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Synthesis and Properties of Homologous Series of Polyallylcarbosilane Dendrimers with Dense Macromolecular Structure

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Summary: Synthesis of the six generations of polyallylcarbosilane dendrimers with tetrafunctional branching center and tetrafunctional base reagent is reported. Obtained dendrimers are compared to carbosilane dendrimers with less dense molecular structure synthesized before. Densification of the dendrimer structure alters some basic dendrimer properties as well as their dependence on generation.

Keywords: dendrimers; density; light scattering; viscosity

Introduction

Dendrimers, regular hyperbranched macromolecules, stay in a focus of researches' attention for about 20 years. The amount of the scientific papers devoted to the different aspects of dendrimer chemistry is still growing. Synthesis of new types of dendrimers, their functionalization and applications in drug delivery, catalysis, etc. are the most popular topics.[1–6] At the same time there is a lack of systematic studies of their physicochemical properties, which hinders finding of structure-properties relationships for this type of polymer objects. One of the reasons of such a gap in dendrimers investigation is the deficit of long/wide/representative homological series of dendrimers.

Among many type of dendrimers carbosilane dendrimers[7–9] are very attractive due to their unique characteristics such as chemical and thermal stability of the molecular structure and high reactivity of the functional groups, which makes their synthetic scheme one of the easiest and the most perfect.[9–11] Besides the simplicity and availability of the reagents, this scheme is interesting because it allows the carry out different modifications both by introduction of the units of different chemical nature[12–15] and within pure carbosilane structure.[16–19] Latter case means utilization of synthetic schemes providing regulation of molecular structure density, which can be varied by adjustment of the functionality of branching center,[20,21] branching reagent[16,17] and the length of branch segments.[17] In some cases structural density is changed via introduction of the layers with lower density.[16,22,23]

For silicon-based/carbosilane dendrimers with point branching center the highest structure density is achieved in case of four-fold core molecule and four-functional branching reagent (4 × 4). Literature data on this species are very inconsistent. Thus in one of the first papers concerning carbosilane dendrimers, synthesis of 5 generations with the use of tetraallysilane as branching center and trichlorosilane as branching reagent was described.[24] 6th generation was said to be highly impure and was not characterized. According to the

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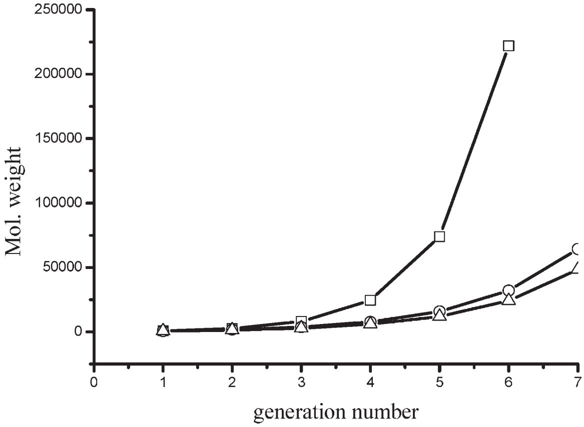


Figure 1.
Molecular weight versus generation number for 3 homologous series of carbosilane dendrimers (□ – (4 × 4), ○ – (4 × 3), △ - (3 × 3)).

authors' molecular modeling calculations higher generation dendrimers could not be prepared due to the surface congestion. In their next paper[17] three series of (4 × 4) carbosilane dendrimers differing in branch segment length (2, 3 and 10 carbon atoms) were compared and for every series generation, where surface congestion is reached, was determined (3rd, 5th and 7th respectively). However these results are questionable, because in contradiction to them (4 × 4) carbosilane dendrimer of 4th generation with branch segment length of 2 carbon atoms was synthesized later,[25] in addition hydrosilylation conditions, described in ref.,[24] were mentioned to be not successful.[26]

At the same time low generation carbosilane dendrimers (4 × 4) are widely used as polyfunctional matrixes[15,22,25,26] and preorganized precursors for sol-gel processes.[20,27,28] Carbosilane monodendrons from 1st till 3rd were synthesized to construct a dendrimer in convergent way with catalytic site in the core.[29,30] Still in case of growing dendrons from the active sites on a polymer backbone an attempt to prepare 3rd generation dendrons with the same to above structure was unsuccessful.[31]

Hence there are serious contradictions in data concerning both mathematic modeling and synthesis of the carbosilane dendrimers with dense molecular structure. While low generation dendrimers are used for some applications, accurate synthesis of high generations of (4 × 4) series is still a challenge. An additional motivation appeared after recent investigation of long homologous series of the carbosilane dendrimers (4 × 3).[11] Further increasing of molecular structure density could efficiently change the dendrimer properties even though chemical nature remains nearly the same. Figure 1 demonstrates dependence of molecular mass of carbosilane dendrimers of different architectures on generation number.

