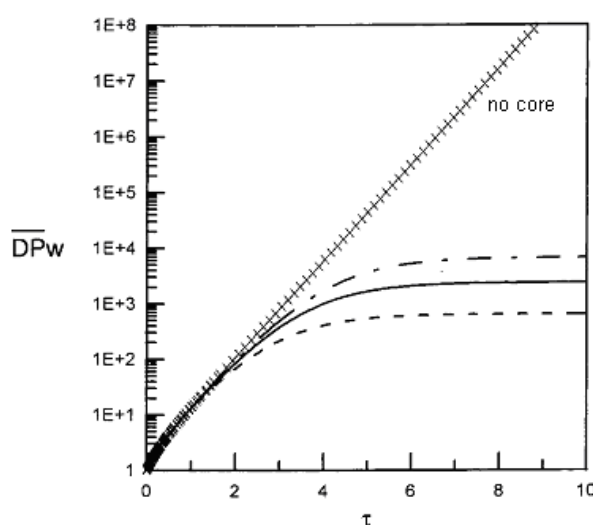


Fig. 5.3 Weight-average degree of polymerization vs. reaction time for core with different reactivities. Reactivity ratio core/monomer $\beta=0.1$ (— — —); $\beta=1$ (——) and $\beta=10$ (----)⁵.

An experimental proof of these theoretical results has been given by Bernal et al., who synthesized hyperbranched poly(arylene ether phosphine oxides) using core molecules of different reactivities⁶. Here, for a polymerization mixture with 10mol% of a B_3 core molecule, the polydispersity could be decreased from 1.62 down to 1.25 by increasing the reactivity of the core through substitution effects.

From a synthetic point of view the copolymerization of an AB_2 monomer with a B_f core is the easiest way to gain control of the synthesis of hyperbranched polymers.

As shown in Figure 5.4 even in batch polymerizations a significant influence on the PDI can be observed, when a multifunctional core is added.

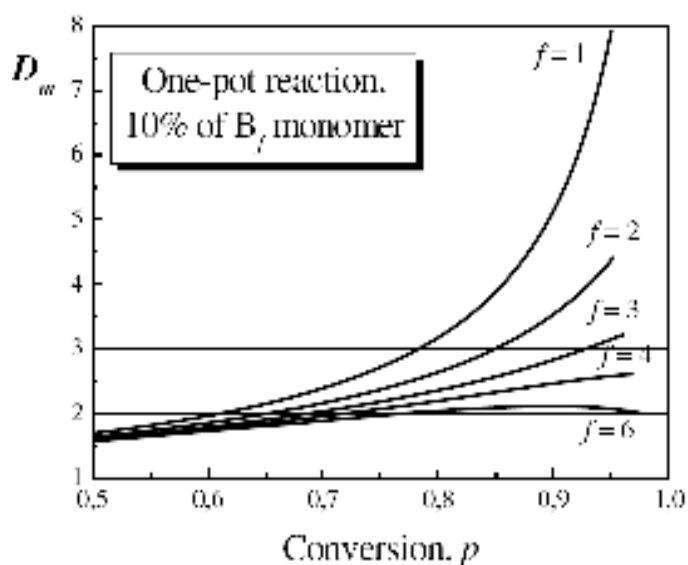


Fig. 5.4 Effect of functionality f of the core on the dispersity D_w of hyperbranched polymers⁷.

This approach was first used for the synthesis of polyesters and polyesteramides⁸⁻¹⁰. In more differentiated examples, the combination of slow monomer addition and application of a core molecule resulted in some well defined hyperbranched polymers^{11, 12}. Moore et al. prepared hyperbranched polyphenylacetylenes by slow addition of the AB_2 monomer to a multifunctional core with polydispersities as low as 1.3. MALDI analysis proved that by this technique cyclization can be suppressed and a completely functionalized polymer is obtained. For the synthesis of hyperbranched polyglycidol the slow monomer addition technique allows control of molecular weight and polydispersity. In this example, a partially deprotonated core molecule, more precisely 1,1,1-tris(hydroxymethyl)propane (TMP), is provided in a high boiling solvent. A dilute solution of the monomer in a low boiling solvent is slowly added and the low boiling solvent removed constantly to retain a high core concentration. Molecular weights between $M_n = 1250\text{--}6500\text{g/mol}$ and $M_w/M_n = 1.13\text{--}1.47$ were obtained¹². As mentioned in chapter 1 hyperbranched polycarbosilanes have been synthesized by the polymerization of triallylsilane in the presence of a functional core, namely 2-(10-decen-1-yl)-1,3-oxazoline (Figure 5.5), as reported by Lach et al.^{13, 14}. The addition of the core molecule allows control of the degree of polymerization by the core to monomer ratio with molecular weights ranging between $17000\text{g/mol} > M_w > 800\text{g/mol}$. The resulting macromonomers bear oxazoline functionality at the core,

which was used for polymerization to obtain hyperbranched analogs of combburst polymers. Unfortunately, the fact that a monofunctional core molecule was used has lead to rather broad molecular weight distributions, especially at low core to monomer ratios. Additionally, there was no analysis concerning the efficiency of polymer attachment to the core, which can only be achieved by detailed mass spectrometry, such as MALDI-ToF.

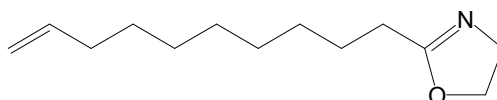


Fig. 5.5 Monofunctional core molecule used by Lach et.al.

Recently, the slow monomer addition of carbosilane monomers to a multifunctional core has been reported by García-Marcos et al.¹⁵. Here, the double bonds of an anionically prepared polystyrene-*b*-1,2-polybutadiene block copolymer have been used as attachment sites for a hyperbranched polycarbosilane block. The resulting linear-hyperbranched block copolymers possess extremely narrow molecular weight distributions ($PDI < 1.1$) with an interesting phase segregation behavior, unique for these new structures.

In this chapter, the synthesis of core-functional hyperbranched polycarbosilane as precursors for block copolymers is described. In order to obtain defined structures, the preparation starts with the synthesis of a low molecular weight ambifunctional core molecule that should allow an efficient attachment of two polymeric blocks (Figure 5.6). As a development compared to the functional polycarbosilanes prepared by Lach et al.¹⁴ the core molecule was modified to contain three double bonds as reactive sites, instead of just one. Besides the reduction of the polydispersity distribution, the molecular weight control should be improved by this approach. Thirdly, simply because of statistical reasons, also the fraction of unfunctionalized polymer, e.g. pure homopolymer, should be minimized in this way. In order to study the influence of the reactivity of the core molecule allyl as well as vinyl groups were introduced as core-functionalities. The allyl functionalities are comparable in reactivity to the employed monomers, while for the core with vinyl groups a higher reactivity is expected in hydrosilylation reactions¹⁶. Depending on the

functionality at the core the resulting polycarbosilanes can be utilized as macroinitiator (Figure 5.6) or can be coupled with a second polymeric block to build up block copolymers. In this case, the attachment of hyperbranched polyglycidol was targeted. To this end, bisglycidolized amines have already been used successfully as macroinitiators¹⁷. Those are readily available by reaction of a primary amine with two equivalents of glycidol. Since amines can interfere with or delay hydrosilylation reactions the amine was introduced in a protected form as phthalimide group and freed after the assembly of the polycarbosilane block. In conclusion, a molecule with three double bonds for the addition of carbosilane monomers on one side and a latent amine functionality on the other side had to be prepared as ambifunctional core for both blocks.

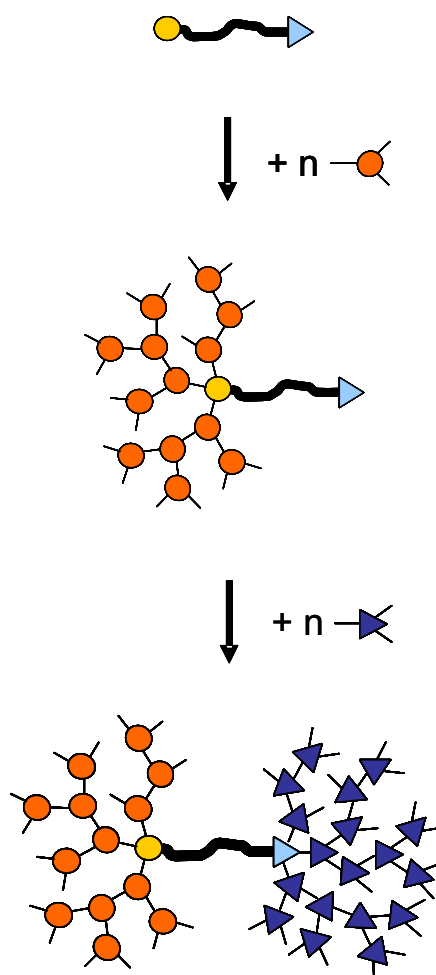


Fig. 5.6 Schematic representation for the synthesis of core functional *hb*-polycarbosilanes and their utilization as macroinitiators.

5.2 Core synthesis

The synthesis of the ambifunctional core should be accomplished starting from a commercially available α , ω -functional molecule. Thus, the choice was 11-bromo-undec-1-ene, which contains a terminal double bond as well as a bromide group. Additionally, the alkyl spacer that links both groups, separates the functionalities allowing an improved attachment of two polymeric blocks. The preparation starts with the addition of trichlorosilane to 11-bromo-undec-1-ene via hydrosilylation using Karstedt catalyst (Figure 5.7)¹⁸⁻²⁰.

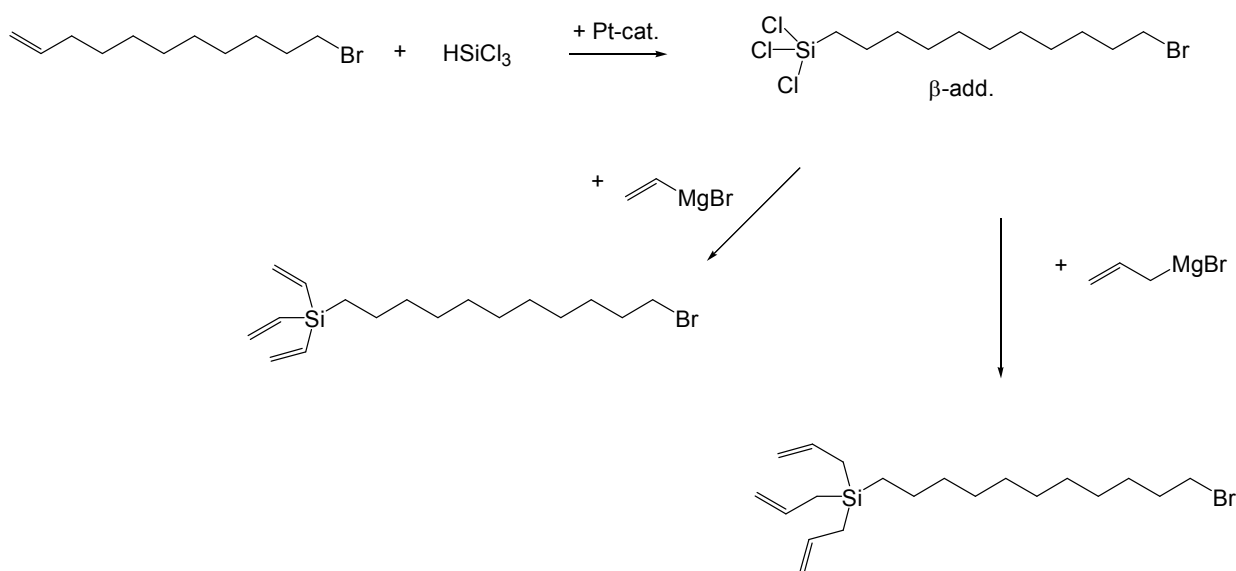


Fig. 5.7 Synthesis of bromofunctional core molecules.

An excess of trichlorosilane is used to complete the reaction, which can easily be distilled off subsequent to the transformation. As a commonly observed side reaction some isomerized undecenylbromide is formed during the reaction, but can be removed by fractionated distillation. In order to limit this side reaction 11-bromoundec-1-en is slowly added to the solution of trichlorosilane and Karstedt catalyst. This also allows controlling the heat evolution during the highly exothermic reaction. The synthesis is regioselective for the β -addition product and gives <5% of the α -addition product (Figure 5.8). This can be derived from ¹H- and ¹³C-NMR spectroscopy by the absence of methyl or methine protons, respectively (see below).

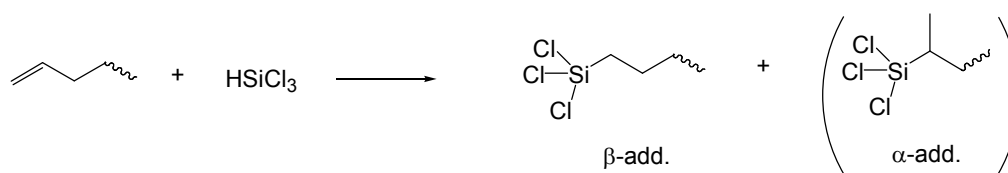


Fig. 5.8 Regioselectivity in the addition of trichlorosilane to double bonds.

The purified chlorosilane was obtained in 83% yield. In a Grignard reaction, i.e. nucleophilic substitution at the silicon, applying either allylmagnesium bromide or vinylmagnesium bromide, results in an exchange of the chlorids to give the double bond-containing derivatives (Figure 5.7). The products, (11-bromoundecyl)triallylsilane and (11-bromoundecyl)trivinylsilane, were purified by distillation or column chromatography in 71% yield each. It should be mentioned that distillation always resulted in a certain fraction of a highly viscous residue in the distillation flask, due to polymerization of the double bonds at elevated temperatures.

The bromo-functionality at the core molecule allows further modification and introduction of miscellaneous functional groups. One of the standard procedures for the synthesis of primary amines is the Gabriel reaction starting from an alkylhalide and potassium phthalimide via the respective phthalimide derivative²¹. The free amine can then be obtained by hydrolytic cleavage using hydrazine. Here, the synthesis of the intermediate 11-(triallylsilanyl)-undecylphthalimide and 11-(trivinylsilanyl)-undecylphthalimide is described. These substances contain a protected amine functionality, that does not interfere with the platinum catalyzed hydrosilylation reaction. The reaction was performed at 60°C in DMF with potassium phthalimide²². Products were purified using column chromatography with yields ranging between 60%-70%.

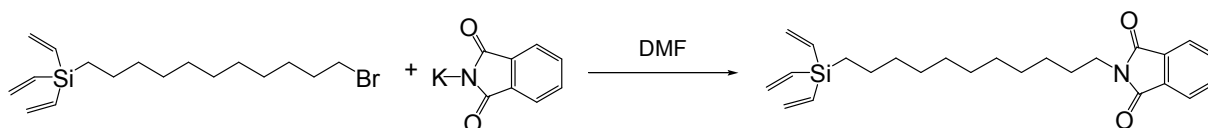


Fig. 5.9 Synthesis of phthalimide derivatives.

Another suitable procedure for the synthesis of primary amines is the Staudinger reaction via an azide group²³. The reduction of the azide can be performed with triphenylphosphine: nucleophilic attack of the phosphorus at the terminal nitrogen gives a phosphazine intermediate, which immediately loses nitrogen to form the iminophosphorane. In the presence of water and ammonia this product is hydrolyzed to give the primary amine (Figure 5.10)²⁴.

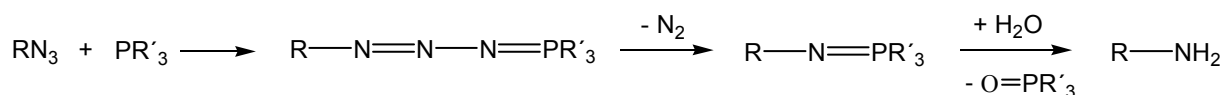


Fig. 5.10 Reaction scheme for the Staudinger reduction.

The azide containing cores can be synthesized by nucleophilic substitution of the bromo-functional molecules using sodium azide in DMF at room temperature.

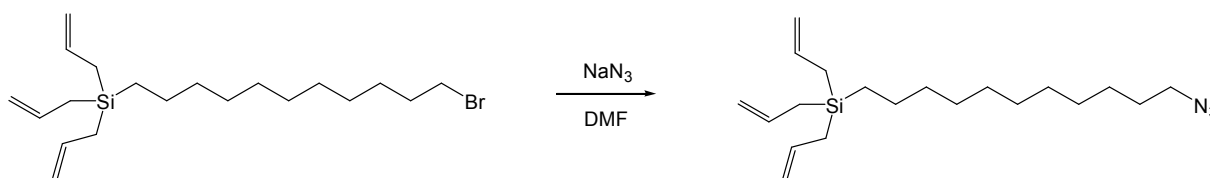


Fig. 5.11 Synthesis of azide-functional cores.

The substitution proceeded smoothly and the raw material was obtained in 70-80% yield. However, due to the low stability of the products purification failed. Especially, in the case of the vinylsilane degradation during purification was observed, possibly because of cycloaddition between azide and Si-vinyl double bonds or decomposition of the azide²⁴. Nonetheless, the reaction can be utilized in the polymer analogous modification as will be discussed in 6.3.

In Figure 5.12 the synthesized core molecules are compiled and labeled as used in the following. The abbreviations include the α - and ω -functionalities on the left and right, respectively, while C₁₁ stands for the alkyl spacer (with the α -functionality originating from the double bond and the ω -functionality from the bromide).

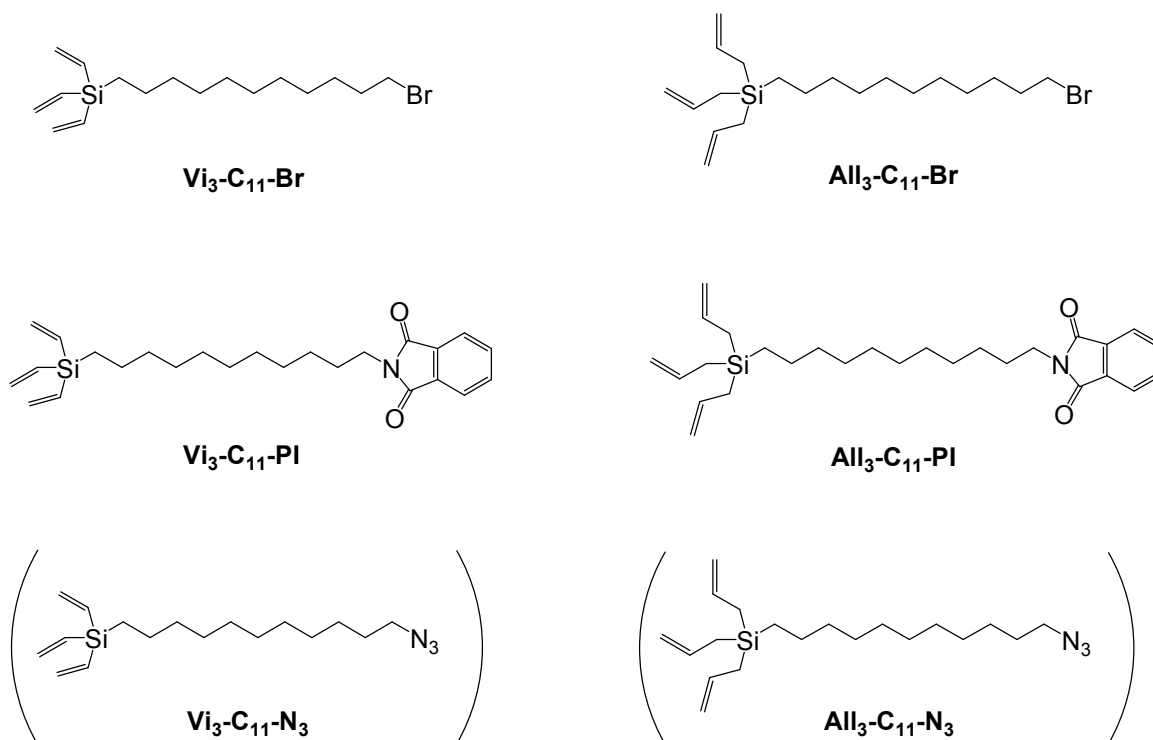


Fig. 5.12 Synthesized core molecules and nomenclature.

5.2.1 Characterization

All products were analyzed using ^1H -, ^{13}C - and ^{29}Si -NMR spectroscopy. The spectra are in agreement with the proposed structures and all signals can be readily assigned. As an example in Figure 5.13 and Figure 5.14 the ^1H - and ^{13}C -NMR spectra of 11-(trivinylsilyl)-undecenylphthalimide are given. In the ^1H -NMR spectrum the chemical shift for the methylene proton f, in this case next to the phthalimide, is very selective for the respective functional group in the ω -position of the spacer and the integral can be used as an internal reference after reaction with monomer. For the vinyl groups three different signals can be observed; an overlapped multiplet between 6.22-6.05ppm for the proton in α -position and in the β -*trans*-position to silicon and at 5.77ppm the signal for the β -*cis*-position. The absence of signals in the range between 1.0-0.8ppm, common for methyl groups, confirms the nearly exclusive formation of the β -addition product.

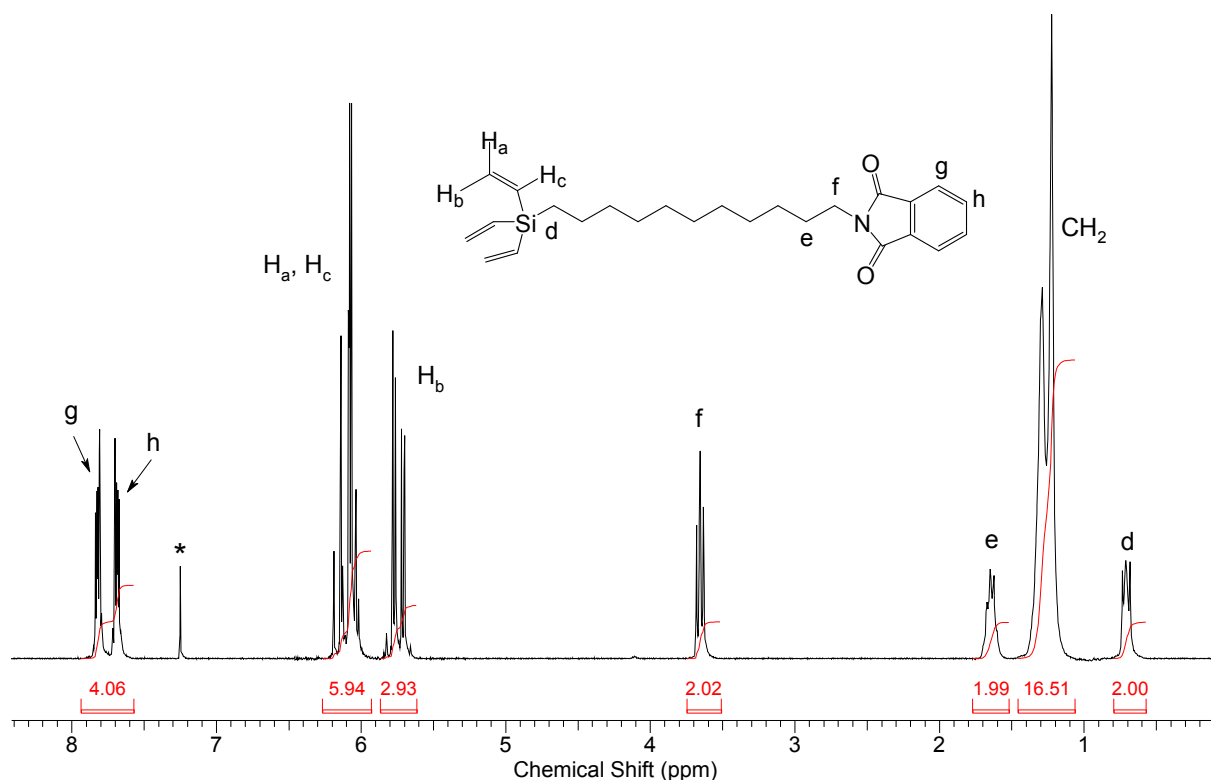


Fig. 5.13 ^1H -NMR spectrum of $\text{Vi}_3\text{-C}_{11}\text{-PI}$ in CDCl_3 .

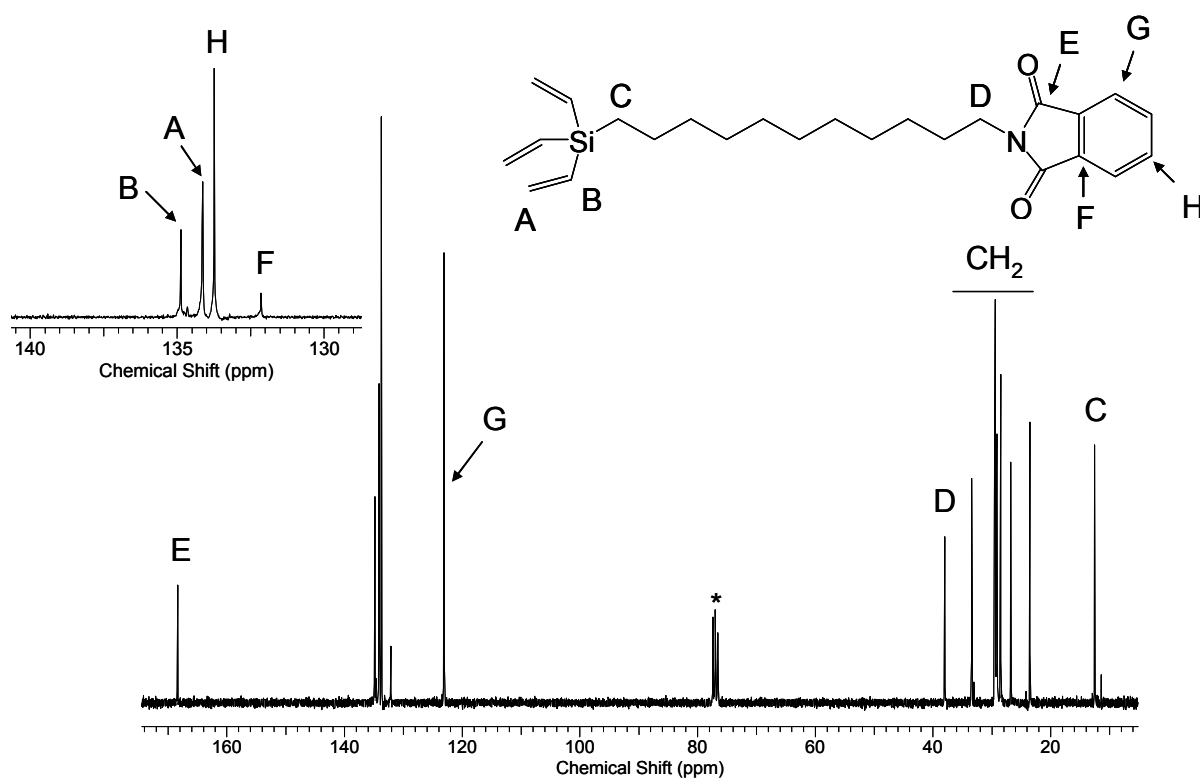


Fig. 5.14 ^{13}C -NMR spectrum of $\text{Vi}_3\text{-C}_{11}\text{-PI}$ in CDCl_3 .

In the ^{13}C -NMR spectrum, in the down-field region, the aromatic carbons belonging to the phthalimide as well as the carbons of the vinyl double bonds can be found. In the

range between 12 and 40ppm the signals for the different methylene carbons of the alkylspacer appear, in which the α - and ω -carbon can be found at 12.57ppm and 38.01ppm, respectively. In the ^{29}Si -NMR spectra a single peak is observed for all products. The ^{29}Si -chemical shifts for the cores are summarized in Table 5.1, together with the carbon shifts for the respective double bonds.

Table 5.1 ^{13}C - and ^{29}Si -NMR shifts (X=Br, PI)

core	$\delta_{\text{C}=\text{C}}$ [ppm]		δ_{Si} [ppm]
$\text{Vi}_3\text{-C}_{11}\text{-X}$	134.87	134.14	-19.53
$\text{AlI}_3\text{-C}_{11}\text{-X}$	134.48	113.40	-0.18

Elemental analysis was applied for the samples and proved the purity of the products. In contrast, FD-MS gave no meaningful results for these samples due to decomposition of the products under the measuring conditions. Instead, GPC was used and showed monodisperse curves with no indication for side products (Figure 5.15). These results were also valuable as a reference after polymerization with monomer.

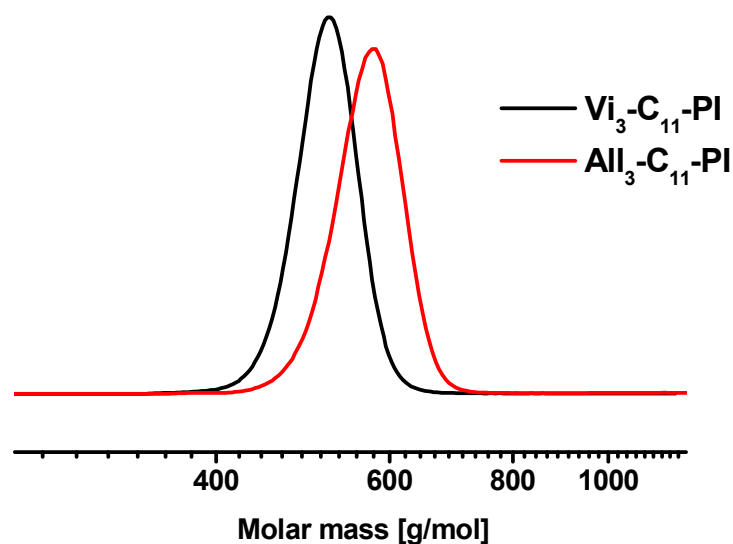


Fig. 5.15 GPC curve in CHCl_3 (RI-signal) for $\text{Vi}_3\text{-C}_{11}\text{-PI}$ and $\text{AlI}_3\text{-C}_{11}\text{-PI}$.

5.3 Synthesis of core-functional branched polycarbosilanes

Different reaction conditions for the polymerization and synthesis of core-functional hyperbranched polycarbosilanes have been tested. At first, the core-functional polycarbosilanes were prepared from dialkenylsilane (AB_2) monomers via the one-pot synthetic procedure. Core molecules of different reactivity were used to study their influence on the polymerization result. 11-Bromo-undec-1-ene, as analog to the oxazoline functional core used by Lach et al.¹⁴, as well as cores with either three vinyl or allyl groups, prepared in the preceding chapter, were applied for the attachment of the branched carbosilane block. Secondary, slow addition techniques were used to enhance molecular weight control. Finally, using different UV-active cores, incorporation of the core into the polymer can be studied applying GPC and MALDI-ToF. The polymers were characterized by NMR spectroscopy.

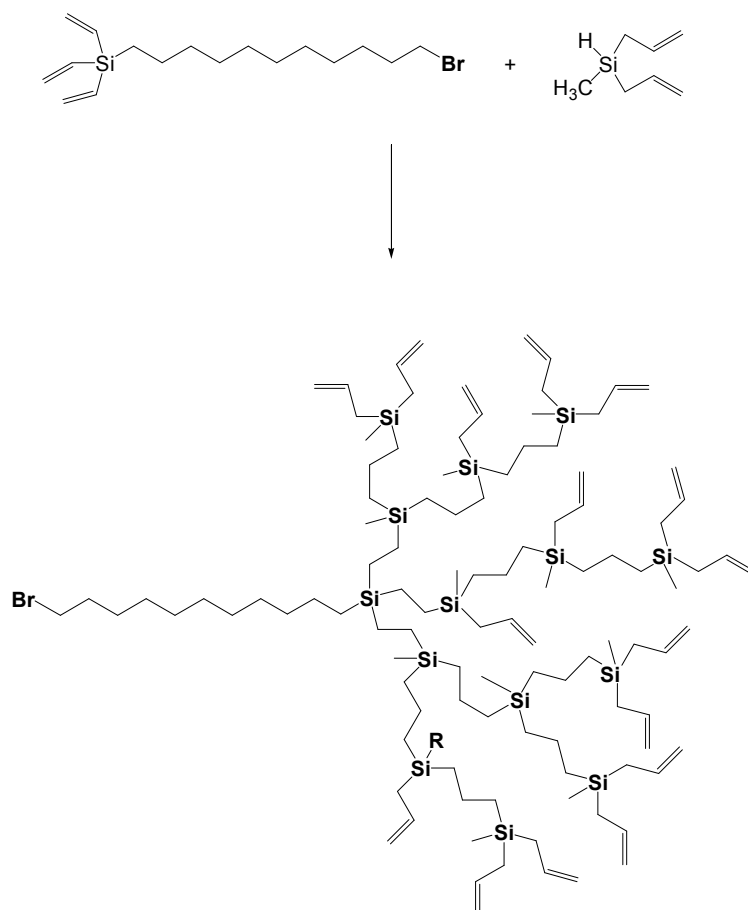


Fig. 5.16 Example for the synthesis of *hb*-PDAMS in the presence of core molecule.

