

Synthesis and study of the properties of the homologous series of polyallylcarbosilane dendrimers and their nonfunctional analogs

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A synthetic route combining the preparation of functional and nonfunctional carbosilane dendrimers has been developed. Using this route, two representative homologous series of carbosilane dendrimers have been prepared. The use of nonfunctional dendrimer derivatives ensures the possibility of performing long-term experiments both in solution and in the bulk. The intrinsic viscosity and the density of the specimens studied do not depend on the generation number. The obtained dendrimers of later generations were studied by atomic force microscopy and light scattering.

Key words: carbosilane dendrimers, intrinsic viscosity of dendrimers, density of dendrimers, atomic force (probe) microscopy of dendrimers.

Synthesis and study of structurally ordered monodisperse nano-sized macromolecules is a foreground line of research in modern chemistry. Dendrimers, regularly branched macromolecules-particles, are the most perfect representatives of this type of polymer.^{1–5} The possibility of controlled regular growth and the almost unlimited potential for modification of the molecular structure account for the attention to and interest in the research in this field.^{6–10}

Despite the substantial advances in the dendrimer synthesis, a number of constraints hold up both the development of the whole line of research and transition from the study of various effects inherent in highly branched molecular systems to their practical application. Attention is drawn by deficiency of data on simple physical properties of dendrimers, in particular, the density, the viscosity, and the glass transition temperature. Systematic investigations of dendrimers by spectroscopic methods, small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), and electron and atomic force microscopy (AFM) remain topical. Therefore, it is necessary to synthesize broad series of dendrimers stable under investigation conditions. The last-mentioned circumstance is very important, because most of dendrimers are highly functional and highly reactive.

A known synthetic route to polycarbosilane dendrimers,^{11,12} which is popular and therefore applicable in

various modifications,^{13–18} represents successive repetition of a two-step sequence consisting of organomagnesium synthesis and hydrosilylation. According to this route, after completion of one step of the sequence, the growing dendrimer occurs alternatively in either of the two functional states: a polyallyl functional dendrimer and a polychlorosilyl dendrimer. In view of the high reactivity of chlorosilyl groups, systematic study of the physicochemical properties of dendrimers shows little promise at this stage. In the allyl functional modification, dendrimers can be isolated in a pure state and are stable when definite storage conditions are observed. However, when subjected to environmental factors, they are hardly suitable for systematic research, which takes a long time. Nonfunctional derivatives of such dendrimers are stable; however, for the same reason, they are incapable of further growth.

The purpose of this study is to synthesize a homologous series of polycarbosilane dendrimers stable under experimental conditions related to their studies by various physical methods and during long-term storage.

This task was solved by elaborating a synthetic route that combined the preparation of functional and nonfunctional dendrimers. As a result, we synthesized two homologous series of carbosilane dendrimers. The first five generations of the polyallyl series have been reported in our previous publication,¹⁹ while five later (sixth to

tenth) polyallylic generations and all eight generations of nonfunctional polybutylcarbosilane dendrimers are described here for the first time.

Results and Discussion

The general scheme shows the known method for the preparation of polyallylcarbosilane dendrimers (Scheme 1, pathway *a*) consisting of the repeating organomagnesium synthesis—hydrosilylation sequence, together with the synthesis of nonfunctional derivatives (Scheme 1, pathway *b*).

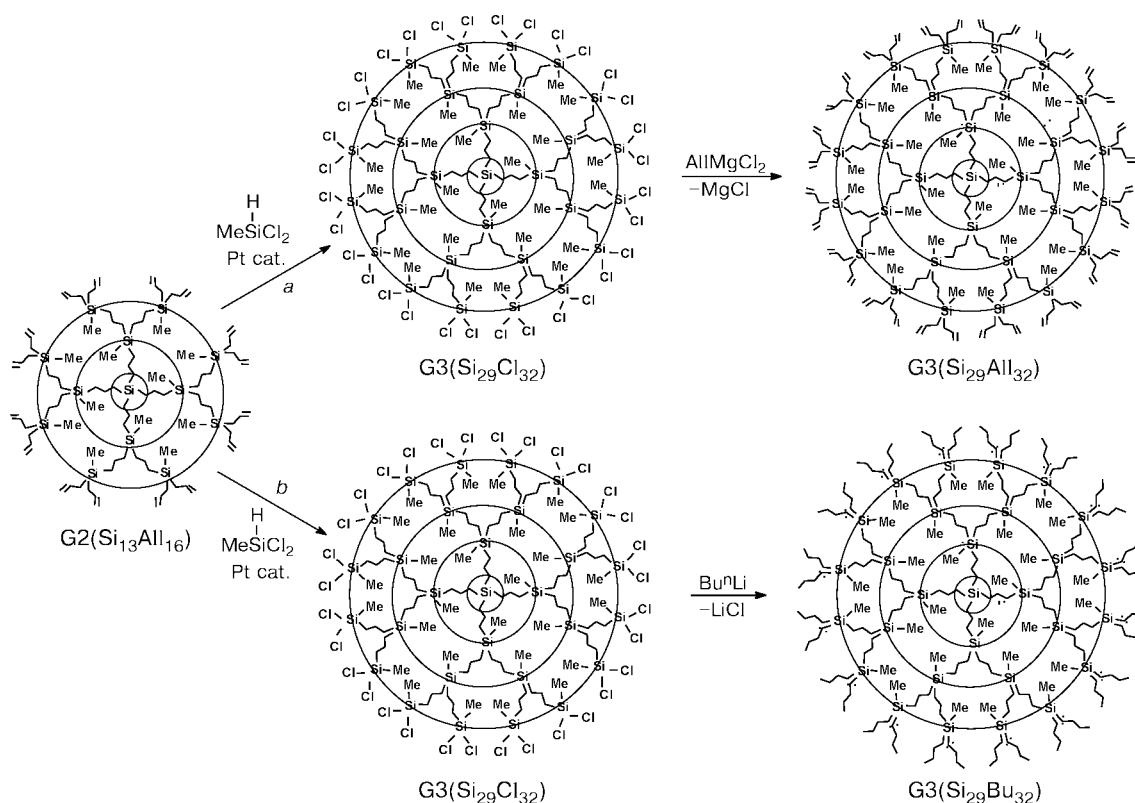
As an example, the scheme shows the repeating sequence of reactions resulting in the formation of third-generation dendrimers. Since stability problems are rather characteristic of dendrimers of later generations, the first two generations of dendrimers with the butyl surface layer have not been synthesized. It can be seen from the Scheme that pathway *b* differs from pathway *a* in the organometallic reagent, in particular, allylmagnesium chloride was replaced by *n*-butyllithium. Due to this replacement, treatment of the chlorosilyl dendrimer affords its nonfunctional analog. The resulting nonfunctional dendrimer derivative is incapable of and is not meant for further building-up of the molecular structure. Therefore, every allylic dendrimer prepared by pathway *a* was used as the starting

compound for the preparation of the next generation both in the functional branch of the scheme and in the non-functional branch. At the first glance, it is reasonable to accomplish separation when the chlorosilyl derivative has been obtained. However, in reality, due to the high reactivity of these compounds, it is more reasonable to carry out separation for the polyallyl-functional generations. The fact that the same dendrimer precursor is used in both parts of the scheme means that the process gives not merely nonfunctional analogs but exact replicas of the functional derivatives, which is rather important for analysis of impurities and possible deviations from the main route of the process.