Thus the aim of present work was to synthesize and characterize high generation dendrimers of (4 × 4) homologous series and to compare them with homologous series (4 × 3) as background. Such a comparison is an important step for the solution of structure-properties relationship problem for all carbosilane dendrimers.

Experimental Part

Materials and Methods

All reactions were carried out in an inert atmosphere and freshly distilled solvents. Organosilanes and chlorosilanes were distilled just before use. Allylchloride was dried via distillation over CaH_2. Platinum 1,3-divinyl-1,1,3,3-tetramethyl-1,3-disiloxane complex in xylene solution (catalyst) was obtained from Aldrich and used as received.

^1H NMR spectra were recorded with "Bruker WP-200" instrument (200.13 MHz) in $CDCl_3$ solution, tetramethylsilane was used as a standard. Gel permeation chromatography was performed in THF (detector – refractometer).

Intrinsic viscosities were measured in toluene with an Ubbelohde viscometer (capillary size 0.3 mm) at 25 °C (accuracy 0.1 °C).

Density was measured using density-bottle method for liquid generations and method of density equilibration[32] with water/ethanol as liquid phase for solid generations.

DLS measurements were conducted in THF at 25 °C and scattering angle 90° on ALV/DLS/SLS-5000 Compact Goniometer System and ALV-5000/60X0 Multiple Tau Digital Real Correlator (ALV-GmbH). He-Ne laser (JDS Uniphase Corporation) ($\lambda = 632.8$ nm) was used as a light source.

The glass transitions were studied by means of differential scanning calorimetry (DSC) using a Mettler DSC-822e thermosystem at heating rate of 10 K/min. Sample weights were typically ~5–10 mg. The glass transition temperatures were estimated from the midpoint of a step corresponding to the heat capacity jump in the course of devitrification.

Tetraallylsilane ($Si(All)_4$) was synthesized according to the standard procedure[10] in organomagnesium synthesis reaction with the use of allylchloride and magnesium turnings.

Polychlorocarbosilane Dendrimer of 1st Generation G1(Si_5^{12}(Cl))

(upper index represents functionality of dendrimer, lower – number of silicon atoms constituted the dendrimer, type of functional groups is shown in brackets). 26.2 g (0.14 mol) of $Si(All)_4$ were dissolved in 40 mL of dry hexane, solution of platinum catalyst (69 μL) was added, 88.7 g (0.65 mol) of trichlorosilane were added dropwise at stirring. Reaction mixture was stirred at room temperature in closed flask equipped with Teflon coated magnetic stirrer bar till full disappearance of allyl functionalities (δ 4.86 ppm ($C\underline{H}_2$=CH–CH_2-Si) И δ 5.74 ppm (CH_2=$C\underline{H}$–CH_2–Si)) controlled by ^1H NMR. Here and further in synthesis of chlorosilyl derivatives the excess of chlorosilane after the end of reaction was removed by distillation. Due to the high reactivity of obtained products they were used for following syntheses without isolation from the solution.

First Generation Polyallylcarbosilane Dendrimer (G1(Si_5^{12}(All))