The structure of the polycarbosilane can be tailored by the choice of monomer: different spacer lengths as well as monomers with either two or three A functionalities can be utilized. In this case, diallylmethylsilane was used as monomer, mainly due to the following reasons: 1. the methyl group at the silane serves as an internal standard for the quantification of the degree of polymerization; 2. compared to the AB₃ monomer the AB₂ monomer is less subjected to steric crowding, which can limit the degree of polymerization 3. polymers based on the long undecenyl spacer are especially susceptible to isomerization of the external double bonds.

5.3.1 Core reactivity

The comparison of the reactivity of the different core molecules appeared to be most important. The reactions were performed in bulk at room temperature by charging the reaction flasks with the cores and different equivalents of monomer. The polymerizations were started by addition of Karstedt catalyst under nitrogen atmosphere. Upon catalyst addition the reaction mixtures instantly turned yellow. The completion of the reaction can conveniently be controlled by IR-spectroscopy owing to the disappearance of the Si-H stretching mode around $\nu = 2100\text{cm}^{-1}$ (Figure 5.17). For the following discussions no purification of the polymers was performed to avoid any removal of unreacted core or low molecular weight species in order to study the conversion of the compounds. All polymers are slightly brown or yellow liquids of moderate viscosity.

In the ideal case, when the core molecule is significantly more reactive than the monomer, the first step in the reaction should be the addition of three monomers to the B₃ core. In this way, a core molecule with six functional groups is created which now have about equal reactivity compared to the monomer functional groups. Nevertheless, due to statistical reasons the probability of monomer addition to the core ($f=6$) is in favor over addition of monomer to monomer ($f=2$). This holds true as long as the concentration of monomer is not considerably higher than the core concentration. Thus, a rather low monomer to core ratio of 5:1 was chosen for the polymerization of diallylmethylsilane with 11-bromoundec-1-ene, (11-bromoundecyl)trivinylsilane and (11-bromoundecyl)triallylsilane in order to compare the reactivities (Table 5.2).

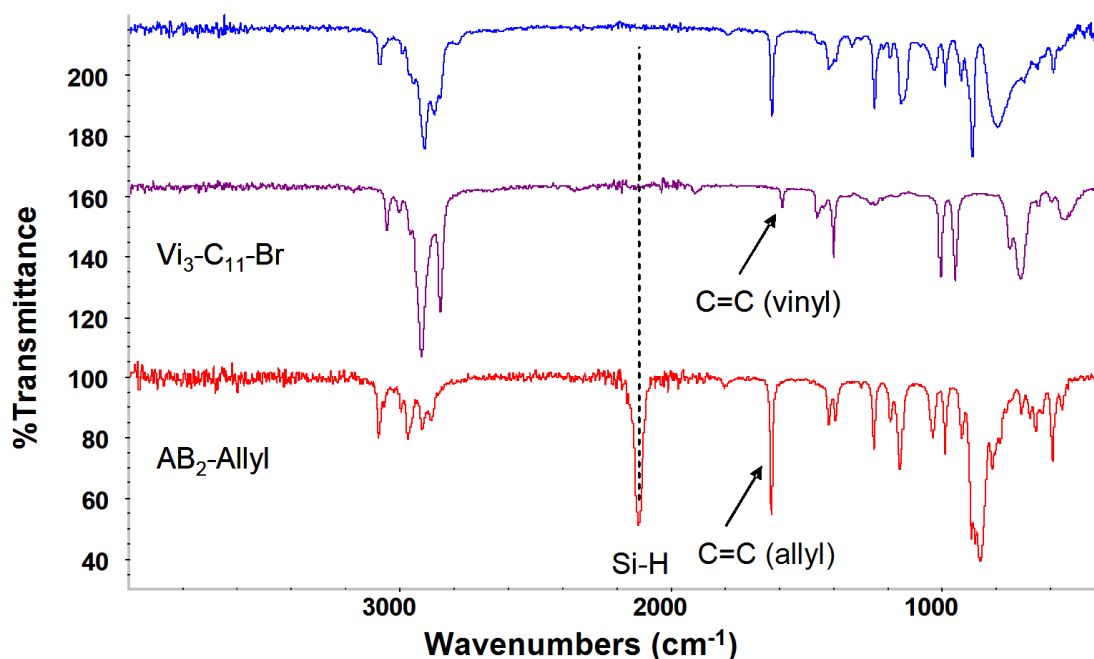


Fig. 5.17 Comparison of FT-IR spectra for AB₂-monomer (red), core Vi₃-C₁₁-Br (purple) and polymerization mixture after complete reaction (blue).

Table 5.2 Bulk polymerization with different core molecules.

core	monomer/core ¹	M(theor.)	GPC(CHCl ₃)	
			M _n	PDI
11-bromo-undec-1-en	4.9	850	840	1.82
All ₃ -C ₁₁ -Br	5.3	1100	1100	2.37
Vi ₃ -C ₁₁ -Br	5.2	1000	940	1.16

¹molar ratio of monomer to core

The GPC results for the polymerizations show the formation of a narrowly distributed oligomer (PDI=1.16) in the case of Vi₃-C₁₁-Br, while for All₃-C₁₁-Br and 11-bromoundec-1ene the distributions are broader with PDI=2.37 and 1.82, respectively. This suggests a well controlled reaction only for (11-bromoundecyl)trivinylsilane. However, in all cases a reduction of molecular weight compared to the neat homopolymerization of diallylmethylsilane is observed (normally M_n~3000g/mol, PDI 2.5-3.5) and the theoretically determined molecular weights and GPC results are in good agreement. Anyway, here the shape of the GPC curves gives a more significant result. In Figure 5.18 it can clearly be seen that for 11-bromoundec-1-ene and (11-bromoundecyl)triallylsilane still a major amount of unreacted core molecule is

present. The finding supports the presumption that these cores show no enhanced reactivity compared to the monomer. Thus, statistical reasons determine the conversion. In this case, remaining core molecules are expected, since the reaction inherently has at least a 2:1 excess of double bonds compared to silicon hydride. Surprisingly, here no apparent advantage can be taken from the fact that a triple functional molecule is used. In contrast, in the case of (11-bromoundecyl)trivinylsilane the core is completely incorporated into the oligomer (Figure 5.19), implying the faster and preferred reaction of the core-functionalities.

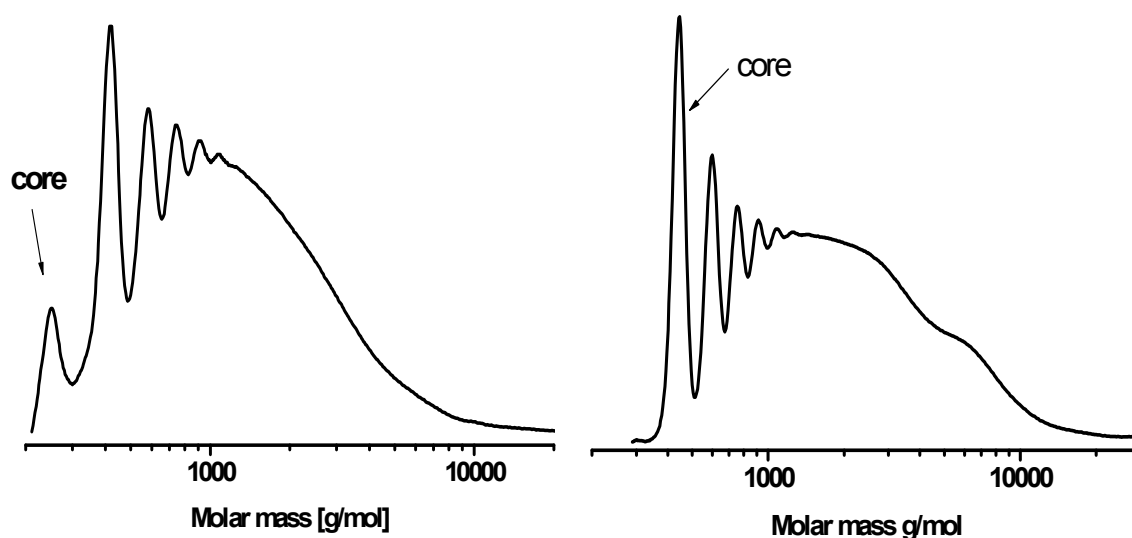


Fig. 5.18 GPC curve in CHCl_3 (RI-signal) for polymerization of DAMS in the presence 11-bromoundec-1-en (left) and $\text{All}_3\text{-C}_{11}\text{-Br}$ (right).

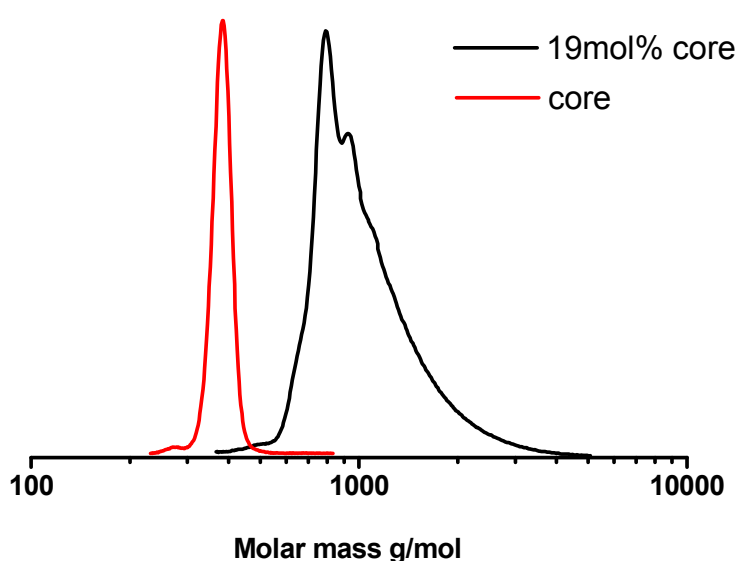


Fig. 5.19 GPC curve in CHCl_3 (RI-signal) for $\text{Vi}_3\text{-C}_{11}\text{-Br}$ and for polymerization of DAMS in the presence of 19%mol $\text{Vi}_3\text{-C}_{11}\text{-Br}$.

Thus, the requirement for a highly reactive core is fulfilled, that should allow a functionalization of the polymers as complete as possible. In order to check the control of the reaction also for higher molecular weights further bulk reactions with different monomer/core ratios were tested (Table 5.3). The samples are named as follows: PCS_x stands for the branched polycarbosilane block with the degree of polymerization x; -C₁₁-Br denotes the alkyl spacer and the ω -functionality.

Table 5.3 Bulk polymerization of DAMS with Vi₃-C₁₁-Br at different monomer/core ratios.

sample	monomer/core ¹	M(theor.)	GPC(CHCl ₃)	
			M _n	PDI
PCS ₄₀ -C ₁₁ -Br	39.6	5300	3300	2.74
PCS ₂₉ -C ₁₁ -Br	28.6	3900	2600	2.57
PCS ₁₉ -C ₁₁ -Br	19.1	2800	1700	1.71
PCS ₁₀ -C ₁₁ -Br	10.4	1700	1300	1.78
PCS ₅ -C ₁₁ -Br	5.2	1000	940	1.16
PCS ₃ -C ₁₁ -Br	3.1	730	720	1.04

¹molar ratio monomer/core in the feed

The test series reveals that a control of molecular weight can be achieved by the amount of core added, as it was intended. Here, lower values for the GPC results compared to the theoretical values can in part be assigned to a general underestimation of hyperbranched structures by this technique. Despite the controlled polymerization for large core fractions, the molecular weight distribution increases for decreasing core to monomer ratios. This is in accord with the considerations made above. For high monomer concentrations the reaction of monomers with each other becomes more favorable and in this way oligomers and polymer without functional core are formed. Due to intramolecular cyclization, which consumes the Si-H in the core, the bonding with core-bearing molecules in later stages of the reaction is also prohibited. The appearance of bi- or multimodal distributions also becomes more distinct for lower core fractions, suggesting side reactions (Figure 5.20). Slow monomer addition techniques have been reported to be a versatile tool to circumvent these problems and are investigated in the next section.

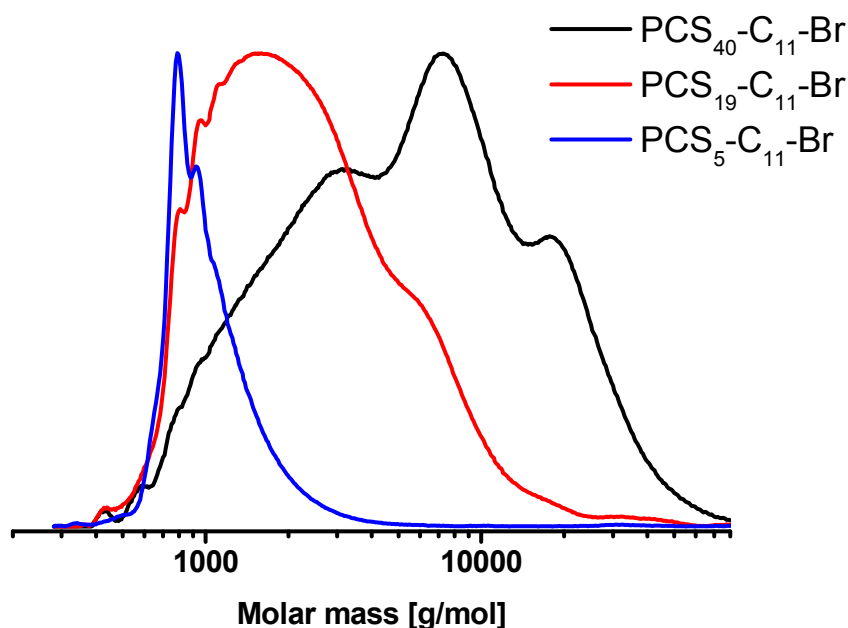


Fig. 5.20 Examples of GPC curves in CHCl_3 (RI-signal) for different monomer to core ratios.

5.3.2 Polymerization control with slow addition techniques

In order to further enhance the control of the synthesis of the core-functional polycarbosilanes slow addition techniques were used. At first a syringe pump, which can be charged with the monomer solution, was used to perform the reaction. This allows the dropwise addition of the monomer to a reaction flask containing the core molecule. Due to the low viscosity of the resulting polymers no solvent was used neither to dissolve the core nor the monomer. This keeps the core concentration high throughout the reaction, avoiding the reaction of monomers with each other. On the other hand, the amount of monomer added per drop can be rather high. Hence, reaction of monomers with each other cannot be completely excluded. A more sophisticated method, circumventing this problem, is the polymerization by the slow monomer addition-dilution technique (SMA). In this case a dilute monomer solution in a low boiling solvent is added slowly to the core molecule. Thus, the low boiling solvent can be removed constantly, keeping the polymerization mixture highly concentrated. Together with the slow addition of the monomer this guarantees that all monomer reacts with the core before new monomer is added. The approach has proven to be a very efficient and controlled method for the synthesis of narrowly distributed linear-hyperbranched PS-*hb*-PCS block copolymers¹⁵. The results for the

polymerization using these methods are given in Table 5.4. Here, in all cases the phthalimide functional cores have been used to allow further reaction.

Table 5.4 Polymerizations of diallylmethylsilane with $\text{Vi}_3\text{-C}_{11}\text{-PI}$ using slow addition techniques.

sample ¹	conditions	monomer/ core ²	M(theor.)	$M_n(\text{NMR})$	GPC(CHCl_3)	
					M_n	PDI
$\text{PCS}_{13}\text{-C}_{11}\text{-PI}$	SMA	10.0	1670	1990	2200	1.35
$\text{PCS}_{39}\text{-C}_{11}\text{-PI}$	SMA	40.1	5470	5300	3200	1.98
$\text{PCS}_{11}\text{-C}_{11}\text{-PI}$	syringe pump	10.0	1670	1760	1700	1.45
$\text{PCS}_{17}\text{-C}_{11}\text{-PI}$	syringe pump	19.2	2830	2530	2100	1.46
$\text{PCS}_{36}\text{-C}_{11}\text{-PI}$	syringe pump	37.4	5130	5010	2600	1.87

¹composition determined by NMR according to 5.3.4 ²molar ratio of monomer to core

Molecular weights determined by NMR are in good agreement with the theoretical values. For the GPC data a deviation from these values is observed for higher molecular weight polymers. Compared to the bulk polymerization even at low core concentrations the polydispersity can be kept <2 using the slow monomer addition technique. Generally, the results are similar for the preparatively laborious addition via the slow monomer addition-dilution technique (see Figure 5.31 for setup) and the simple dropwise addition of the neat monomer with a syringe pump. Consequently, the addition via syringe pump is privileged, due to the ease in procedure. The GPC traces show that a high molecular weight shoulder is formed for low core/monomer ratios (Figure 5.21 and 5.22). Here, it is rather interesting to compare the shape and maxima of the curves with the results obtained in the neat homopolymerization of diallylmethylsilane, where the occurrence of a multimodal distribution has been observed before (see 3.2). In Figure 5.23 the peak maxima are essentially the same in all cases with the high molecular weight shoulders being less pronounced for the core-functional polymers. This has to be associated with the observation made by Drohmann et al., who reported the appearance of a limiting molecular weight for these polymers: after repeated addition of new monomer to a polymerization mixture for allyl-based monomers no enhancement of the molecular weight took place any more²⁵. Even though rather implausibly, this was explained by the rising sterical hindrance that prevents interaction of the polymer double bonds with the catalyst at a certain point. More likely the non-increase in molecular weight is probably due to cyclization consuming Si-H functionalities as suggested by Fréchet et al.²⁶ and Frey

et al.²⁷. Despite this, obviously also side reactions became kinetically more important when a certain molecular weight is achieved. For example rearrangements can lead to the formation of A_2B molecules, which can act as crosslinkers and in minor concentration cause the formation of dimers and trimers, which constitute the high molecular weight shoulder.

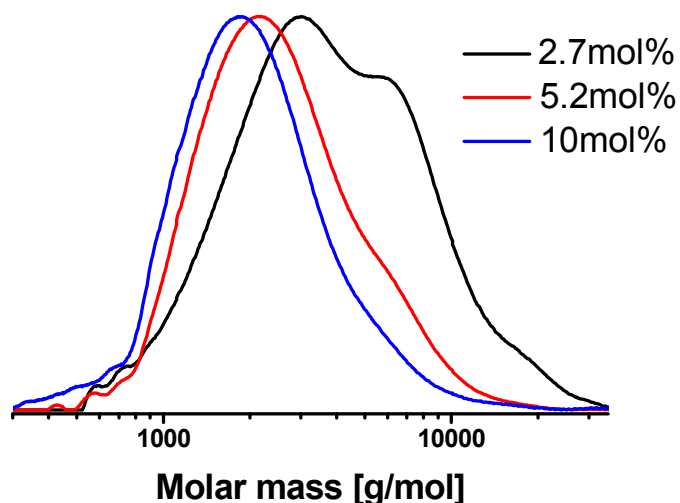


Fig. 5.21 GPC curve in CHCl_3 (RI-signal) for the polymerization of diallylmethylsilane with $\text{Vi}_3\text{-C}_{11}\text{-PI}$ core using a syringe pump.

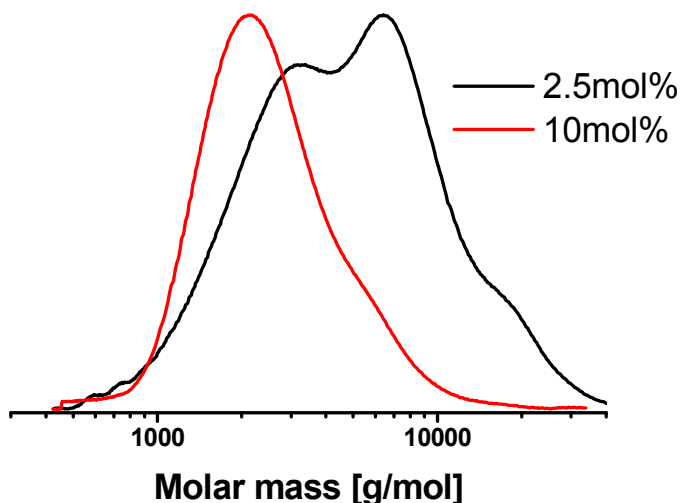


Fig. 5.22 GPC curve in CHCl_3 (RI-signal) for the polymerization of diallylmethylsilane with $\text{Vi}_3\text{-C}_{11}\text{-PI}$ core applying slow-monomer-addition.

Nonetheless, this approach allows the synthesis of well-defined structures with $\text{PDI} < 1.5$ up to $M_n \sim 3000$. This limitation in molecular weight does not impede further application in block copolymer synthesis, since a large block prevents the attachment

of the second polymer due to shielding of the core-functionality. This also holds true when it comes to polymer analogous reactions, e.g. removal of the phthalimide group. Further modifications of the core-functional polymers and their application in block copolymer synthesis are discussed in chapter 6.

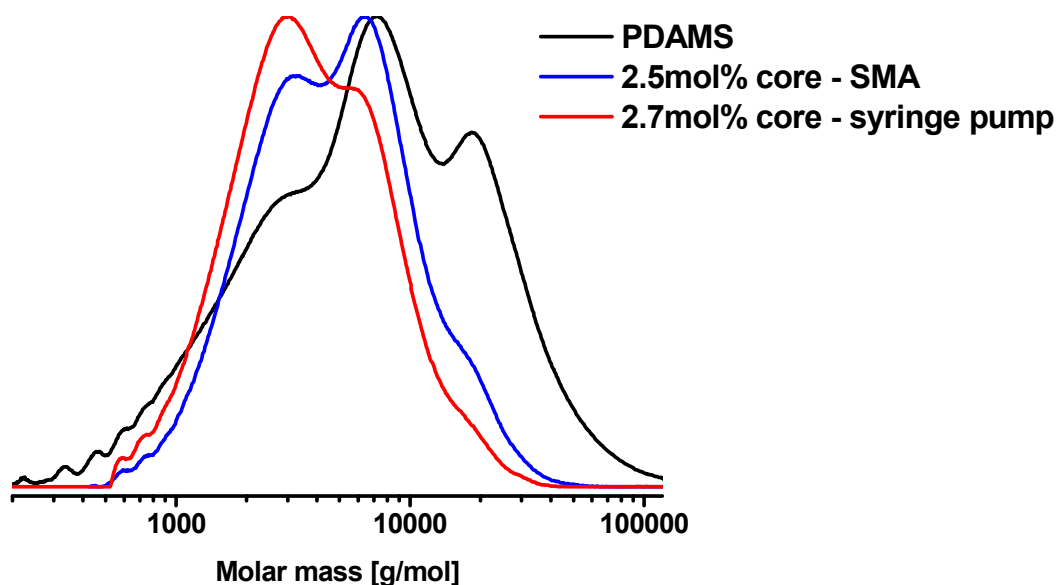


Fig. 5.23 GPC curve in CHCl_3 (RI-signal) for the polymerization of diallylmethylsilane with and without core.

5.3.3 Distribution of core in the polymer

The results concerning the core reactivity and the different reaction procedures obtained in the last sections can be additionally confirmed, when polymers with UV-active cores are compared. Unfunctionalized hyperbranched polycarbosilanes are not UV-active, thus normally only the refractive index signal can be used for analysis in the GPC elugramm. Aromatic phthalimides, however, exhibit UV-bands, thus the incorporation of a phthalimide-containing core leads to the detection of an UV-signal for these polymers. Depending on the course of reaction, the UV-active molecule can be accumulated in the low molecular weight material or be distributed throughout the whole molecular weight range. In the following the polymerization results for polymerizations with monomer/core ratios of 10:1 (Table 5.5) and some examples of the respective GPC curves are shown (Figure 5.24). In agreement with the results for the analysis of the core reactivities, the UV- and RI-signals for polymers with *N*-undec-10-enylphthalimide ($\text{C}_{11}\text{-PI}$) as well as with the allyl-bearing core exhibit large discrepancies. Molecular weights are underestimated by the UV curves, resulting

from the severe decay of the signal for higher molecular weights (fig. 5.24 (A)). While there is still a difference between the shapes of the curves when $\text{Vi}_3\text{-C}_{11}\text{-PI}$ is used in bulk polymerizations, the curves are almost congruent with each other for the slow addition techniques.

Table 5.5 Polymerization results for the reaction with UV-active phthalimide-containing cores.

core	conditions	M(theor.)	GPC(CHCl_3 , RI)		GPC(CHCl_3 , UV)	
			M_n	PDI	M_n	PDI
$\text{C}_{11}\text{-PI}$	bulk	1560	1920	2.96	660	2.62
$\text{AlI}_3\text{-C}_{11}\text{-PI}$	bulk	1700	1460	2.64	890	1.85
$\text{Vi}_3\text{-C}_{11}\text{-PI}$	bulk	1670	1680	1.47	1400	1.37
$\text{Vi}_3\text{-C}_{11}\text{-PI}$	syringe pump	1670	1700	1.45	1660	1.42
$\text{Vi}_3\text{-C}_{11}\text{-PI}$	SMA	1670	2190	1.35	2150	1.43

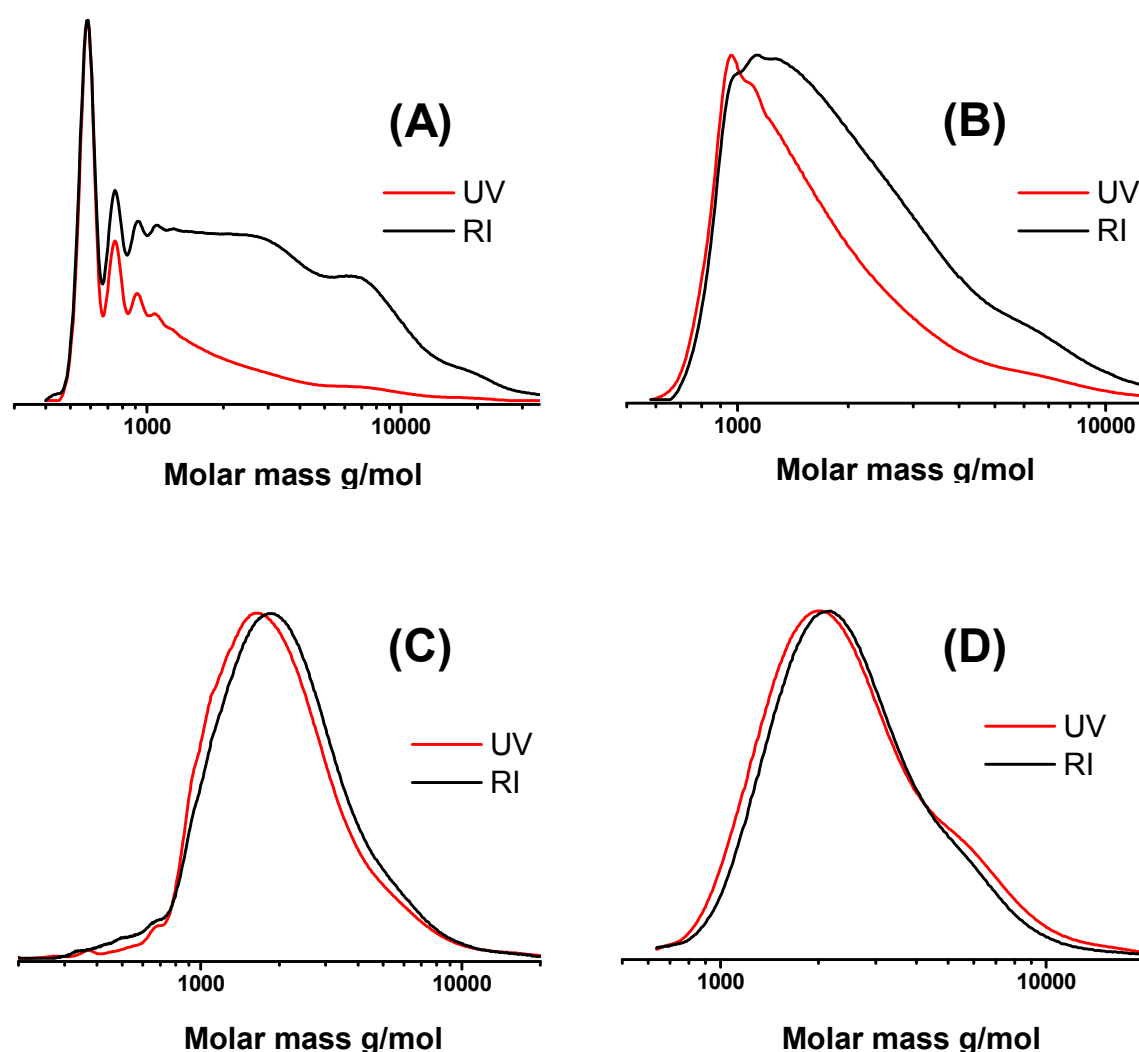


Fig. 5.24 GPC curves in CHCl_3 for polymerization results with monomer/core ratio of 10:1 (A) bulk polymerization with $\text{AlI}_3\text{-C}_{11}\text{-PI}$, (B) bulk polymerization with $\text{Vi}_3\text{-C}_{11}\text{-PI}$, (C) addition with syringe pump to $\text{Vi}_3\text{-C}_{11}\text{-PI}$ and (D) reaction by slow monomer addition to $\text{Vi}_3\text{-C}_{11}\text{-PI}$.

Finally, the conclusion can be drawn that for the reactive core ($\text{Vi}_3\text{-C}_{11}\text{-X}$) the functional group is present throughout the whole molecular weight range, suggesting the presence of at most a small amount of unfunctional polymer in the sample. Instead, for unreactive cores the discrepancy between the curves for the UV- and RI-signal for higher molecular weights suggests the formation of homopolymer besides core-functional material. Additionally, diagrams **(B)**-**(D)** reflect the influence of the polymerization technique underlining the advantages of the slow addition techniques.

MALDI-ToF is another possibility to confirm the incorporation of the core into the polymer. In Figure 5.25 the mass distribution for a polymer obtained by reaction of diallylmethylsilane with 10mol% $\text{Vi}_3\text{-C}_{11}\text{-PI}$ is displayed. Each peak can be assigned to $[\text{core} + n \times \text{monomer} + \text{Ag}]^+$ with $n \geq 3$. Unfortunately, polycarbosilanes are generally hard to detect by MALDI experiments, thus the presence of homopolymer cannot be fully excluded by this result. Worth mentioning is the fact that no peaks can be detected lower than the triple substituted core, confirming conversion of all core-functionalities.

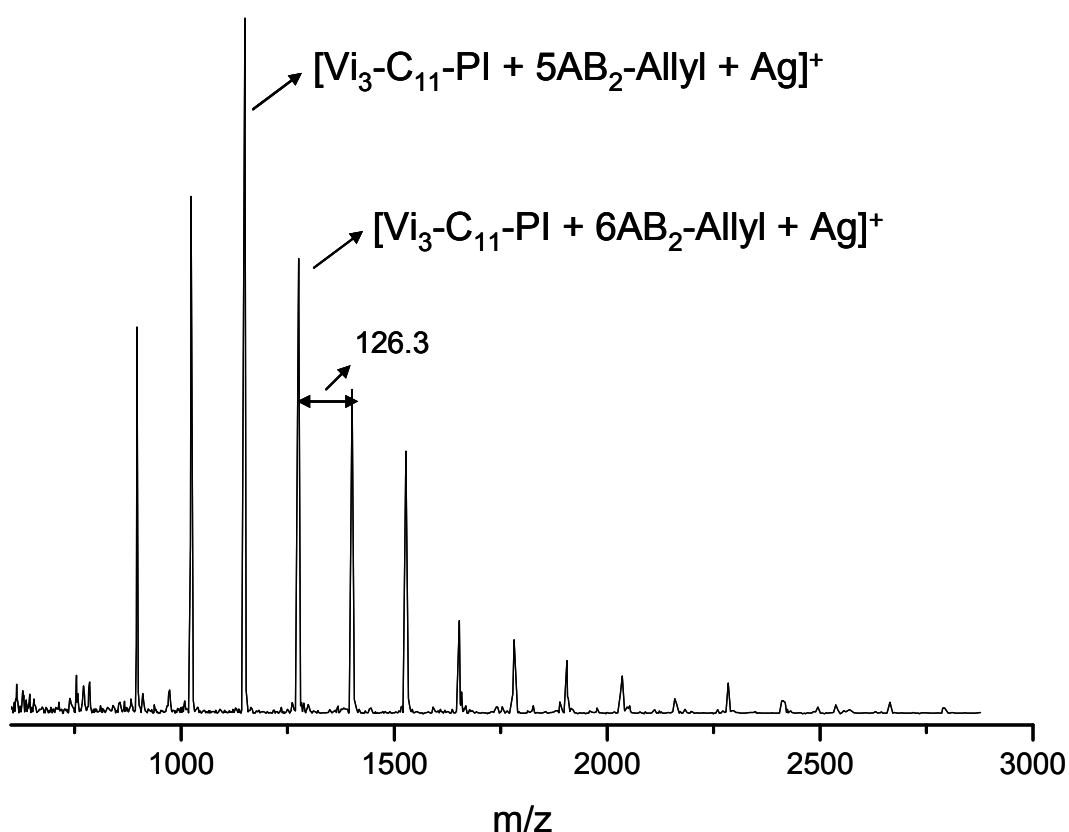


Fig. 5.25 MALDI-ToF spectrum of $\text{PCS}_{10}\text{-C}_{11}\text{-PI}$ (pencil, Ag^+).