Hydrosilylation was carried out in hexane or toluene solutions in an excess of chlorosilane until the signals for allyl group protons completely disappeared from the ^1H NMR spectra. The chlorosilyl derivatives were not isolated and were used without additional purification.

Both sorts of dendrimers were isolated *via* the same sequence of operations. The allyl and butyl generations of dendrimers isolated from reaction mixtures (so-called crude) were dissolved in toluene, passed through a silica gel column, and isolated on a preparative chromatograph. The dendrimers of both the allyl and butyl series were identified similarly. The purity of samples after chromatography was estimated by GPC in an analytical mode;

Scheme 1



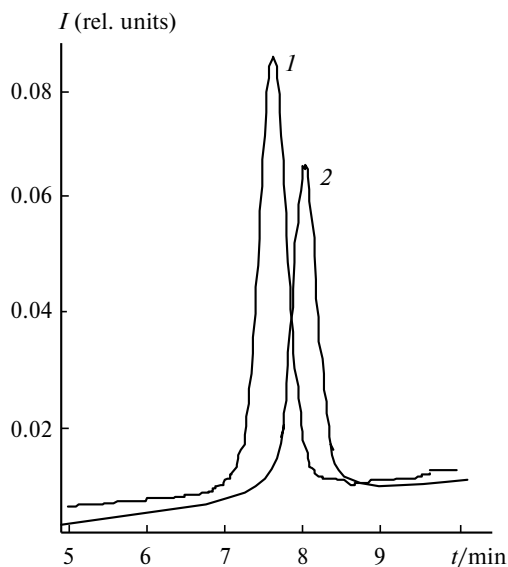


Fig. 1. GPC curves of polycarbosilane dendrimers G9(Bu) (1) and G8(AlI) (2).

the content of the major substance was found to be 99.5–99.8%. As an example, Figure 1 shows the chromatograms of the ninth butyl and eighth allyl generations of dendrimers after their preparative isolation.

The compliance of dendrimer composition with the calculated values was confirmed by elemental analysis data (see Experimental). In all cases, the experimental and calculated values were in good agreement. The structures of the products were analyzed by ^1H NMR. As an example, Figs. 2 and 3 show the spectra of the ninth butyl and eighth allyl generations of dendrimers. The Figures show the key assignment of proton signals for various structural elements. The good resolution of signals and the satisfactory ratio of the integral intensities of the signals of protons of various groups is the main argument favoring the correspondence of the obtained products to the given structures.

Later generations of dendrimers were studied by light-scattering methods. For the dendrimers of the ninth butyl and eighth allyl generations, the hydrodynamic radii determined by dynamic light scattering (DLS) in heptane are 4.6 and 3.9 nm, respectively. It can be seen from the presented data (Fig. 4) that the samples are monodisperse and, as in the case of GPC, they can be reliably detected as nonassociated globular objects.

Static scattering measurements of the molecular mass for the ninth-generation butyl dendrimer (G9(Bu)) in heptane showed a good correspondence between the calculated and obtained values (see Table 1). This result is important not only by itself but also for the whole homologous series. Taking into account the fact that generations were obtained successively without intermediate fractionation, the good agreement between the results of

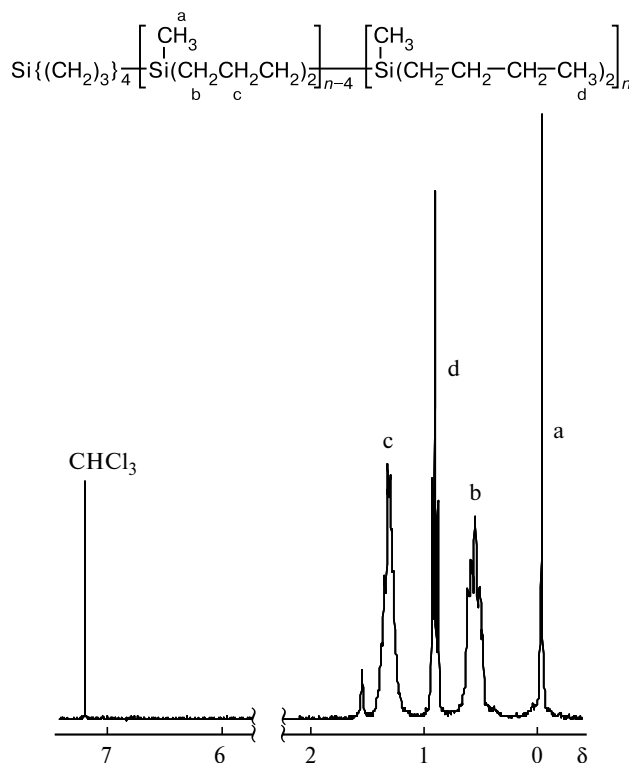


Fig. 2. ^1H NMR spectrum of the polycarbosilane dendrimer G9(Bu).

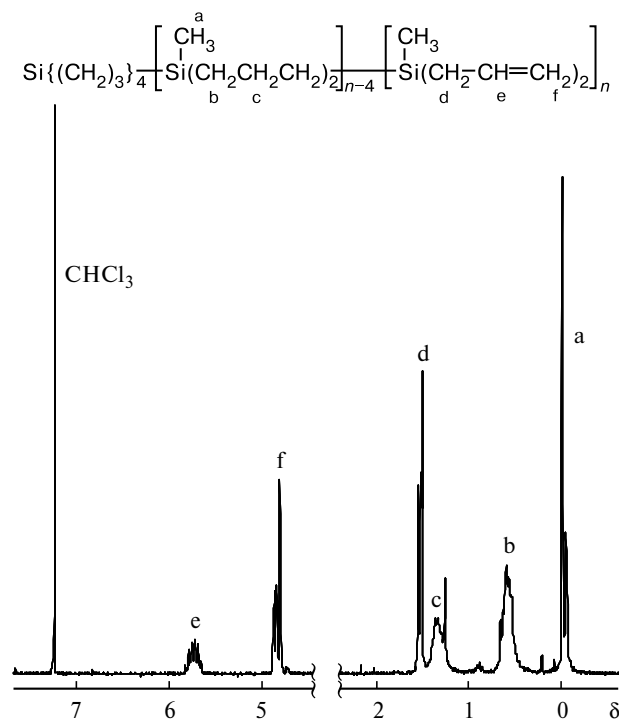


Fig. 3. ^1H NMR spectrum of the polycarbosilane dendrimer G8(AlI).

measurements and the calculated value attest to the lack of deviations of the obtained dendrimers from their theo-

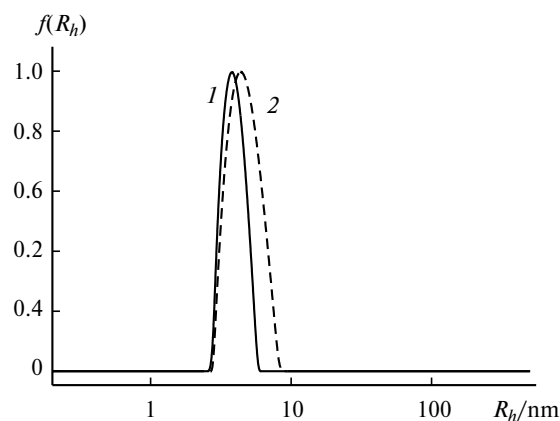


Fig. 4. Distribution function over the hydrodynamic radii for the dendrimers G8(Al) (1) and G9(Bu) (2).

retical structural models for the whole homologous series including the ninth generation.

