Diphilic carbosilane dendrimers with different densities of the hydrophilic layer

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A universal method for the synthesis of hydrophilic dendrimers was considered. The method is based on a combination of carbosilane dendrimers with different molecular organizations and hydrophilizing agents, *viz.*, substituted hydride silanes containing one and three protected hydroxyl groups. The combination of a limited set of the mentioned reagents makes it possible to control the ratio of hydrophilic and hydrophobic moieties of the molecular structure in wide limits. A simple and convenient method for the removal of trimethylsilyl protection of hydroxyl groups in the surface layer of dendrimers was developed.

Key words: hydrophilizing reagents, hydrosilylation, polyhydroxyl carbosilane dendrimers.

Polyhydroxyl derivatives of carbosilane dendrimers are of increasing interest, first of all, as core—shell molecular systems. Like many other hydrophilic dendrimers,[1—5] the carboxylane analogs[6—8] have good prospects for use in biology and medicine if they are based on water-soluble systems. Wide possibilities for controlling the molecular structure of dendrimer-matrix[9—13] and the method developed for chemical modification of the external functional layer[8,9,13—21] make it possible to choose the required ratios of sizes and density of the external and internal spheres.

The available methods for the synthesis of dendrimers with the hydrophilic layer are very diverse. One of the most striking examples for the preparation of such systems is the synthesis of "sugar balls."[22—25] Other approaches to the formation of the hydrophilic layer are also known. For example, polymer-analogous transformations of the poly(etheramide) and poly(propyleneimine) dendrimers afforded their carboxyl derivatives.[26,27] Hydroboration followed by hydrolysis was used for the poly-allylcarbosilane dendrimers.[9,14,20]

We have previously proposed the method for preparation of hydroxyl-containing carbosilane dendrimers: grafting of hydride silane with the protected hydroxyl group in the organic radical on the functional surface layer.[15] The main advantage of the method is that it is naturally incorporated into the synthetic scheme for the synthesis of the dendrimer-matrix and uses a simple and efficient procedure of the deprotection by transetherification of the trimethylsiloxy derivative.

The purpose of this work is the application of this approach to the preparation of hydroxyl derivatives of carbosilane dendrimers, the study of its specific features
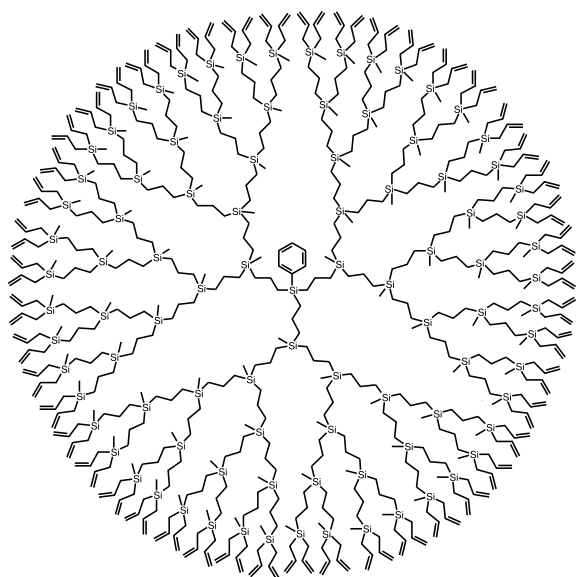
exemplified by the synthesis of a series of diphilic carbosilane dendrimers with different ratios of the hydrophobic and hydrophilic moieties of the molecular structure, and the demonstration of possibilities of fine tuning the structure and properties of polyhydroxyl carbosilane dendrimers.
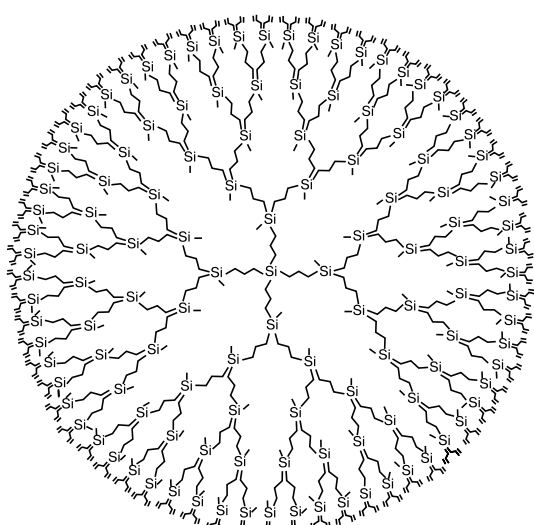
Results and Discussion

To solve the problem stated, we varied (1) the density of the molecular structure of the carbosilane core of the dendrimer and (2) the functionality of the hydrophilizing agent. Possibilities of the density control of the dendrimer molecular structure were provided by several homological series of carbosilane dendrimers different by functionality of the initial branching center and the main reagent. Taking into account that dendrimers from different generations can be used, it is evident that the parameters of the hydrophobic dendrimer-matrix can be varied within very wide limits.