5.3.4 Spectroscopic characterization of the functional polymers

The polymers were characterized using ^1H , ^{13}C and ^{29}Si -NMR spectroscopy. The spectra for the core-functional polymers are similar to the spectra of the neat homopolymer, so that many of the assignments can be readily transferred. Additionally, of course the core signals are present. In Figure 5.26, as a representative example, the ^1H -NMR spectrum of $\text{PCS}_{39}\text{-C}_{11}\text{-PI}$ is given. Here, the aromatic protons of the phthalimide at 8.85-8.65ppm (red), as well as the triplet for the methylene group next to the phthalimide at 3.66ppm (blue) can be identified. The remaining CH_2 groups of the spacer are part of the broad signal between 1.15-1.45ppm, giving rise to a sharp spike at 1.26ppm. All further signals are equivalent to the spectrum of *hb*-PDAMS and can be assigned as done before (see chapter 3.3). For polymers with bromofunctional core molecules the functional group can be identified by a triplet at 3.42ppm for the methylene group bearing the bromide and a signal for the adjoining methylene centered at 1.86ppm. Since the signal for the CH_2 in α -position to the functional groups can be readily distinguished from the other signals, it can be used as an internal reference to determine the degree of polymerization. The calculation was based on the relative intensities of this signal ($I_{\text{X-CH}_2}$) compared to the signal for the Si-CH_3 groups ($I_{\text{Si-CH}_3}$):

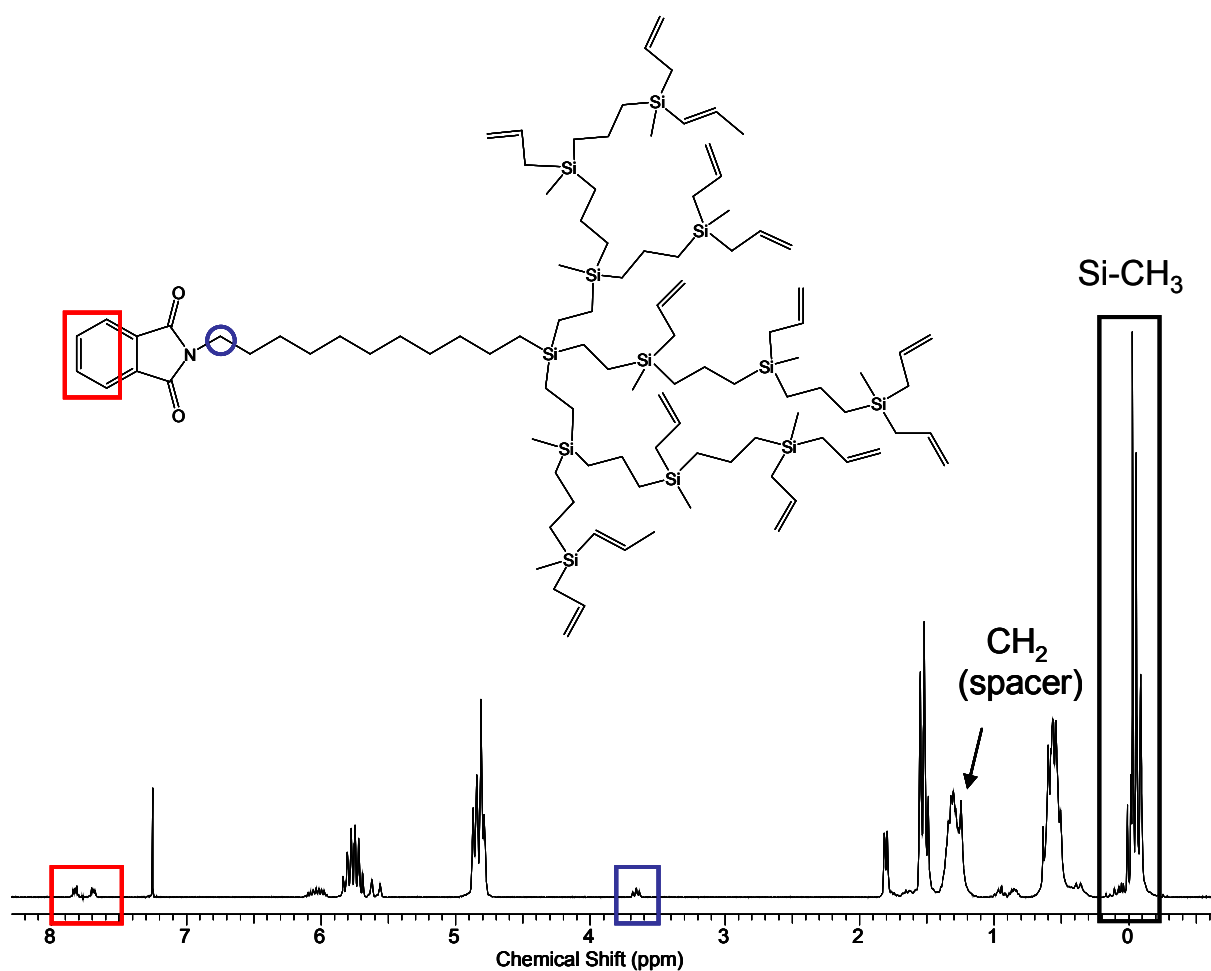
$$DP = \frac{I_{\text{Si-CH}_3}}{3} : \frac{I_{\text{X-CH}_2}}{2}.$$

The results of this calculation are presented in Tables 5.6 and 5.4 and are in good agreement with the employed monomer to core ratios. In all cases a small amount of isomerized double bonds is observed, usually <6% for polymers prepared via syringe pump. This effect is more severe for the polymers obtained via SMA with more than 10% isomerization, due to the longer contact times with the catalyst. For the polymers summarized in Table 5.6, the signals for the vinyl groups belonging to the core have completely disappeared, implying full conversion of the core. However, it has to be mentioned that in the ^1H -NMR spectra for polymerization mixtures with 3 to 5 equivalents of monomers some unreacted vinyl groups are still present (<15%). Probably, the reaction of the first two double bonds of the core results in a shielding of the remaining vinyl group and favors reaction at the novel external double bonds.

Table 5.6 Degree of polymerization and amount of isomerized double bonds calculated by NMR.

sample	conditions	monomer/ core ¹	DP(NMR)	%isom. DB ²
PCS ₁₃ -C ₁₁ -PI	SMA	10.0	13	14
PCS ₃₉ -C ₁₁ -PI	SMA	40.1	39	12
PCS ₁₁ -C ₁₁ -PI	syringe pump	10.0	11	4
PCS ₁₇ -C ₁₁ -PI	syringe pump	19.2	17	6
PCS ₃₆ -C ₁₁ -PI	syringe pump	37.4	36	5

¹molar ratio of monomer to core ²percentage of isomerized double bonds.

**Fig. 5.26** ¹H-NMR in CDCl₃ for PCS₃₉-C₁₁-PI.

In Figure 5.27 a comparison of the ¹³C-NMR spectra for the functional polycarbosilane, *hb*-PDAMS and the core Vi₃-C₁₁-PI is given, allowing to determine which signals result from the core and which from the branched polymer structure. Principally, the spectrum for PCS₁₀-C₁₁-PI is an overlap of the core and the *hb*-PDAMS spectra, however some signals disappear or are shifted.

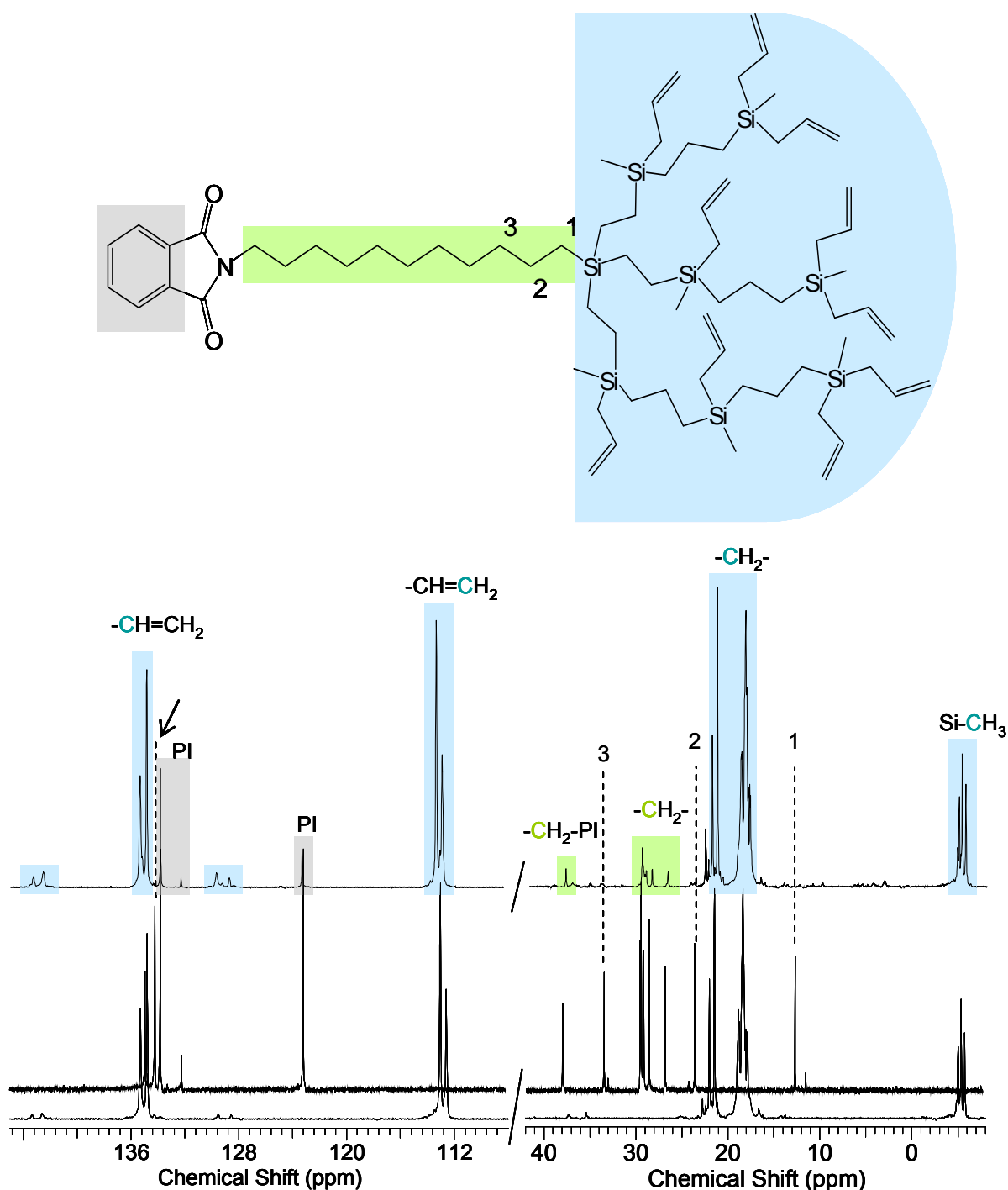


Fig. 5.27 ^{13}C -NMR in CDCl_3 of $\text{PCS}_{39}\text{-C}_{11}\text{-PI}$, $\text{Vi}_3\text{-C}_{11}\text{-PI}$ and *hb*-PDAMS from top to bottom.

The peaks belonging to the branched structure are highlighted turquoise, starting up-field with up to five peaks between -5.02ppm and -6.31ppm for the Si-CH_3 carbons of the different branching units. The CH_2 groups of the short alkyl spacer give rise to a number of signals between 17.5 and 19.2ppm, followed by two signals at 21.5ppm and 22.0ppm belonging to the allylic carbons. In the olefinic region two pairs of

signals resulting from the methine and methylene carbons of the double bond can be identified, as well as smaller signal for the isomerized double bonds. The signals for the phthalimide functionality, incorporated into the polymer, are retained at 168.4ppm, 133.78ppm, 132.2ppm and 123.1ppm (highlighted grey), together with most of the signals for the alkyl spacer (highlighted green). Linking of the core and the branched structure is proven by the deviations from a spectrum obtained from a pure overlap of the individual spectra of the components.

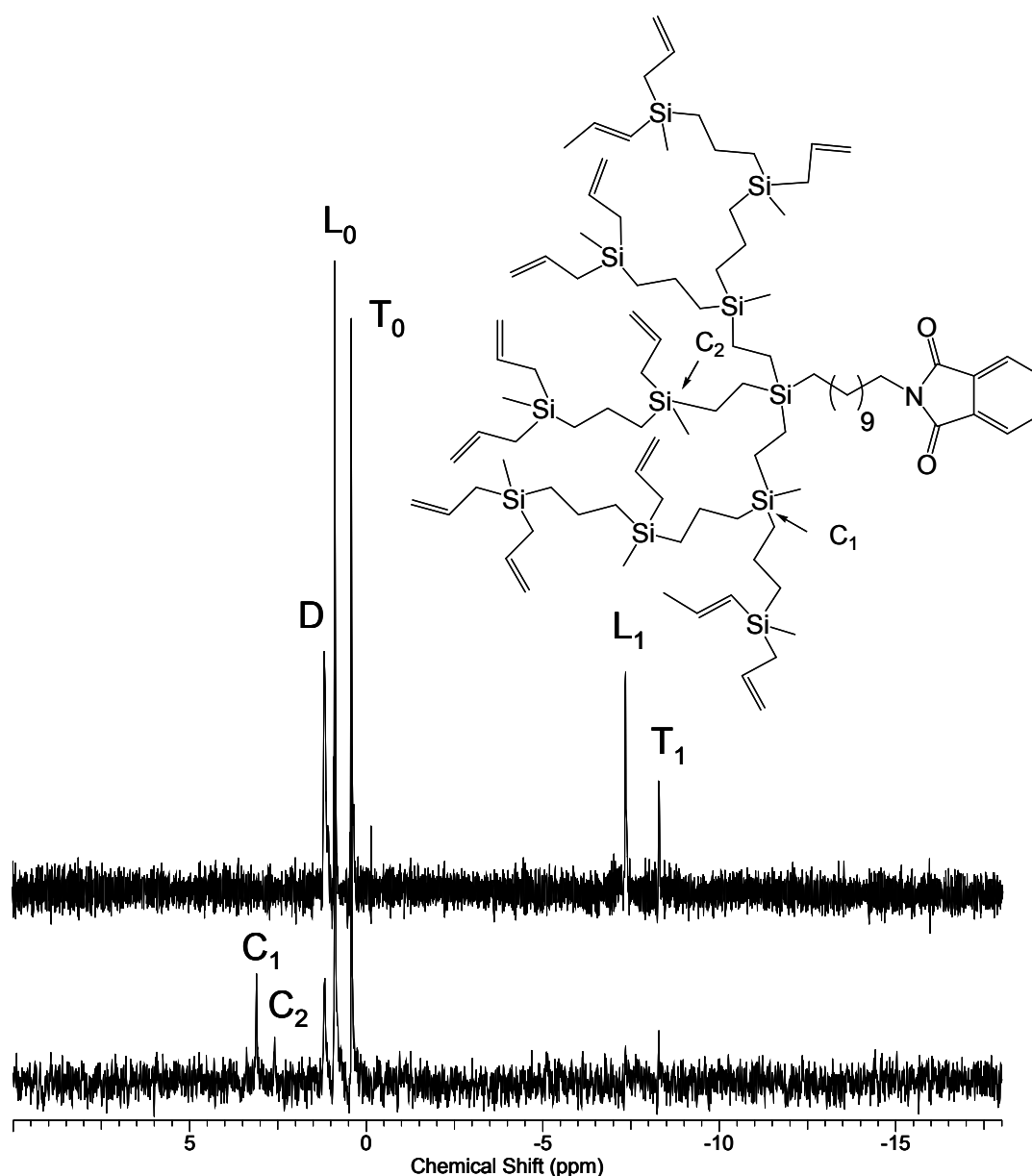


Fig. 5.28 ²⁹Si-NMR in CDCl₃ for PCS₃₉-C₁₁-PI (upper) and PCS₁₇-C₁₁-PI (lower).

The attachment of the polymeric block to the core results in the disappearance of the vinyl carbons at 134.9 and 134.1ppm (indicated with an arrow). Additionally, a shift

can be observed for all CH₂ groups of the spacer in proximity to the polymeric block, this is in 1-,2- and 3- position to silicon (dashed line).

At large monomer to core ratios the ²⁹Si-NMR for the functional polycarbosilane is identical with the pure homopolymer *hb*-PDAMS. Here, the three signals for dendritic (D), linear (L₀) and terminal units (T₀) can be seen as well as two smaller signals (L₁, T₁) for branching units bearing isomerized double bonds (Figure 5.28 upper). If the polycarbosilane block is small (<20 monomers) two additional signals (C₁, C₂) appear at 3.11ppm and 2.61ppm (Figure 5.28 lower). The HSQC spectrum for the Si-H correlation (Figure 5.29) shows that coupling between these signals and the methyl protons occurs, which permits to conclude that the peaks are a result of monomer branching units directly bound to the core. The silicon of the core molecule can not be identified, probably due to the low relative amount in the sample. Because of the new signals that cannot be doubtlessly assigned to the respective branching units, a degree of branching (DB) was not calculated. However, the splitting of the signals in the silicon-NMR, as well as the different peaks for the Si-CH₃ group in the ¹H- and ¹³C-NMR confirm the branched structure of the functional polymers.

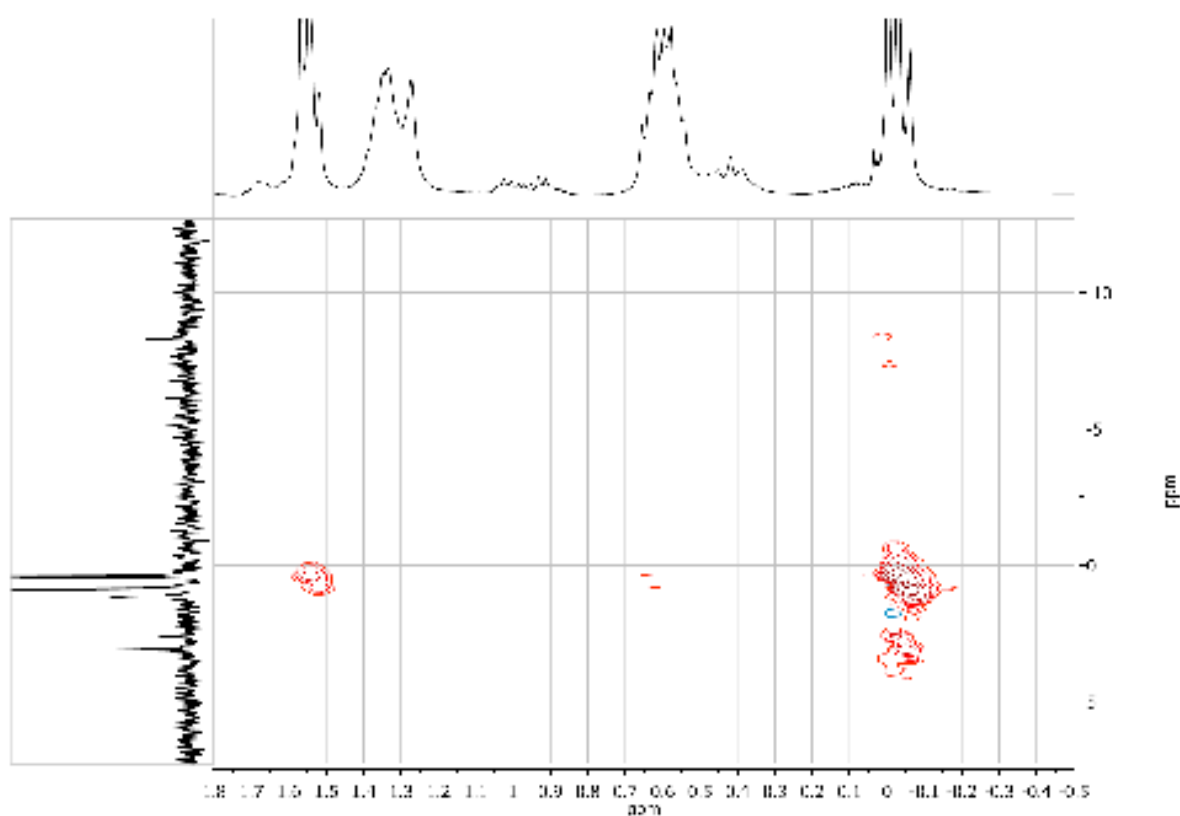


Fig. 5.29 HSQC spectrum of PCS₁₇-C₁₁-PI in CDCl₃ for the Si-H correlation.

5.4 Conclusion

Starting from a commercially available α - ω -functional molecule, a novel type of low molecular weight ambifunctional core, that permits the attachment of two polymeric blocks, has been synthesized. The cores contain multiple double bonds permitting the polyaddition of AB₂-alkenylsilane monomers via hydrosilylation. In order to study the influence of the core reactivity on the polymerization result, cores with one and three double bonds of different reactivity were synthesized (Figure 5.30). In agreement with theory, in simple one-pot polymerizations the superiority of the reactive vinyl containing core Vi₃-C₁₁-X could be proven, resulting in a controlled reaction with complete conversion of the core molecule. In contrast, for All₃-C₁₁-X and C₁₁-X a major amount of unreacted core molecules was still present after completed polymerization. The synthetic approach was further optimized using slow monomer addition techniques, which allowed the preparation of functional polymers with M_n up to 5300 g/mol and PDI between 1.35-1.98 (Table 5.7), approaching the theoretical value of 1.33 for a B₃ type core. The polycarbosilanes with phthalimide as functionality at the core showed a UV-signal, which allowed to trace the distribution of the core molecule in the polymer. In this way, it was verified that the combination of a highly reactive core with slow addition techniques results in integration of the core throughout the whole molecular weight distribution, while for the less reactive molecules an accumulation of the core can be seen in the low molecular weight region.

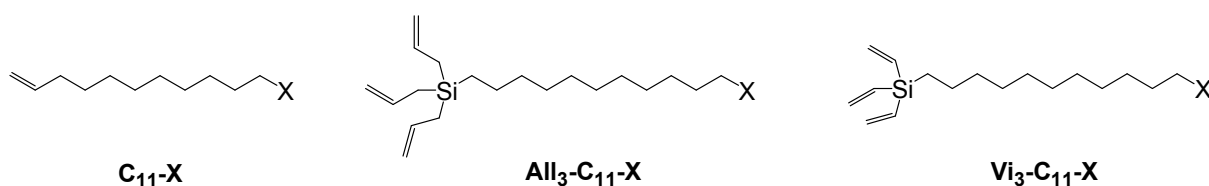


Fig. 5.30 Ambifunctional core molecules (X=Br, PI).

The core molecules were analyzed with ¹H-, ¹³C and ²⁹Si-NMR spectroscopy and checked for their purity using elemental analysis and GPC. NMR spectra for the functional polymers revealed the analogy to the pure homopolymers. ¹H-NMR was used to calculate the degree of polymerization since the core-functionality represents an internal reference. Results are in accord with the utilized monomer to core ratio and confirm that GPC underestimates the absolute molecular weight values. Analysis

of the ^{13}C -NMR reinforces the complete conversion of the core molecule by the disappearance of the vinyl carbon signals and a shift in the methylene protons adjacent to the attachment site. Additionally, especially the silicon NMR proves the branched structure of the polymers displaying distinguishable signals for the different branching units.

Table 5.7 Summary of the synthesized PI-functional polymers.

sample	conditions	$M_n(\text{NMR})$	GPC(CHCl_3)	
			M_n	PDI
$\text{PCS}_{13}\text{-C}_{11}\text{-PI}$	SMA	1990	2200	1.35
$\text{PCS}_{39}\text{-C}_{11}\text{-PI}$	SMA	5300	3200	1.98
$\text{PCS}_{11}\text{-C}_{11}\text{-PI}$	syringe pump	1760	1700	1.45
$\text{PCS}_{17}\text{-C}_{11}\text{-PI}$	syringe pump	2530	2100	1.46
$\text{PCS}_{36}\text{-C}_{11}\text{-PI}$	syringe pump	5010	2600	1.87

5.5 Experimental

5.5.1 Materials

Trichlorosilane, 11-bromoundec-1-ene, dimethylformamide, potassium phthalimide, sodium azide and vinylmagnesium bromide (1M in THF) were used as received. Allylmagnesium bromide solutions in diethyl ether were prepared according to literature procedures using a threefold excess magnesium²⁸. *N*-undec-10-enylphthalimide was prepared according to a modified literature procedure²². The solvents, diethyl ether and tetrahydrofuran, were dried by refluxing them over sodium/benzophenone and were freshly distilled prior to use. Platinum-divinyltetramethyldisiloxane complex (Karstedt catalyst) in xylene with 2.1-2.4% platinum concentration was purchased from Gelest.

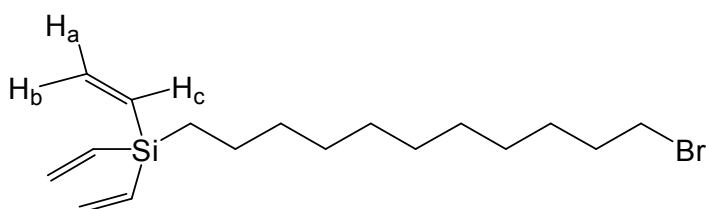
(11-Bromoundecyl)trichlorosilane ($\text{Cl}_3\text{Si-C}_{11}\text{-Br}$). In a dry flask 10.57g trichlorosilane (78mmol) and 84 μl of Karstedt catalyst were combined and stirred for 15min. To the yellow solution 13.99g 11-bromoundec-1-ene (60mmol) were slowly added and stirred at room temperature for 1h. The product was purified by vacuum

distillation (bp. 91-93°C/7·10⁻²mbar; Lit. 170°C/1mm). Yield: 18.45g (83%) of a colorless liquid.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 3.42 (t, 2H, J=6.81 Hz, -CH₂Br); 1.86 (m, 2H, -CH₂CH₂Br); 1.69-1.50 (m, 2H, CH₂); 1.49-1.10 (m, 16H, CH₂). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm]: 33.98 (-CH₂Br); 32.80; 31.77; 29.42; 29.36; 29.27; 28.95; 28.71; 28.13; 24.28; 22.21.

(11-Bromoundecyl)trivinylsilane (Vi₃-C₁₁-Br). Under an inert atmosphere 100ml of a 1.6M solution of vinylmagnesium chloride (0.16mol) in THF were placed in a three-necked flask equipped with reflux condenser and addition funnel. A solution of 16.59g (11-bromoundecyl)trichlorosilane (45mmol) in 10ml of dry THF was added at 0°C. After complete addition an extra 70ml of THF were added and the reaction was heated under reflux. After 18h the reaction mixture was evaporated to dryness and diluted with 100ml of diethyl ether. At 0°C first 40ml sat. NH₄Cl-solution and then 70ml H₂O were added. The organic layer was separated and washed twice with 20ml of a sat. NaHCO₃-solution, followed by H₂O until neutral reaction of the aqueous layer. The organic layer was dried with MgSO₄ and the solvent evaporated. The product was purified by fractionated distillation (117-127°C/3·10⁻²mbar). Yield: 11.1g (71%) of a colorless liquid.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 6.22-6.05 (m, 6H, H_a,H_c); 5.77 (dd, 3H, H_b); 3.42 (t, 2H, J=6.99 Hz, -CH₂Br); 1.86 (m, 2H, -CH₂CH₂Br); 1.52-1.07 (m, 16H, CH₂); 0.75 (m, 2H, -CH₂Si). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm]: 134.87 (-CH=CH₂); 134.17 (-CH=CH₂); 33.92 (-CH₂Br); 33.49; 32.82; 29.52; 29.48; 29.40; 29.22; 28.74; 28.16; 23.59; 12.61 (-CH₂Si). ²⁹Si-NMR (60 MHz, CDCl₃) δ [ppm]: -19.53.



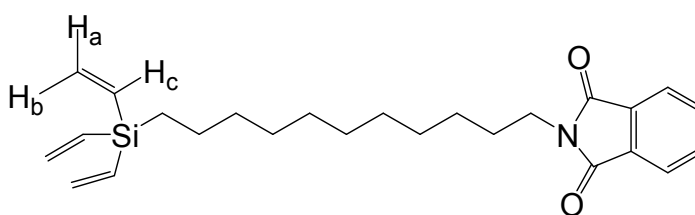
(11-Bromoundecyl)triallylsilane (AlI₃-C₁₁-Br). Under an inert atmosphere a solution of freshly prepared allylmagnesium bromide (0.43mol) in diethyl ether was placed in a three-necked flask equipped with reflux condenser and addition funnel. A solution of 44.23g (11-bromoundecyl)trichlorosilane (0.12mol) in 25ml of dry diethyl ether was

added at 0°C. After complete addition the reaction was heated under reflux for 18h. The reaction mixture was cooled to 0°C and 80ml sat. NH_4Cl -solution and then 120 ml H_2O were added. The organic layer was separated and washed twice with 50ml of a sat. NaHCO_3 -solution, followed by H_2O until neutral reaction of the aqueous layer. The organic layer was dried with MgSO_4 and the solvent evaporated. The product was purified by column chromatography in PE. Yield: 32.8g (71%).

^1H -NMR (300 MHz, CDCl_3) δ [ppm]: 5.90-5.71 (m, 3H, $-\text{CH}=\text{CH}_2$); 4.92-4.85 (m, 6H, $-\text{CH}=\text{CH}_2$); 3.42 (t, 2H, $J=6.81$ Hz, $-\text{CH}_2\text{Br}$); 1.86 (q, 2H, $-\text{CH}_2\text{CH}_2\text{Br}$); 1.60 (d, 6H, $J=8.09$ Hz, $-\text{CH}_2-\text{CH}=\text{CH}_2$); 1.52-1.07 (m, 16H, CH_2); 0.58 (m, 2H, $-\text{CH}_2\text{Si}$). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: 134.48 ($-\text{CH}=\text{CH}_2$); 113.43 ($-\text{CH}=\text{CH}_2$); 34.00 ($-\text{CH}_2\text{Br}$); 33.59; 32.82; 29.52; 29.48; 29.42; 29.19; 28.76; 28.16; 23.39; 19.62 ($-\text{CH}_2-\text{CH}=\text{CH}_2$); 11.40 ($-\text{CH}_2\text{Si}$). ^{29}Si -NMR (60 MHz, CDCl_3) δ [ppm]: -0.18.

(11-Trivinylsilanyl-undecyl)-isoindol-1,3-dion ($\text{Vi}_3\text{-C}_{11}\text{-PI}$). In a flask equipped with reflux condenser 8.59g (11-bromoundecyl)trivinylsilane (25mmol) and 5.09g potassium phthalimide (27,5mmol) were suspended in 45ml DMF. The solution was stirred at 60°C for 24h. The precipitate was removed by filtration. A 1:1 solution of brine/ H_2O (45ml) was added and the resulting mixture extracted with diethylether for three times. The organic layer was washed with brine, dried over K_2CO_3 and evaporated to dryness. Remaining DMF was removed by washing the residue with methanol. The product was purified by column chromatography in PE/ CHCl_3 2:1. Yield: 6.3g (62%) of a colorless liquid.

^1H -NMR (300 MHz, CDCl_3) δ [ppm]: 7.82 (m, 2H, H_{Ar}); 7.69 (m, 2H, H_{Ar}); 6.22-6.05 (m, 6H, $\text{H}_{\text{a}}, \text{H}_{\text{c}}$); 5.77 (dd, 3H, H_{b}); 3.65 (t, 2H, $J=7.36$ Hz, $-\text{CH}_2\text{Phth}$); 1.65 (m, 2H, $-\text{CH}_2\text{CH}_2\text{Phth}$); 1.45-1.12 (m, 16H, CH_2); 0.71 (m, 2H, $-\text{CH}_2\text{Si}$). ^{13}C -NMR (75 MHz, CDCl_3) δ [ppm]: 168.36 ($\text{C}=\text{O}$); 134.87 ($-\text{CH}=\text{CH}_2$); 134.14 ($-\text{CH}=\text{CH}_2$); 133.74 (C_{Ar}); 132.15 ($\text{C}_{\text{Ar, quar.}}$); 123.06 (C_{Ar}); 38.01 ($-\text{CH}_2\text{Phth}$); 33.46; 29.51; 29.45; 29.40; 29.18; 28.13; 28.53; 26.79; 23.54; 12.57 ($-\text{CH}_2\text{Si}$). ^{29}Si -NMR (60 MHz, CDCl_3) δ [ppm]: -19.53. Elemental Analysis: C, 73.35%; H, 8.55%; N, 3.41 (cal. for $\text{C}_{25}\text{H}_{35}\text{NO}_2\text{Si}$: C, 73.30%; H, 8.61%; N, 3.42).