Allyl chloride (5 mL) was added to magnesium turnings (68.62 g, 2.82 mol) in 30 mL of THF to initiate the reaction, and a solution consisting of dendrimer Si_5^{12}(Cl) (100.06 g, 0.14 mol), THF (500 mL), hexane (250 mL), and allyl chloride (187.5 g, 2.45 mol) was added dropwise at stirring. The reaction mixture was stirred at reflux for 14 h. To determine if all chlorosilyl groups have reacted, the probe with preliminary neutralized Grignard reagent was titrated. After completion of the reaction, the reaction mixture was treated with a saturated aqueous solution of NH_4Cl. The precipitate was filtered off. The filtrate was kept over anhydrous Na_2SO_4 for 24 h and filtered. Removing of the solvents gave 102 g (96.6% crude yield) of a transparent liquid. The content of Si_5^{12}(All) determined by GPC was 98.9%. The products obtained in this and in the subsequent syntheses were purified by means of column chromatography before being used for the synthesis of later generations. Monodispersed samples for investigations were obtained by preparative exclusion chromatography. Found (%): C, 71.94; H, 10.53; Si, 17.41. $Si_5C_{48}H_{84}$. Calculated (%): C, 71.92; H, 10.56; Si, 17.52. Mol. weight (calc.) 801.63. ^1H NMR ($CDCl_3$), δ: 5.74 (m, 12H, CH_2=$C\underline{H}$–CH_2–Si); 4.86 (m, 24H, $C\underline{H}_2$=CH–CH_2–Si); 1.58 (d, 24H, CH_2=CH–$C\underline{H}_2$–Si); 1.33 (m, 8H,

$Si{-}CH_2{-}C\underline{H}_2{-}CH_2{-}Si$); 0.60 (m, 16H, $-C\underline{H}_2{-}Si{-}C\underline{H}_2-$).

Second Generation Polychlorocarbosilane Dendrimer (G2 (Si_{17}^{36} (Cl))

The same procedure that used in preparation of Si_5^{12}(Cl) was utilized in the reaction of 4 g (0.11 mol) of Si_5^{12}(All) in 150 mL of hexane with 281.31 g (2.08 mol) of trichlorosilane in presence of 0.28 mL of platinum catalyst solution, except the temperature was raised up to 50 °C.

Second Generation Polyallylcarbosilane Dendrimer (G2(Si_{17}^{36}(All))

The reaction of magnesium turnings (174.07 g, 7.16 mol), Si_{17}^{36}(Cl) (279.74 g 0.11 mol) and AllCl (476.32 g, 6.22 mol) in solution of THF and hexane (1300 mL and 650 mL respectively) was conducted under conditions similar to the synthesis of Si_5^{12}(All) and gave 294.3 g (97.1% crude yield) of a transparent liquid. The content of Si_{17}^{36}(All) was 71.8%. Found (%): C, 71.22; H, 10.56; Si, 18.15. $Si_{17}C_{156}H_{276}$. Calc. (%): C, 71.26; H, 10.58; Si, 18.16. d_4^{25} 0.9016 g/cm^3. $[\eta]^{25}$ 0.0237 dL/g. Mol. weight (calc.) 2629.39. ^{1}H NMR ($CDCl_3$), δ: 5.74 (m, 36H, $CH_2{=}C\underline{H}{-}CH_2{-}Si$); 4.86 (m, 72H, $C\underline{H}_2{=}CH{-}CH_2{-}Si$); 1.58 (d, 72H, $CH_2{=}CH{-}C\underline{H}_2{-}Si$); 1.33 (m, 32H, $Si{-}CH_2{-}C\underline{H}_2{-}CH_2{-}Si$); 0.60 (m, 64H, $-C\underline{H}_2{-}Si{-}C\underline{H}_2-$).

Third Generation Polychlorocarbosilane Dendrimer (G3(Si_{53}^{108}(Cl))

The same procedure that used in preparation of Si_5^{12}(Cl) was utilized in the reaction of 23.14 g (8.8 mmol) of Si_{17}^{36}(All) in 47 mL of hexane with 64.37 g (0.47 mol) of trichlorosilane in presence of 0.06 mL of platinum catalyst solution, except after 90 hours of stirring at 30 °C, 6 mL of trichlorosilane were added along with 0.05 mL of platinum catalyst solution and stirring was continued for 90 hours at 35 °C and then for 125 hours at 40 °C.