The hydrophilic component of the system was more difficult to deal with. The monofunctional reagent bearing one OH group could not provide the solution of the problem. Therefore, the synthetic scheme providing the synthesis of the hydrophilic reagent with three protected OH groups was developed in the first step of the present work.

The distinctive feature of the chosen approach is the introduction of the hydrophilizing agent containing the OH group in the latent position using the hydrosilylation reaction. This made it possible to vary easily the degree of hydrophilicity of the agent due to changing its length and the number of OH groups and polar moieties. Two hydride

Scheme 1

$HOCH_2CH_2OH$ $\xrightarrow[\text{Na}]{CH_2=CHCH_2Cl}$ $H_2C=CHCH_2OCH_2CH_2OH$ **1** $\xrightarrow{\text{AcCl, Py}}$ $H_2C=CHCH_2OCH_2CH_2OAc$ **2** $\longrightarrow$

$\xrightarrow{Me_2SiHCl}$ $\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Cl-Si}}CH_2CH_2CH_2OCH_2CH_2OAc$ **3** $\xrightarrow[\text{2) } Me_3SiCl]{\text{1) } LiAlH_4}$ $\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{H-Si}}CH_2CH_2CH_2OCH_2CH_2OSiMe_3$ **4**

(hereinafter $HZOSiMe_3$)

silyl reagents containing one and three terminal OH groups in the latent position were synthesized in this work.

The synthesis of hydrophilizing agent **4** with one OH group according to a previously described method[15] is presented in Scheme 1.

The synthesis of the hydrophilizing agent with three OH groups (**7**) was not described in literature. The development of its synthesis was based on the previous scheme, which was, however, modified substantially (Scheme 2).

In the first step, monoallyl ether of polyatomic alcohol (**5**) was obtained. In the second step, the free OH groups were protected by trimethylsilyl groups instead of acetyl groups. Only one hydrosilylation step is needed to introduce the hydride silyl group into the synthesized reagent by Scheme 2, while, according to Scheme 1, the reduction reaction is required in addition to hydrosilylation.

The use of this scheme made it possible to considerably simplify the synthesis and also to enhance the yield of the target product. Hydride siloxane **7** differs in structure from the hydrophilizing agent bearing one OH group (**4**) by the presence of the siloxane bond but contains the same functional units: the active hydride silyl group, ether bond, and protected OH groups.

In all steps of the synthesis, the structures of the resulting products were confirmed by ^1H NMR spectra. The spectrum of pentaerythritol monoallyl ether (**5**) contains a signal of protons of the OH groups at δ 3.1, signals of protons of the CH_2O groups at δ 3.5, 3.7, and 4.0, and signals of protons of the allyl group at δ 5.2 and 5.9. The

spectrum of compound **6** exhibits no signal of OH groups but the signal of protons of the trimethylsiloxy group appears at δ 0.06.

The ^1H NMR spectrum of compound **7** contains no signals of protons at the double bond. It exhibits only signals of the Me protons at the hydride silyl group (δ 0.2) and protons of the $SiCH_2$ (δ 0.5), CH_2 (δ 1.6), and SiH groups (δ 4.7). In addition, the signal of protons of the CH_2O group, which was at the double bond (δ 3.9), undergoes the upfield shift (δ 3.3) due to a change in the environment.

Hydrophilizing reagents **4** and **7** were used in the syntheses of polyhydroxycarbosilane dendrimers. Polyallylcarbosilane dendrimer (**8**) of the fifth generation with the trifunctional branching center (synthesized according to a procedure analogous to the synthesis of the second generation dendrimer[11]) and polyallylcarbosilane dendrimer (**9**) of the fifth generation with the tetrafunctional branching center[12] were chosen as modified starting carbosilane dendrimers.

The allyl groups of the dendrimers were hydrosilylated in the presence of the Pt catalysts, and the completeness of the reaction was monitored by the disappearance of the signals of protons at the double bond in the ^1H NMR spectrum. The resulting dendrimers with OH groups in the latent position were further transformed into the polyhydroxyl dendrimers by the removal of the trimethylsilyl protective group.

The removal of the protective groups from the synthesized dendrimers was studied under different conditions.