(11-Triallylsilanyl-undecyl)-isoindol-1,3-dione (All₃-C₁₁-PI). In a flask equipped with reflux condenser 2.0g (11-bromoundecyl)triallylsilane (5.2mmol) and 1.06g potassium phthalimide (5.7mmol) were suspended in 10ml DMF. The solution was stirred at 60°C for 24h. The precipitate was removed by filtration. A 1:1 solution of brine/H₂O (10ml) was added and the resulting mixture extracted with diethyl ether three times. The organic layer was washed with brine, dried over K₂CO₃ and evaporated to dryness. Remaining DMF was removed by washing the residue with methanol. The product was purified by column chromatography in PE/CHCl₃ 2:1. Yield: 1.59g (68%) of a colorless liquid.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 7.82 (m, 2H, H_{Ar}); 7.69 (m, 2H, H_{Ar}); 5.84-5.70 (m, 3H, -CH=CH₂); 4.95-4.80 (m, 6H, -CH=CH₂); 3.66 (t, 2H, J=7.36 Hz, -CH₂Phth); 1.65 (m, 2H, -CH₂CH₂Phth); 1.60 (d, 6H, J=8.45 Hz, -CH₂-CH=CH₂); 1.45-1.12 (m, 16H, CH₂); 0.55 (m, 2H, -CH₂Si). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm]: 168.41 (C=O); 134.48 (-CH=CH₂); 133.77 (C_{Ar}); 132.16 (C_{Ar}, quar.); 123.09 (C_{Ar}); 113.40 (-CH=CH₂); 38.03 (-CH₂Phth); 33.59; 29.52; 29.48; 29.45; 29.16; 28.56; 26.82; 23.38; 19.59 (-CH₂-CH=CH₂); 11.38 (-CH₂Si). Elemental Analysis: C, 74.32%; H, 8.91%; N, 3.20 (cal. for C₂₈H₄₁NO₂Si: C, 74.45%; H, 9.15%; N, 3.10).

(11-Azidoundecyl)trivinylsilane (Vi₃-C₁₁-N₃). In a flask 2.51g NaN₃ (38mmol) were suspended in 110ml DMF. At room temperature 11.1g (11-Bromoundecyl)trivinylsilane (32mmol) were added and the mixture stirred for 15h. After complete reaction DMF was removed under reduced pressure and the residue was dissolved in hexane. The hexane layer was washed with water, dried with MgSO₄ and evaporated to dryness. The product contained byproduct, however partial decomposition occurred during purification. Yield: 7.8 g (70%).

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 6.27-5.99 (m, 6H, H_a, H_c); 5.77 (dd, 3H, H_b); 3.26 (t, 2H, J=6.81 Hz, -CH₂N₃); 1.73-1.47 (m, 2H, -CH₂CH₂N₃); 1.47-1.07 (m, 16H, CH₂); 0.74 (m, 2H, -CH₂Si).

(11-Azidoundecyl)triallylsilane ($\text{All}_3\text{-C}_{11}\text{-N}_3$). In a flask 2.1g NaN_3 (32mmol) were suspended in 120ml DMF. At room temperature 10.9g (11-Bromoundecyl)triallylsilane (28mmol) were added and the mixture was stirred for 15h. After complete reaction DMF was removed under reduced pressure and the residue was dissolved in hexane. The hexane layer was washed with water, dried with MgSO_4 and evaporated to dryness. Yield: 6.9g (70%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm]: 5.84-5.73 (m, 3H, $-\text{CH}=\text{CH}_2$); 4.95-4.82 (m, 6H, $-\text{CH}=\text{CH}_2$); 3.27 (t, 2H, $J=6.99$ Hz, $-\text{CH}_2\text{N}_3$); 1.60 (d, 6H, $J=8.09$ Hz, $-\text{CH}_2\text{-CH}=\text{CH}_2$); 1.44-1.06 (m, 18H, CH_2); 0.58 (m, 2H, $-\text{CH}_2\text{Si}$). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ [ppm]: 134.48 ($-\text{CH}=\text{CH}_2$); 113.41 ($-\text{CH}=\text{CH}_2$); 51.46 ($-\text{CH}_2\text{N}_3$); 33.59; 29.52; 29.48; 29.19; 29.13, 28.82; 26.69, 23.39, 19.61 ($-\text{CH}_2\text{-CH}=\text{CH}_2$); 11.40 ($-\text{CH}_2\text{Si}$).

Polymerization with multifunctional core ($\text{PCS}_x\text{-C}_{11}\text{-X}$)

All polymerizations were performed under an inert atmosphere using dried glassware.

Bulk polymerizations. The functional core, monomer and Karstedt catalyst were combined and stirred at room temperature until complete reaction was confirmed by IR-spectroscopy. In a standard reaction for example 0.25g (0.61mmol) $\text{Vi}_3\text{-C}_{11}\text{-PI}$, 0.77g (6.1mmol) diallylmethylsilane and 30 μl Karstedt catalyst were combined.

Syringe pump. The core and Karstedt catalyst were mixed and the neat monomer was added slowly and dropwise (normally during 6-12h). For example 6.31g (50mmol) diallylmethylsilane were added to a mixture of 2.05g (5mmol) $\text{Vi}_3\text{-C}_{11}\text{-PI}$ and 108 μl Karstedt catalyst.

Slow monomer addition. The polymerization was performed in the apparatus pictured in Figure 5.31. For example 3.08g (24.4mmol) diallylmethylsilane dissolved in 500ml dry pentane were added slowly via a dosing pump to a mixture of 1.0g (2.44mmol) $\text{Vi}_3\text{-C}_{11}\text{-PI}$ and 80 μl (0.007mmol) Karstedt catalyst at 60°C. Pentane was removed by distillation during the addition of the monomer.

In all cases the catalyst was inactivated by addition of methanol or by precipitation of the polymer from methanol after complete reaction.

PCS_x-C₁₁-PI. ¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 7.82 (H_{arom.}); 7.69 (H_{arom.}); 5.92-5.67 (-CH=CH₂); 4.95-4.80 (-CH=CH₂); 3.66 (t, -CH₂Phth); 1.65-1.45 (-CH₂-CH=CH₂); 1.45-1.10 (CH₂); 0.79-0.30 (-CH₂Si); -0.01 (-SiCH₃(t)); -0.03 (-SiCH₃(l)); -0.07 (-SiCH₃(d)). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm]: 168.38 (-C=O); 143.29, 142.54 (-CH=CH-CH₃); 135.28 (-CH=CH₂, T), 134.78 (-CH=CH₂, L); 133.75 (C_{Ar}); 132.21 (C_{Ar}; quart.); 129.54, 128.58 (-CH=CH-CH₃); 123.10 (C_{Ar}); 113.04 (-CH=CH₂, L); 112.60 (-CH=CH₂, T); 38.01 (-CH₂-PI); 30.03-29.06, 28.61, 26.88 (-CH₂, core); 22.75 (-CH=CH-CH₃); 22.42 (-CH₂, core); 22.02, 21.46 (-CH₂-CH=CH₂); 19.64-17.31 (CH₂); -4.82, -5.00, -5.20, -5.33, -5.74 (Si-CH₃). ²⁹Si-NMR (60 MHz, CDCl₃) δ [ppm]: 1.18 (D); 0.89 (L₀); 0.43 (T₀); -7.33 (L₁), -8.29 (T₁).

PCS_x-C₁₁-Br. ¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 5.92-5.67 (-CH=CH₂); 4.95-4.80 (-CH=CH₂); 3.41 (t, -CH₂CH₂Br); 1.86 (-CH₂CH₂Br); 1.65-1.45 (-CH₂-CH=CH₂); 1.45-1.10 (CH₂); 0.79-0.30 (-CH₂Si); -0.01 (-SiCH₃(t)); -0.03 (-SiCH₃(l)); -0.07 (-SiCH₃(d)). ¹³C-NMR (75 MHz, CDCl₃) δ [ppm]: 143.29, 142.54 (-CH=CH-CH₃); 135.28 (-CH=CH₂, T), 134.78 (-CH=CH₂, L); 129.54, 128.58 (-CH=CH-CH₃); 113.04 (-CH=CH₂, L); 112.60 (-CH=CH₂, T); 33.97(-CH₂-Br); 32.85, 29.61, 29.48, 29.34, 28.80, 28.19 (-CH₂, core); 22.75 (-CH=CH-CH₃); 22.02, 21.47 (-CH₂-CH=CH₂); 20.85 (-CH₂, core); 19.19-17.39 (CH₂); -5.00, -5.33, -5.72, -5.89, -6.28 (Si-CH₃). ²⁹Si-NMR (60 MHz, CDCl₃) δ [ppm]: 1.18 (D); 0.89 (L₀); 0.43 (T₀); -7.33 (L₁), -8.29 (T₁).

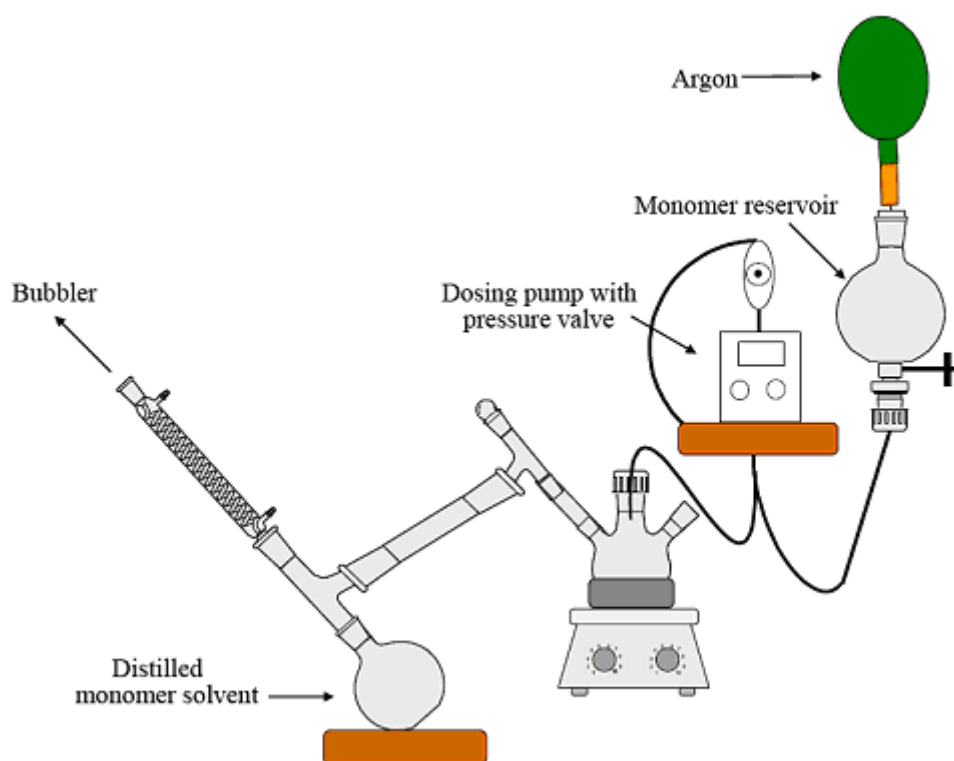


Fig. 5.31 Apparatus used for the slow monomer addition procedure.

5.6 References

1. Hanselmann, R.; Holter, D.; Frey, H. *Macromolecules* **1998**, 31, (12), 3790-3801.
2. Holter, D.; Frey, H. *Acta Polymerica* **1997**, 48, (8), 298-309.
3. Radke, W.; Litvinenko, G.; Muller, A. H. E. *Macromolecules* **1998**, 31, (2), 239-248.
4. Cheng, K. C. *Polymer* **2003**, 44, (4), 1259-1266.
5. Cheng, K. C.; Wang, L. Y. *Macromolecules* **2002**, 35, (14), 5657-5664.
6. Bernal, D. P.; Bedrossian, L.; Collins, K.; Fossum, E. *Macromolecules* **2003**, 36, (2), 333-338.
7. Galina, H.; Krawczyk, M. *Polymer Bulletin* **2007**, 58, (1), 83-91.
8. Feast, W. J.; Stainton, N. M. *Journal of Materials Chemistry* **1995**, 5, (3), 405-411.
9. Kricheldorf, H. R.; Lohden, G. *Macromolecular Chemistry and Physics* **1995**, 196, (6), 1839-1854.
10. Kricheldorf, H. R.; Stober, O.; Lubbers, D. *Macromolecules* **1995**, 28, (7), 2118-2123.
11. Bharathi, P.; Moore, J. S. *Macromolecules* **2000**, 33, (9), 3212-3218.
12. Sunder, A.; Hanselmann, R.; Frey, H.; Mulhaupt, R. *Macromolecules* **1999**, 32, (13), 4240-4246.
13. Lach, C.; Hanselmann, R.; Frey, H.; Mulhaupt, R. *Macromolecular Rapid Communications* **1998**, 19, (9), 461-465.
14. Lach, C.; Muller, P.; Frey, H.; Mulhaupt, R. *Macromolecular Rapid Communications* **1997**, 18, (3), 253-260.
15. Marcos, A. G.; Pusel, T. M.; Thomann, R.; Pakula, T.; Okrasa, L.; Geppert, S.; Gronski, W.; Frey, H. *Macromolecules* **2006**, 39, (3), 971-977.
16. Brook, M. A., *Silicon in Organic, Organometallic and Polymer Chemistry*. Wiley: Canada, 2000.
17. Istratov, V.; Kautz, H.; Kim, Y. K.; Schubert, R.; Frey, H. *Tetrahedron* **2003**, 59, (22), 4017-4024.
18. Chupa, J. A.; Xu, S.; Fischetti, R. F.; Strongin, R. M.; McCauley, J. P.; Smith, A. B.; Blasie, J. K. *Journal of the American Chemical Society* **1993**, 115, 4383-4384.

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19. McGovern, M. E.; Thompson, M. *Canadian Journal of Chemistry-Revue Canadienne De Chimie* **1999**, 77, (10), 1678-1689.
 20. Shyue, J. J.; Tang, Y.; De Guire, M. R. *Journal of Materials Chemistry* **2005**, 15, (2), 323-330.
 21. Gabriel, S. *Journal of the Chemical Society, Abstracts* **1892**, 62, 157-158.
 22. Gagné, M. R.; Stern, C. L.; Marks, T. J. *Journal of the American Chemical Society* **1992**, 114, 275-294.
 23. Staudinger, H.; Meyer, J. *Helvetica Chimica Acta* **1919**, 2, 635-646.
 24. Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angewandte Chemie. Int. Ed.* **2005**, 44, 5188-5240.
 25. Drohmann, C.; Moller, M.; Gorbatshevich, O. B.; Muzafarov, A. M. *Journal of Polymer Science Part a-Polymer Chemistry* **2000**, 38, (4), 741-751.
 26. Gong, C. G.; Miravet, J.; Frechet, J. M. J. *Journal of Polymer Science Part a-Polymer Chemistry* **1999**, 37, (16), 3193-3201.
 27. Burgath, A.; Sunder, A.; Frey, H. *Macromolecular Chemistry and Physics* **2000**, 201, 782.
 28. G. Marcos, A. *Dissertation, University of Mainz* **2006**.

6 Synthesis of hyperbranched polycarbosilane-containing block copolymers

6.1 Introduction

Block copolymers consist of at least two chemically different polymers, which are covalently linked. Owing to their mutual repulsion, the different blocks segregate into different domains, leading to the self-assembly into ordered nanoscopically structured morphologies¹⁻⁴. The scale of the microdomains (tens of nanometers) fosters their application in nanotechnology applications, e.g., micelles for drug delivery, nanostructured membranes, photonic crystals and nanopattern masks for the fabrication of high-density information storage. The broad variety of self-organized structures formed in bulk and solution is shown in Figure 6.1. Size and shape of the microstructure can be conveniently tuned by the chemical structure and composition of the polymer blocks.

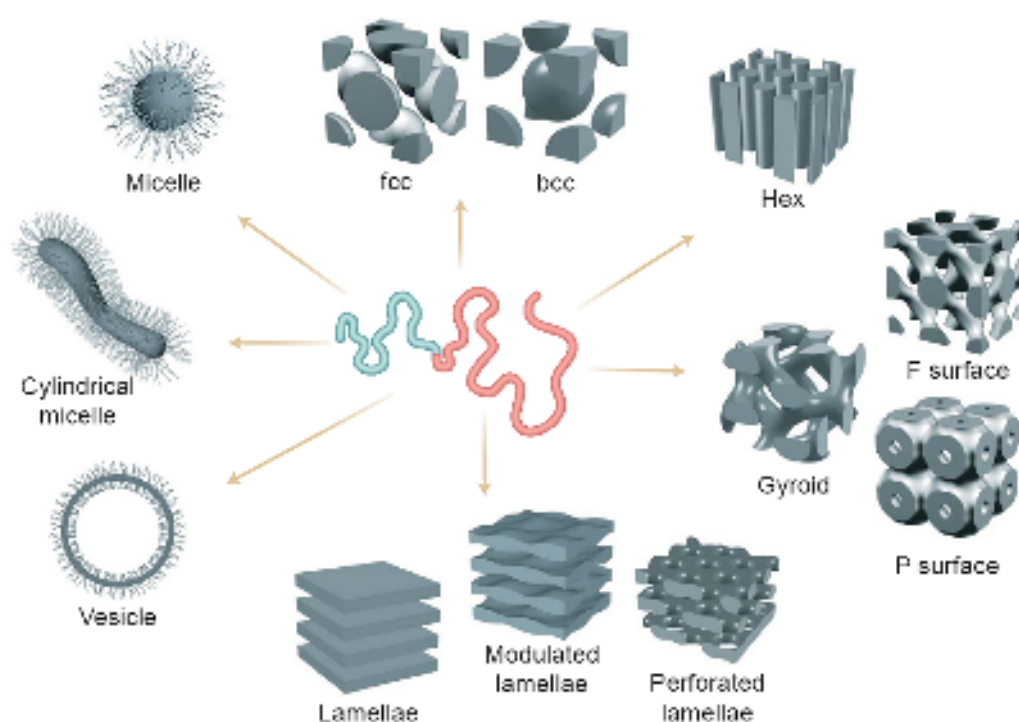


Fig. 6.1 Self-organization of block copolymers in solution (spherical and cylindrical micelles, and vesicles) and bulk (spheres with face-centered cubic (fcc) and body-centered cubic (bcc) packing, hexagonally packed cylinders (Hex), minimal surfaces (gyroid, F and P surface) and lamellar structures).

The majority of the reported structures are based on linear molecular architectures. However, in recent years the development of synthetic approaches for the preparation of more complex well-defined block copolymers containing non-linear architectures has begun. Besides the synthesis and examination of star-block, miktoarm star and graft copolymers^{5,6} the integration of dendritic structural elements into block copolymers has set in with the rapid development of dendrimers and hyperbranched polymers⁷. The general approaches towards the synthesis of linear-dendritic block copolymers are depicted in Figure 6.2 and can be applied for the preparation of AB as well as ABA structures. The combination of a dendritic segment (dendron) with a linear chain is possible via three different strategies: a) coupling of a precasted dendron with a linear polymer chain, b) the chain-first route and c) the dendron-first route.

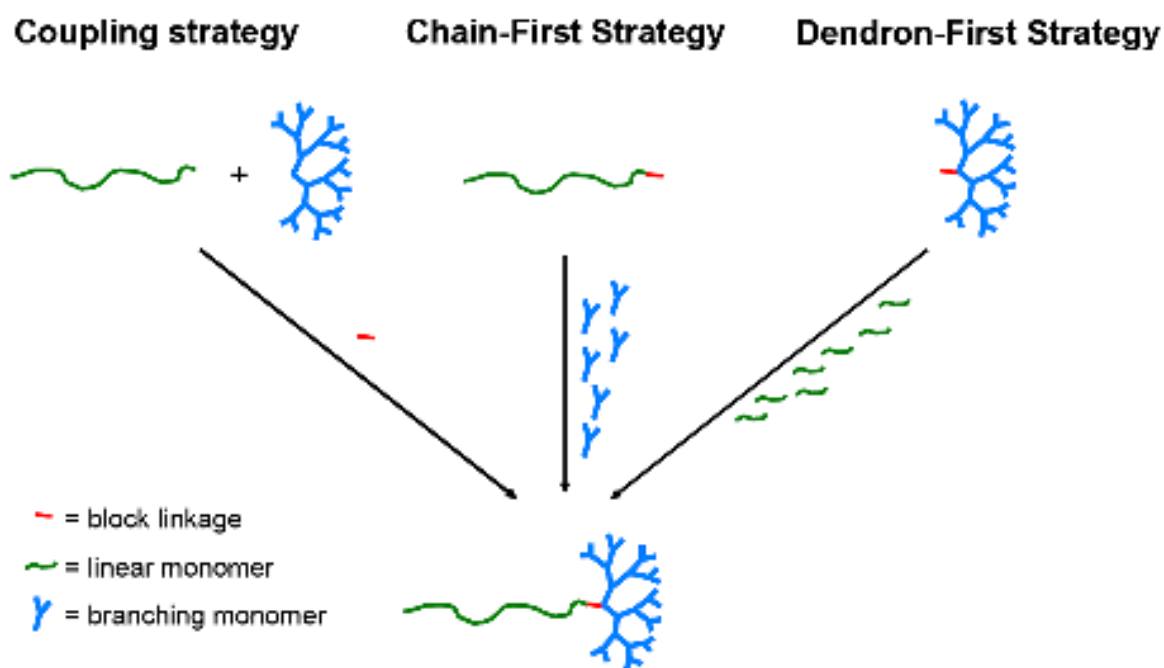


Fig. 6.2 Synthetic strategies for the synthesis of linear-dendritic block copolymers.

The chain-first strategy was used for the synthesis of the first linear-hyperbranched structures. In chapter 1 the synthesis of PS-*b*[PB-*hb*-PCS] has been described starting from a PS-PB linear block, where the small double bond-containing PB block was employed for the attachment of the carbosilane monomers⁸. In a similar approach amphiphilic PS-*hb*-PG was synthesized using a hydroborated PS-PB as initiator for the ring opening polymerization of glycidol (Figure 6.3).

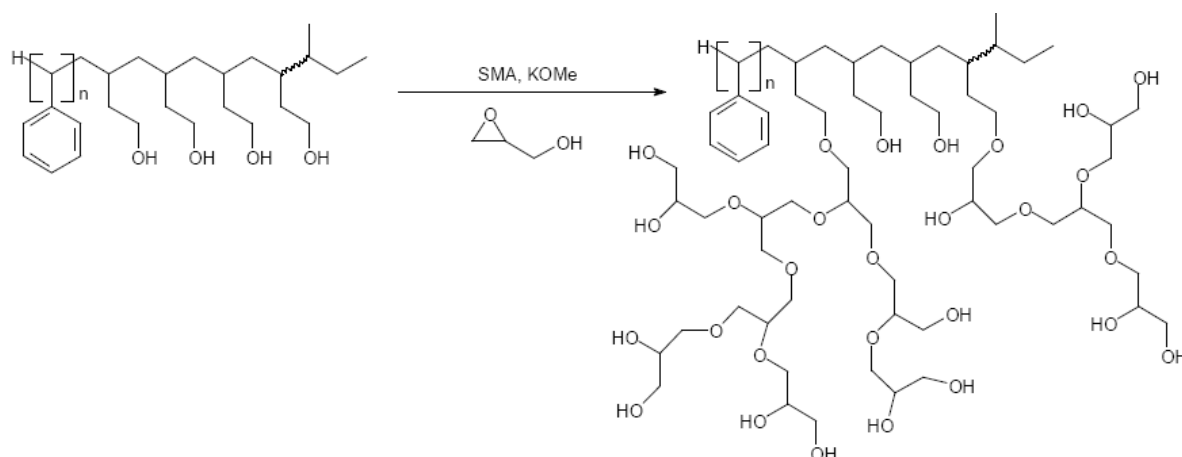


Fig. 6.3 Synthesis of amphiphilic PS-*hb*-PG.

The coupling approach was applied for the synthesis of block co-dendrimers. In these structures two dendrimer blocks, either of different chemical structure or different peripheral functionalization, are covalently linked. Despite the interesting structure-property relations to be expected for these structures only a limited number of articles concerning this topic have been published so far. In 1992 Hawker et al. reported the coupling of prefabricated aromatic ester and ether wedges to a polyfunctional core resulting in segmented block copolymers⁹. An amphiphilic diblock dendrimer was synthesized by Okada et al., who divergently prepared core functional poly(amido amine) (PAMAM) dendritic wedges that were functionalized with hydrophilic sugar moieties or hydrophobic phthaloyl groups. After activation of the core the hemi-spherical blocks were linked through an urea bond¹⁰. In the groups of Nierengarten and Gallani the interfacial properties of amphiphilic diblock dendrimers were studied systematically. They varied the generation of the dendritic wedges modified with either hydrophobic or hydrophilic groups on the periphery, and thus the hydrophobic/hydrophilic balance¹¹⁻¹³. A deviation in the behavior from traditional amphiphiles was observed for larger generation dendrimers exhibiting more complicated isotherms, with a non straightforward temperature dependence. Interestingly, the formation of stable Langmuir films could be achieved, although bulky functional groups like fullerenes were incorporated in the diblock dendrimers. The first report on the formation of self-assembled supramolecular structures was reported by Wegner et al. for block codendrimers consisting of [G3]-poly(benzyl ether) (PBE) and an aliphatic [G3]-poly(methallyl dichloride) (PMDC) (Figure 6.4 left)¹⁴. In selective solvents vesicles with a diameter of 100nm are formed. The special architecture of the polymer results in a membrane thickness that is less than

the thickness of membranes formed by linear-linear copolymers of the same molecular weight. The formation of microdomains in the melt was observed with a slightly modified hydrogen bond-containing diblock codendrimer [G3]-PBE-*b*-[G3]-poly(2,2-bis(hydroxymethyl) propionic acid). SAXS diffraction patterns showed the presence of a layered structure below 50°C and a transition to the disordered melt above 50°C, when the hydrogen bonds are broken¹⁵. Click chemistry also found its way into the preparation of diblock codendrimers. Jin et al. reported the coupling of an azide-functionalized PBE and PAMAM dendrons bearing a propargyl group at the focal point (Figure 6.4 right)¹⁶.

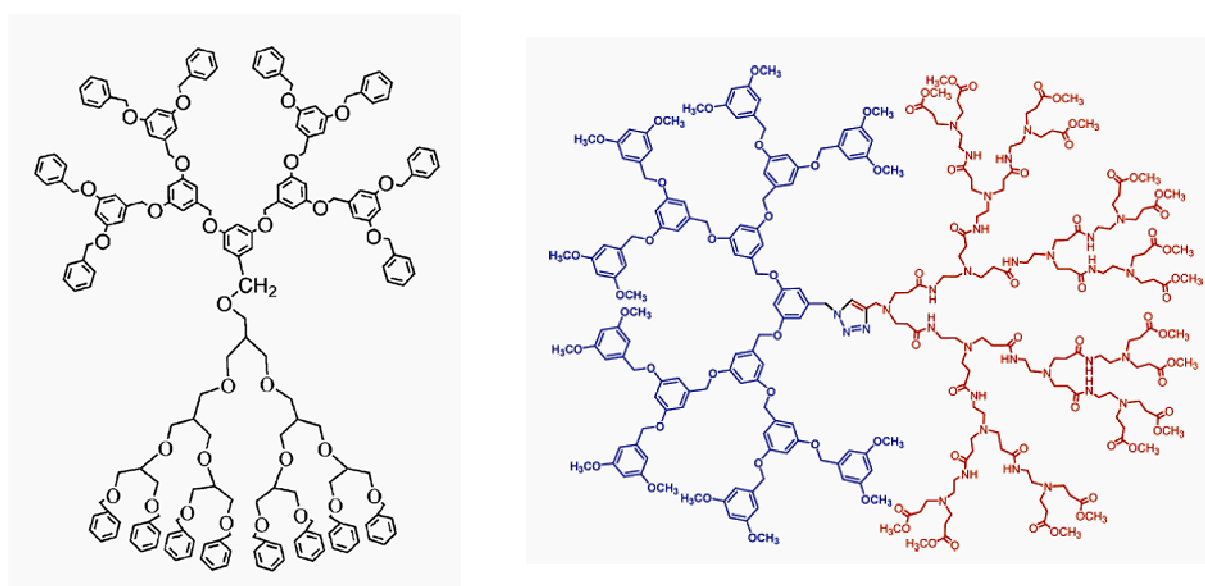


Fig. 6.4 Examples for block codendrimers: PBE-*b*-PMDC (left) and PBE-*b*-PAMAM (right).

The application of dendrimer wedges in block codendrimers is always limited by the time consuming stepwise synthesis. Additionally, molecular weights are limited to the respective dendrimer generations. So far no example of block copolymers with two chemically different hyperbranched blocks has been reported.

In this chapter the modification of the core-functional polycarbosilanes towards their application as macroinitiators in the ROMBP of glycidol leading to novel hyperbranched-hyperbranched amphiphiles is discussed. Carbosilane dendrimer wedges with an amine group at the focal point have been reported by van Heerbeek et al. They introduced the amine by reaction of a halide with liquid ammonia or through the intermediate azide or phthalimide¹⁷⁻¹⁹. Thus, similar reaction conditions can be applied for hyperbranched wedges. The macroinitiators obtained after

biglycidolization of the amine-functional cores were used for the attachment of the second branched block resulting in the targeted block copolymers.

Polycarbosilanes functionalized with azide cores constitute potential building blocks in 1,3-dipolar cycloadditions with alkynes. This approach was successfully used for the synthesis of *hb*-PCS-*b*-*lin*-PG by reaction between azide functional polycarbosilane wedges and linear polyglycerol (Fig. 6.5). Prior to a discussion of the modifications at the core, several functionalizations of the terminal double bonds are presented.

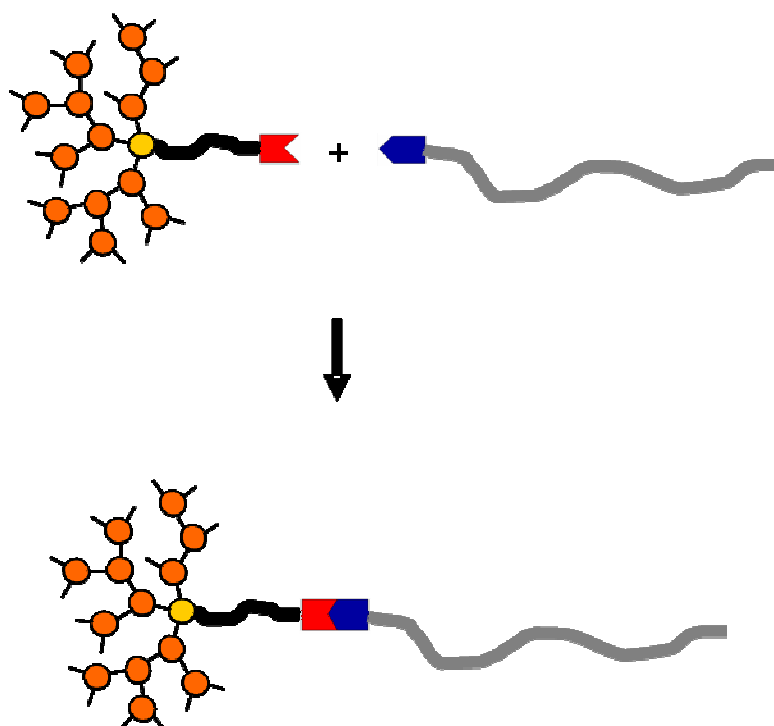


Fig. 6.5 Preparation of linear-hyperbranched block copolymer via the coupling strategy.

6.2 Functionalization of hyperbranched polycarbosilanes

6.2.1 Hydrogenation

The allylic groups at the periphery and at the linear branching points of the carbosilane reduce the stability of these structures under harsh reaction conditions and due to their sensitivity to light. On the other hand, these units permit to introduce functional groups into the polymer. This represents an additional possibility to alter the polymer properties. In order to enhance the inertness of the polymers before the attachment of a second block the allylic groups were hydrogenated. This seemed to

be necessary for the preparation of the polyglycerol block, since strong basic conditions and high reaction temperatures are applied. Contrary to allylic groups which can form a stabilized anion, the propyl groups obtained after hydrogenation are not prone to nucleophilic substitution. Additionally, the long term stability of the samples is improved, since radically induced crosslinking of the double bonds is inhibited. The catalytic hydrogenations were performed in ethyl acetate/methanol using Pd/carbon in a hydrogen atmosphere (Figure 6.6).