Third Generation Polyallylcarbosilane Dendrimer (G3(Si_{53}^{108}(All))

The reaction of magnesium turnings (76.27 g, 3.14 mol), Si_{53}^{108}(Cl) (66.054 g, 8.8 mmol) and AllCl (120.01 g, 1.57 mol) in solution of THF and hexane (300 mL and 250 mL respectively) was conducted under conditions similar to the synthesis of Si_5^{12}(All) (the content of residual chlorine after reaction completion was ~0.3–0.5%) and gave 52 g (72.8% crude yield) of a transparent liquid. The content of the Si_{53}^{108}(All) was 41.8%. Found (%): C, 70.90; H, 10.60; Si, 18.41. $Si_{53}C_{480}H_{852}$. Calc (%): C, 71.07; H, 10.59; Si, 18.35. d_4^{25} 0.9114 g/cm^3. $[\eta]^{25}$ 0.0304 dL/g. Mol. weight (calc.) 8112.65. ^{1}H NMR ($CDCl_3$), δ: 5.74 (m, 108H, $CH_2{=}C\underline{H}{-}CH_2{-}Si$); 4.86 (m, 216H, $C\underline{H}_2{=}CH{-}CH_2{-}Si$); 1.58 (d, 216H, $CH_2{=}CH{-}C\underline{H}_2{-}Si$); 1.34 (m, 104H, $Si{-}CH_2{-}C\underline{H}_2{-}CH_2{-}Si$); 0.61 (m, 208H, $-C\underline{H}_2{-}Si{-}C\underline{H}_2-$).

Fourth Generation Polychlorocarbosilane Dendrimer (G4 (Si_{161}^{324} (Cl))

The same procedure that used in preparation of Si_5^{12}(Cl) was utilized in the reaction of 20 g (2.46 mmol) of Si_{53}^{108}(All) in 23 mL of toluene with 54.09 g (0.4 mol) of trichlorosilane in presence of 0.042 mL of platinum catalyst solution, except after 20 hours of stirring at room temperature and 112 hours at 50 °C, 10 mL of trichlorosilane were added along with 0.042 mL of platinum catalyst solution and stirring was continued for 312 hours at 50 °C; subsequently 5 mL of trichlorosilane were added and stirring was continued for 48 hours at 50 °C .

Fourth Generation Polyallylcarbosilane Dendrimer (G4(Si_{161}^{324}(All))

The reaction of magnesium turnings (69.9 g, 2.87 mol), Si_{161}^{324} (Cl) (56.1 g, 2.46 mmol) and AllCl (110.02 g, 1.44 mol) in solution of THF and toluene (375 mL and 250 mL respectively) was conducted under conditions similar to the synthesis of Si_5^{12}(All) (the content of residual chlorine after reaction completion was ~0.3%) and gave 50.65 g (83.6% crude yield) of a transparent liquid. The content of the Si_{161}^{324}(All) was 40.2%.

Found (%): C, 70.92; H, 10.51; Si, 18.38. $Si_{161}C_{1452}H_{2580}$.. Calc. (%): C, 71.00; H, 10.59; Si, 18.41. d_4^{25} 0.9235 g/cm^3. $[\eta]^{25}$ 0.0297 dL/g. Mol. weight (calc.) 24562.46. ^{1}H NMR($CDCl_3$), δ: 5.74 (m, 324H, $CH_2{=}C\underline{H}{-}CH_2{-}Si$); 4.86 (m, 648H, $C\underline{H}_2{=}CH{-}CH_2{-}Si$); 1.57 (d, 648H, $CH_2{=}CH{-}C\underline{H}_2{-}Si$); 1.35 (m, 320H, $Si{-}CH_2{-}C\underline{H}_2{-}CH_2{-}Si$); 0.63 (m, 640H, $-C\underline{H}_2{-}Si{-}C\underline{H}_2-$).

Fifth Generation Polychlorocarbosilane Dendrimer (G5 (Si_{485}^{972} (Cl))

The same procedure that used in preparation of Si_5^{12}(Cl) was utilized in the reaction of 20 g (0.81 mmol) of Si_{161}^{324}(All) in 28 mL of toluene with 53.6 g (0.39 mol) of trichlorosilane in presence of 0.044 mL of platinum catalyst solution, except after 374 hours of stirring at 50 °C, 20 mL of trichlorosilane were added along with 0.044 mL of platinum catalyst solution and stirring was continued for 216 hours at 50 °C; subsequently 0.088 mL of platinum catalyst solution were added and stirring continued for 312 h; afterwards 18 mL of trichlorosilane along with 0.044 mL of platinum catalyst solution were added and stirring was continued for 96 hours at 65 °C .