Scheme 2

$\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{HOCH_2-C-CH_2OH}}$ $\xrightarrow[\text{NaOH}]{CH_2=CHCH_2Br}$ $\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{H_2C=CHCH_2OCH_2-C-CH_2OH}}$ **5** $\xrightarrow[(Me_3Si)_2NH]{Me_3SiCl}$

$\longrightarrow$ $\underset{\underset{CH_2-O-SiMe_3}{|}}{\overset{\overset{CH_2-O-SiMe_3}{|}}{H_2C=CHCH_2OCH_2-C-CH_2O-SiMe_3}}$ **6** $\xrightarrow{(Me_2SiH)_2O}$ $\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{H-Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-(CH_2)_3OCH_2-\underset{\underset{CH_2-O-SiMe_3}{|}}{\overset{\overset{CH_2-O-SiMe_3}{|}}{C}}-CH_2O-SiMe_3$ **7**

8 (hereinafter ⬡—CH₂CH=CH₂)

9 (hereinafter ⊕—CH₂CH=CH₂)

In the general case, the trimethylsilyl protective group can be removed by water or alcohols in acidic or basic media. It was found that, unlike monomeric compounds,[28,29] the Si—O—C bond in all studied dendrimers was not cleaved in either water or MeOH in the presence of ammonia or an alkali solution. The trimethylsilyl derivatives were recovered in ~100% yields upon the prolonged treatment of the reaction mixture under alkaline conditions. Probably, this result is related to the strong hydrophobic effect of the trimethylsilyl protection when the process is heterogeneous.

Attempts of desilylation by water or MeOH in the presence of inorganic acids gave insoluble products. It is most likely that the side formation of ether bonds occurs

along with the main reaction. In this case, even an insignificant and almost undetectable intermolecular interaction results in the solubility loss due to the formation of cross-linked polymers.

The treatment of the dendrimers with MeOH in the presence of minor additives of AcOH does not result in a noticeable Si—O—C bond cleavage. However, the elimination of the trimethylsilyl groups is substantially accelerated with an increase in the acid concentration in the reaction mixture.

At an AcOH concentration of 20 vol.% the process occurs in ~100% yield. In essence, this is the transetherification reaction with the formation of volatile MeOSiMe₃.

Thus, there are at least two factors shifting the equilibrium toward the desilylated product: a large excess of MeOH and the distillation of MeOSiMe₃ during the reaction. Due to this, the process of trimethylsilyl protection removal is almost 100%, which is confirmed by a considerable decrease in the integral intensity of signals of protons of the trimethylsilyl groups in the ¹H NMR spectra of the target polyhydroxyl derivatives after the reaction completion. The absence of side intermolecular processes is confirmed by the GPC data. The chromatograms of the dendrimer before (**10**) and after (**11**) removal of the trimethylsilyl protection are presented in Fig. 1. After the treatment the dendrimer is characterized by the monomodal distribution within the sensitivity of the method. Taking into account that dendrimers of the neighboring generations[12] are reliably detected by GPC, we are sure that the simplest product of intermolecular reactions (dimer) would certainly be found in the reaction mixture.

The general reaction scheme is presented for dendrimer **8** with the trifunctional branching center and for substituted hydride silane reagent **7** with three protected OH groups (Scheme 3).

The developed scheme was successively applied for the synthesis of protected carbosilane dendrimers **10**, **12**, and **14** and the related hydroxyl derivatives, namely, dendrimer **11** of the fifth generation with the trifunctional
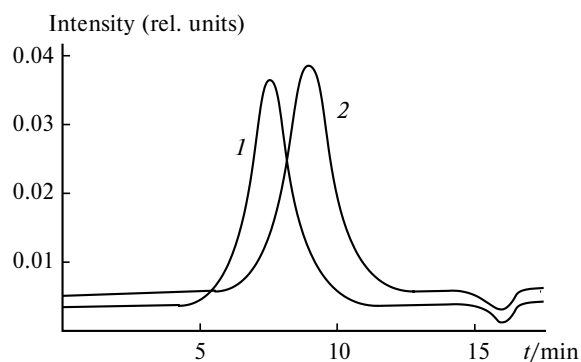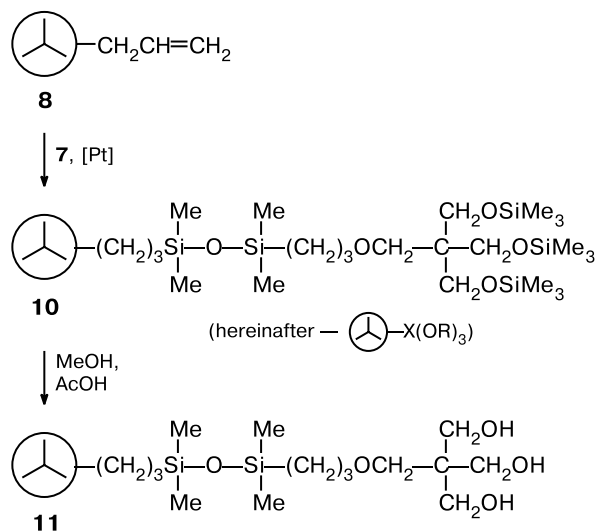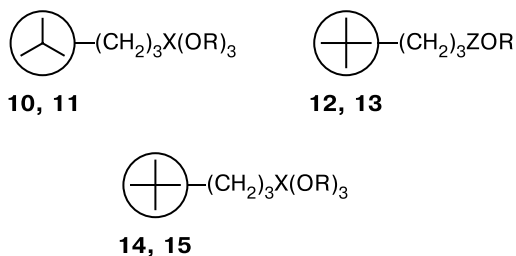
Fig. 1. GPC profiles of dendrimers **10** (*1*) and **11** (*2*).