The calculated molecular masses and the yields of the polyallylcarbosilane dendrimers are summarized in Table 2. The product yields were estimated after the preparation of the crude dendrimer (before the preparative isolation). These values characterize qualitatively the high degree of conversion of functional groups throughout the whole process. The content of the major substance, *i.e.*, the dendrimer of a specified generation, in the crude was determined from the data of analytical exclusion chromatography. The content of the major substance drops especially sharply (see Table 2) on passing to later generations, mainly due to an increase in the content of the high-molecular-mass component, which results, as proposed previously, from side reactions.

Table 1. Some characteristics of nonfunctional carbosilane dendrimers

Compound	Generation	M^a (calculation)	Yield (%)	Y^b	$[\eta]$ /dl g ⁻¹	d_4^{25} /g cm ⁻³
Si ₂₉ Bu ₃₂	G3	4241.4	67.7	85	0.036	0.8767
Si ₆₁ Bu ₆₄	G4	8795.6	60.8	68	0.04	—
Si ₁₂₅ Bu ₁₂₈	G5	17903.9	88.5	66	0.042	0.8877
Si ₂₅₃ Bu ₂₅₆	G6	36120.7	68.5	60	0.036	—
Si ₅₀₉ Bu ₅₁₂	G7	72554.1	95.2	47	0.046	0.8734
Si ₁₀₂₁ Bu ₁₀₂₄	G8	145420.9	91.1	30	0.038	—
Si ₂₀₄₅ Bu ₂₀₄₈	G9	291154.5 ^c	93.9	27	0.043	0.8838
Si ₄₀₉₃ Bu ₄₀₉₆ ^d	G10	582621.8	95.8	22	—	—

^a M is the molecular mass.

^b Y is the content of the major compound in the crude material.

^c The molecular mass measured by LS is 295600.

^d The sample G10 was obtained in a quantity of several tens milligram; therefore, no investigations except for structure identification were carried out.

Table 2. Some characteristics of polyallylcarbosilane dendrimers

Compound	Generation	M^a (calculation)	Yield ^b	Y^c
			(%)	
Si ₅ Al ₈	G1	697.5	97.9	98
Si ₁₃ Al ₁₆	G2	1707.7	91.6	90
Si ₂₉ Al ₃₂	G3	3728.1	87.9	86
Si ₆₁ Al ₆₄	G4	7768.9	97.0	80
Si ₁₂₅ Al ₁₂₈	G5	15850.5	99.4	78
Si ₂₅₃ Al ₂₅₆	G6	32013.7	99.6	65
Si ₅₀₉ Al ₅₁₂	G7	64340.1	98.5	59
Si ₁₀₂₁ Al ₁₀₂₄	G8	128992.9	99.1	31
Si ₂₀₄₅ Al ₂₀₄₈	G9	258298.5	94.6	28.5
Si ₄₀₉₃ Al ₄₀₉₆	G10	516909.7	93	24

^a M is the molecular mass.

^b The yield of crude dendrimer.

^c Y is the content of the main component in the crude material.

In this study we did not take any special measures for increasing the content of the major product; in other words, the tenth generation was prepared in the same way as the first one. The decrease in the content of the major substance to 17% in the 11th generation precluded the possibility of isolation of a sufficiently large pure sample. This served as the reason to stop further synthesis, although no objective indications of the "limit generation phenomena"^{13–15,20–23} were observed. Apart from the increase in the functionality and the concomitant risk of side reactions, the disproportionate decrease in the yield of the target products on passing to later generations may be due to accumulation of platinum in the system. The platinum complexes with a changed structure or the products of platinum transformation into colloid or cluster forms can exhibit an absolutely different activity and selectivity in hydrosilylation. Some characteristics of dendrimers of the nonfunctional polybutylcarbosilane homologous series of the third to tenth generation are listed in Table 1.

The product yields mainly characterize the isolation and drying of the samples; therefore, they are rather subjective. For example, the lower yields for the third to six generations compared to the polyallyl analogs reflect rather the process of dendrimer separation from magnesium lithium chloride and not the difference in the course of chemical processes.

The properties of dendrimers were studied using dendrimer samples purified and isolated from the reaction mixture by chromatographic techniques (see Experimental). The properties of such samples have been studied previously by adiabatic calorimetry,^{24,25} SAXS and SANS,²⁶ and NMR spectroscopy.²⁷ We measured the viscosity of dendrimers in dilute solutions in toluene and the dendrimer density. The dependence of intrinsic viscosity on the generation number measured for the third to ninth

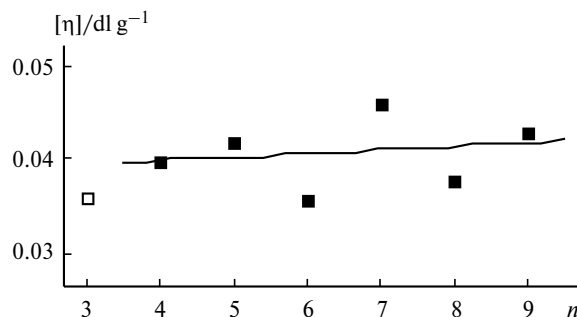


Fig. 5. Intrinsic viscosity vs. the generation number for polybutylcarbosilane dendrimers.

generations of the homologous series with butyl substituents has no extrema (as was observed previously^{28,29}), but is described by a straight line almost parallel to the abscissa axis (Fig. 5).

This is at variance with some published data²⁸ and with the results of modeling.²⁹ However, examples of a different sort can also be cited. Thus in a study,³⁰ a constant intrinsic viscosity was observed for all samples ranging from the first to eighth generation. The discrepancies in the patterns of dependence of the intrinsic viscosity on the number of generation has been attributed²⁸ to the specific chemical nature (the presence of strong specific intermolecular interactions) of polylysine dendrimers, resulting in a higher density of the molecular structure similar to that of globular systems. In another case,¹ a similar result has been attributed to the asymmetry of the branching sites in the polylysine dendrimers, leading to a denser packing of their molecular structure. In both cases, the reason is related to a high density of the molecular structure. The data obtained in this work do not confirm any of the assumptions made. Indeed, polybutylcarbosilane dendrimers contain neither structural fragments apt to specific intramolecular interactions, nor asymmetric branching sites but, nevertheless, they have an almost invariable viscosity for the whole studied series starting from the fourth generation. The presence or the absence of a maximum on the dependence of viscosity on the number of generation might be dictated by particular parameters of the molecular structure of dendrimers, as follows from the results of numerical modeling,³¹ which either predicts an extremum or not, depending on parameters that are different for different homologous series of dendrimers. This discussion calls for further research along this line in order to separate general features (inherent in all dendrimers) from specific ones (typical of particular types of dendrimers).