Fifth Generation Polyallylcarbosilane Dendrimer (G5(Si_{485}^{972}(All))

The reaction of magnesium turnings (69.3 g, 2.85 mol), Si_{485}^{972} (Cl) (55.7 g, 0.81 mmol) and AllCl (109.03 g, 1.42 mol) in solution of THF and toluene (370 mL and 250 mL respectively) was conducted under conditions similar to the synthesis of Si_5^{12}(All) (the content of residual chlorine after reaction completion was ~0.4%.) and gave 48.26 g (80.2% crude yield) of a white solid. The content of the Si_{485}^{972}(All) was 39.1%. Found (%): C, 70.79; H, 10.58; Si, 18.51. $Si_{485}C_{4368}H_{7764}$. Calc. (%): C, 70.98; H, 10.59; Si, 18.43. d_4^{25} 0.9344 g/cm^3. $[\eta]^{25}$ 0.0276 dL/g. Mol. weight (calc.) 73911.87. ^{1}H NMR ($CDCl_3$), δ: 5.74 (m, 972H, $CH_2{=}C\underline{H}{-}CH_2{-}Si$); 4.86 (m, 1944H, $C\underline{H}_2{=}CH{-}CH_2{-}Si$); 1.57 (d, 1944H, $CH_2{=}CH{-}C\underline{H}_2{-}Si$); 1.38 (m, 968H, $Si{-}CH_2{-}C\underline{H}_2{-}CH_2{-}Si$); 0.65 (m, 1936H, $-C\underline{H}_2{-}Si{-}C\underline{H}_2-$).

Sixth Generation Polychlorocarbosilane Dendrimer (G6 (Si_{1457}^{2916} (Cl))

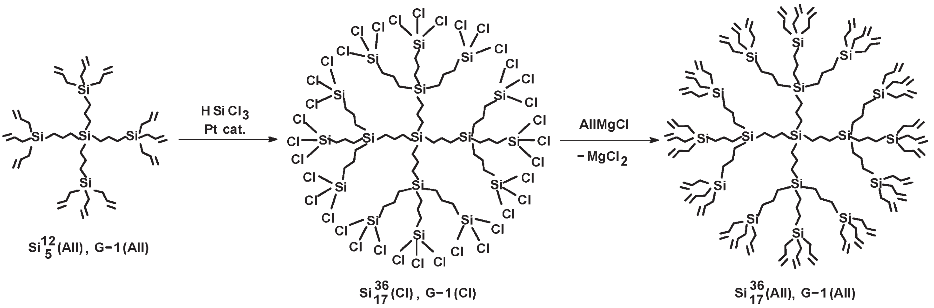
The same procedure that used in preparation of Si_5^{12}(Cl) was utilized in the reaction of 25 g (0.3 mmol) of Si_{1487}^{2916}(All) in 50 mL of toluene with 53.7 g (0.4 mol) of trichlorosilane in presence of 0.13 mL of platinum catalyst solution, except after 65 hours of stirring at 50 °C and 63 hours at 70 °C 7 mL of trichlorosilane were added along with 0.1 mL of platinum catalyst solution and stirring was continued for 72 hours at 70 °C.

Sixth Generation Polyallylcarbosilane Dendrimer (G6(Si_{1457}^{2916}(All))

The reaction of magnesium turnings (48 g, 1.97 mol), Si_{1457}^{2916}(Cl) (51.12 g, 0.2 mmol) and AllCl (76.13 g, 0.99 mol) in THF (700 mL at the beginning and 450 mL were added after 6 hours of stirring at reflux) was conducted under conditions similar to the synthesis of Si_5^{12}(All) (the content of residual chlorine after reaction completion was ~0.4%) and gave 53 g (96%) of a white solid. The content of $\mathbf{Si_{1457}^{2916}}$(All) was 38.9%. Found (%): C, 71.09; H, 10.56; Si, 18.25. $Si_{1457}C_{13116}H_{23316}$. Calc. (%): C, 70.97; H, 10.59; Si, 18.44. d_4^{25} 0.944 g/cm^3. $[\eta]^{25}$ 0.038 dL/g. Mol. weight (calc.) 221960.1. ^{1}H NMR ($CDCl_3$), δ: 5.74 (m, 2916H, $CH_2{=}C\underline{H}{-}CH_2{-}Si$); 4.86 (m, 5832H, $C\underline{H}_2{=}CH{-}CH_2{-}Si$); 1.57 (d, 5832H, $CH_2{=}CH{-}C\underline{H}_2{-}Si$); 1.38 (m, 2912H, $Si{-}CH_2{-}C\underline{H}_2{-}CH_2{-}Si$); 0.65 (m, 5824H, $-C\underline{H}_2{-}Si{-}C\underline{H}_2-$).