Scheme 3

$$\text{8} \quad \bigtriangleup\!\!\!\!-\text{CH}_2\text{CH}=\text{CH}_2$$

7, [Pt]

10   $\bigtriangleup\!\!\!\!-(\text{CH}_2)_3\text{Si}-\text{O}-\text{Si}-(\text{CH}_2)_3\text{OCH}_2-\text{C}-\text{CH}_2\text{OSiMe}_3$

with Me, Me, and $\text{CH}_2\text{OSiMe}_3$ substituents

(hereinafter — $\bigtriangleup\!\!\!\!-\text{X(OR)}_3$)

MeOH, AcOH

11   $\bigtriangleup\!\!\!\!-(\text{CH}_2)_3\text{Si}-\text{O}-\text{Si}-(\text{CH}_2)_3\text{OCH}_2-\text{C}-\text{CH}_2\text{OH}$

Note. For designation $\bigtriangleup$, see above.

branching center and three OH groups at each spacer (on the whole, 288 OH groups), dendrimer **13** of the fifth generation with the tetrafunctional branching center and one OH group at each spacer (on the whole, 128 OH groups), and dendrimer **15** of the fifth generation with the tetrafunctional branching center and three OH groups at each spacer (on the whole, 384 OH groups).

10, 11 $\bigtriangleup\!\!\!\!-(\text{CH}_2)_3\text{X(OR)}_3$ **12, 13** $\boxplus\!\!\!\!-(\text{CH}_2)_3\text{ZOR}$

14, 15 $\boxplus\!\!\!\!-(\text{CH}_2)_3\text{X(OR)}_3$

R = SiMe₃ (**10, 12, 14**), H (**11, 13, 15**)

Note. For designation Z, see in Scheme 1.

After the solvent was removed, the polyhydroxyl dendrimers are transparent gel-like substances highly soluble in MeOH and EtOH, unlike the starting carbosilane dendrimers and their trimethylsilyl derivatives. When water is gradually added to methanol solutions of these substances, at first they become turbid and then, due to further aggregation, the dendrimers are deposited on the flask walls as a white precipitate. It is worth mentioning that dendrimer **13** is precipitated when <5% water of the MeOH weight are added, while at least 20% water are needed for dendrimer **15**. The enrichment in MeOH of a mixture of solvents results in the complete dissolution of the precipitate. Polyhydroxyl carbosilane dendrimers are diphilic systems with the hydrophobic core—hydro-

philic shell structure, and even the most compact shell (of those presented above) does not provide the complete isolation of the core (otherwise, the dendrimers would be water-soluble). At the same time, taking into account that the density of the hydrophilic shell could increase further, we believe it evident that the complete solubility can be achieved due to both the additional compactness of the external shell in the framework of the approach used and other methods providing an analogous compactness of the hydrophilic layer.

Fine control of the ratio of the hydrophilic and hydrophobic moieties of the dendrimer molecule makes it possible to change the character of their self-organization. All dendrimers obtained are prone to form monolayers on the water surface. However, the properties of these monolayers differ noticeably in each particular case. These specific features of organization of the synthesized dendrimers on the water surface are presently under study.