Of equal importance is the dependence of the density of polycarbosilane dendrimers from the generation number (Fig. 6). The dependence of density on the generation number is an important function that allows one to decide between different models of the molecular arrangement

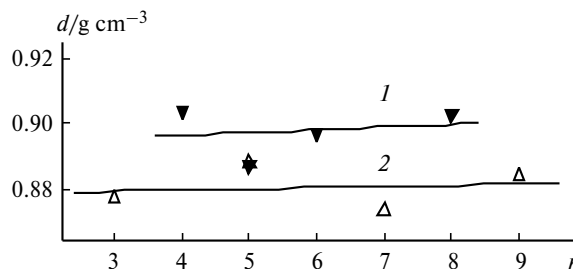


Fig. 6. Density vs. the generation number for the homologous series of polyallylcarbosilane dendrimers (1) and for their polybutylcarbosilane analogs (2).

of dendrimers. Owing to the invariable density within the homologous series of dendrimers, they can be regarded as compact particles with a nonrigid molecular structure.

No systematic data on density measurements have been reported for most dendrimers. A special review⁵ devoted to the properties of dendrimers does not make any mention of measurements of the dendrimer density depending on the generation number. The concentration of a dendrimer in an area confined by the hydrodynamic volume of the molecule, *i.e.*, the ratio of the dendrimer molecular mass to the hydrodynamic volume, is often taken to be the measure of density. An exception is the study³² in which the so-called apparent density of the fourth- and fifth-generation polypropyleneimine dendrimers is calculated from the density of dendrimer solutions of specified concentrations. The values of density (1.12 and 1.13 g mL⁻¹ for the fourth and fifth generations, respectively) were markedly higher than the density of these dendrimers in the block, which is equals to 1.01 g mL⁻¹ for the third- to fifth-generation polypropyleneimine dendrimers, according to Aldrich, 2004. Unfortunately, data for the subsequent generations were missing.

The obtained data on the density and intrinsic viscosity were used to determine the ratio of the weight of the solvated solvent to the polymer weight from the formula³³

$$[\eta] = 2.5[1 + m_1\rho_2/(m_2\rho_1)]/\rho_2,$$

where ρ_1 and ρ_2 are the densities of the solvent and the polymer, respectively, m_1/m_2 is the solvated solvent to polymer weight ratio, and $[\eta]$ is the intrinsic viscosity of the polymer in this solvent. Having substituted $[\eta] = 4.6 \text{ mL g}^{-1}$, $\rho_2 = 0.8734 \text{ g mL}^{-1}$, and $\rho_1 = 0.8669 \text{ g mL}^{-1}$ (with toluene as the solvent) for G7(Bu), we found that $m_1/m_2 = 0.61$ or, for the volume fraction of the solvent in the dendrimer bulk, $\phi_s/\phi_0 = 0.38$, which is consistent with the SANS data³⁴ concerning the content of the solvent in the dendrimer bulk.

The data in Table 1 provide almost the first opportunity to follow the variation of the dendrimer density and intrinsic viscosity vs. the generation number and thus they introduce a certain factual ground into the numerous debates aroused by different versions of computer modeling

and theoretical calculations. The dendrimers of parallel homologous series have quite similar densities, and for the fifth generations, the points almost coincide (see Fig. 6). Generally, the density of dendrimers of the polyallylcarbosilane series is somewhat higher than that for the polybutylcarbosilane dendrimers; however, in view of the extra methyl group present at the silicon atoms of the organic substituents in the outer layer of polybutylcarbosilane dendrimers, this difference appears quite natural.

The visualization of the objects synthesized is of obvious interest. The images of dendrimers obtained by various methods, including scanning probe microscopy, have been already reported.^{35,36} The fact of obtaining these micrographs is becoming customary. In addition, AFM images for a particular type of dendrimers may provide a large bulk of indirect, but very important information. Naturally, this implies performing systematic research us-

ing an extensive range of objects. We present (Fig. 7) the images of the ninth-generation polybutylcarbosilane dendrimer, first of all, to demonstrate that AFM study of these structures has a serious potential.

It can be seen in these images that dendrimers deposited on a mica surface have a fairly regular shape and are uniform in size. The geometric dimensions of separate particles obtained from the AFM data are in rather good agreement with the results of DLS measurements for the same samples. Analysis of the images indicates that the dendrimers under study are sufficiently rigid molecular particles to be detected by a microscope tip and to retain their shape; they are dense enough to exclude interpenetration.

The obtained clear images open up the possibilities for more detailed investigation of dendrimers as molecular particles taking into account the density of the molecular structure, the nature of the surface layer, the affinity to the substrate surface, and deposition conditions.

Thus, the synthesis of nonfunctional analogs of carbosilane dendrimers we carried out markedly extends the possibility of investigating these objects by various physical methods. In addition to ten generations of polyallylcarbosilane dendrimers, we synthesized a representative homologous series of nonfunctional analogs. Currently, functional dendrimers are extensively used to prepare various derivatives, in particular, polyhydroxylated,³⁷ fluorinated multi-arm star polymers.³⁸ Nonfunctional polybutylcarbosilane systems are the focus of research by a number of physical methods and thus confirm good prospects of the chosen approach as regards the synthesis of functional and nonfunctional homologous series of dendrimers. The absence of principle difficulties in attaining the complete conversion of functional groups in the synthesis of the tenth and eleventh generations demonstrates the absence of the "limit generation phenomenon" for dendrimers with the chosen molecular parameters.

Experimental

All the reactions were carried out under inert atmosphere and in anhydrous solvents. The organic solvents, *viz.*, hexane and toluene, were additionally dried and distilled from CaH_2 ; THF was stored over NaOH and distilled from CaH_2 . Dichloromethylsilane was distilled immediately prior to use. Allyl chloride was dried by refluxing and distilling over CaH_2 .

^1H NMR spectra were recorded on a Bruker WP-200 SY spectrometer (200.13 MHz) using Me_4Si as the internal standard. GPC analysis was performed on a GTsP instrument (Czechoslovakia) using a RIDK-102 refractometer as the detector, LiChrosphere 100, 300 and Silasorb 600 (4×250 mm) columns, and THF as the eluent. The resulting allylic functional dendrimers were used for the synthesis of the subsequent generations without further purification. Chromatographically pure polyallyl and polybutyl dendrimer samples for investigations