Results and Discussion

Polyallylcarbosilane dendrimers were synthesized according to the known procedure, used before for the synthesis of 10 generations of polyallylcarbosilane dendrimers (4 × 3) and their non-functional polybutylcarbosilane counterparts.[11] Dendrimer synthesis was carried out in two iterative steps: organomagnesium synthesis and hydrosilylation. In the present work synthesis of polyallylcarbosilane dendrimers was accomplished with the use of trichlorosilane in hydrosilylation reaction



Scheme 1.

and allylmagnesium chloride in Grignard reaction; tetraallylsilane was used as branching center (Scheme 1)

Reaction conditions were similar to the syntheses of (4 × 3) dendrimers, at the same time it should be noted, that in case of this homologous series the reactions run slower relative to less structurally dense series. Increase of time, needed for full conversion, leaded to increase of the side products, such as high molecular weight impurities as a result of side reactions. To shorten reaction time and reduce the fraction of side products we assumed following measures: hydrosilylation reaction was carried out at 30–50 °C for generations from 1st to 4th and at 60–70 °C – for 5th and 6th; realization of Grignard reaction in more dilute solution decreased the reaction time; purification of the end products of Grignard reactions by column chromatography on silica-gel to remove polar impurities and platinum catalyst increased the fraction of desired product. The adjustments introduced to the reaction procedures allowed the successive synthesis of 6 generations of polyallylcarbosilane dendrimers with dense molecular structure.

Full conversion of functional groups was reached in all reaction steps. To control the conversion chlorine ion analysis was used for Grignard reaction and ^{1}H NMR spectroscopy for hydrosilylation. Chlorosilyl derivatives were used for further syntheses without additional purification. The quality of the synthesized dendrimers was checked for allylfunctional ones.

The resulting polyallylcarbosilane dendrimers were purified by means of preparative chromatography (Figure 2) to obtain monodisperse products with the content of desired dendrimer about 99.5–99.8%.

Identity and purity of obtained dendrimers were confirmed by analytical GPC (Figure 3), and their structure by ^{1}H NMR spectroscopy (Figure 4). Integral intensities ratios for signals corresponding to different protons types are in good agreement with calculated values.

It should be noted, that ^{1}H NMR spectra for low and high generations have the same set of signals matching structure elements and differ only in resolution. Lower resolution and broadening of the signals in case of high generation are the consequences of its polymeric nature unlike the 1st generation, which is actually an oligomeric compound. The composition of

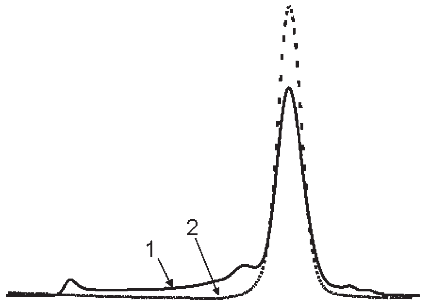


Figure 2.

Analytical GPC trace of G2(All) before (1) and after (2) purification by preparative chromatography.

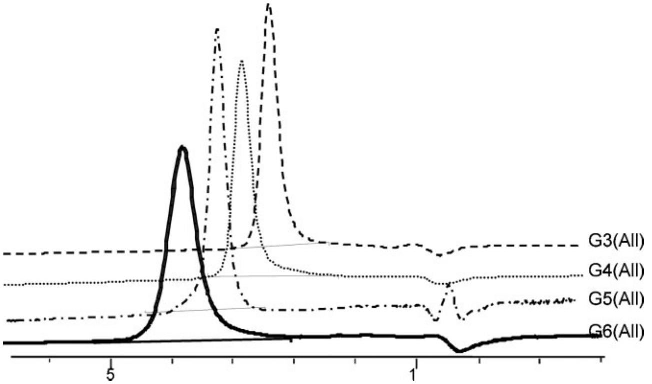


Figure 3.
GPC traces of G3(All)-G6(All) after purification.

the dendrimers, measured by elemental analysis is also in good agreement with calculated values.