Experimental

GLC analysis was carried out on a 3700 chromatograph (Russia) with a katharometer as the detector (helium as the carrier gas, columns 2 m × 3 mm, stationary phase SE-30 (5%) supported on Chromaton-H-AW). GPC analysis was carried out on a Laboratorni pristroje liquid chromatograph (Czechia) with a RIDK-102 refractometer used as the detector (column 300×7.8 mm, sorbent Phenogel 10×4 Å (particle size 5 μm) (Phenomenex, USA), eluent THF). ¹H NMR spectra were recorded on a Bruker WP-200 SY instrument (200.13 MHz) using Me₄Si as the internal standard. IR spectra were recorded on a Bruker Equinox 55/S instrument. A xylene solution (2.1—2.4% Pt) of the (divinyltetramethyldisiloxane)platinum(0) complex[30] (Aldrich) was used as the catalyst. Commercial reagents were used.

2-Allyloxyethanol (1) was synthesized from ethylene glycol monosodium salt (synthesized *in situ* from ethylene glycol and sodium metal) and allyl bromide using a known procedure.[31] The yield was 76%, b.p. 159—160 °C, n_D^{20} 1.4358 (Ref. 31: b.p. 159 °C, n_D^{20} 1.4360). ¹H NMR (CDCl₃), δ: 2.33 (t, 1 H, OH); 3.54 (m, 2 H, CH₂=CHCH₂OCH₂); 3.70 (m, 2 H, CH₂OH); 4.01 (d, 2 H, CH₂=CHCH₂, *J* = 5.6 Hz); 5.21 (m, 2 H, CH₂=CH); 5.88 (m, 1 H, CH₂=CH).

2-Allyloxyethyl acetate (2). Acetyl chloride (49.93 g, 45.2 mL, 0.80 mol) was added dropwise to a stirred solution of compound **1** (68 g, 0.67 mol) in toluene (150 mL) and Py (63.2 g, 64.4 mL, 0.52 mol). The mixture was stirred for 2 h at 40—50 °C and for 3 h at 90—100 °C. After cooling to ~20 °C, the mixture was poured to acidified water (2—4% HCl). The organic layer was washed with water to the neutral reaction and dried above Na₂SO₄. The solvents were distilled off above the copper plate and in an argon flow, and the residue was distilled at 177—179 °C. The yield of compound **2** was 63.8 g (66.5%). Found (%): C, 58.32; H, 8.39. C₇H₁₂O₃. Calculated (%): C, 58.35; H, 8.43. ¹H NMR (CDCl₃), δ: 2.03 (s, 3 H, Ac); 3.59 (m, 2 H, CH₂=CHCH₂OCH₂); 3.98 (m, 2 H, CH₂=CHCH₂); 4.17 (m, 2 H, CH₂OAc); 5.19 (m, 2 H, CH₂=CH); 5.84 (m, 1 H, CH₂=CH). IR, ν/cm⁻¹: 3080 (CH=), 1740 (C=O), 1648 (C=C).

3-(Dimethylchlorosilyl)propyloxyethyl acetate (3). A mixture of compound **2** (56.24 g, 0.39 mol), Me_2SiHCl (44.9 mL, 0.41 mol), and a solution of the catalyst (105 μL) was kept in a tightly closed flask (which was preliminarily flushed with argon) for 5 days at 30—36 °C until the signals of protons at the double bond disappeared completely from the ^1H NMR spectra of samples of the reaction mixture. A Me_2SiHCl excess was distilled off by a vacuum pump for 10 min, and the product was used for further transformations without additional purification (it decomposes during distillation). The yield was 93.15 g (100%). Functional analysis (titration with 0.1 *M* NaOH after hydrolysis with an $H_2O—Me_2CO$ mixture), found (%): Cl, 14.60. Calculated (%): Cl, 14.85. ^1H NMR ($CDCl_3$), δ: 0.37 (s, 6 H, SiMe); 0.81 (m, 2 H, $SiCH_2$); 1.68 (m, 2 H, CH_2); 2.05 (s, 3 H, Ac); 3.44 (m, 2 H, $OCH_2(CH_2)_2Si$); 3.61 (m, 2 H, $CH_2O(CH_2)_3Si$); 4.18 (m, 2 H, CH_2OAc).

Dimethyl{3-[2-(trimethylsiloxy)ethyloxy]propyl}silane (4). A solution of compound **3** (42.7 g, 0.18 mol) in anhydrous THF (50 mL) was added dropwise in an argon flow to $LiAlH_4$ (10.5 g, 0.28 mol) suspended in anhydrous THF (150 mL). The reaction mixture was refluxed with stirring for 6 h, and Me_3SiCl (95 mL, 0.75 mol) was added dropwise to the cooled reaction mixture. The mixture was refluxed with stirring for 4 h. The organic phase was separated by decantation from the inorganic precipitate. The precipitate was washed with anhydrous THF (50 mL), decanted, and combined with the reaction solution. The combined solution was filtered under argon, light solvents were distilled off, and the residue was distilled *in vacuo*. The yield was 17.6 g (42%), b.p. 59—60 °C (1 Torr), n_D^{20} 1.4257. Found (%): C, 51.11; H, 10.99; Si, 23.85. $C_{10}H_{26}O_2Si_2$. Calculated (%): C, 51.22; H, 11.18; Si, 23.95. ^1H NMR ($CDCl_3$), δ: 0.05 (d, 6 H, CH_2SiMe, *J* = 3.8 Hz); 0.11 (s, 9 H, OSiMe); 0.57 (m, 2 H, $SiCH_2$); 1.62 (m, 2 H, CH_2); 3.45 (m, 4 H, CH_2OCH_2); 3.70 (t, 2 H, CH_2OSi, *J* = 11.0 Hz); 3.85 (m, 1 H, SiH).