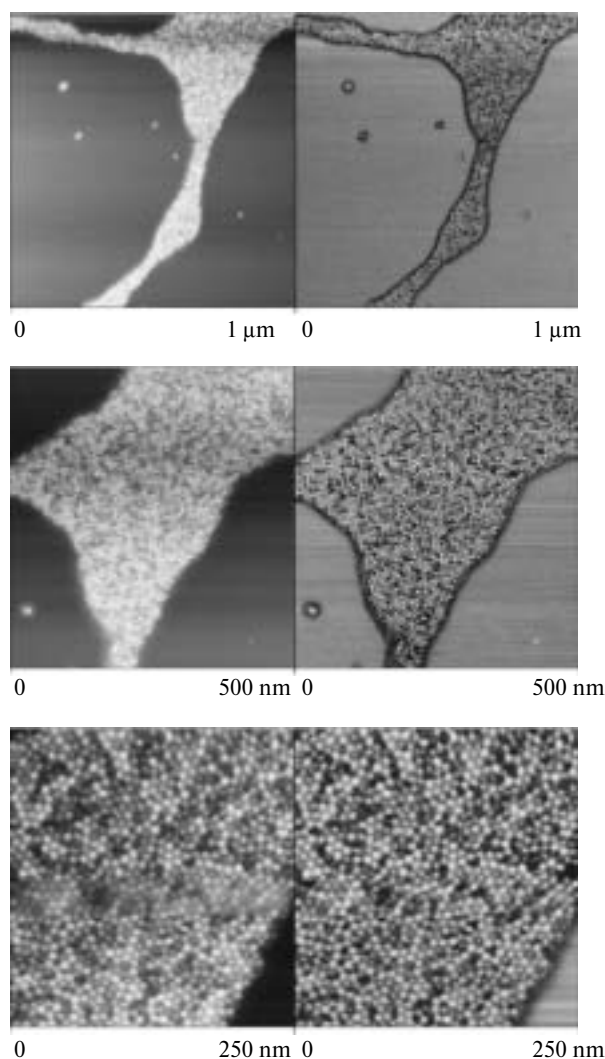


Fig. 7. AFM images of the polybutylcarbosilane dendrimer G9(Bu) on a mica surface obtained with different scanning scales.

were prepared by column chromatography on Silica gel 60 (0.063–0.100 mm, Merck, toluene as the solvent) followed by preparative isolation by exclusion gel filtration. The preparative chromatographic system consisted of a high-pressure isocratic pump (Akvilon), a RIDK-102 refractometric detector (Czechia), and 300×21.2 mm Phenomenex preparative columns (USA) packed with the Phenogel sorbent (particle size 10 μm). Depending on the molecular masses of the components of the mixtures being separated, columns with pore sizes of 10^3 , 10^4 , and 10^5 Å were used and THF was used as the eluent. The solvents were removed by evacuation to 1 Torr at 60 °C.

The intrinsic viscosity was measured on a Ubbelohde viscometer (capillary diameter 0.3 mm) using toluene as the solvent. The temperature was maintained to an accuracy of 0.1 °C.

Density measurements were performed by a pycnometer for early generations and by the density equilibration method for later generations; a water–ethanol mixture was used as the liquid phase.

The dynamic and static light scattering studies of dendrimers were carried out at 25 °C using an ALV/CGS-8F Compact goniometer with an angle range of 10–155° and an angular resolution of 0.003° and a He–Ne laser (JDS Uniphase Corporation) with a wavelength of 632.8 nm and a power of 22 mW.

All experiments using dynamic light scattering were carried out at a scattering angle of 90° with heptane as the solvent; the concentration of samples in heptane was 1 mg mL⁻¹.

In the case of static light scattering, the measurements were carried out at four different concentrations of the dendrimer. For each concentration, the intensity of light scattering was recorded at 12 angles in the 40–150° range with a step of 10°.

AFM studies were carried out in air in the intermittent contact mode with a Nanoscope-IIIa microscope (Digital Instruments, USA). Silicon cantilevers with a resonance frequency of ~300 kHz were used. The samples were prepared in air by applying a drop of a toluene solution of the polymer onto a freshly cleaved mica surface followed by centrifugation at a constant velocity of 2000 rpm. The concentration of the polymer solution was 1 mg mL⁻¹. The images were processed using the Nanoscope and FemtoScan programs.³⁹

The polycarbosilane dendrimers G0(Si₁All₄)–G5(Si₁₂₅All₁₂₈) were synthesized by standard procedures^{19,40} via a sequence including organomagnesium synthesis using allyl chloride and metallic magnesium and hydrosilylation using dichloromethylsilane and a platinum catalyst (Aldrich), in particular, the complex of zerovalent platinum with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (a solution in xylene).

Elemental analysis of the chloride derivatives of dendrimers was not carried out.

Sixth-generation polychlorocarbosilane dendrimer G6(Si₂₅₃Cl₂₅₆). The fifth-generation dendrimer G5(Si₁₂₅All₁₂₈) (100.01 g, 6.3 mmol) was dissolved in 120 mL of hexane, a solution of the platinum catalyst (0.17 mL) was added under argon, dichloromethylsilane (130.03 g, 1.13 mol) was added dropwise with stirring, and the mixture was stirred for 25 h at room temperature. The reaction was considered to be completed when the signals for the protons of the allyl group, δ 4.86 ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$) and δ 5.74 ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$), disappeared from the ¹H NMR spectra of the samples taken from the reaction mixture. In this and in the subsequent experiments on the synthesis of chlorosilyl derivatives, the excess of dichloro-

methylsilane and a part of the solvent were distilled after the reaction until the temperature of the distillate was ~68 °C. Due to its high reactivity, the product was used to prepare the polyallyl derivative without isolation from the solution.

Sixth-generation polyallylcarbosilane dendrimer (G6(Si₂₅₃All₂₅₆)). Allyl chloride (10 mL) was added to Mg (94.86 g, 3.90 mol) in 150 mL of THF to initiate the reaction, and a solution consisting of dendrimer G6(Si₂₅₃Cl₂₅₆) (192.89 g, 6.3 mmol), THF (550 mL), hexane (500 mL), and allyl chloride (259.5 g, 3.39 mol) were added dropwise with stirring. The reaction mixture was stirred at reflux for 60 h. The reaction was monitored using the data of functional analysis for chloride ions (negative test). After completion of the reaction, the reaction mixture was treated with a saturated aqueous solution of NH₄Cl. The precipitate was filtered off. The filtrate was kept over anhydrous Na₂SO₄ for 24 h and filtered. Evaporation of the solvents gave 201.16 g (99.6%) of a product. The content of the major substance determined by GPC was 65.2%. The products obtained in this and in the subsequent experiments were used for the synthesis of later generations without further purification. Chromatographically pure samples for investigations were obtained by a sequence including column chromatography on silica gel (with toluene as the solvent) and preparative exclusion chromatography. Si₂₅₃C₁₇₇₆H₃₅₄₈, d_4^{25} 0.8974 g cm⁻³. Mol. weight (calc.) 32013.68. ¹H NMR (CDCl₃), δ : 5.74 (m, 256 H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$); 4.86 (m, 512 H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$); 1.55 (d, 512 H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$, J = 8.0 Hz); 1.30 (m, 504 H, Si–CH₂–CH₂–CH₂–Si); 0.54 (m, 1008 H, –CH₂–Si–CH₂–); –0.03 (s, 372 H, –CH₂–Si(CH₃)CH₂–CH₂–CH₂–Si); –0.07 (s, 384 H, Si(CH₃)–CH₂–CH=CH₂).

Seventh-generation polychlorocarbosilane dendrimer (G7(Si₅₀₉Cl₅₁₂)). The reaction of G6(Si₂₅₃All₂₅₆) (30 g, 0.9 mmol) and dichloromethylsilane (38.63 g, 0.33 mol) in the presence of a solution of the platinum catalyst (0.05 mL) was carried out in hexane (36 mL) under conditions similar to those used to prepare G6(Si₂₅₃Cl₂₅₆). The reaction mixture was stirred for 25 h at room temperature. Completion of the reaction was detected as the disappearance of the proton signals of the allyl group, δ 4.86 ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$) and δ 5.74 ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$), from the ¹H NMR spectra.