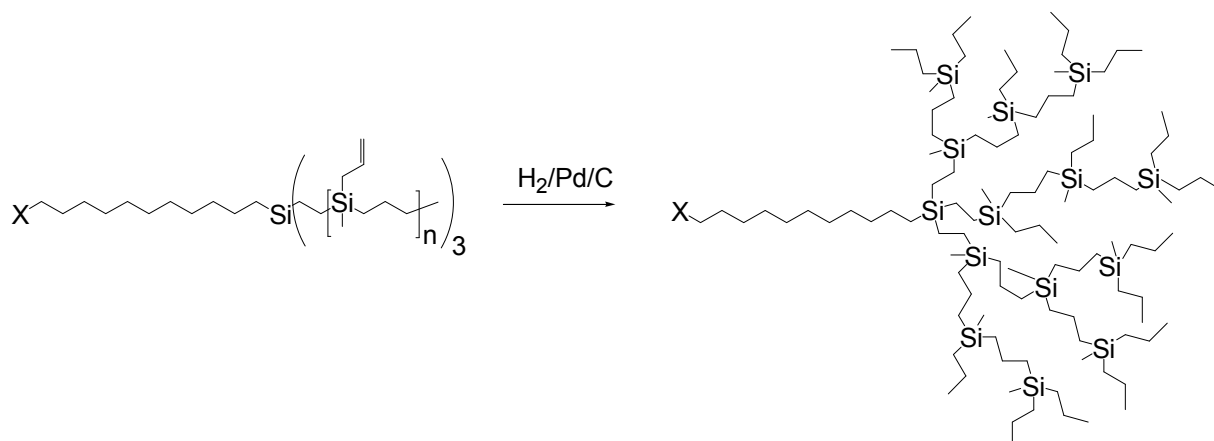


Fig. 6.6 Hydrogenation of polycarbosilane wedges.

Completion of the reaction was monitored using ^1H -NMR (Fig 6.7) and was usually achieved after 1-3 days. The spectrum clearly shows the disappearance of the double bonds at 5.76ppm and at 4.85ppm. The hydrogenated polymers are obtained in excellent yields after filtration over Celite. The reaction is applicable for phthalimide as well as bromide groups at the focal point. As expected, no significant change in the hydrodynamic radius and accordingly the molecular weight obtained by GPC was observed after hydrogenation (Table 6.1). Hydrogenated samples are indicated as H-PCS-C₁₁-X.

Table 6.1 Examples of hydrogenated polycarbosilanes.

	before hydrogenation		after hydrogenation	
	GPC(THF, RI)		GPC(THF, RI)	
	M _n	PDI	M _n	PDI
H-PCS ₅ -C ₁₁ -Br	1190	1.17	1090	1.26
H-PCS ₁₁ -C ₁₁ -PI	1810	1.50	1820	1.53
H-PCS ₂₀ -C ₁₁ -Br	2220	1.54	2320	1.52

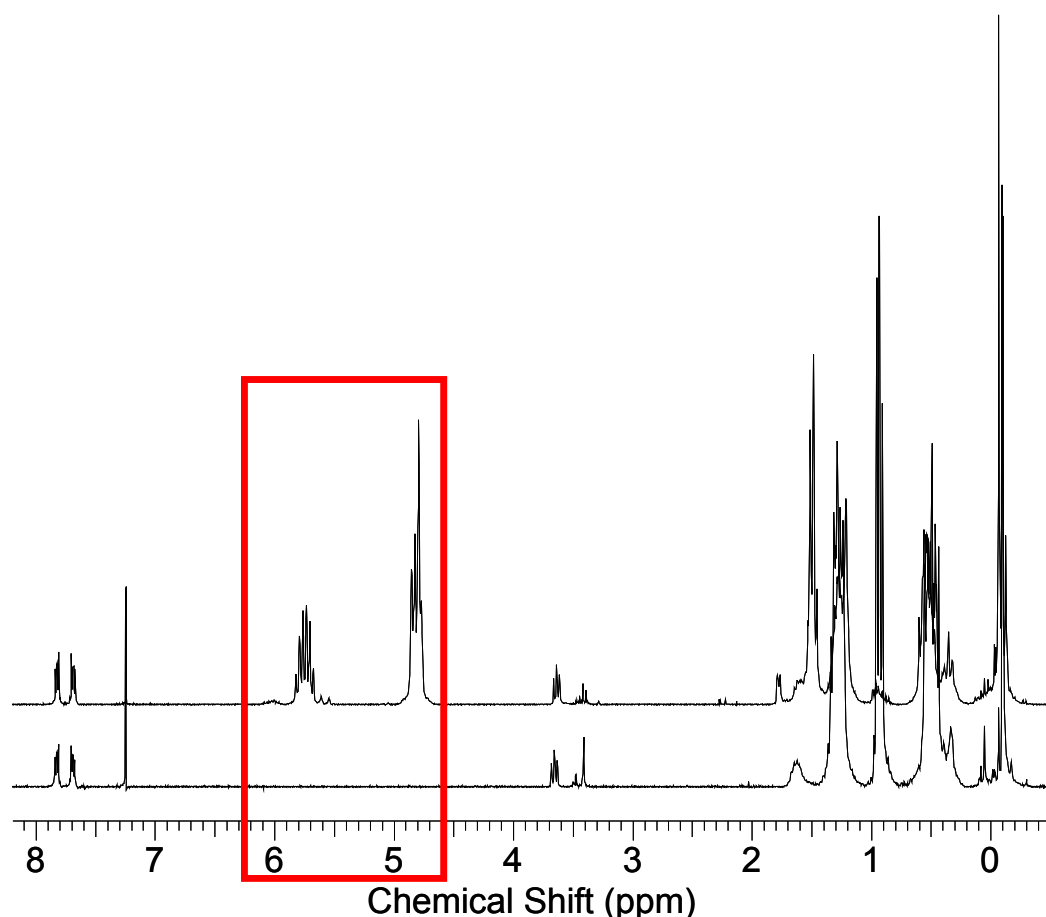


Fig. 6.7 ¹H-NMR spectrum in CDCl₃ for PCS₁₁-C₁₁-PI before (top) and after (bottom) hydrogenation.

6.2.2 Functionalization

The addition of a silane to the free double bonds is a further possibility to convert the allylic groups and simultaneously introduce functionality into the polymer. The integration of functional groups by hydrosilylation addition was studied with different silanes (Fig. 6.8), namely dimethylphenylsilane, diferrocenylmethylsilane and triethylsilane, for the core-functionalized sample (nomenclature of the samples Ph-PCS-, Fc₂-PCS- or Et₃-PCS-, respectively). Dimethylphenylsilane is highly reactive in hydrosilylations and can be added to the reaction mixture right after completed polymerization (see 5.3.2). This means that the polymerization and the subsequent functionalization can be performed in two consecutive steps without intermediate purification. The phenylsilane was applied in slight excess and the reaction proceeded very fast to completion within 1h. The polymer was purified by precipitation from methanol. Diferrocenylmethylsilane and triethylsilane are less reactive and hydrosilylation reactions were performed at 60°C for 3 days.

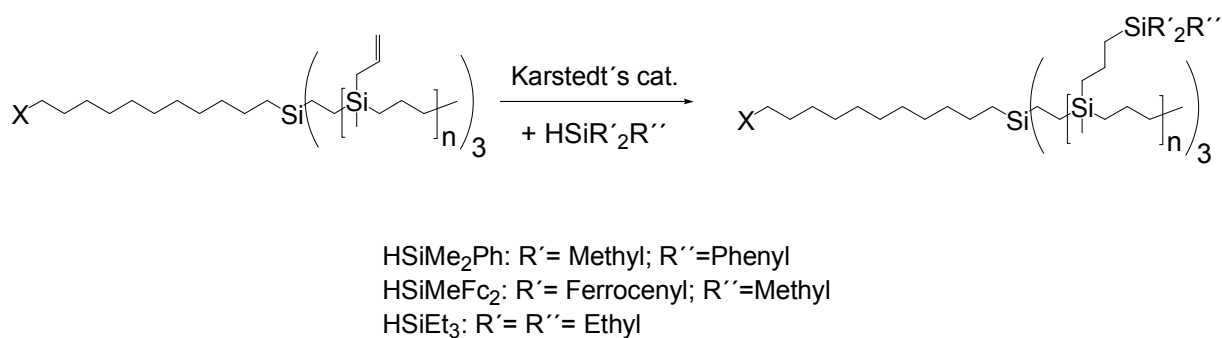


Fig. 6.8 Modification of hyperbranched polycarbosilanes.

However, in all cases a degree of functionalization of the carbosilane wedges >90% was achieved as determined by NMR. In Figure 6.9 two spectra for functionalized polycarbosilanes with phthalimide cores are given. In both spectra the disappearance of signals between 4.5–6.0 ppm indicates the full conversion of double bonds.

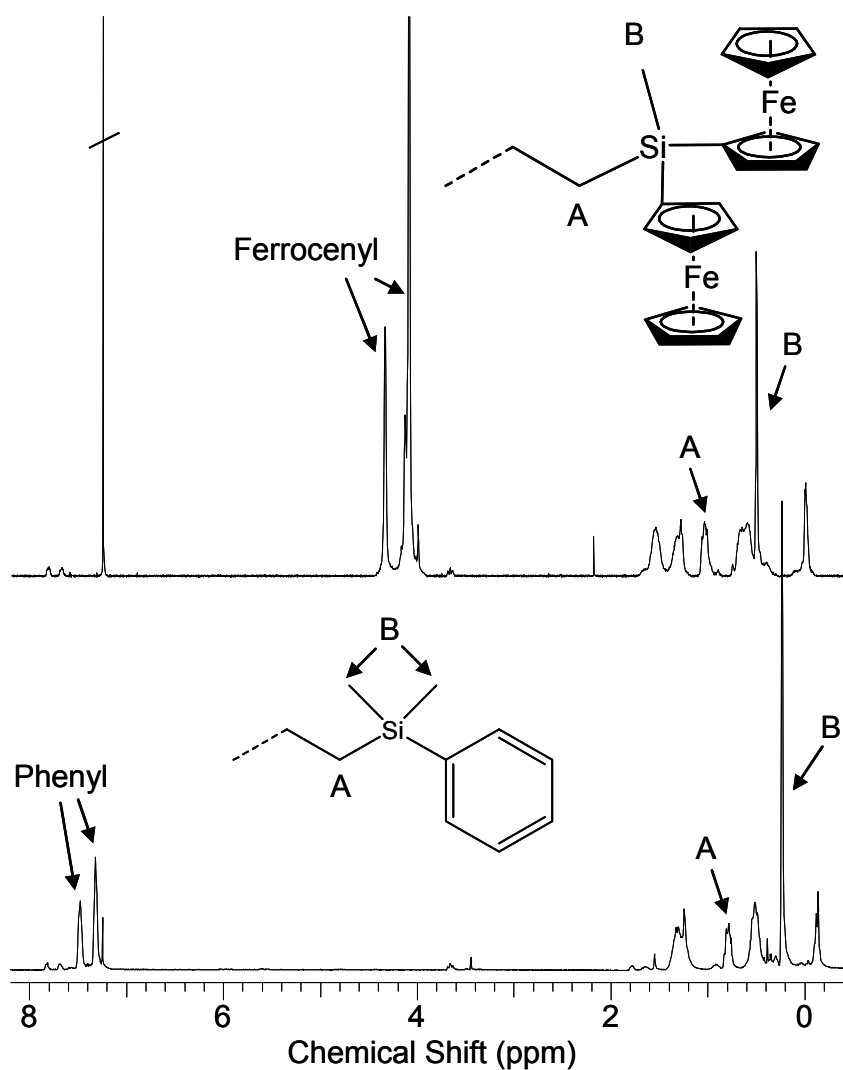


Fig. 6.9 ¹H-NMR in CDCl₃ for diferrocenylmethylsilane- (top) and dimethylphenylsilane-functionalized polymers (bottom).

The characteristic signals for the functional moieties ferrocenyl (4.33 and 4.08ppm) or phenyl (7.48 and 7.32ppm) are clearly observed. Additionally, new signals for the methylene protons adjacent to the functional groups emerge in the spectra (denoted A). Functionalized samples with bromo-cores can be converted to the respective azides as described in chapter 6.3.

GPC results for two different starting polymers are shown in Table 6.2 and reveal a molecular weight increase after functionalization. The reaction with dimethyl phenylsilane proceeds without any detectable side-reaction and the molecular weight distribution is retained. In contrary, after functionalization with triethylsilane, and less pronounced for diferrocenylmethylsilane, a high molecular weight shoulder is visible (Fig 6.10). The polymers obtained after functionalization were analyzed regarding their thermal properties using DSC. The nature of the end groups has a significant influence on the T_g of the samples with an increase from -84°C for the unfunctionalized polymer to 5°C for the ferrocenyl-functionalized one. In hyperbranched polymers, the number of branches (a factor that tends to increase T_g) and the number of end groups (a factor that tends to diminish T_g) grow in parallel. Therefore, the T_g is mainly influenced by the nature of the end groups and not significantly by molecular weight.

Table 6.2 Examples of functionalized polycarbosilanes

sample	silane	GPC(THF, RI)		DSC
		M_n	PDI	T_g [$^\circ\text{C}$]
PCS ₃ -C ₁₁ -Br	-	800	1.09	n.d. ^a
Et ₃ -PCS ₃ -C ₁₁ -Br	HSiEt ₃	1480	1.26	n.d.
Ph-PCS ₃ -C ₁₁ -Br	HSiMe ₂ Ph	1390	1.07	-57
Fc ₂ -PCS ₃ -C ₁₁ -Br	HSiMeFc ₂	1390	1.19	0
PCS ₁₀ -C ₁₁ -PI	-	1810	1.46	-84
Et ₃ -PCS ₁₀ -C ₁₁ -PI	HSiEt ₃	3080	1.81	-71
Ph-PCS ₁₀ -C ₁₁ -PI	HSiMe ₂ Ph	3230	1.52	-55
Fc ₂ -PCS ₁₀ -C ₁₁ -PI	HSiMeFc ₂	3680	1.86	5

a) not detectable

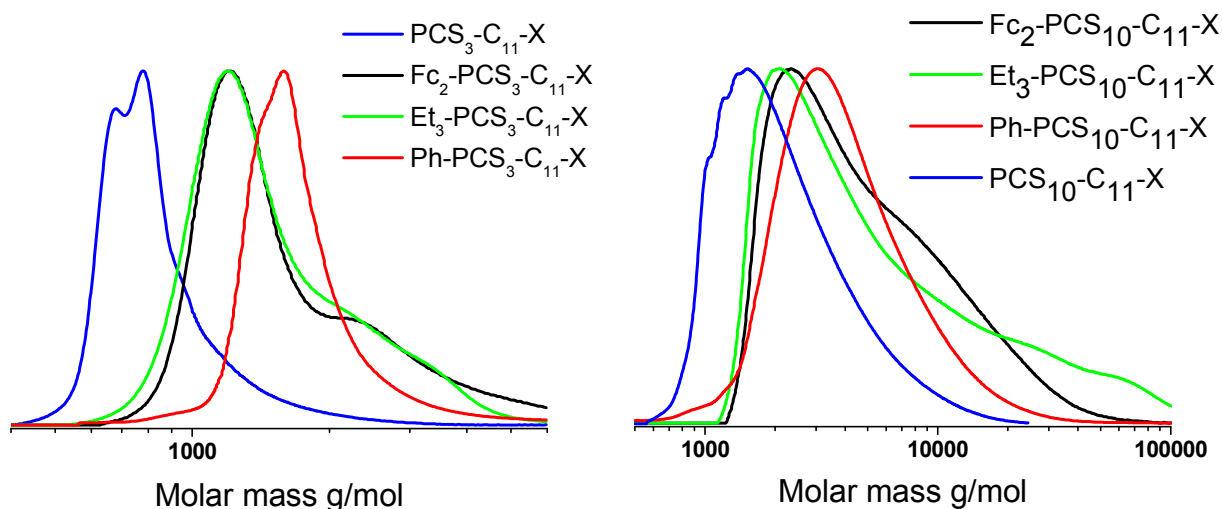


Fig. 6.10 GPC curves for functionalized polycarbosilanes.

6.3 Modifications at the core

6.3.1 Amine-functional polycarbosilanes

The synthesis of amine-functional polycarbosilanes can be accomplished using two different synthetic strategies. Phthalimide functional polymers can be hydrolyzed using hydrazine to give the free amine (Fig. 6.10 left). The reaction is performed in ethanol at 60°C leading to the precipitation of phthalhydrazide. The major amount of this side product was removed by filtration. However, complete purification of the amine-functional polymer was only possible after column chromatography or dialysis, both methods decreasing the yield significantly (Yield~50%). The second possibility for the synthesis is the preparation via an azide intermediate (Fig. 6.10 right). After functionalization of the peripheral double bonds in the polymer no side reactions are expected and observed, when an azide group is introduced into the polymer core. The reaction is performed at 60°C in DMF/THF by reaction of sodium azide with the bromo-functional polymer. The reaction proceeds smoothly for molecular weights of up to 2000g/mol. For larger molecules higher temperature, an excess of sodium azide (up to 10 equivalents) and longer reaction time are necessary. Additionally, the solubility of the polymer in the required polar solvents decreases. The yield for the azide-functional polymers is normally >80% after work-up. The free amine can be obtained from the azide-functional polymer using the Staudinger reduction, i.e., the

reaction with triphenylphosphin and subsequent treatment with ammonia (see Figure 5.10). In order to remove the byproduct triphenylphosphite column chromatography was necessary resulting in low yields between 40-60%. An excellent alternative circumventing the laborious purification is the reduction of the azide with hydrogen catalyzed by Pd/carbon (Fig. 6.8). The reaction proceeds smoothly at room temperature and the pure product is obtained after filtration over Celite to remove the catalyst in yields >90%. In summary, different synthetic pathways have been examined for the synthesis of amine-functional polycarbosilanes. The method of choice clearly depends on the targeted molecular weight. Amine-functional polymers with $M_n < 3000 \text{ g/mol}$ are best prepared through the sequence: preparation of the bromo-functional polymer, conversion to the azide and reduction with hydrogen. For higher molecular weight polymers (>3000 g/mol) nucleophilic substitution at the core is hindered due to a decrease in the solubility in polar solvents and a decreased accessibility of the focal group. Here, the approach via the phthalimide-functional polymer is preferential, in which the nitrogen is already incorporated into the core. Larger hydrodynamic radii for these polymers inhibit their diffusion through the dialysis membrane, resulting in reasonable yields.

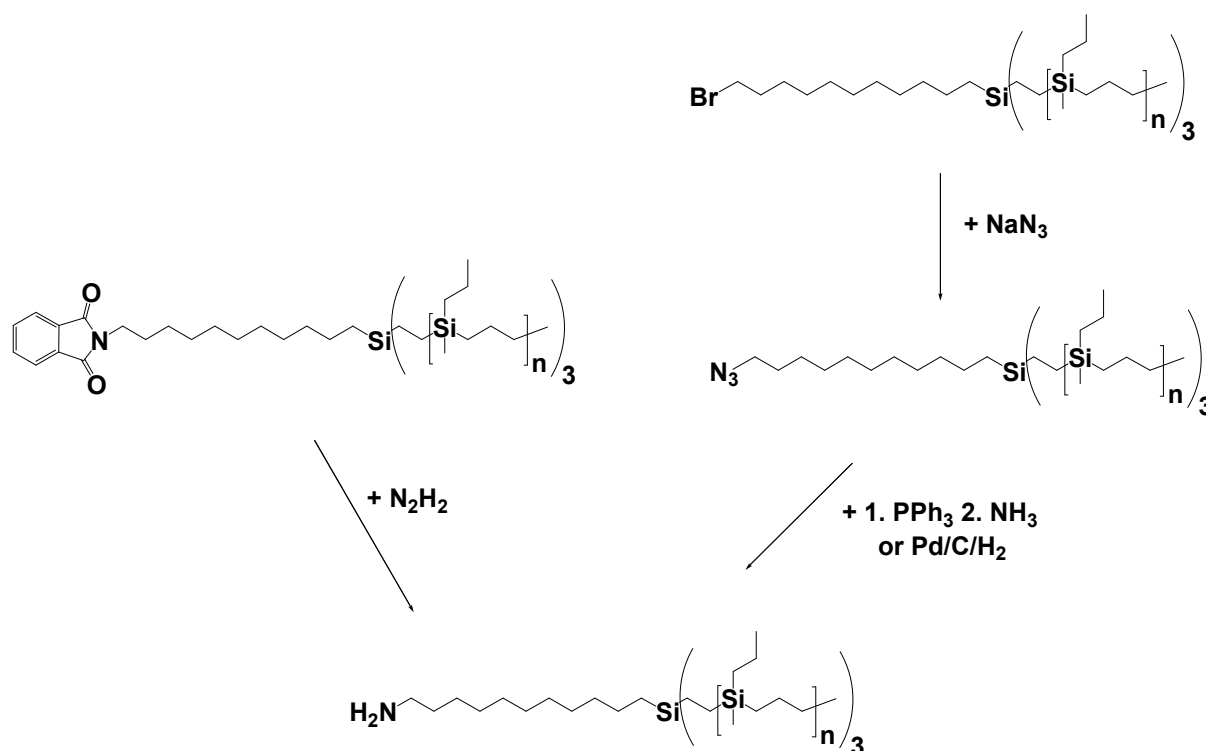


Fig. 6.11 Preparation of amine-functionalized polycarbosilanes.

6.3.2 Bisglycidolized polycarbosilanes

Bisglycidolized amines are obtained by reaction of the amine-functional polycarbosilanes with two equivalents of glycidol (Figure 6.11). The higher nucleophilicity of the amine compared to the hydroxyl groups results in a preferred two-fold reaction at the primary amine.

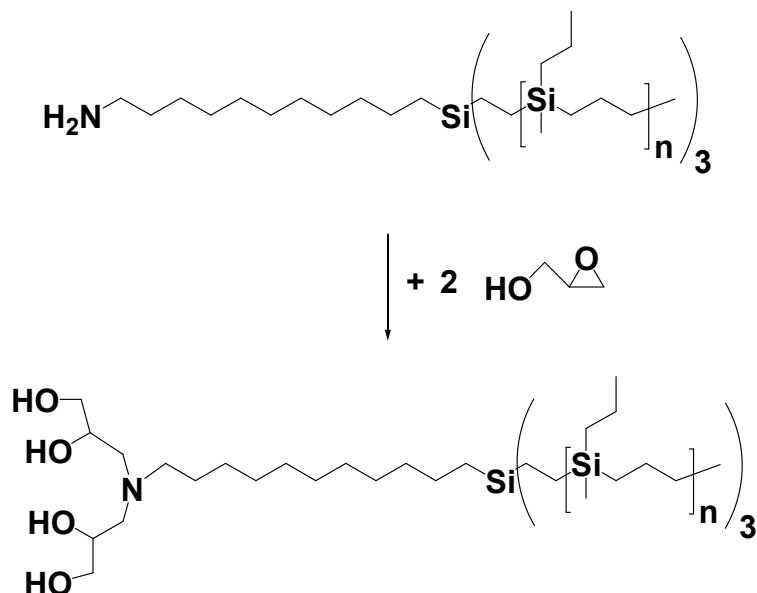


Fig. 6.12 Synthesis of bisglycidolized macroinitiators.

In order to realize good control in the synthesis of the polyglycerol no free amines are allowed in the reaction, hence a slight excess of glycidol is used (2.2-3 equivalents) and the reaction is completed at 60°C. Remaining glycidol can be removed under high vacuum. In some cases the NMR spectra revealed a higher degree of substitution, i.e. three or four glycidols attached to the core. This is a result of ring opening of glycidol by hydroxyl groups which can occur at increased temperatures. However, this is not detrimental for the reaction control.

6.3.2 Characterization and results

The reactions at the focal group of the polycarbosilane can be observed by NMR spectroscopy. An example of ^1H -NMR spectra for amine-functional polycarbosilane and macroinitiator obtained after bisglycidolization is shown in Figure 6.13. After hydrogenation or cleavage of the phthalimide group, the methylene protons adjacent to the primary amine give rise to a triplet at 2.67ppm, distinct from the starting

material with signals at 3.24ppm for the azide or 3.66ppm for the phthalimide. Bisglycidolization results in broad signals between 3.88-3.39ppm and 2.75-2.39ppm belonging to the methylene groups next to oxygen and amine, respectively. The integral ratio for these signals indicates that 2.5 to 3 equivalents of glycidol are added per amine group.

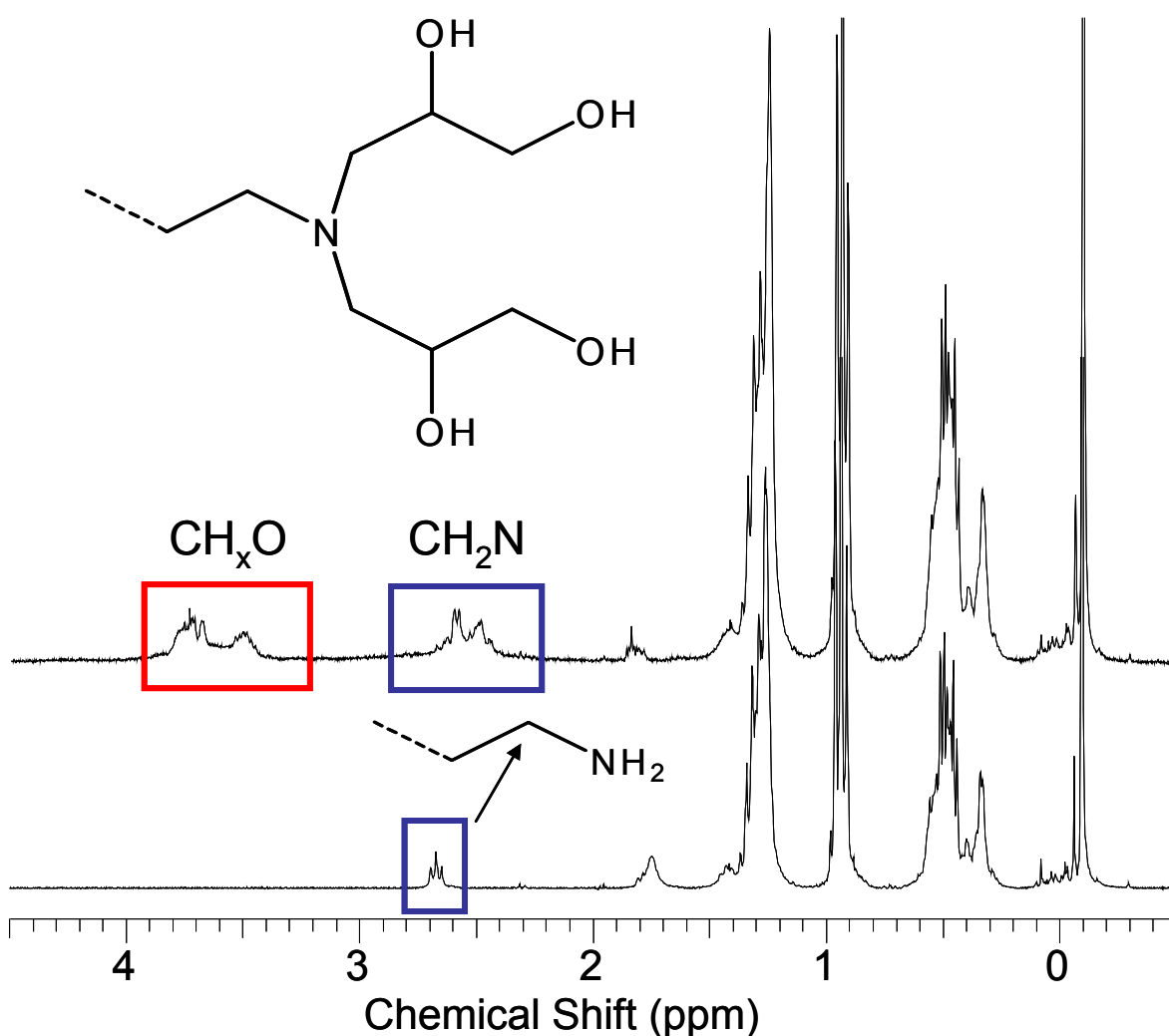


Fig. 6.13 Examples of ^1H -NMR spectra in CDCl_3 for amine-functional PCS (bottom) and bisglycidolized macroinitiator (top).

The reaction sequence leading to polycarbosilanes macroinitiators via azide reduction can also be conveniently followed by IR-spectroscopy as shown in Figure 6.14. The hydrogenation of double bonds is accompanied by the disappearance of the characteristic signal for the $\text{C}=\text{C}$ valence vibration at $\tilde{\nu} = 1630\text{cm}^{-1}$. The nucleophilic substitution with sodium azide results in a strong absorption at $\tilde{\nu} = 2100\text{cm}^{-1}$, which in turn disappears after reduction. Although the primary amine is not

detected in the respective spectrum, after bisglycidolization the hydroxyl groups are clearly visible with a broad signal between $\tilde{\nu} = 3100\text{--}3300\text{cm}^{-1}$.

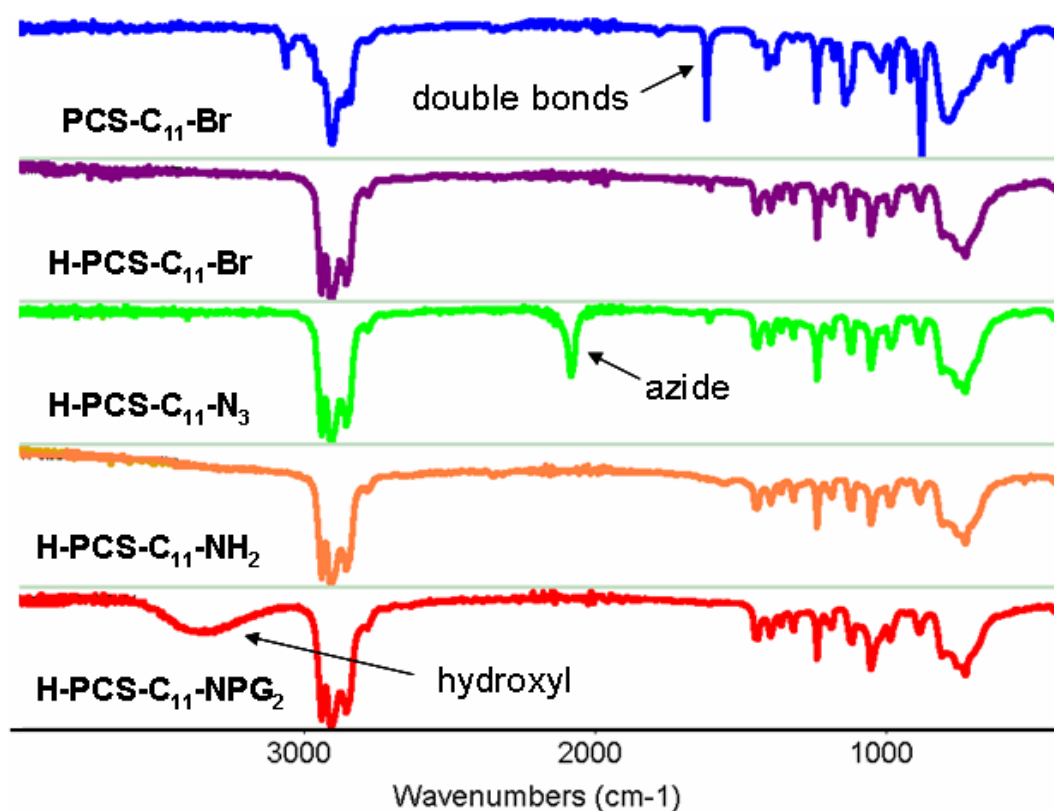


Fig. 6.14 IR-spectra for the reaction sequence targeting polycarbosilane macroinitiators.

In Table 6.3 GPC results for different polycarbosilanes with amines at the focal point are summarized and compared with the respective bisglycidolized macroinitiators. For the lowest molecular weight polymer (H-PCS₅-C₁₁-X), GPC results in THF are not analyzable (dashed line, Fig 6.15 **(A)**) probably due to the strong amphiphilic character of the sample. Besides a higher molecular weight shoulder, which can be explained by weak aggregation, the distribution revealed a distinct signal at lower molecular weights. Unfunctionalized polycarbosilanes are insoluble in polar solvents, however, with the bisglycidolized core attached, low molecular weight samples became slightly soluble in DMF. Thus, the GPC curve for H-PCS₅-C₁₁-NPG₂ was measured in DMF showing a narrow molecular weight distribution with only a small low molecular weight shoulder. Further analysis by NMR and MALDI confirmed that no degradation of the sample occurred. For higher molecular weight samples monomodal curves are obtained in THF for all stages of the reaction. The GPC curve for H-PCS₂₂-NPG₂ in DMF (Figure 6.15 **(B)**) shows a narrow distribution (PDI~1.2)

indicating the collapsed nature of the carbosilane block. For H-PCS₅₄-NPG₂ the apolar nature of the polycarbosilane is dominant, rendering the polymer insoluble in DMF.