3-Allyloxy-2,2-bis(hydroxymethyl)propanol (5) was synthesized by a known procedure.[32] Pentaerythritol (107 g, 0.79 mol) and dioxane (175 mL) were placed in a flask, and a solution of NaOH (31.44 g, 0.79 mol) in water (14 mL) was gradually added. The contents of the flask was stirred for 0.5 h at 45 °C, and then $CH_2=CHCH_2Br$ (68 mL, 0.79 mol) was added dropwise. The reaction mixture was stirred for 12—15 h at 45—47 °C. The precipitate of NaBr and unreacted pentaerythritol was filtered off and washed with dioxane (~100 mL) on the filter. Solvents were distilled from the combined filtrates, and the residue was twice distilled *in vacuo*. The fractions with b.p. 130—133 °C (1 Torr) and 150—155 °C (1 Torr) were obtained. The first fraction was **2,2-bis(allyloxymethyl)propane-1,3-diol** obtained in 21% yield (34 g), n_D^{20} 1.4758 (*cf.* Ref. 32: n_D^{20} 1.4729). ^1H NMR ($CDCl_3$), δ: 2.92 (br.s, 2 H, OH); 3.48 (d, 4 H, $CH_2=CHCH_2OCH_2$, *J* = 5.0 Hz); 3.67 (m, 4 H, CH_2OH); 3.94 (m, 4 H, $CH_2=CHCH_2$); 5.18 (m, 2 H, $CH_2=CH$); 5.83 (m, 1 H, $CH_2=CH$). The second fraction was **compound 5** obtained in 27.8% yield (39 g), n_D^{20} 1.4813 (*cf.* Ref. 32: n_D^{20} 1.4843). ^1H NMR ($CDCl_3$), δ: 3.08 (br.s, 3 H, OH); 3.45 (s, 2 H, $CH_2=CHCH_2OCH_2$); 3.68 (d, 6 H, CH_2OH, *J* = 4.8 Hz); 3.96 (d, 2 H, $CH_2=CHCH_2$, *J* = 5.4 Hz); 5.20 (m, 2 H, $CH_2=CH$); 5.85 (m, 1 H, $CH_2=CH$).

1-Allyloxy-2,2,2-tris(trimethylsiloxymethyl)ethane (6). A mixture of $(Me_3Si)_2NH$ (64.6 g, 0.4 mol) and Me_3SiCl (43.5 g,

0.4 mol) was added dropwise to compound **5** (19.9 g, 0.11 mol) in dioxane (15 mL), and the suspension was refluxed for 3 h. The precipitate was filtered off, the solvents were distilled off above the copper plate and in an argon flow, and the residue was distilled *in vacuo*. Compound **6** was obtained in 85.5% yield (37.9 g), b.p. 100—102 °C (0.5 Torr). ^1H NMR ($CDCl_3$), δ: 0.06 (s, 27 H, SiMe); 3.29 (s, 2 H, $CH_2=CHCH_2OCH_2$); 3.47 (s, 6 H, CH_2OSi); 3.90 (m, 2 H, $CH_2=CHCH_2$); 5.17 (m, 2 H, $CH_2=CH$); 5.87 (m, 1 H, $CH_2=CH$).