Seventh-generation polyallylcarbosilane dendrimer (G7(Si₅₀₉All₅₁₂)). The reaction of Mg (28.2 g, 1.16 mol), G7(Si₅₀₉Cl₅₁₂) (57.6 g, 0.9 mmol), and allyl chloride (77.11 g, 1.01 mol) in a mixture of 175 mL of THF and 146 mL of hexane was carried out under conditions similar to those used to prepare G6(Si₂₅₃All₂₅₆). The reaction mixture was stirred at reflux for 60 h. The reaction was monitored using the data of functional analysis for chloride ions (negative test). Evacuation (1 Torr) at 50 °C gave 59.38 g (98.5%) of the product G7(Si₅₀₉All₅₁₂). The content of the major compound in the crude material was 58.7%. Si₅₀₉C₃₅₆₈H₇₁₃₂. Mol. weight (calc.) 64340.08. ¹H NMR (CDCl₃), δ : 5.74 (m, 512 H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$); 4.86 (m, 1024 H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$); 1.55 (d, 1024 H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}$, J = 7.4 Hz); 1.3 (m, 1016 H, Si–CH₂–CH₂–CH₂–Si); 0.54 (m, 2032 H, –CH₂–Si–CH₂–); –0.03 (s, 756 H, –CH₂–Si(CH₃)CH₂–CH₂–CH₂–Si); –0.07 (s, 768 H, Si(CH₃)–CH₂–CH=CH₂).

Eighth-generation polychlorocarbosilane dendrimer (G8(Si₁₀₂₁Cl₁₀₂₄)). The reaction of G7(Si₅₀₉All₅₁₂) (15 g, 0.23 mmol) and dichloromethylsilane (19.22 g, 0.17 mol) in the presence of a solution of the platinum catalyst (0.025 mL) was

carried out in hexane (18 mL) under conditions similar to those used to prepare G6(Si₂₅₃Cl₂₅₆). The reaction mixture was stirred at room temperature for 60 h. Completion of the reaction was detected as the disappearance of the proton signals of the allyl group, δ 4.86 (CH₂=CH—CH₂—Si) and δ 5.74 (CH₂=CH—CH₂—Si), from the ¹H NMR spectra.

Eighth-generation polyallylcarbosilane dendrimer (G8(Si₁₀₂₁All₁₀₂₄)). The reaction of Mg (16.81 g, 0.69 mol), G8(Si₁₀₂₁Cl₁₀₂₄) (24.9 g, 0.2 mmol), and allyl chloride (46 g, 0.60 mol) in a mixture of 105 mL of THF and 87 mL of hexane was carried out under conditions similar to those used to prepare G6(Si₂₅₃All₂₅₆). The reaction mixture was stirred at reflux for 70 h. The reaction was monitored using the data of functional analysis for chloride ions (negative test). Evacuation (1 Torr) at 50 °C gave 25.83 g (99.1%) of the product G8(Si₁₀₂₁All₁₀₂₄). The content of the major compound in the crude material was 31.3%. Si₁₀₂₁C₇₁₅₂H₁₄₃₀₀. d_4^{25} 0.9028 g cm⁻³. Mol. weight (calc.) 128992.88. ¹H NMR (CDCl₃), δ : 5.74 (m, 1024 H, CH₂=CH—CH₂—Si); 4.86 (m, 2048 H, CH₂=CH—CH₂—Si); 1.55 (d, 2048 H, CH₂=CH—CH₂—Si, J = 8.3 Hz); 1.3 (m, 2040 H, Si—CH₂—CH₂—CH₂—Si); 0.54 (m, 4080 H, —CH₂—Si—CH₂—); -0.03 (s, 1524 H, —CH₂—Si(CH₃)CH₂—CH₂—CH₂—Si); -0.07 (s, 1536 H, Si(CH₃)—CH₂—CH=CH₂).

Ninth-generation polychlorocarbosilane dendrimer (G9(Si₂₀₄₅Cl₂₀₄₈)). The reaction of G8(Si₁₀₂₁All₁₀₂₄) (13.07 g, 0.1 mmol) and dichloromethylsilane (16.7 g, 0.14 mol) in the presence of a solution of the platinum catalyst (0.022 mL) was carried out in hexane (16 mL) under conditions used to prepare G6(Si₂₅₃Cl₂₅₆). The reaction mixture was stirred for 60 h at room temperature. Completion of the reaction was defined as disappearance of the proton signals of the allyl group, δ 4.86 (CH₂=CH—CH₂—Si) and δ 5.74 (CH₂=CH—CH₂—Si), from the ¹H NMR spectrum.

Ninth-generation polyallylcarbosilane dendrimer (G9(Si₂₀₄₅All₂₀₄₈)). The reaction of Mg (12.18 g, 0.5 mol), G9(Si₂₀₄₅Cl₂₀₄₈) (25 g, 0.1 mmol), and allyl chloride (33.34 g, 0.43 mol) was carried out in a mixture of 76 mL of THF and 63 mL of hexane under conditions similar to those used to prepare G6(Si₂₅₃All₂₅₆). The reaction mixture was stirred at reflux for 70 h. The reaction was monitored using the data of functional analysis for chloride ions (negative test). Evacuation (1 Torr) at 50 °C gave 24.75 g (94.6%) of the product G9(Si₂₀₄₅All₂₀₄₈). The content of the major compound in the crude material was 28.5%. Si₂₀₄₅C₁₄₃₂₀H₂₈₆₃₆. Mol. weight (calc.) 258298.48. ¹H NMR (CDCl₃), δ : 5.74 (m, 2048 H, CH₂=CH—CH₂—Si); 4.86 (m, 4096 H, CH₂=CH—CH₂—Si); 1.55 (d, 4096 H, CH₂=CH—CH₂—Si); 1.3 (m, 4088 H, Si—CH₂—CH₂—CH₂—Si); 0.54 (m, 8176 H, —CH₂—Si—CH₂—); -0.03 (s, 3060 H, —CH₂—Si(CH₃)CH₂—CH₂—CH₂—Si); -0.07 (s, 3072 H, Si(CH₃)—CH₂—CH=CH₂).

Tenth-generation polychlorocarbosilane dendrimer (G10(Si₄₀₉₃Cl₄₀₉₆)). The reaction of G9(Si₂₀₄₅All₂₀₄₈) (5 g, 0.02 mmol) and dichloromethylsilane (6.84 g, 0.06 mol) in the presence of a solution of the platinum catalyst (0.007 mL) was carried out in toluene (6 mL) under conditions similar to those used to prepare G6(Si₂₅₃Cl₂₅₆). The reaction mixture was stirred for 60 h at room temperature. Completion of the reaction was defined as disappearance of the proton signals of the allyl group, δ 4.86 (CH₂=CH—CH₂—Si) and δ 5.74 (CH₂=CH—CH₂—Si), from the ¹H NMR spectra.