Dendrimers from 1st till 4th generation are transparent viscous liquids, whose viscosity increases along with the generation; 5th and 6th generation dendrimers are white solids. It should be noted, that in case of (4 × 3) series the transition from liquid to solid state occurs between 5th and 6th generations. Also important is that the dendrimers with the same structure synthesized before[17] are reported to be solid already at 3rd generation. This fact indicates some deviations in molecular structure of dendrimers in cited paper, which could be caused by side reactions or different ratio of Markovnikov and anti-Markovnikov addition during the hydrosilylation step.

Our attempt to synthesize 7th generation according to the same reaction scheme was unsuccessful: hydrosilylation of G6(All) resulted in the formation of insoluble gel. According to the ^{1}H NMR spectrum of the last soluble probe conversion before

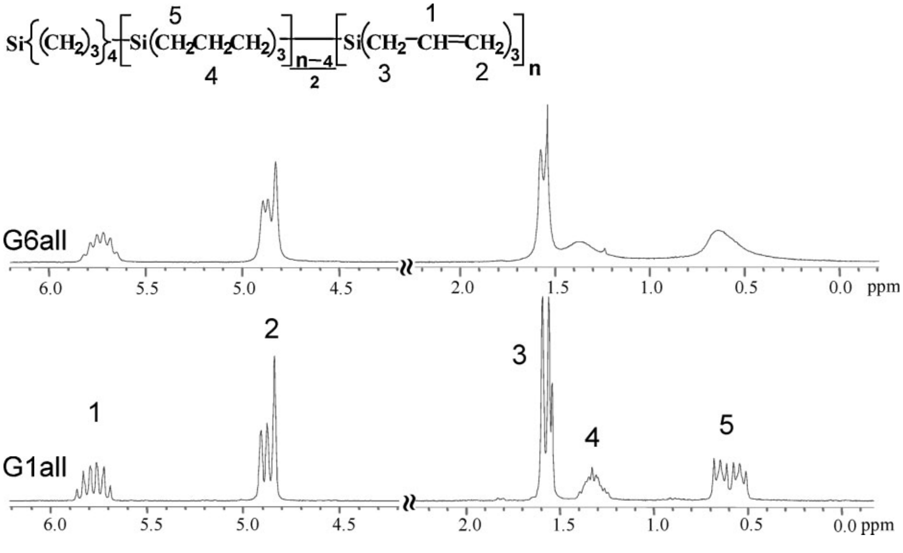


Figure 4.
^{1}H NMR spectra of G1(All) and G6(All).

Table 1.
Some characteristics of synthesized dendrimers.

Dendrimer	Generation	MM (calc.)	Crude yield, %	Major product yield, %	[η], dL/g	d_4^{25}, g/cm^3
Si_5^{12}(All)	1	801.6	96.6	99	–	–
Si_{17}^{36}(All)	2	2629.4	97.1	72	0.0237	0.9016
Si_{53}^{108}(All)	3	8112.6	72.8	42	0.0304	0.9114
Si_{161}^{324}(All)	4	24562.4	83.6	40	0.0297	0.9235
Si_{485}^{972}(All)	5	73911.9	80.2	39	0.0276	0.9344
Si_{1457}^{2916}(All)	6	221960.1	96.0	39	0.0380	0.9440

Table 2.
Glass transition temperatures and hydrodynamic radii of dendrimers of (4 × 4) and (4 × 3) homologous series.

Generation	T_g, K		R_h, nm	
	(4 × 4)	(4 × 3) [32,33]	(4 × 4)	(4 × 3)[32]
1	–	154 ± 1	–	–
2	178 ± 2	172 ± 1	–	–
3	187 ± 2	173 ± 1	–	–
4	–	172 ± 1	1.7	–
5	200 ± 2	179 ± 1	2.5	2.0
6	200 ± 2	180 ± 1	3.5	2.6
7	–	181 ± 1	–	3.5

cross-linking was 65–70%. We do not consider yet this fact as a proof of existence of limiting generation in this particular homologous series. This problem will be further investigated in a separate paper. Some characteristics of the dendrimers are shown in Table 1.

Hydrodynamic radii of dendrimers of generations from 4 to 6, measured by means of dynamic light scattering, increase linearly with generation (Table 2). Hydrodynamic radius distribution functions also proved monodispersity of synthesized products (Figure 5).