1-[2,2,2-Tris(trimethylsiloxymethyl)ethoxy]propyl-1,1,3,3-tetramethyldisiloxane (7). A mixture of compound **6** (35.7 g, 0.091 mol), $(Me_2SiH)_2O$ (48.8 g, 0.36 mol), and a solution of the catalyst (100 μL) was kept in a tightly closed flask (which was preliminarily flushed with argon) for 30 h at 35—40 °C until the signals of protons at the double bond completely disappeared in the ^1H NMR spectra of samples of the reaction mixture. An excess of $(Me_2SiH)_2O$ was distilled off, and the residue was twice distilled *in vacuo*. Compound **7** was obtained in 50.1% yield (24 g), b.p. 125—128 °C (1 Torr). Found (%): C, 47.88; H, 10.44; Si, 26.16. $C_{21}H_{54}O_5Si_5$. Calculated (%): C, 47.85; H, 10.33; Si, 26.64. ^1H NMR ($CDCl_3$), δ: 0.07 (s, 33 H, OSiMe); 0.15 (d, 6 H, $MeSiH$, *J* = 3.0 Hz); 0.52 (m, 2 H, $SiCH_2$); 1.55 (m, 2 H, CH_2); 3.26 (s, 2 H, $CH_2OCH_2CR_3$); 3.31 (t, 2 H, $CH_2CH_2OCH_2CR_3$, *J* = 13.8 Hz); 3.47 (s, 6 H, CH_2OSiMe); 4.68 (m, 1 H, SiH).

Polyallylcarbosilane dendrimer of the fifth generation with the trifunctional branching center (8, G-5(96All)) was synthesized in two steps according to a known method.[11] The polychlorocarbosilane dendrimer was synthesized in the first step and transformed into the target products by the Grignard reaction in the second step.

Polychlorocarbosilane dendrimer. $MeSiCl_2H$ (0.7 g, 6.08 mmol) was added dropwise in an argon atmosphere to a solution of the polyallylcarbosilane dendrimer of the fourth generation[11] (0.5 g, 0.0845 mmol) in anhydrous hexane (1 mL) and a solution of the catalyst (2 μL). The mixture was stirred for 24 h at ~20 °C. After volatile admixtures were removed from the reaction mixture by evacuation at 1 Torr, the product (0.99 g) was obtained. Functional analysis (titration with 0.1 *M* NaOH after hydrolysis with an $H_2O—Me_2CO$ mixture), found (%): Cl, 30.5. Calculated (%): Cl, 29.8. ^1H NMR ($CDCl_3$), δ: −0.08 (s, 63 H, SiMe); −0.03 (s, 72 H, SiMe); 0.52—0.66 (m, 276 H, $SiCH_2$); 0.76 (s, 144 H, Cl_2SiMe); 1.18 (m, 96 H, CH_2); 1.28 (m, 90 H, CH_2); 1.47—1.60 (m, 96 H, Cl_2SiCH_2); 7.26—7.44 (m, 5 H, Ph).

Polyallylcarbosilane dendrimer. $CH_2=CHCH_2Cl$ (0.1 mL) was added with vigorous stirring to a mixture of Mg (0.34 g, 0.014 mol) and anhydrous THF (5 mL) in an argon atmosphere. After the reaction mixture simmered, a solution of a mixture of the polychlorocarbosilane dendrimer (0.99 g) and $CH_2=CHCH_2Cl$ (0.98 g, 0.0128 mol) in anhydrous THF (10 mL) was slowly added dropwise. The reaction mixture was stirred during boiling for 8 h, an excess of the Grignard reagent was decomposed by a saturated aqueous solution of NH_4Cl, the precipitate was filtered off, and the filtrate was dried above anhydrous Na_2SO_4. The solvent and volatile reaction products were removed at a reduced pressure (1 Torr). A colorless transparent product was obtained in 87% yield (0.9 g), whose preparative liquid chromatography gave pure dendrimer **8** (0.5 g). ^1H NMR ($CDCl_3$), δ: −0.07 (s, 144 H, SiMe); −0.03 (s,

135 H, SiMe); 0.53 (m, 372 H, SiCH$_2$); 1.28—1.37 (m, 186 H, CH$_2$CH$_2$CH$_2$); 1.52—1.56 (d, 192 H, SiCH$_2$CH=CH$_2$, J = 8.0 Hz); 4.85 (m, 192 H, CH$_2$=CH); 5.82 (m, 96 H, CH$_2$=CH); 7.26—7.44 (m, 5 H, Ph).

Polyallylcarbosilane dendrimer of the fifth generation with the tetrafunctional branching center (9, G-5(128All)) was synthesized by a known procedure.[8]

Dendrimer with the tetrafunctional branching center and one terminal protected OH group at each branch (12). A mixture of dendrimer **9** (0.3868 g, 0.024 mmol), compound **4** (0.7606 g, 3.2 mmol), anhydrous hexane (2.5 mL), and a solution of the catalyst (3.5 µL) was kept in a tightly closed flask (which was preliminarily flushed with argon) for 15 days at 30—35 °C until signals of protons at the double bond almost completely disappeared from the ^{1}H NMR spectra of samples of the reaction mixture. ^{1}H NMR (CDCl$_3$), δ: −0.06 (s, 1140 H, SiMe); 0.11 (s, 1152 H, OSiMe); 0.52 (m, 1256 H, SiCH$_2$); 1.28 (m, 504 H, SiCH$_2$CH$_2$CH$_2$Si); 1.55 (m, 256 H, CH$_2$CH$_2$O); 3.38 (t, 256 H, CH$_2$CH$_2$CH$_2$O, J = 18.0 Hz); 3.47 (t, 256 H, OCH$_2$CH$_2$OSi, J = 11.0 Hz); 3.71 (t, 256 H, CH$_2$OSiMe, J = 18.0 Hz).