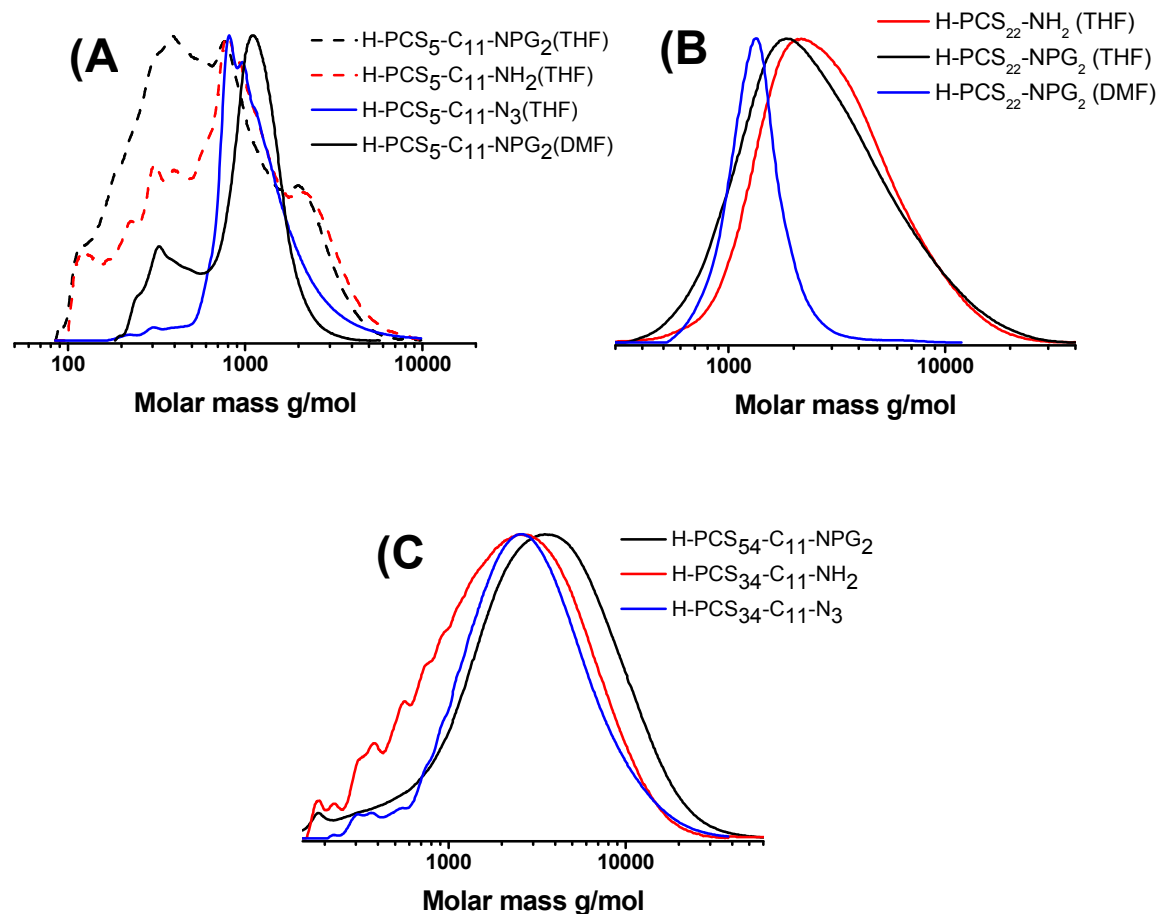


Fig. 6.15 GPC curves for different examples of core-functional polycarbosilanes: **(A)** H-PCS₅-C₁₁-X, **(B)** H-PCS₂₂-C₁₁-X, **(C)** H-PCS₃₄-C₁₁-X.

Table 6.3 GPC results for core-functional polycarbosilanes

	GPC(THF, RI)	
	M _n	PDI
H-PCS ₅ -C ₁₁ -N ₃	1070	1.23
H-PCS ₅ -C ₁₁ -NH ₂	-	-
H-PCS ₅ -C ₁₁ -NPG ₂	-	-
H-PCS ₂₂ -C ₁₁ -NH ₂	2390	1.54
H-PCS ₂₂ -C ₁₁ -NPG ₂	1830	1.82
H-PCS ₃₄ -C ₁₁ -NH ₂	1210	2.65
H-PCS ₅₄ -C ₁₁ -NPG ₂ ^a	2490	2.05

a) composition calculated from ¹H-NMR; b) after dialysis

MALDI-ToF spectrometry of the bisglycidolized samples was performed in order to verify the structure of the samples. Analysis of the spectra is complex, since a distribution of the polycarbosilane block as well as a distribution of the glycidol moiety is observed (normally 2 or 3). The intensity of the respective distributions in the spectra is dependent on the measuring conditions, e.g. salt added, detection mode or laser intensity. Thus, no quantification of the amount of each species in the sample can be given. The absolute mass values for the peaks are not very precise due to the isotope pattern of silicon, however the repeating units and the different distributions can clearly be assigned. As an example in Figure 6.16 the spectra for H-PCS₃₄-C₁₁-NH₂ and the corresponding macroinitiator H-PCS₅₄-C₁₁-NPG₂ are compared. The mass of the carbosilane monomer (128,3g/mol-dashed arrow) can be found in both spectra as the repeating unit.

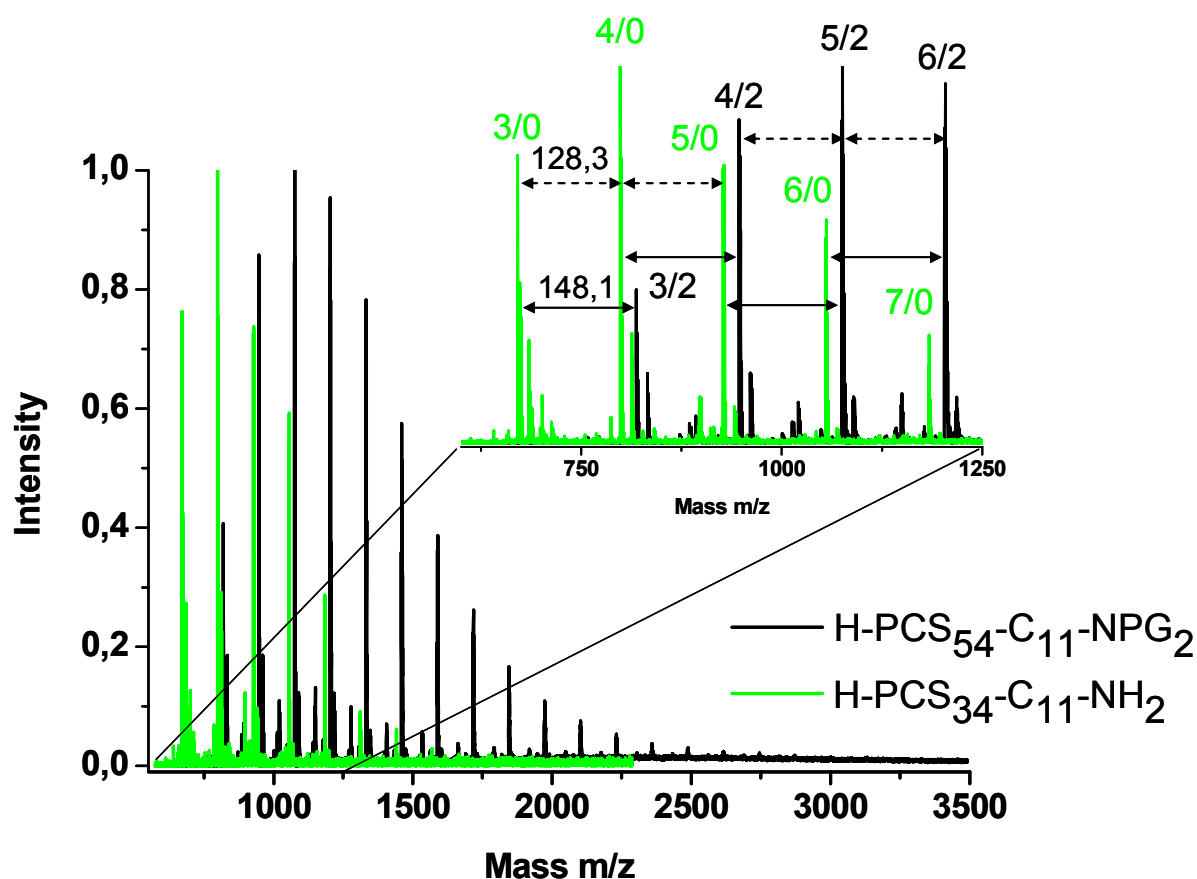


Fig. 6.16 MALDI-ToF spectrum for amine-functional polymer and resulting macroinitiator (peak assignment x/y corresponds to number of carbosilane and glycidol repeating units).

The lowest molecular weight peak in the distribution for the amine-functional polymer belongs to the core reacted with three carbosilane monomers (denoted 3/0 in the inset). Addition of two glycidol units (148,1) results in the bisglycidolized reaction

product (denoted 3/2). This in turn is the lowest molecular weight peak observed for the macroinitiator. Thus, the spectra are exactly shifted by two glycidol units which confirms the quantitative transformation. In other cases the distributions belonging to three or four glycidol units are observed as well, rendering the analysis even more intricate.

6.4 Synthesis of *hb*-PCS- C_{11} -*hb*-PG

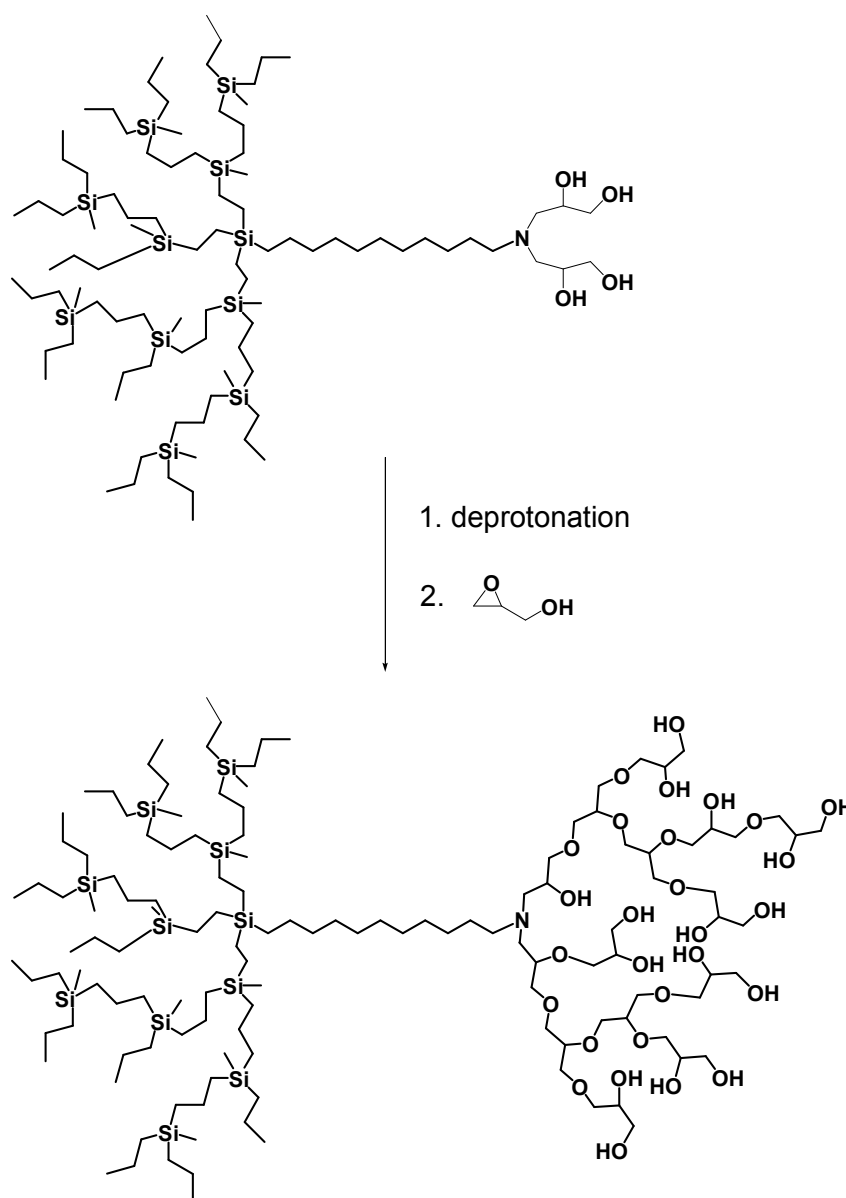


Fig. 6.17 Ring-opening polymerization of glycidol applying polycarbosilane macroinitiator.

Bisglycidolized carbosilane macroinitiators can be applied for the synthesis of hyperbranched-hyperbranched amphiphiles containing a hydrophobic carbosilane

block and a hydrophilic polyglycerol block (Figure 6.17). The synthesis of these block copolymer structures was realized in collaboration with J. Nieberle. In order to obtain nucleophilic species that are capable of ring opening multibranching polymerization (ROMBP) of glycidol, the macroinitiators were partially deprotonated using cesium hydroxide or potassium *tert*-butylate. Degree of deprotonation of around 30% is advantageous to retain a certain solubility of the initiator and thus a homogeneous reaction mixture. The formed byproducts water or *tert*-butanol were completely removed under vacuum, since they may act as initiators in the polymerization of glycidol as well. The polymerization reaction was performed by slow addition of the respective amount of glycidol dissolved in THF to a suspension/solution of the deprotonated initiator in diglyme or THF at 60°C. After completed polymerization the products were treated with ion exchange resin and purified by precipitation or dialysis.

6.4.1 Results and characterization

The ring opening polymerization of glycidol was performed with macroinitiators containing 5, 22 or 54 carbosilane units. The polymerization results are summarized in Table 6.4.

Table 6.4 Polymerization results for polycarbosilane macroinitiators.

	GPC(THF,RI)		DSC
	M _n	PDI	T _g [°C]
H-PCS ₅ -C ₁₁ -N ₃	1070	1.23	-
H-PCS ₅ -C ₁₁ -PG ₅₅	5060 ^a	1.57	-32
H-PCS ₅ -C ₁₁ -PG ₅₅ Bz	5540	1.26	n.d.
H-PCS ₂₂ -C ₁₁ -NPG ₂	1830	1.82	-75/-58
H-PCS ₂₂ -C ₁₁ -PG ₁₅	2800	2.15	-83
H-PCS ₂₂ -C ₁₁ -PG ₁₅ Si	2340	1.89	-81/58
H-PCS ₅₄ -C ₁₁ -NPG ₂	2490	2.05	-79
H-PCS ₅₄ -C ₁₁ -PG _x	no attachment of PG		

a) GPC in DMF.

The size of the carbosilane block is crucial for the accessibility of the initiating moiety. While the oligomeric initiator was suitable for the polymerization of glycidol, initiation

was completely inhibited for the largest macroinitiator and hence no polyglycerol block could be attached. In Figures 6.18 and 6.19 GPC results for the PCS- C_{11} -PG polymers are compared with the respective initiators.

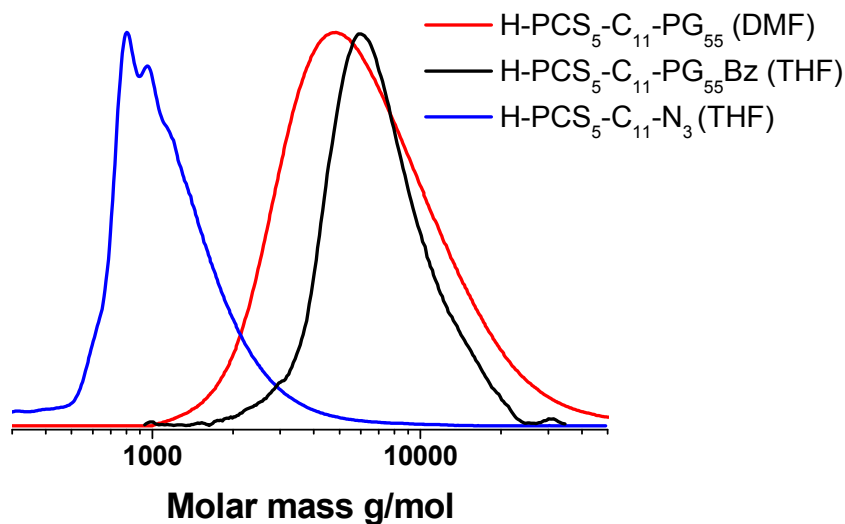


Fig. 6.18 GPC curves for H-PCS₅-C₁₁-X.

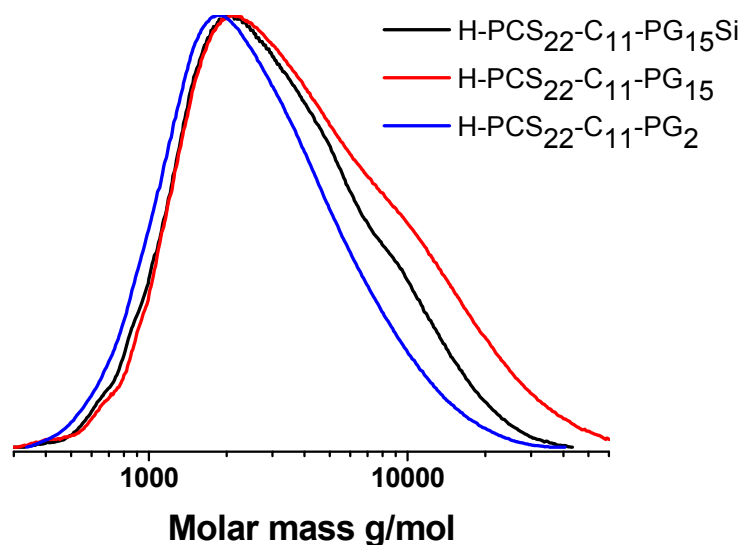


Fig. 6.19 GPC curves for H-PCS₂₂-C₁₁-X in THF.

The molecular weight increase is palpable, though accompanied by an increase in polydispersity. The latter is caused by a high molecular weight tailing, likely due to weak hydrogen bond interactions. Chemical masking of the free hydroxyl groups of the polyglycerol block with benzoyl (-PGBz) or trimethylsilyl (-PGSi) protecting groups removes the amphiphilic properties of the polymer (Fig. 6.20). Analysis for these

samples shows that the actual polydispersity is smaller than observed for the amphiphile and equal to the respective macroinitiator (see Table 6.4).

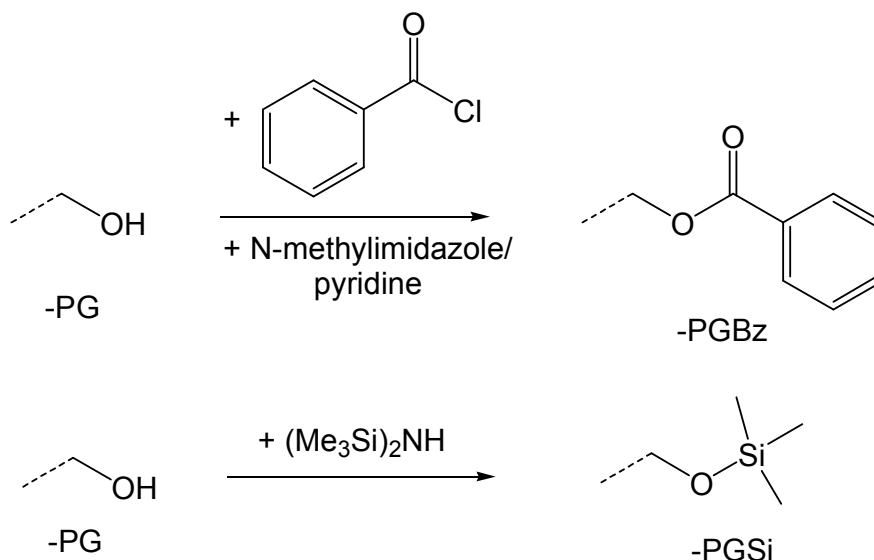


Fig. 6.20 Protection of hydroxyl groups using benzoyl chloride or hexamethyldisilazane.

Growth of the polyglycerol block can be observed in the $^1\text{H-NMR}$ spectrum. In Figure 6.21 the spectra for macroinitiator and a typical block copolymer are presented. As reference for the carbosilane block the signal for Si-CH_3 is marked (blue). Compared to this signal the increased size of the polyether structure (red) is obvious. MALDI-ToF spectrometry is a versatile tool to analyze the structural composition of a polymer. However, for block copolymer structures analysis is often complex and not straightforward due to an overlap of different distributions resulting from the presence of a large variety of combinations of all monomer units present. In Figure 6.22 the spectrum for $\text{H-PCS}_{22}\text{-C}_{11}\text{-PG}_{15}$ is given showing a monomodal distribution with a peak maximum at ~ 3500 g/mol. However, peak assignment is futile because of the large number of peaks representing manifold possible combinations of carbosilane and glycerol units in the polymer.

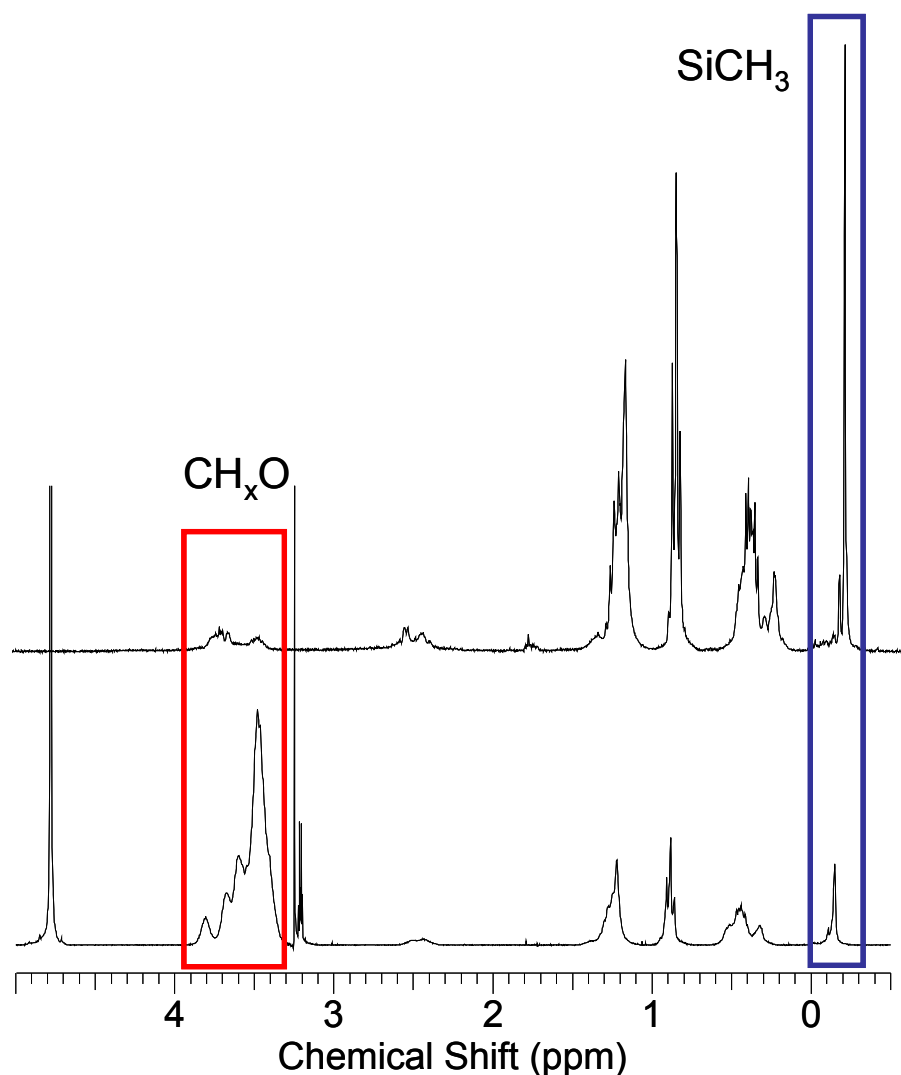


Fig. 6.21 ^1H -NMR spectra for $\text{H-PCS}_5\text{-C}_{11}\text{-PG}_{55}$ in MeOD-d_4 (bottom) and $\text{H-PSC}_5\text{-C}_{11}\text{-PG}_2$ in CDCl_3 (top).

In contrast a diminished number of possible combinations is expected for $\text{H-PCS}_5\text{-C}_{11}\text{-PG}_{55}$ with an oligomeric carbosilane block. And indeed, three distributions of major intensity are visible in the spectrum (Fig. 6.23). The enlarged section shown in Figure 6.24 reveals that the mass increment in each distribution equals 74.1g/mol, corresponding to a glycidol repeating unit. Thus, the main distributions can be assigned to polymers containing 3, 4 or 5 etc. carbosilane units and increasing amounts of glycidol.

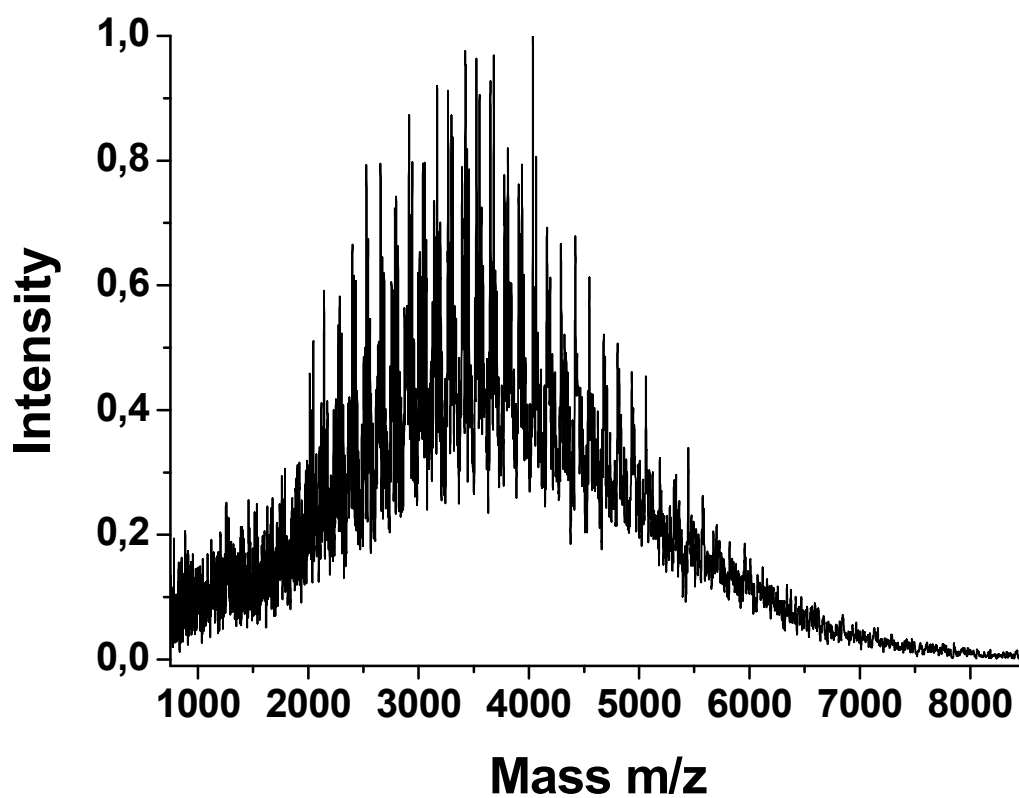


Fig. 6.22 MALDI-ToF spectrum for H-PCS₂₂-C₁₁-PG₁₅.

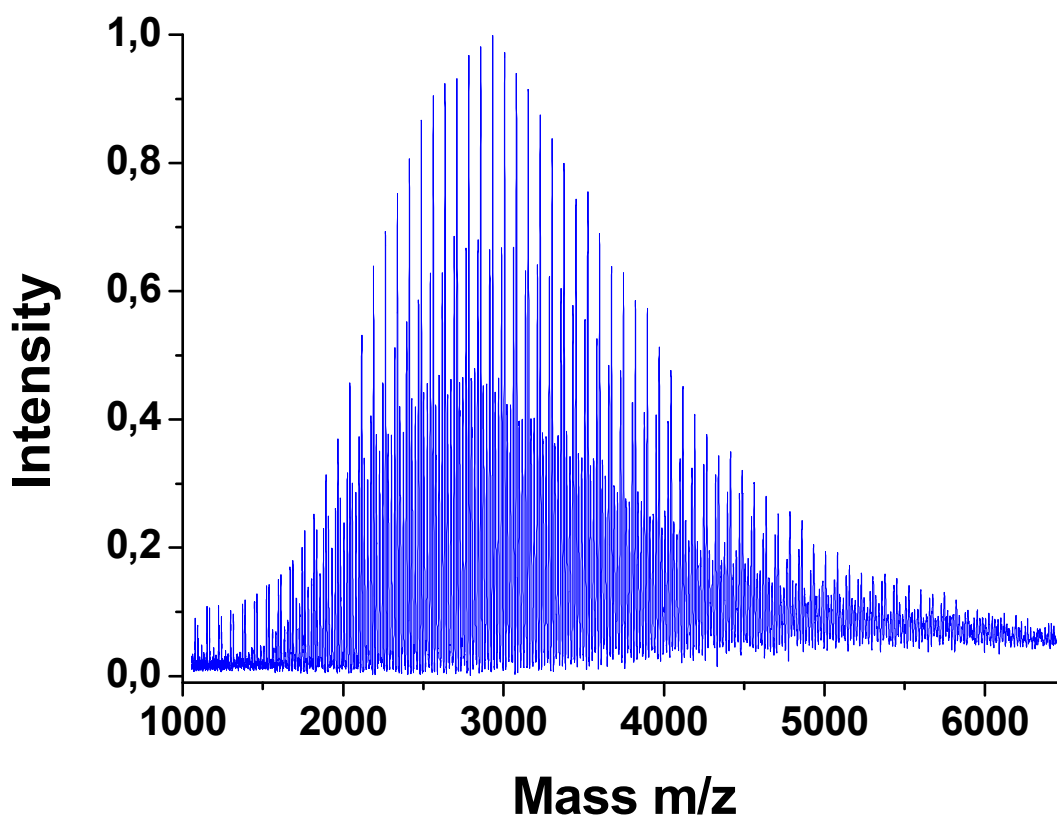


Fig. 6.23 MALDI-ToF spectrum for H-PCS₅-C₁₁-PG₅₅.

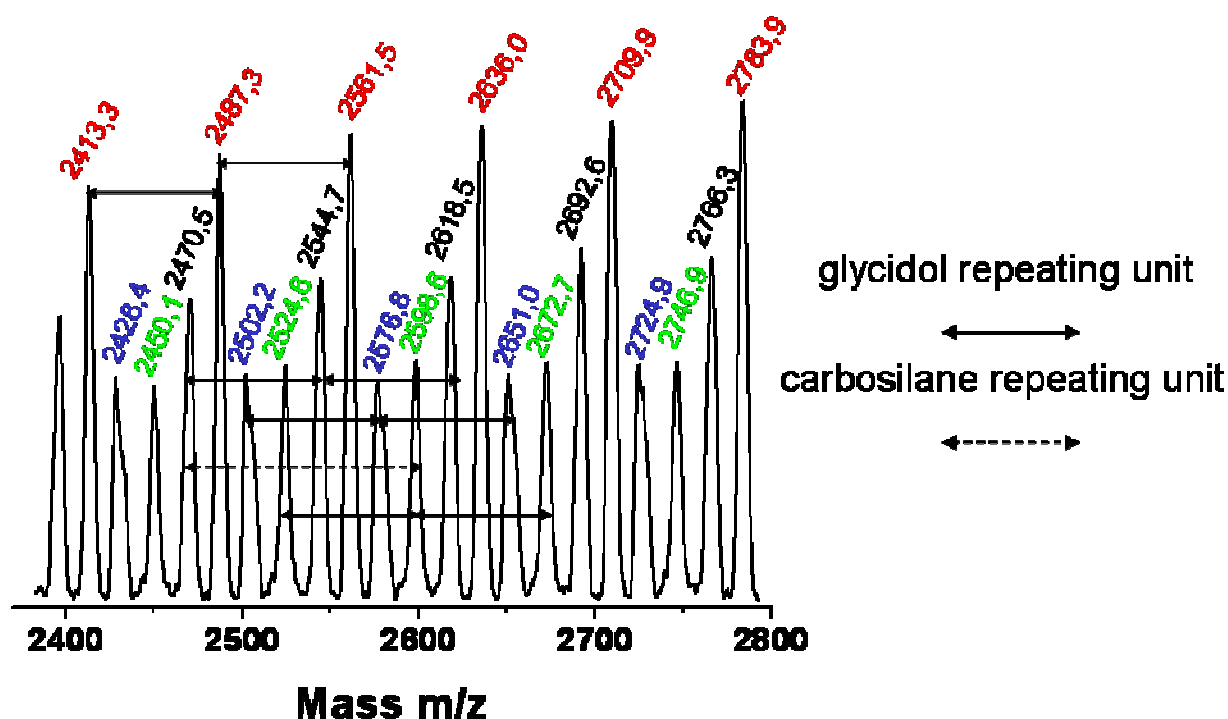


Fig. 6.24 Section of MALDI-ToF spectrum for H-PCS₅-C₁₁-PG₅₅.

The amphiphilic character of the samples can be demonstrated using an extraction experiment. Therefore, aqueous solutions of methyl orange, rose bengal and congo red (each ~5mg/ml) were prepared. These dyes are insoluble in chloroform, thus upon addition of chloroform to the dye solution no coloring of the chloroform layer is visible after vigorous shaking. The result of this blank test can be seen in Figure 6.25 left with a colorless chloroform layer at the bottom and a colored aqueous solution on top. The amphiphilic block copolymer H-PCS₂₂-C₁₁-PG₁₅ is soluble in chloroform. However, due to the insolubility of polyglycerol in this solvent the formation of micelles with a polycarbosilane exterior is expected.