Tenth-generation polyallylcarbosilane dendrimer (G10(Si₄₀₉₃All₄₀₉₆)). The reaction of Mg (4.99 g, 0.205 mol), G10(Si₄₀₉₃Cl₄₀₉₆) (9.56 g, 0.02 mmol), and allyl chloride (13.65 g, 0.18 mol) in a mixture of 31 mL of THF and 26 mL of toluene was carried out under conditions similar to those used to prepare G6(Si₂₅₃All₂₅₆). The reaction mixture was stirred at reflux for 70 h. The reaction was monitored using the data of functional analysis for chloride ions (negative test). Evacuation (1 Torr) at 50 °C gave 9.3 g (93%) of the product G10(Si₄₀₉₃All₄₀₉₆). The content of the major compound in the crude material was 24%. Si₄₀₉₃C₂₈₆₅₆H₅₇₃₀₈. Mol. weight (calc.) 516909.68. ¹H NMR (CDCl₃), δ : 5.74 (m, 4096 H, CH₂=CH—CH₂—Si); 4.86 (m, 8192 H, CH₂=CH—CH₂—Si); 1.55 (d, 8192 H, CH₂=CH—CH₂—Si); 1.3 (m, 8184 H, Si—CH₂—CH₂—CH₂—Si); 0.54 (m, 16368 H, —CH₂—Si—CH₂—); -0.03 (s, 6132 H, —CH₂—Si(CH₃)CH₂—CH₂—CH₂—Si); -0.07 (s, 6144 H, Si(CH₃)—CH₂—CH=CH₂).

Eleventh-generation polychlorocarbosilane dendrimer (G11(Si₈₁₈₉Cl₈₁₉₂)). The reaction of G10(Si₄₀₉₃All₄₀₉₆) (3.5 g, 0.007 mmol) and dichloromethylsilane (4.78 g, 0.04 mol) in the presence of a solution of the platinum catalyst (0.006 mL) was carried out in toluene (4.5 mL) under conditions similar to those used to prepare G6(Si₂₅₃Cl₂₅₆). The reaction mixture was stirred for 60 h at room temperature. Completion of the reaction was defined as disappearance of the proton signals of the allyl group, δ 4.86 (CH₂=CH—CH₂—Si) and δ 5.74 (CH₂=CH—CH₂—Si), from the ¹H NMR spectra.

Third-generation polybutylcarbosilane dendrimer (G3(Si₂₉Bu₃₂)). G3(Si₂₉Cl₃₂) (10.39 g, 2.93 mmol) in 40 mL of hexane was added dropwise with stirring to a solution of BuLi in hexane (240 mL) with a BuLi concentration of 0.713 mol L⁻¹. Then 50 mL of THF was added. The reaction mixture was stirred at reflux for 20 h. Excess BuLi was quenched with ethanol. The reaction mixture was washed with distilled water to neutral wash water and dried with anhydrous Na₂SO₄. Evaporation of the solvents and evacuation of the residue (1 Torr) at 60 °C gave 8.4 g (67.7%) of the target product. The content of the major compound in the crude material was 85%. Found (%): C, 68.31; H, 12.71; Si, 18.98. Si₂₉C₂₄₀H₅₄₀. Calculated (%): C, 67.96; H, 12.83; Si, 19.20. d_4^{25} 0.8767 g cm⁻³, $[\eta]^{25}$ 0.036 dl g⁻¹. Mol. weight (calc.) 4241.45. ¹H NMR (CDCl₃), δ : 1.3 (m, 184 H, Si—CH₂—CH₂—CH₂—Si, —Si—CH₂—CH₂—CH₂—CH₃); 0.86 (m, 96 H, —CH₂—CH₃); 0.54 (m, 176 H, —CH₂—Si—CH₂—, —Si—CH₂—CH₂—CH₂—CH₃); -0.05 (s, 84 H, Si—CH₃).

Fourth-generation polybutylcarbosilane dendrimer (G4(Si₆₁Bu₆₄)). The reaction of a solution of BuLi in hexane (220 mL) (BuLi concentration, 0.713 mol L⁻¹) with G4(Si₆₁Cl₆₄) (9.94 g, 1.34 mmol) in 40 mL of hexane was carried out under conditions similar to those used to prepare dendrimer G3(Si₂₉Bu₃₂) to give 7.18 g (60.84%) of the target product G4(Si₆₁Bu₆₄). The content of the major compound in the crude material was 68%. Found (%): C, 67.81; H, 12.69; Si, 19.32. Si₆₁C₄₉₆H₁₁₁₆. Calculated (%): C, 67.73; H, 12.79; Si, 19.48. $[\eta]^{25}$ 0.04 dL g⁻¹. Mol. weight (calc.) 8795.63. ¹H NMR (CDCl₃), δ : 1.3 (m, 376 H, Si—CH₂—CH₂—CH₂—Si, —Si—CH₂—CH₂—CH₂—CH₃); 0.86 (m, 192 H, —CH₂—CH₃); 0.54 (m, 368 H, —CH₂—Si—CH₂—, —Si—CH₂—CH₂—CH₂—CH₃); -0.05 (s, 180 H, Si—CH₃).

Fifth-generation polybutylcarbosilane dendrimer (G5(Si₁₂₅Bu₁₂₈)). The reaction of a solution of BuLi in hexane

(210 mL) (BuLi concentration, 0.713 mol L^{-1}) with G5(Si₁₂₅Cl₁₂₈) (9.74 g, 0.64 mmol) in 40 mL of hexane was carried out under conditions similar to those used to prepare dendrimer G3(Si₂₉Bu₃₂) to give 10.2 g (88.5%) of the target product G5(Si₁₂₅Bu₁₂₈). The content of the major compound in the crude material was 66%. Found (%): C, 67.76; H, 12.65; Si, 19.49. Si₁₂₅C₁₀₀₈H₂₂₆₈. Calculated (%): C, 67.62; H, 12.77; Si, 19.61. d_4^{25} 0.8877 g cm⁻³. $[\eta]^{25}$ 0.042 dl g⁻¹. Mol. weight (calc.) 17903.98. ¹H NMR (CDCl₃), δ : 1.3 (m, 760 H, Si-CH₂-CH₂-CH₂-Si, -Si-CH₂-CH₂-CH₂-CH₃); 0.86 (m, 384 H, -CH₂-CH₃); 0.54 (m, 752 H, -CH₂-Si-CH₂-, -Si-CH₂-CH₂-CH₂-CH₃); -0.05 (s, 372 H, Si-CH₃).

Sixth-generation polybutylcarbosilane dendrimer (G6(Si₂₅₃Bu₂₅₆)). The reaction of a solution of BuLi in hexane (220 mL) (BuLi concentration, 0.713 mol L^{-1}) with G6(Si₂₅₃Cl₂₅₆) (9.64 g, 0.315 mmol) in 40 mL of hexane was carried out under conditions similar to those used to prepare dendrimer G3(Si₂₉Bu₃₂) to give 7.8 g (68.54%) of the target product G6(Si₂₅₃Bu₂₅₆). The content of the major compound in the crude material was 60%. Found (%): C, 67.66; H, 12.60; Si, 19.47. Si₂₅₃C₂₀₃₂H₄₅₇₂. Calculated (%): C, 67.57; H, 12.76; Si, 19.67. $[\eta]^{25}$ 0.036 dl g⁻¹. Mol. weight (calc.) 36120.686. ¹H NMR (CDCl₃), δ : 1.3 (m, 1528 H, Si-CH₂-CH₂-CH₂-Si, -Si-CH₂-CH₂-CH₂-CH₂-CH₃); 0.86 (m, 768 H, -CH₂-CH₃); 0.54 (m, 1520 H, -CH₂-Si-CH₂-, -Si-CH₂-CH₂-CH₂-CH₃); -0.05 (s, 756 H, Si-CH₃).