Hence structure, purity and composition of the dendrimers and their correlation with calculated values were confirmed by the combination of analytical methods (GPC, NMR, elemental analysis, DLS).

Figure 6 shows densities of the dendrimers of homological series (4 × 3) and (4 × 4) plotted against generation number. One can see that unlike (4 × 3) series, where density is constant (doesn't depend on generation number), density of (4 × 4) dendrimer significantly increases in line with the generation number. This implies that despite the noticeable increase of hydrodynamic dimensions in comparison with (4 × 3) series (Table 2) inner sphere of (4 × 4) dendrimers is filled up more efficiently. In other words the potentialities of increasing of hydrodynamic volume at the expense of conformational rearrangements are almost exhausted. Seeing that, the measurement of the free volume, available

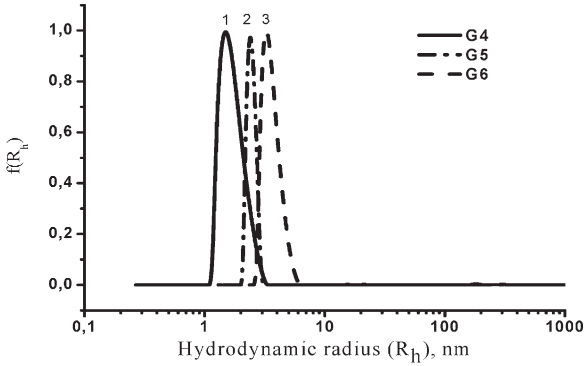


Figure 5.
Hydrodynamic radius distribution functions for dendrimers G4-G6(All).

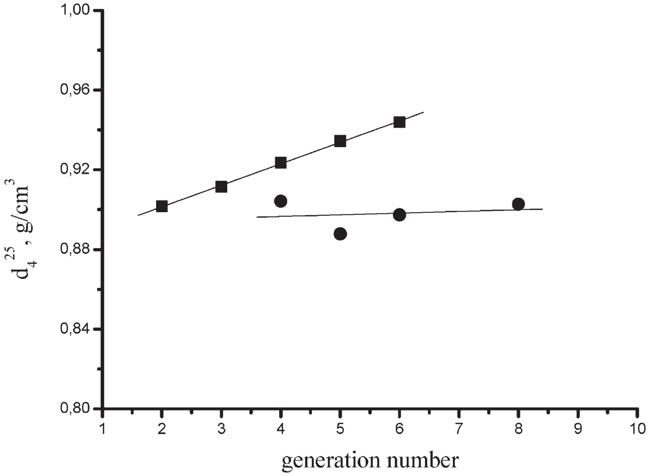


Figure 6.
Density of (4 × 3) (●) and (4 × 4) (■) dendrimers plotted versus generation number. Straight lines are linear approximations.

for the solvent molecules, which have been done before for less dense homologous series,[34] can be regarded as a relevant experiment.

The comparison of the glass transition temperatures measured by DSC (Table 2) also demonstrates considerable increment, increasing with the generation. This fact could be also interpreted as reflection of the lack of space for the dendrimer's branches mobility.

In the framework of the accuracy of the intrinsic viscosity measurements its value for studied dendrimers does not depend on the generation number. Since 2nd generation dendrimer is rather oligomeric than polymeric molecule, it has lower viscosity, than other generations. The same trend was observed for the carbosilane dendrimers of (4 × 3) homologous row.[11] Due to very low intrinsic viscosity values, close to the value 0.025 dL/g for hard spheres, these dendrimers can be attributed to a compact objects with solvent content lower than for less structurally dense series (4 × 3).

Conclusion

Contrary to the previous studies we have shown, that it is possible to synthesize up to six generations of carbosilane dendrimers (4 × 4). The difficulties with the synthesis of 7th and following generations are likely to be consequences of not surface congestion, but rather changing of the main and side reactions ratio.

Densification of the molecular structure leads to the significant changes in dendrimers properties compared with the dendrimers of the same generation but another homologous series.

Considering dendrimers as objects of dualistic nature, which have both macromolecular and nanoparticle properties, it could be stated that compared objects have different proportion of features belonging to both forms. As it was shown earlier for even higher generations of the (4 × 3) series dendrimers they are still first of all macromolecules. Passing on to the dendrimers of (4 × 4) series the significance of particle features is increasing. The question is how far we could move in this direction staying in the frames of regular growth?

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