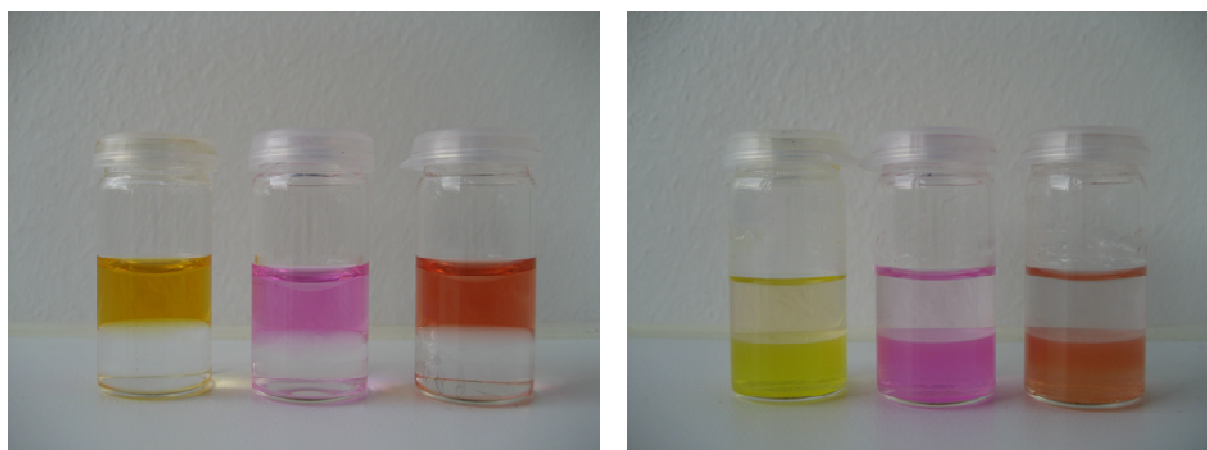


Fig. 6.25 Extraction experiments: left) blank test and right) test with amphiphile (each with methyl orange, rose bengal and congo red).

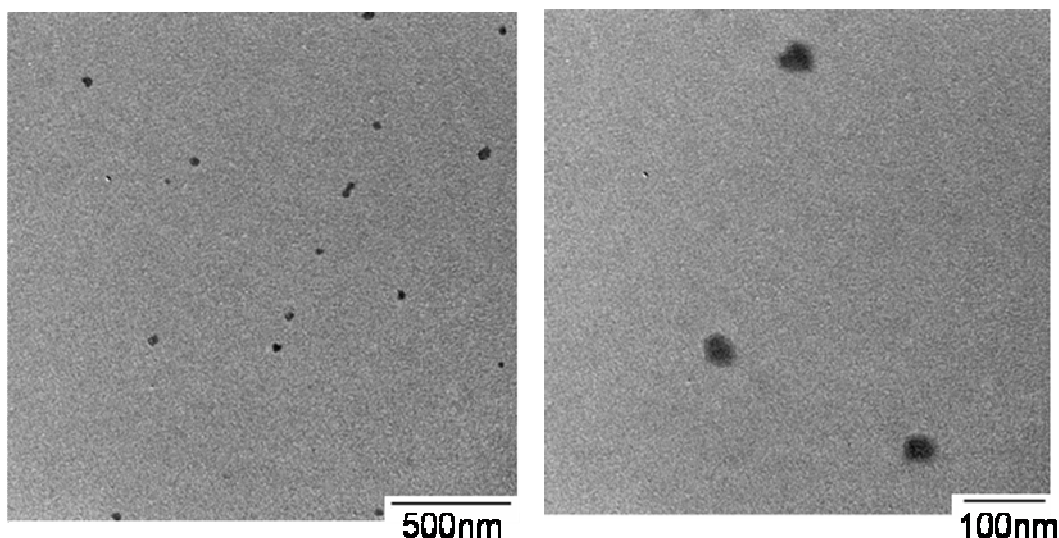


Fig. 6.26 TEM images of solution cast sample of H-PCS₂₂-C₁₁-PG₁₅ (prepared from 0.5mg/ml solutions in CHCl₃).

Mixing of equal volumes of dye solution with a solution of the polymer in chloroform (~4mg/ml) results in a complete extraction of the dye from the aqueous into the chloroform layer (Figure 6.25 right). Thus, the dye is efficiently encapsulated into the polar interior of the micelles, confirming the polymers amphiphilic character. The micelles are also visible when dried chloroform solutions of the polymer are examined using transmission electron microscopy (TEM). The spherical structures are uniform in size and visible without staining due to the strong scattering contrast of silicon (Figure 6.26).

6.5 Synthesis of *hb-PCS-b-lin-PG*

In order to demonstrate the versatility of the core-functional polymers, synthesis of block copolymers was targeted using azide-functional polycarbosilane wedges. Azides and alkynes can react in the Huisgen 1,3-dipolar cycloaddition to give 1,2,3-triazoles^{20, 21}. This reaction has found its way into organic chemistry and especially polymer chemistry^{22, 23}, due to its high yields and mild reaction conditions. The reaction can be used to combine two preformed polymer blocks with the appropriate terminal functionalities, e.g., reaction of azide-functional polycarbosilane with alkyne-terminated linear polyglycerol to give linear-hyperbranched polymers. The feasibility of this approach was first tested using phenyl acetylene as a low molecular weight

coupling agent (Fig. 6.27). The reaction was performed using CuI and 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) as the chelating agent in THF at 20°C. The polymer was purified by filtration over a silica gel column. The resulting phenyl-terminal polymer is denoted H-PCS-C₁₁-tr-Ph with tr marking the triazole linkage.

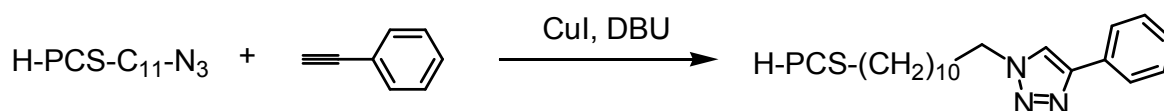


Fig. 6.27 Cycloaddition of phenyl acetylene and azide-functional polycarbosilane.

¹H-NMR spectroscopy (Fig. 6.28) confirms the formation of the triazole ring with a singlet at 7.73ppm belonging to the proton in the 5-position. Quantitative conversion is proven by the disappearance of the focal azide group (-CH₂-N₃ at 3.24ppm); while a new signal arises at 4.38ppm for -CH₂-triazole (denoted A in Fig.6.28). The attachment of the phenyl group to the polymer became noticeable by the appearance of a strong UV signal in GPC, as well (Fig. 6.29).

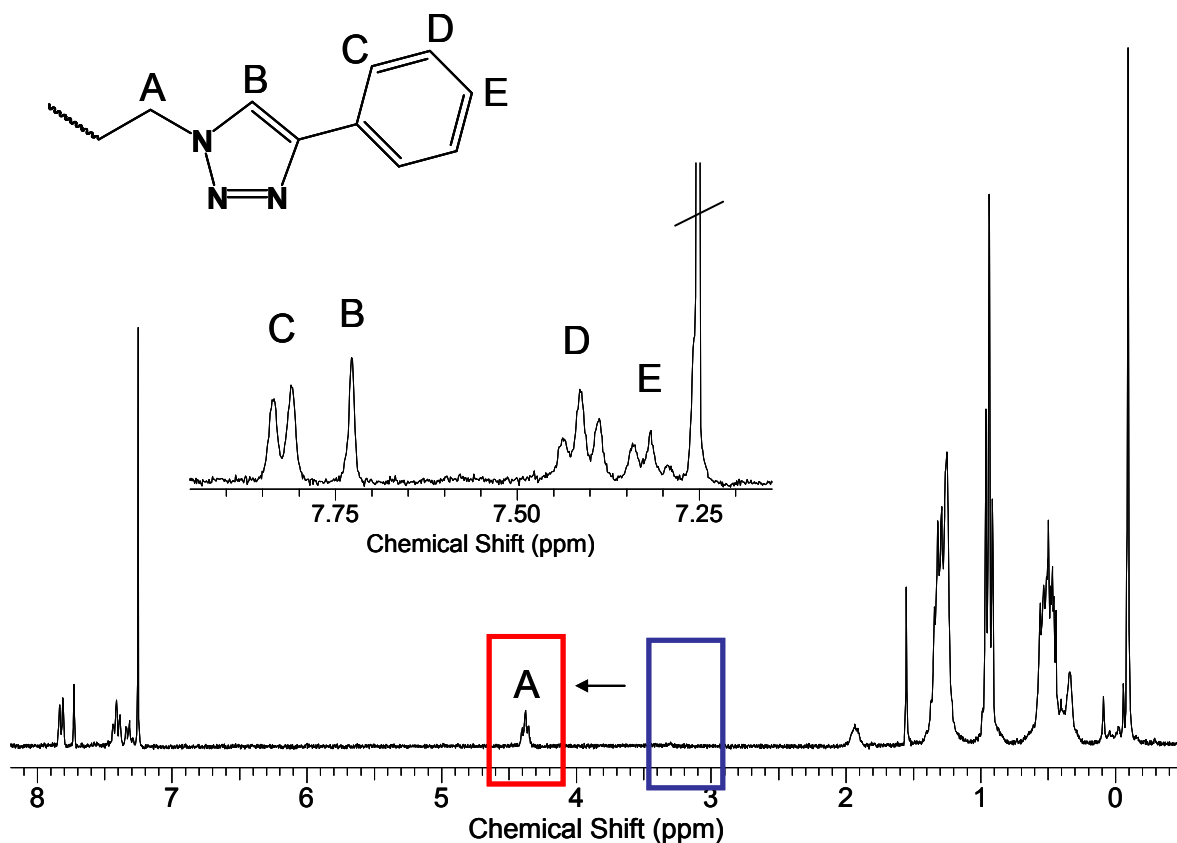


Fig. 6.28 ¹H-NMR spectrum in CDCl₃ for H-PCS-C₁₁-tr-Ph.

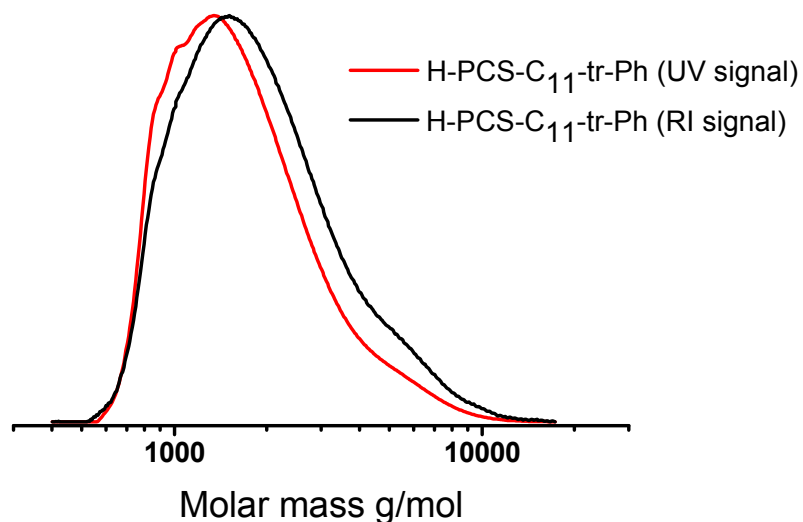


Fig. 6.29 GPC in CHCl_3 for H-PCS- C_{11} -tr-Ph.

Consequently, the reaction was adapted for the synthesis of block copolymers. Linear polyglycerol can be prepared by anionic polymerization of vinyl ether protected glycidol²⁴. Termination of the polymerization with propargyl bromide results in the alkyne-functional polymer (Fig 6.27). This polymer was made available by F. Wurm. The acetal groups of protected polyglycerol (poly(ethoxyethyl glycidylether), PEEGE) can be cleaved off under acidic conditions to give linear polyglycerol (*lin*-PG).

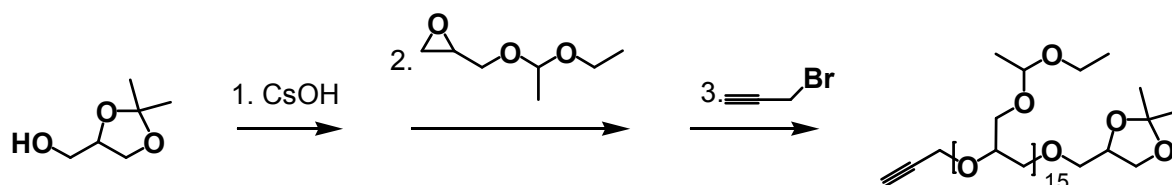


Fig. 6.30 Synthesis of alkyne-terminated protected linear polyglycerol (alkyne-PEEGE₁₅).

Exemplarily, the cycloaddition reaction was carried out with different oligomeric polycarbosilane wedges functionalized with phenylsilane or diferrocenylsilane, again using the CuI/DBU system (Figure 6.31).

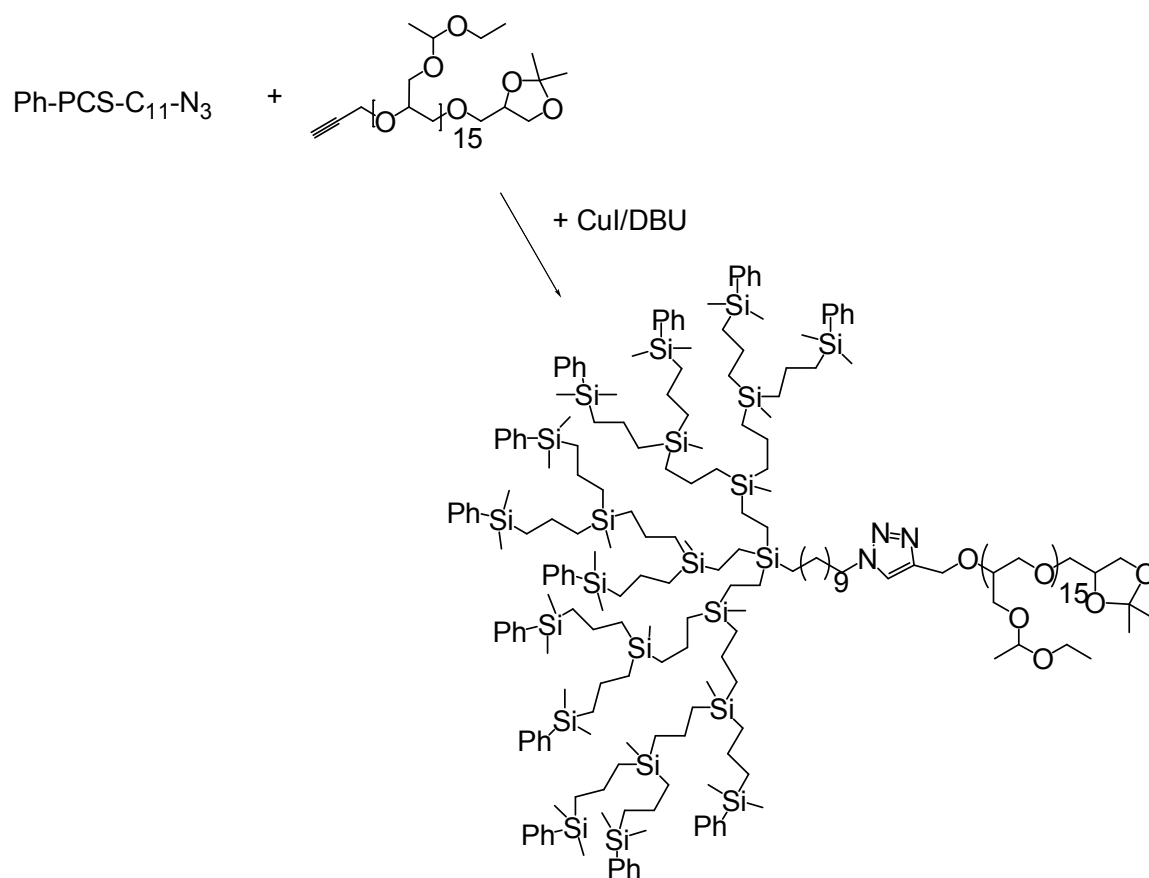


Fig. 6.31 Synthesis of linear-hyperbranched polymers via cycloaddition.

Unlike PEEGE these polymers show strong UV-absorption facilitating the distinction of the reacting polymers in GPC and thus reaction control during synthesis. Coupling reaction was performed with an excess of alkyne-PEEGE and stopped after 2 to 3 days when GPC results remained unchanged. In all cases PCS as well as PEEGE was still present in the reaction mixture. This may be a result of incomplete functionalization of the polymers. The crude product was purified by column chromatography removing most of the starting polymers. Remaining PEEGE could be separated by precipitation from cooled methanol. Isolated block copolymer yields are between 50-60%. In Table 6.5 the starting polymers as well as the block copolymers resulting after purification are summarized. The block copolymers show the expected molecular weight increase compared to the starting components. Polydispersities are still narrow between 1.3-1.4. The GPC curves for the phenyl-substituted polymers are presented in Figures 6.32 and 6.33. It can clearly be seen that the starting polymers were completely removed during purification. The block copolymers show a high molecular weight tailing, which might be due to a partial

cleavage of acetal protecting groups during work up. Here, it also has to be mentioned, that phenylsilanes are susceptible to an attack by strong electrophiles resulting in substitution at the aromatic system. However, no indication of a cleavage of the phenylsilane was observed in NMR. The ferrocenyl-substituted block copolymer (Fig. 6.34) can be obtained under the same reaction conditions, again supporting the variability of the presented system. In conclusion it can be stated that although the reactions did not go to completion the general practicability of this approach could be unambiguously proven.

Table 6.5 Cycloaddition between alkyne-PEEGE and azide-functional PCS.

	$M_n(\text{NMR})$	GPC(THF, RI)	
		M_n	PDI
PEEGE ₁₅ -alkyne	-	2100	1.08
Ph-PCS ₈ -C ₁₁ -N ₃	2800	2200	1.15
Ph-PCS ₈ -C ₁₁ -tr-PEEGE ₁₅	4900	4900	1.31
Ph-PCS ₃ -C ₁₁ -N ₃	1540	1650	1.17
Ph-PCS ₃ -C ₁₁ -tr-PEEGE ₁₅	3640	4100 ^a	1.36
Fc ₂ -PCS ₃ -C ₁₁ -N ₃	3260	1700 ^a	1.20
Fc ₂ -PCS ₃ -C ₁₁ -tr-PEEGE ₁₅	5360	3570	1.36

a) GPC in CHCl₃

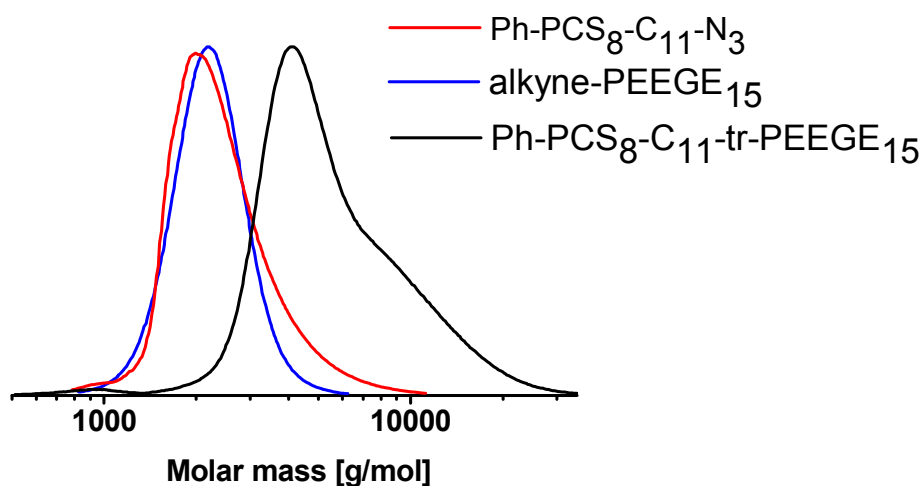


Fig. 6.32 GPC results for Ph-PCS₈-C₁₁-N₃, alkyne-PEEGE₁₅ and block copolymer.

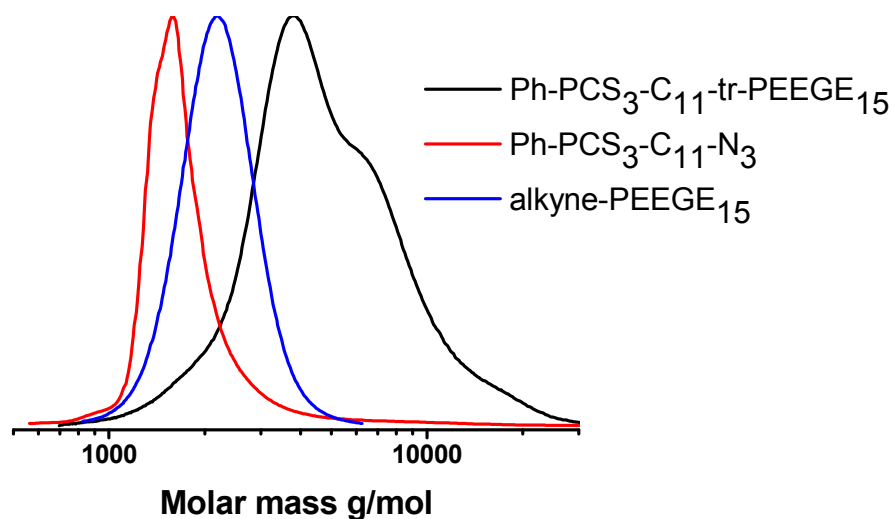


Fig. 6.33 GPC results for Ph-PCS₃-C₁₁-N₃, alkyne-PEEGE₁₅ and block copolymer.

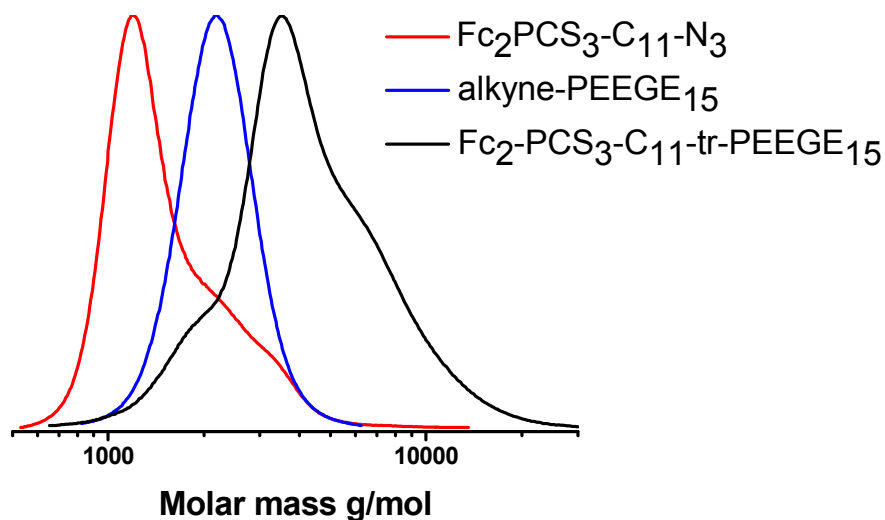


Fig. 6.34 GPC results for Fc₂-PCS₃-C₁₁-N₃, alkyne-PEEGE₁₅ and block copolymer.

Finally, the preparation of linear-hyperbranched analogs to the hyperbranched-hyperbranched PG-PCS block copolymers presented in 6.4 is shown. Acetale protecting groups of the synthesized block copolymers can be removed under acidic conditions (Fig. 6.35). To this end, the polymer is dissolved in THF and stirred after addition of HCl²⁵. After precipitation from cold acetone the amphiphilic block copolymer is obtained.

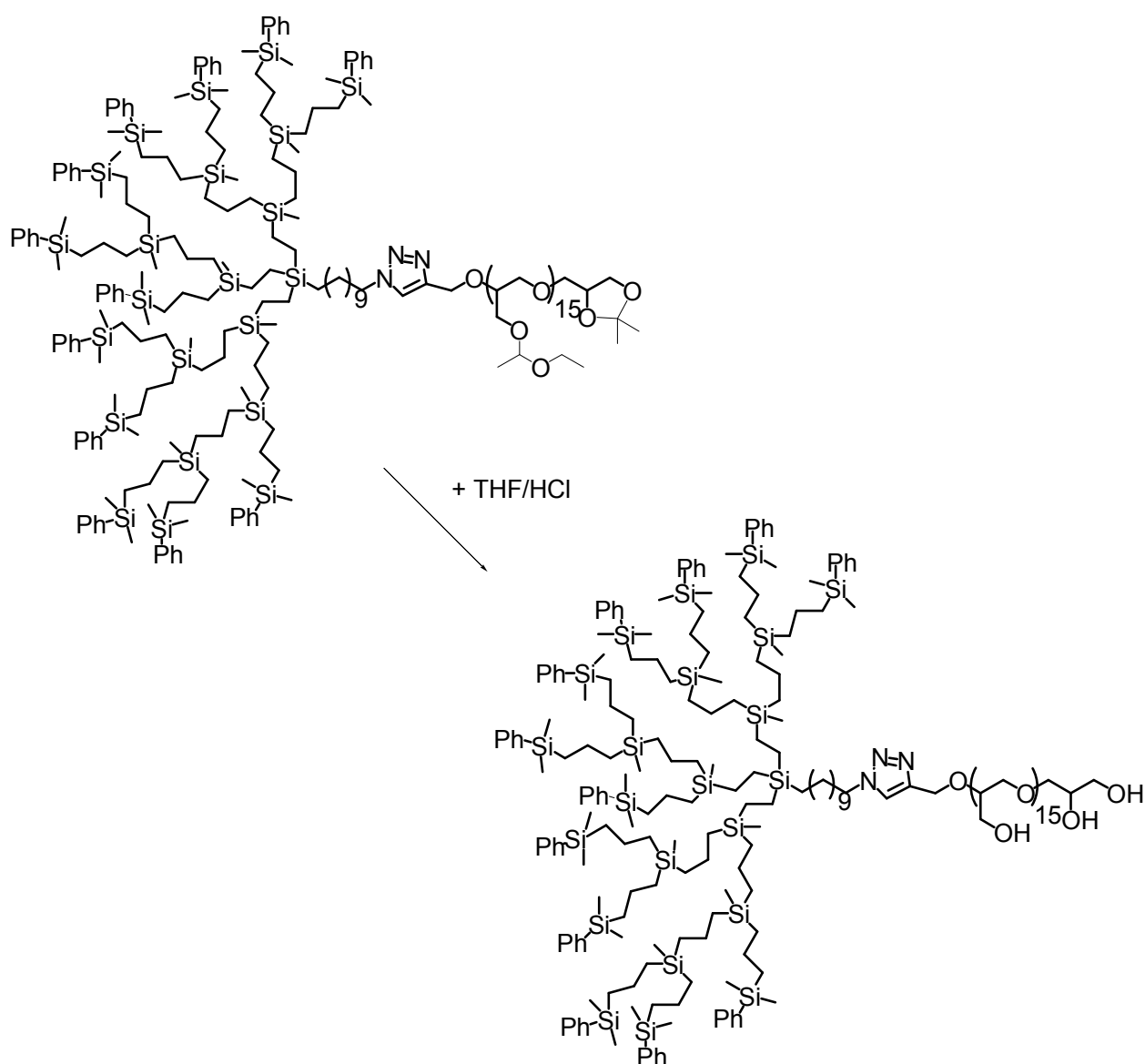


Fig. 6.35 Cleavage of acetal protecting groups to give Ph-PCS-C₁₁-tr-lin-PG.

GPC diagrams of the PG-PCS block copolymers were measured in THF and DMF (Fig. 6.36). The results are summarized in Table 6.6. Removal of the protecting groups results in a molecular weight loss observed in THF and in DMF. The THF curve is broad and resembles the shape of the curve obtained for *hb*-PCS-*hb*-PG. In DMF the signal is sharper, indicating a suppression of hydrogen bonding. Nevertheless, a high molecular weight shoulder is visible. In Figure 6.37 the NMR spectra for the protected and deprotected block copolymer are compared. By means of following the intensity of the signal of the methine proton (red) of the acetal group

the cleavage can be followed spectroscopically. Additionally, the methylene groups next to the triazole ring are observable.

Table 6.6 GPC results after deprotection of block copolymer

	solvent	GPC(RI)	
		M_n	PDI
Ph-PCS ₈ -C ₁₁ -tr-PEEGE ₁₅	THF	4900	1.31
Ph-PCS ₈ -C ₁₁ -tr- <i>lin</i> -PG ₁₅	THF	1300	1.71
Ph-PCS ₈ -C ₁₁ -tr- <i>lin</i> -PG ₁₅	DMF	3310	1.65

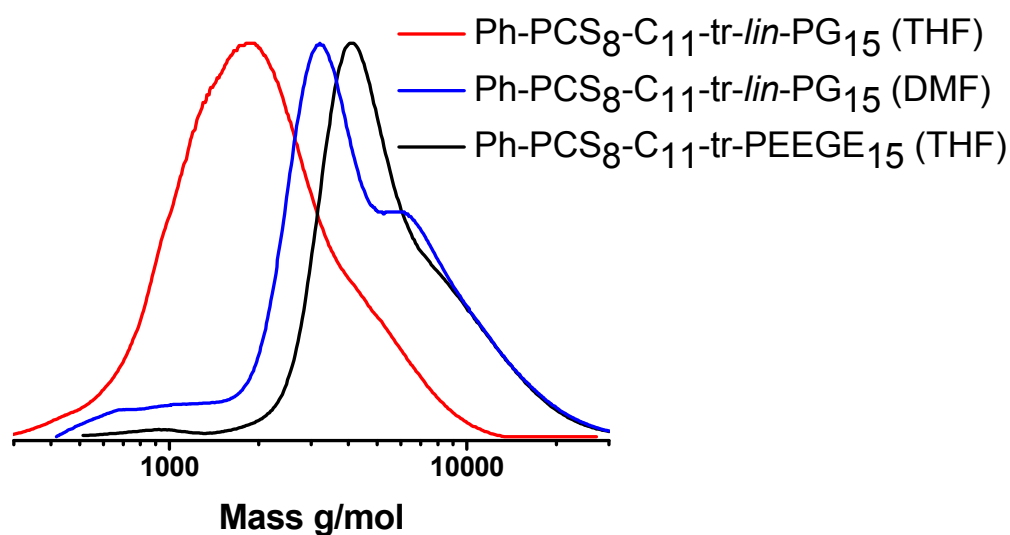


Fig. 6.36 GPC results for linear-hyperbranched block copolymer before and after deprotection of the glycidol block.

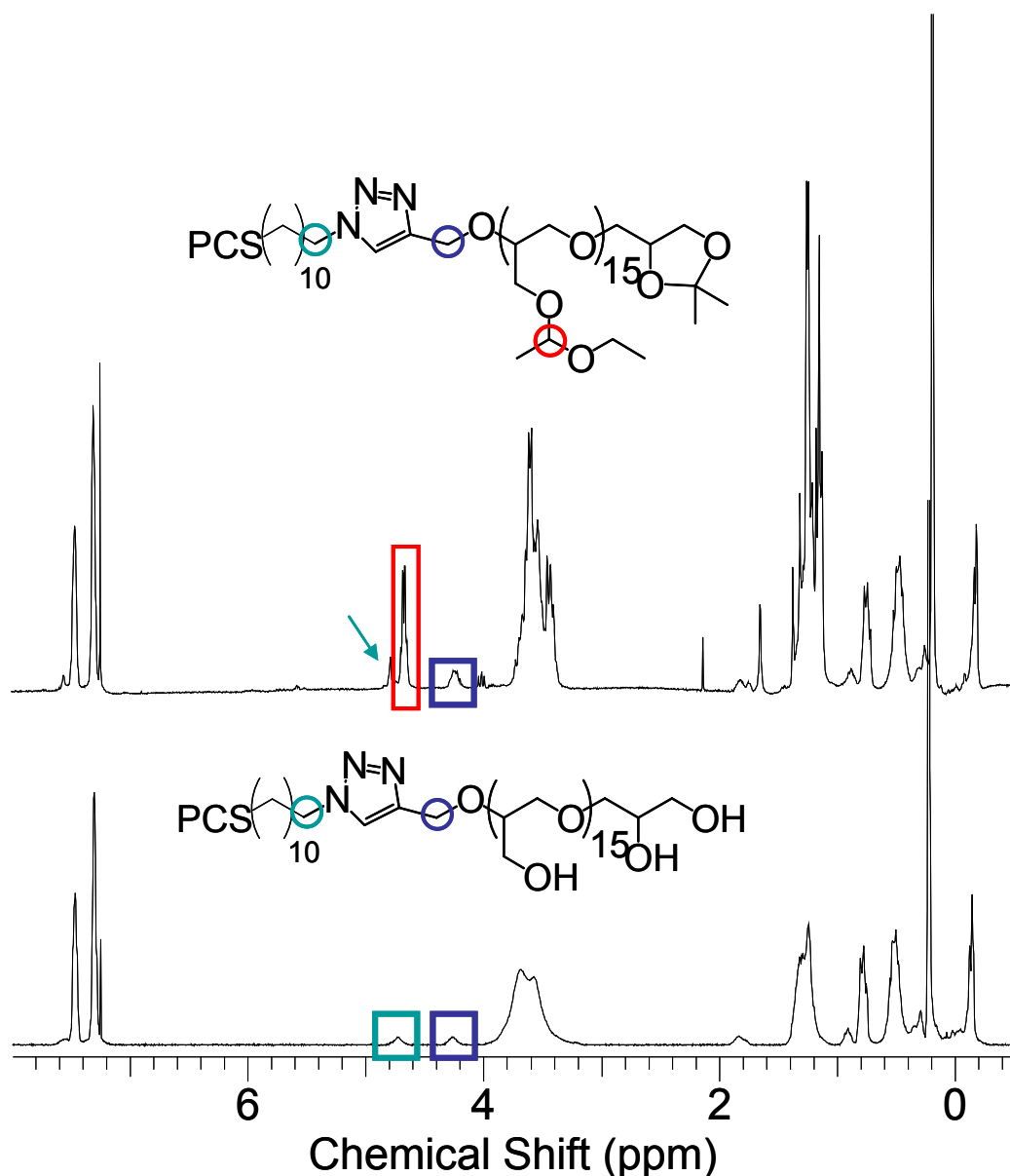


Fig. 6.37 ^1H -NMR in CDCl_3 for PCS-C₁₁-tr-PEEGE (top) and deprotected PCS-C₁₁-tr-PG.