Dendrimer with the tetrafunctional branching center and one terminal OH group at each branch (13) was synthesized from compound **12** purified from the catalyst by chromatography on silica gel (Kieselgel (Merck), hexane as the eluent). A mixture of compound **12** (0.126 g, 0.0027 mmol), toluene (3 mL), MeOH (2 mL), and glacial AcOH (1 mL) was heated with stirring for 48 h at 70 °C. The solvents were evaporated to dryness, and the dendrimer was dried *in vacuo* at 1 Torr. IR, ν/cm^{-1}: 3420 (OH). ^{1}H NMR (CD$_3$OD), δ: 0.02 (s, 1140 H, SiMe); 0.64 (m, 1256 H, SiCH$_2$); 1.42 (m, 504 H, SiCH$_2$CH$_2$CH$_2$Si); 1.60 (m, 256 H, CH$_2$CH$_2$O); 3.44 (t, 256 H, CH$_2$CH$_2$CH$_2$O, J = 9.2 Hz); 3.51 (t, 256 H, OCH$_2$CH$_2$OH, J = 10.0 Hz); 3.66 (t, 256 H, CH$_2$OH, J = 10.3 Hz).

Dendrimer with the trifunctional branching center and three terminal protected OH groups at each branch (10) was synthesized similarly to compound **12** from dendrimer **8** (0.465 g, 0.039 mol), petroleum ether (15.5 mL), compound **7** (2.0882 g, 4.0 mmol), and a solution of the catalyst (18 µL). ^{1}H NMR (CDCl$_3$), δ: 0.02—0.14 (m, 4023 H, SiMe); 0.51 (m, 948 H, SiCH$_2$); 1.28 (m, 378 H, SiCH$_2$CH$_2$CH$_2$Si); 1.52 (m, 192 H, CH$_2$CH$_2$O); 3.24—3.67 (m, 960 H, CH$_2$O); 7.26—7.44 (m, 5 H, Ph).

Dendrimer with the trifunctional branching center and three terminal OH groups at each branch (11) was synthesized from compound **10** similarly to the synthesis of compound **13**. IR, ν/cm^{-1}: 3400 (OH). ^{1}H NMR (CD$_3$OD), δ: 0.02—0.14 (m, 1431 H, SiMe); 0.62 (m, 948 H, SiCH$_2$); 1.43 (m, 378 H, SiCH$_2$CH$_2$CH$_2$Si); 1.62 (m, 192 H, CH$_2$CH$_2$O); 3.46—3.62 (m, 960 H, CH$_2$O); 7.26—7.44 (m, 5 H, Ph).

Dendrimer with the tetrafunctional branching center and three terminal protected OH groups at each branch (14) was synthesized similarly to compound **12** from dendrimer **9** (0.4005 g, 0.025 mmol), compound **7** (1.7047 g, 3.2 mmol), anhydrous hexane (2.9 mL), and a solution of the catalyst (5 µL). ^{1}H NMR (CDCl$_3$), δ: 0.02 (m, 1908 H, SiMe); 0.06 (s, 3456 H, OSiMe); 0.52 (m, 1264 H, SiCH$_2$); 1.28 (m, 504 H, SiCH$_2$CH$_2$CH$_2$Si); 1.52 (m, 256 H, CH$_2$CH$_2$O); 3.27 (m, 512 H, CH$_2$OCH$_2$); 3.45 (m, 768 H, CH$_2$OSi).

Dendrimer with the tetrafunctional branching center and three terminal OH groups at each branch (15) was prepared from compound **14** similarly to the synthesis of compound **13**. IR, ν/cm^{-1}: 3400 (OH). ^{1}H NMR (CD$_3$OD), δ: 0.01—0.12 (m, 1908 H, SiMe); 0.63 (m, 1264 H, SiCH$_2$); 1.44 (m, 504 H, SiCH$_2$CH$_2$CH$_2$Si); 1.61 (m, 256 H, CH$_2$CH$_2$O); 3.45 (m, 512 H, CH$_2$OCH$_2$); 3.63 (m, 768 H, CH$_2$OSi).

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