6.6 Conclusion

In the preceding chapter a variety of reactions were summarized that allow the synthesis of tailored hyperbranched polycarbosilanes. The allyl end groups of the polymer can be converted to saturated alkyls via hydrogenation to enhance the stability of the molecules. Hydrosilylation addition of different silanes results in functionalized polymers with modified properties. Besides the transformations of the end groups also the core is susceptible to reactions. The synthesis of polymers with azide, amine and hydroxyl-functionalities at the focal point was demonstrated. The versatile modification possibilities are summarized in Figure 6.38.

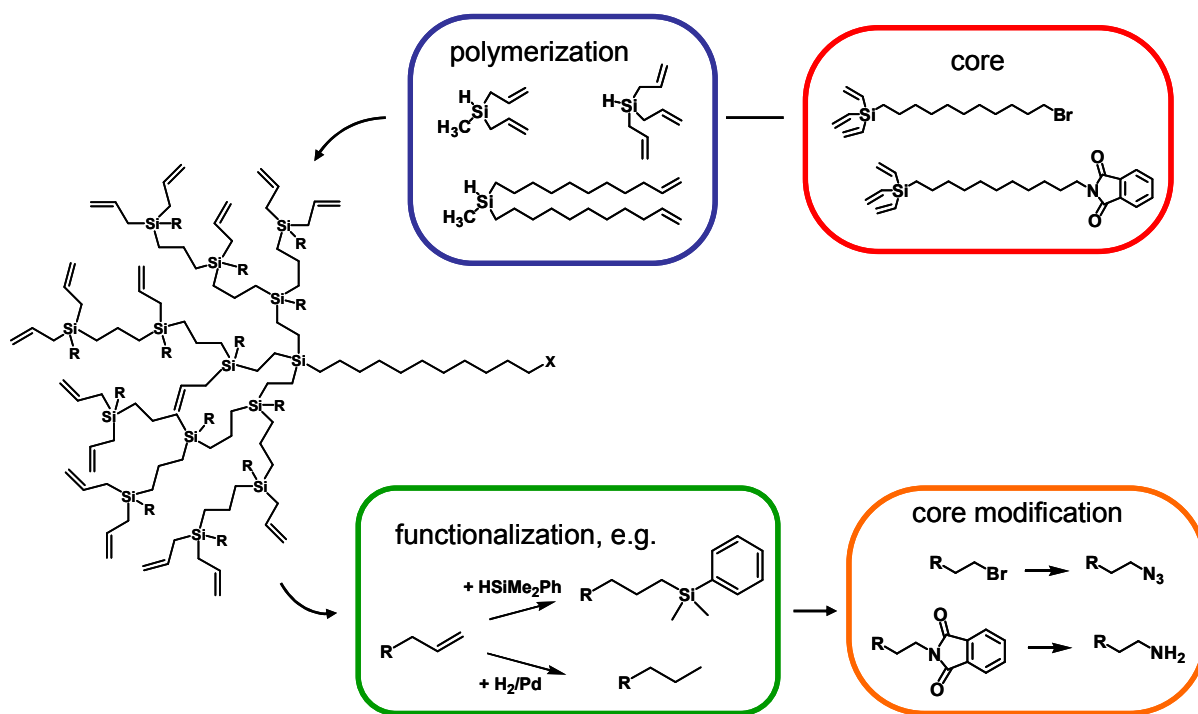


Fig. 6.38 Modifications routes for hyperbranched polycarbosilane wedges.

Core-functional carbosilane wedges allow further application in block copolymer synthesis. Bisglycidolized amine functional polymers were successfully employed as macroinitiators for glycidol polymerization. This resulted in the first example of amphiphilic hyperbranched-hyperbranched polymer structures (Fig 6.39). Utilizing copper-catalyzed cycloaddition between azide-functional polycarbosilane and alkyne-functional poly(ethoxyethyl glycidylether) resulted in linear-hyperbranched block copolymers. Removal of acetal protecting groups provided a convenient access to *lin*-PG-*hb*-PCS.

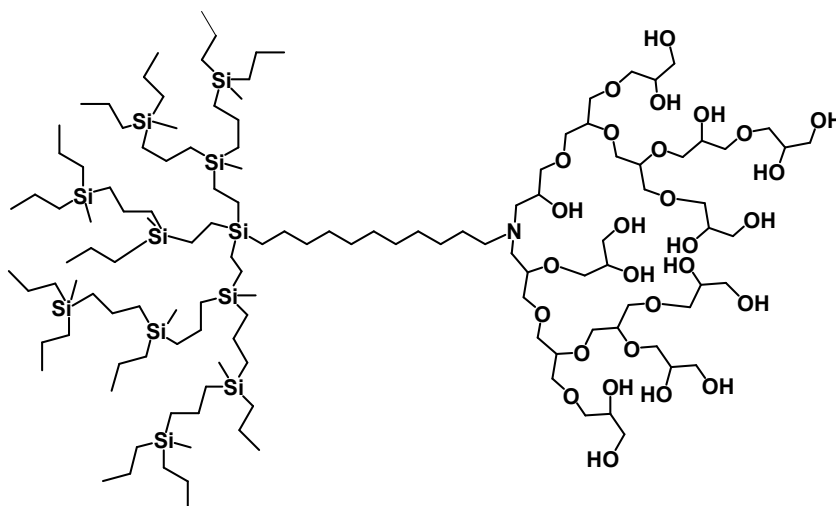


Fig. 6.39 *hb*-PCS- C_{11} -*hb*-PG.

6.7 Experimental

6.7.1 Materials

Palladium on activated charcoal (10%), dimethylphenylsilane, triethylsilane, sodium azide, hydrazine monohydrate and triphenylphosphine were purchased from Acros or Aldrich and used as received. Glycidol was distilled before usage. If not noted otherwise solvents were used as received. Platinum-divinyltetramethyldisiloxane complex (Karstedt catalyst) in xylene with 2.1-2.4% platinum concentration was purchased from Gelest.

Hydrogenation of double bonds (H-PCS_x-C₁₁-X)

Hydrogenation reactions were performed using Pd/C as catalyst under a hydrogen atmosphere. As an example 7.8g PCS₁₀-C₁₁-PI (M=1700; 4.6mmol) were dissolved in 30ml of a 3:1 mixture of ethyl acetate/methanol, followed by addition of 450mg Pd/C (10%). Hydrogen was bubbled through the solution until complete conversion was confirmed by NMR (normally ~24h). The catalyst was removed by filtration through a column filled with Celite®. Yield: 85-95%.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 1.45-1.10 (CH₂); 0.93 (CH₃); 0.73-0.24 (-CH₂Si); -0.10 (-SiCH₃); additionally depending on core used: X=Phth: 7.82 (H_{Ar}); 7.69 (H_{Ar}); 3.66 (t, -CH₂Phth); X=Br: 3.41 (t, -CH₂CH₂Br); 1.86 (-CH₂CH₂Br).

Functionalization of the double bonds

The following reaction procedures are applicable for bromo- as well as phthalimide-functional polymers.

Ph-PCS_x-C₁₁-Br. For example 2.01g (15.84mmol) diallylmethylsilane and 1.81g (5.28mmol) Vi₃-C₁₁-Br are polymerized by addition of 34μl Karstedt catalyst. After complete conversion of the monomer 4.75g (34.85mmol) dimethylphenylsilane are added drop wise to the cooled flask. Reaction of the double bonds is controlled by IR, eventually new catalyst was added. The polymer is purified by precipitation from methanol.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm]: 7.52-7.43 (H_{Ar}); 7.36-7.27 (H_{Ar}); 3.38 (t, $-\text{CH}_2\text{Br}$); 1.91-1.74 ($-\text{CH}_2\text{CH}_2\text{Br}$); 1.47-1.12 (CH_2); 0.84-0.73 ($-\text{CH}_2\text{SiMe}_2\text{Ph}$); 0.66-0.40 ($-\text{CH}_2\text{Si}$); 0.23 ($-\text{SiPhCH}_3$); -0.15 ($-\text{SiCH}_3$).

$\text{Fc}_2\text{-PCS}_x\text{-C}_{11}\text{-PI}$. In a dry flask 51mg (0.03mmol) $\text{PCS}_{10}\text{-C}_{11}\text{-PI}$ and 181mg (0.42mmol) diferrocenylmethylsilane are dissolved in 0.25ml chlorobenzene. After addition of 10 μl Karstedt catalyst the solution is heated to 60°C for 24h. The polymer is purified by dialysis (MWC 1000, Aldrich) in chloroform. Yield: 96%.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm]: 7.81 (H_{Ar}); 7.68 (H_{Ar}); 4.39-4.27 ($\eta\text{-C}_5\text{H}_4$); 4.19-4.01 ($\eta\text{-C}_5\text{H}_4$); 3.66 (t, $-\text{CH}_2\text{Phth}$); 1.70-1.17 (CH_2); 1.08-0.91 ($-\text{CH}_2\text{SiMeFc}_2$); 0.72-0.51 ($-\text{CH}_2\text{Si}$); 0.48 ($-\text{SiFc}_2\text{CH}_3$); 0.04-(-0.14) ($-\text{SiCH}_3$).

$\text{Et}_3\text{-PCS}_x\text{-C}_{11}\text{-PI}$. In a dry flask 102mg (0.06mmol) $\text{PCS}_{10}\text{-C}_{11}\text{-PI}$ and 97mg (0.86mmol) triethylsilane are dissolved in 0.1ml chlorobenzene. After addition of 10 μl Karstedt catalyst the solution is heated to 60°C for 24h. Excess triethylsilane is removed under vacuum. Yield: quant.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm]: 3.39 (t, $-\text{CH}_2\text{CH}_2\text{Br}$); 1.82 ($-\text{CH}_2\text{CH}_2\text{Br}$); 1.43-1.18 (CH_2); 0.91 (t, CH_3); 0.66-0.28 ($-\text{CH}_2\text{Si}$); 0.49 (q, $\text{CH}_3\text{CH}_2\text{Si}$); -0.9 ($-\text{SiCH}_3$).

All functionalized polymers with a bromide at the focal point can be converted to the respective azide according to the procedure described in 6.7.3.

Modifications at the core

$\text{H-PCS}_x\text{-C}_{11}\text{-N}_3$. Reactions were performed in DMF/THF at 60°C employing 2-20 equivalents sodium azide. As an example 1.81g (0.62mmol) $\text{PCS}_{20}\text{-C}_{11}\text{-Br}$ and 0.81g (12.4mmol) sodium azide were suspended in 10ml DMF/THF and heated at 60°C for 24h. The solvents were removed under vacuum and the residue dissolved in chloroform. The solution was washed with water and dried with MgSO_4 .

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm]: 3.24 ($-\text{CH}_2\text{N}_3$); 1.45-1.10 (CH_2); 0.93 (CH_3); 0.73-0.24 ($-\text{CH}_2\text{Si}$); -0.10 ($-\text{SiCH}_3$).

H-PCS_x-C₁₁-NH₂**a) Via the phthalimide.**

A solution of 6.5g H-PCS-C₁₁-PI (M=1700; 3.8mmol) and 0.9g (18mmol) hydrazine in 40ml ethanol/THF were heated at 60°C for 18h. The white precipitate was removed by filtration and the solution evaporated to dryness. The residue was dissolved in diethyl ether and washed with a 1M NaOH-solution. Remaining phthalhydrazide was removed by dialysis (MWCO = 1000g/mol).

b) Via the azide.

Staudinger reduction. A solution of 2.0g PCS-C₁₁-N₃ (M=1400; 1.4mmol) and 0.75g triphenylphosphine in 10ml THF were stirred for 18h (evolution of gas normally ceased after the first hours). After addition of aqueous ammonia solution (0.7ml, 35%) the reaction mixture was stirred for another 18h. The solvent was removed and the triphenylphosphite separated by a short column in CHCl₃/MeOH 9:5. The amine-functional polymer was eluted from the column by addition of triethylamine to the eluent. Yield: 1.2g (60%).

Reduction with hydrogen. Hydrogen was bubbled through a solution of 1.39g (0.48mmol) PCS₂₀-C₁₁-N₃ in 5ml ethyl acetate/methanol (4:1) and 50mg Pd/C. After complete reduction of the azide the solution was filtered over Celite and the pure polymer obtained after removal of the solvent. Yield: quant.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 2.67 (-CH₂NH₂); 1.84-1.64 (-NH₂); 1.45-1.10 (CH₂); 0.93 (CH₃); 0.73-0.24 (-CH₂Si); -0.10 (-SiCH₃).

H-PCS_x-C₁₁-NPG₂. A solution of 67mg (0.9mmol) glycidol in 1ml dry THF is added drop wise to a solution of 1.20g (0.04mmol) PCS₂₀-C₁₁-NH₂. After complete addition the reaction mixture is heated to 60°C for 18h. Unreacted glycidol is removed under vacuum at 100°C. Yield: quant.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 3.84-3.42 (CH_xO); 2.72-2.38 (CH_xN); 1.45-1.10 (CH₂); 0.93 (CH₃); 0.73-0.24 (-CH₂Si); -0.10 (-SiCH₃).

Hyperbranched-hyperbranched block copolymers

Hb-H-PCS-C₁₁-hb-PG. Bisglycidolized amine functionalized *hb*-PCS (H-PCS-C₁₁-PG₂) was dissolved in benzene and partially deprotonated (30% of the OH-groups) by adding cesium hydroxide. The solution was stirred for one hour at 90°C at atmospheric pressure and subsequently for two more hours under vacuum to remove benzene and water. The completely dried macroinitiator was dissolved in THF and heated till reflux. The polymerization reaction was performed by slow addition of the respective amount of a 10% solution of glycidol in THF via a syringe pump (Lambda VIT-FIT syringe pump). After addition was completed, a cation exchange resin (Dowex[®] 50WX8, 200-400 mesh) was added and the mixture was stirred for one more hour. Subsequently, the solution was filtered over a sintered filter (pore size 1) and washed with CHCl₃, Et₂O or MeOH, depending on the size of the blocks. The resulting polymer was purified by dialysis in the respective solvent. Yields: 80-90%.

¹H-NMR (300 MHz, MeOD) δ [ppm]: 3.86-3.30 (CH_xO); 2.59-2.29 (CH_xN); 1.48-1.07 (CH₂); 0.97-0.76 (CH₃); 0.61-0.24 (-CH₂Si); -0.04-(-0.24) (-SiCH₃).

Hb-H-PCS-C₁₁-hb-PGSi. A solution of 8mmol HMDS in 10ml chloroform was added dropwise to a stirred suspension of *hb*-H-PCS-C₁₁-*hb*-PG (10mmol OH groups) and iodine (0.1mmol) in chloroform (40ml). After stirring for 24h a clear solution was obtained. 3g of powdered Na₂S₂O₃ were added portion-wise. The mixture was stirred for another 30 minutes, filtered and washed twice with chloroform. The solvents were removed under vacuum and the product was purified by dialysis in CHCl₃.

Hb-H-PCS-C₁₁-hb-PGBz. A solution of *hb*-H-PCS-C₁₁-*hb*-PG (3mmol OH groups), benzoyl chloride (3.3ml) and *N*-methylimidazole (0.1ml) in pyridine (30ml) was heated to 80°C and stirred for 12h. After removal of most of the solvent, 2.6g K₂CO₃ was added to the residue, dissolved in 100ml toluene. The solution was filtered and washed with toluene. Pyridine impurities were removed by azeotropic distillation of the toluene. The product was purified by dialysis in CHCl₃.

Linear-hyperbranched block copolymers

Hb-H-PCS-C₁₁-tr-Ph. A flask was filled with 100mg (M=1400g/mol, 0.067mmol) H-PCS-C₁₁-N₃ and 3mg (0.13mmol) CuI and was oxygen removed under vacuum. Under a nitrogen atmosphere 13mg (0.13mol) phenyl acetylene, 200mg DBU (1.3mmol) and 2.5ml THF were added and the solution stirred over night. The product was purified by filtration over a silica column in CHCl₃.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 7.83 (d, J = 7.72Hz, H_{Ar}); 7.73 (s, N-CH=CR₂); 7.47-7.37 (m, H_{Ar}); 7.36-7.28 (m, H_{Ar}); 4.38 (m, CH₂-triazole); 1.94 (CH₂); 1.45-1.14 (CH₂); 0.94 (CH₃); 0.68-0.23 (-CH₂Si); -0.09 (-SiCH₃).

Hb-Ph-PCS₈-C₁₁-tr-PEEGE₁₅. A flask was filled with 0.94g (M=2100g/mol, 0.45mmol) Ph-PCS-C₁₁-N₃, 1.88g (M=2100g/mol, 0.9mmol) PEEGE and 21mg (0.1mmol) CuI and oxygen was removed under vacuum. Under a nitrogen atmosphere 1.52g DBU (10mmol) and 25ml THF were added and the solution stirred at 40°C for 48h. The product was purified by column chromatography in CHCl₃/PE 1:1 and THF. Remaining DBU and PEEGE were removed by dissolving the polymer in CHCl₃ and precipitation from methanol cooled with acetone/dry ice. Yield: 1.14g (61%).

Hb-Ph-PCS₃-C₁₁-tr-PEEGE₁₅. Reaction was performed according to the previous procedure using 1.0g (M=1490g/mol, 0.67mmol) Ph-PCS-C₁₁-N₃ and 1.68g (M=2100g/mol, 0.8mmol) PEEGE. Yield: 50%.

Hb-Fc₂-PCS₃-C₁₁-tr-PEEGE₁₅. Reaction was performed according to the previous procedure using 0.5g (M=3260g/mol, 0.15mmol) Fc₂-PCS-C₁₁-N₃ and 0.97g (M=2100g/mol, 0.46mmol) PEEGE.

¹H-NMR (300 MHz, CDCl₃) δ [ppm]: 7.56 (s, N-CH=CR₂); 7.46 (m, H_{Ar}); 7.31 (m, H_{Ar}); 4.80 (m, CH₂-PEEGE); 4.69 (q, CH-acetal); 4.25 (m, CH₂-triazole); 3.80-3.38 (CH₂O); 1.93-1.73 (CH₂); 1.43-1.09 (CH₂, CH₃-acetal); 0.85-0.70 (-CH₂SiMe₂Ph); 0.68-0.23 (-CH₂Si); 0.22 (-SiPhCH₃); -0.08-(-0.20) (-SiCH₃).

Hb-Ph-PCS₈-C₁₁-tr-lin-PG₁₅. Conc. HCl (6ml) were added to a stirred solution of 0.67g Ph-PCS₈-C₁₁-tr-PEEGE₁₅ in 35ml THF. After 1h the solution was evaporated to

dryness. The polymer was dissolved in warm methanol and precipitated into cold acetone.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ [ppm]: 7.56 (s, N-CH=CR_2); 7.47 (m, H_{Ar}); 7.31 (m, H_{Ar}); 4.73 (m, $\text{CH}_2\text{-PEEGE}$); 4.27 (m, $\text{CH}_2\text{-triazole}$); 3.80-3.38 (CH_2O); 1.93-1.73 (CH_2); 1.44-1.09 (CH_2); 0.85-0.70 ($-\text{CH}_2\text{SiMe}_2\text{Ph}$); 0.68-0.23 ($-\text{CH}_2\text{Si}$); 0.22 ($-\text{SiPhCH}_3$); -0.08-(-0.20) ($-\text{SiCH}_3$).

6.8 References

1. Ruzette, A. V.; Leibler, L. *Nat Mater* **2005**, 4, (1), 19.
2. Lodge, T. P. *Macromol Chem Phys* **2003**, 204, (2), 265.
3. Bucknall, D. G.; Anderson, H. L. *Science* **2003**, 302, (5652), 1904.
4. Forster, S.; Plantenberg, T. *Angew Chem Int Edit* **2002**, 41, (5), 689.
5. Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem Rev* **2001**, 101, (12), 3747.
6. Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Advances in Polymer Science* **1998**, 135, 1.
7. Gitsov, I., Linear-Dendritic Block Copolymers. Synthesis and Characterization. In *Advances in Dendritic Macromolecules*, Newkome, G. R., Ed. Elsevier Science: Amsterdam, 2002; Vol. 5, pp 45.
8. G. Marcos, A.; Pusel, T. M.; Thomann, R.; Pakula, T.; Okrasa, L.; Geppert, S.; Gronski, W.; Frey, H. *Macromolecules* **2006**, 39, (3), 971.
9. Hawker, C. J.; Fréchet, J. M. J. *J Am Chem Soc* **1992**, 114, 8405.
10. Aoi, K.; Itoh, K.; Okada, M. *Macromolecules* **1997**, 30, (25), 8072.
11. Bury, I.; Donnio, B.; Gallani, J. L.; Guillon, D. *Langmuir* **2007**, 23, (2), 619.
12. Nierengarten, J. F.; Eckert, J. F.; Rio, Y.; Carreon, M. D.; Gallani, J. L.; Guillon, D. *J Am Chem Soc* **2001**, 123, (40), 9743.
13. Zhang, S.; Rio, Y.; Cardinali, F.; Bourgoigne, C.; Gallani, J. L.; Nierengarten, J. F. *J Org Chem* **2003**, 68, (25), 9787.
14. Yang, M.; Wang, W.; Yuan, F.; Zhang, X. W.; Li, J. Y.; Liang, F. X.; He, B. L.; Minch, B.; Wegner, G. *J Am Chem Soc* **2005**, 127, (43), 15107.
15. Yuan, F.; Wang, W.; Yang, M.; Zhang, X. J.; Li, J. Y.; Li, H.; He, B. L. *Macromolecules* **2006**, 39, (12), 3982.
16. Lee, J. W.; Kim, B. K.; Kim, J. H.; Shin, W. S.; Jin, S. H. *J Org Chem* **2006**, 71, (13), 4988.
17. Amore, A.; van Heerbeek, R.; Zeep, N.; van Esch, J.; Reek, J. N. H.; Hiemstra, H.; van Maarseveen, J. H. *J Org Chem* **2006**, 71, (5), 1851.
18. van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. N. M. W.; Reek, J. N. H. *Org Biomol Chem* **2006**, 4, (2), 211.
19. van Heerbeek, R.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron Lett* **1999**, 40, (39), 7127.
20. Huisgen, R.; Szeimies, G.; Möbius, L. *Chem. Ber.* **1967**, 100, 2494.
21. Huisgen, R. *Angew. Chem.* **1963**, 75, (13), 604.
22. Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew Chem Int Edit* **2001**, 40, (11), 2004.
23. Binder, W. H.; Sachsenhofer, R. *Macromol Rapid Comm* **2007**, 28, (1), 15.
24. Taton, D.; Leborgne, A.; Sepulchre, M.; Spassky, N. *Macromol Chem Phys* **1994**, 195, (1), 139.
25. Istratov, V.; Kautz, H.; Kim, Y. K.; Schubert, R.; Frey, H. *Tetrahedron* **2003**, 59, (22), 4017.

7 Summary

Polycarbosilanes are a class of polymers at the interface between organic and inorganic chemistry. They are characterized by a high thermal and chemical inertness and high flexibility, especially pronounced for branched structures. Linear polycarbosilanes are well known as precursors for the preparation of SiC_x ceramics. Additionally, more sophisticated architectures like dendrimers, hyperbranched polymers or block copolymers have been the subject of research for more than a decade.

The scope of this work was to expand the properties and fields of application for polycarbosilane-containing structures. Thus, the work is divided in two major parts. The first part covers the synthesis and characterization of hyperbranched polycarbosilanes containing organometallic moieties. Hyperbranched poly-carbosilanes were synthesized using hydrosilylation of diallylmethylsilane and methyldiundecenylsilane. The degree of branching for polydiallylmethylsilane was determined using standard ^1H -NMR spectroscopy. The functional building blocks ferrocenyldimethylsilane and diferrocenylmethylsilane were synthesized which contain an isolated ferrocene unit or two ferrocenes bridged by silicon, respectively. Hyperbranched polycarbosilanes functionalized with ferrocenyl moieties were synthesized by modification of preformed polymers or by copolymerization of AB_2 carbosilane monomers with AX-type ferrocenylsilanes. Polymers with $M_n = 2500\text{--}9000\text{g/mol}$ and ferrocene contents of up to 67wt% were obtained. Electrochemical characterization by cyclic voltammetry revealed that polymers functionalized with isolated ferrocene units showed a single reversible oxidation wave, while voltammograms for polymers functionalized with diferrocenyl silane exhibited two well-separated reversible oxidation-reduction waves. This shows that the polymer bound ferrocenes bridged by silicon are electronically communicating and thus oxidation of the first ferrocene shifts the oxidation potential for the adjacent one. The polymers were utilized successfully for the preparation of modified electrodes with persistent and reproducible electrochemical response in organic solvents as well as in aqueous solution. The presented work has proven that ferrocenyl-functionalized hyperbranched polymers exhibit similar electrochemical properties as the analogous dendrimers. In a further approach it was shown that hyperbranched polymers containing organometallic moieties can be synthesized by polymerization of a new ferrocene-containing AB_2 monomer - diallylferrocenylsilane.

The second part of this work is dedicated to the preparation of core-functional hyperbranched polycarbosilanes. Low molecular weight ambifunctional molecules were synthesized that contain double bonds for the attachment of a polycarbosilane polymer as well as a second functionality available for further reaction and modification. Reactive vinyl groups in the core molecule allow an efficient attachment of hyperbranched polycarbosilane which was proven by MALDI-ToF and GPC. In combination with slow monomer addition techniques molecular weight and polydispersity of the polymers were controlled successfully. Core-functional polymers were characterized by NMR-spectroscopy, MALDI-ToF and GPC. Polymers with polydispersities <2 and molecular weights up to 5300g/mol were obtained. Transformation of the double bonds of the carbosilane was demonstrated with various silanes using hydrosilylation reaction or hydrogenation. Additionally, the core-functionality was varied resulting in polymers with bromo-, phthalimide-, amine- or azide moieties. Thus, a versatile synthetic strategy was developed that allows the synthesis of tailor-made polymers.

A promising approach is the application of the polymer building blocks in copolymer synthesis. Bisglycidolization of amine-functional polycarbosilanes produces macro-initiators that are suitable for the multibranching-ring opening polymerization of glycidol. This experiments lead to the first example of hyperbranched-hyperbranched amphiphilic block copolymers, *hb*-PG-*b*-*hb*-PCS. Furthermore, the implementation of copper-catalyzed cycloaddition between azide-functional polycarbosilane and alkyne-functional poly(ethoxyethyl glycidylether) resulted in linear-hyperbranched block copolymers. The facile removal of acetal protecting groups provided convenient access to *lin*-PG-*b*-*hb*-PCS.

8 Experimental methods and instrumentation

Matrix Assisted Laser Desorption Ionization – Time of Flight (MALDI-ToF) mass spectrometry

All spectra were recorded on a Kratos Axima-CFR mass spectrometer (Shimadzu) equipped with a nitrogen laser delivering 3ns laser pulses at 337nm. The samples were measured in positive ion and in linear or reflectron mode of the spectrometer.

MALDI-ToF of hyperbranched ferrocenysilanes

Dithranol (1,8-dihydroxy-9(10H)-anthracetone, Aldrich, 97%) was used as matrix. Potassium (Aldrich, 98%) or silver trifluoroacetate (Aldrich, 99.99%) were added for ion formation. Best results were obtained for samples which were prepared from trichloromethane solution by mixing matrix (10 mg/mL), polymer (10 mg/mL) and salt (0.1N solution in methanol) in a ratio of 10:1:1. A total volume of 0.9 μ L was pipetted onto the MALDI sample slide and allowed to dry to a thin film at room temperature for 2 h prior to measurement.

MALDI-ToF of amphiphilic *hb*- PG-*hb*-PCS

In this case, CHCA (α -cyano-4-hydroxy-cinnamic acid, Acros, 97%) was the matrix of choice. Sodium and lithium trifluoro acetate were utilized for ion formation as 0.1N solutions in methanol. Sample preparation was performed in analogy to the procedure described above.

Field Desorption (FD) mass spectrometry

FD mass spectra were measured on a Finnigan MAT 95.

Infra Red (IR)-Spectroscopy

IR spectra were recorded on a Thermo Nicolet 5DXC FT-IR spectrometer equipped with an ATR-Unit.

Nuclear Magnetic Resonance (NMR) Spectrometry

^1H / ^{13}C -NMR spectra were recorded at 300/75 MHz on a Bruker AC or on at 400/100 MHz on a Bruker AMX 400. All samples were referenced internally to the residual Proton signal of the deuterated solvents.

^{29}Si -NMR spectra were acquired with a 10mm multinuclear probe, pulse program: inverse gated decoupling ($D_1 = 40\text{s}$, $P_1 = 30^\circ$ deg. transmitter pulse, sweep width = 200 ppm, TD= 64K) at 80 MHz on a Bruker DRX 400 and were referenced externally to TMS at 79.49 MHz.

Gel Permeation Chromatography (GPC)

GPC in trichloromethane (TCM) or tetrahydrofuran (THF) was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P 100 pump and a set of three PSS SDV columns ($10^4/500/50 \text{ \AA}$). Elution of samples was followed by measuring the specific refractive index increment (dn/dc) at 30°C on a Wyatt Optilab DSP interferometric refractometer (RI detector) and by UV absorption detection on a TSP Spectra System UV 2000 (UV detector, $\lambda = 254 \text{ nm}$). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service.

For these systems, MALLS-detection (Multi Angle Laser Light Scattering) was carried out on a Wyatt Dawn 18 angle online light scattering detector.

For measurements in dimethylformamide (DMF) (containing 1 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument including a PSS Gral column ($10^4/10^4/10^2 \text{ \AA}$ porosity), a UV (275 nm) and a RI detector. Calibration was performed using poly(styrene) standards provided by Polymer Standards Service.

UV/VIS-Spektroskopie

Die UV/VIS-Messungen wurden mit einem Lambda 2 UV/VIS Spektralphotometer der Firma Perkin Elmer durchgeführt. Die Aufzeichnung und Auswertung der Daten erfolgte mit der UV Winlab V2.85.04 Software.

Transmission electron microscopy (TEM)

High-resolution TEM studies were conducted on a Philips Tecnai F30 analytical TEM at an operating voltage of 300 kV and on a TEM EM420 electron microscope at an operating voltage of 120 kV.

Differential scanning calorimetry (DSC)

DSC curves were recorded on a Perkin Elmer DSC 7 operated with a Perkin Elmer Thermal Analysis Controller TAC 7/DX in sealed aluminium pans under nitrogen atmosphere. Measurements were performed in the temperature range between -90°C and 100°C at scan rates of 10K/min or 20K/min. Sample weights were ~10mg. The instrument was calibrated using milipore water ($T_m=0^\circ\text{C}$) and high-purity indium ($T_m=156^\circ\text{C}$).

Cyclovoltammetry

Cyclic voltammetry (CV) was performed using a BAS CV-50W potentiostat using dichloromethane as a solvent under an inert atmosphere (N_2). The supporting electrolyte was tetra-n-butylammonium hexafluorophosphate in organic solvents and lithium perchlorate in water. The supporting electrolyte concentration was typically 0.1M. All experiments were performed at 25 °C, in a conventional three-electrode cell using a platinum-disk working electrode ($A=0.020\text{cm}^2$) which was polished prior to use with 1 μm diamond paste (Buehler) and rinsed thoroughly with purified water. All potentials are referenced to the saturated calomel electrode (SCE). A coiled platinum wire was used as the counter electrode. Solutions for CV were typically 0.1mM or 1mM in the redox active species and were deoxygenated by purging with prepurified nitrogen. The modification of electrode surfaces was effected either by controlled potential electrolysis or by repeated cycling of the potential.