Seventh-generation polybutylcarbosilane dendrimer (G7(Si₅₀₉Bu₅₁₂)). The reaction of a solution of BuLi in hexane (495 mL) (BuLi concentration, 0.758 mol L^{-1}) with G7(Si₅₀₉Cl₅₁₂) (26.34 g, 0.43 mmol) in 80 mL of hexane was carried out under conditions similar to those used to prepare dendrimer G3(Si₂₉Bu₃₂) to give 29.6 g (95.2%) of the target G7(Si₅₀₉Bu₅₁₂). The content of the major compound in the crude material was 47%. Found (%): C, 67.63; H, 12.59; Si, 19.52. Si₅₀₉C₄₀₈₀H₉₁₈₀. Calculated (%): C, 67.54; H, 12.75; Si, 19.70. d_4^{25} 0.8734 g cm⁻³, $[\eta]^{25}$ 0.046 dl g⁻¹. Mol. weight (calc.) 72554.09. ¹H NMR (CDCl₃), δ : 1.3 (m, 3064 H, Si-CH₂-CH₂-CH₂-Si, -Si-CH₂-CH₂-CH₂-CH₂-CH₃); 0.86 (m, 1536 H, -CH₂-CH₃); 0.54 (m, 3056 H, -CH₂-Si-CH₂-, -Si-CH₂-CH₂-CH₂-CH₃); -0.05 (s, 1524 H, Si-CH₃).

Eighth-generation polybutylcarbosilane dendrimer (G8(Si₁₀₂₁Bu₁₀₂₄)). The reaction of a solution of BuLi in hexane (254 mL) (BuLi concentration, 0.753 mol L^{-1}) with G8(Si₁₀₂₁Cl₁₀₂₄) (13.71 g, 0.11 mmol) in 45 mL of hexane was carried out under conditions similar to those used to prepare the dendrimer G3(Si₂₉Bu₃₂) to give 16.03 g (91.1%) of the target product G8(Si₁₀₂₁Bu₁₀₂₄). The content of the major compound in the crude material was 30%. Found (%): C, 67.61; H, 12.55; Si, 19.44. Si₁₀₂₁C₈₁₇₆H₁₈₃₉₆. Calculated (%): C, 67.53; H, 12.75; Si, 19.72. $[\eta]^{25}$ 0.038 dl g⁻¹. Mol. weight (calc.) 145420.9. ¹H NMR (CDCl₃), δ : 1.30 (m, 6136 H, Si-CH₂-CH₂-CH₂-Si, -Si-CH₂-CH₂-CH₂-CH₂-CH₃); 0.54 (m, 6128 H, -CH₂-Si-CH₂-, -Si-CH₂-CH₂-CH₂-CH₃); -0.05 (s, 3060 H, Si-CH₃); 0.86 (m, 3072 H, -CH₂-CH₃).

Ninth-generation polybutylcarbosilane dendrimer (G9(Si₂₀₄₅Bu₂₀₄₈)). The reaction of a solution of BuLi in hexane (610 mL) (BuLi concentration, 0.956 mol L^{-1}) with G9(Si₂₀₄₅Cl₂₀₄₈) (25 g, 0.101 mmol) in 80 mL of hexane was carried out under conditions similar to those used to prepare the

dendrimer G3(Si₂₉Bu₃₂) to give 27.5 g (93.86%) of the target product G9(Si₂₀₄₅Bu₂₀₄₈). The content of the major compound in the crude material was 27%. Found (%): C, 67.61; H, 12.50; Si, 19.39. Si₂₀₄₅C₁₆₃₆₈H₃₆₈₂₈. Calculated (%): C, 67.52; H, 12.75; Si, 19.73. d_4^{25} 0.8838 g cm⁻³, $[\eta]^{25}$ 0.043 dl g⁻¹. Mol. weight 291154.53 (calc.); 295600 (determined by static light scattering in heptane). ¹H NMR (CDCl₃), δ : 1.3 (m, 12280 H, Si-CH₂-CH₂-CH₂-Si, -Si-CH₂-CH₂-CH₂-CH₂-CH₃); 0.54 (m, 12272 H, -CH₂-Si-CH₂-, -Si-CH₂-CH₂-CH₂-CH₃); -0.05 (s, 6132 H, Si-CH₃); 0.86 (m, 6144 H, -CH₂-CH₃).

Tenth-generation polybutylcarbosilane dendrimer (G10(Si₄₀₉₃Bu₄₀₉₆)). The reaction of a solution of BuLi in hexane (316 mL) (BuLi concentration, 0.753 mol L^{-1}) with G10(Si₄₀₉₃Cl₄₀₉₆) (9.56 g, 0.019 mmol) in 40 mL of toluene was carried out under conditions similar to those used to prepare the dendrimer G3(Si₂₉Bu₃₂) to give 10.8 g (95.83%) of the target product G10(Si₄₀₉₃Bu₄₀₉₆). The content of the major compound in the crude material was 22%. Found (%): C, 67.67; H, 12.46; Si, 19.49. Si₄₀₉₃C₃₂₇₅₂H₇₃₆₉₂. Calculated (%): C, 67.52; H, 12.75; Si, 19.73. Mol. weight (calc.) 582621.79. ¹H NMR (CDCl₃), δ : 1.3 (m, 24568 H, Si-CH₂-CH₂-CH₂-Si, -Si-CH₂-CH₂-CH₂-CH₃); 0.86 (m, 12288 H, -CH₂-CH₃); 0.54 (m, 24560 H, -CH₂-Si-CH₂-, -Si-CH₂-CH₂-CH₂-CH₃); -0.05 (s, 12276 H, Si-CH₃).

Eleventh-generation polybutylcarbosilane dendrimer (G11(Si₈₁₈₉Bu₈₁₉₂)). The reaction of a solution of BuLi in hexane (140 mL) (BuLi concentration, 0.729 mol L^{-1}) with G11(Si₈₁₈₉Cl₈₁₉₂) 6.69 g (0.007 mmol) in 30 mL of toluene was carried out under conditions similar to those used to prepare the dendrimer G3(Si₂₉Bu₃₂) to give 6.46 g (81.87%) of the target product G11(Si₈₁₈₉Bu₈₁₉₂). The content of the major compound in the crude material was 17%. Si₈₁₈₉C₆₅₅₂₀H₁₄₇₄₂₀. Calculated (%): C, 67.52; H, 12.75; Si, 19.73. Mol. weight (calc.) 1165556.3. ¹H NMR (CDCl₃), δ : 1.3 (m, 49144 H, Si-CH₂-CH₂-CH₂-Si, -Si-CH₂-CH₂-CH₂-CH₂-CH₃); 0.86 (m, 24576 H, -CH₂-CH₃); 0.54 (m, 49136 H, -CH₂-Si-CH₂-, -Si-CH₂-CH₂-CH₂-CH₃); -0.05 (s, 24564 H, Si-CH₃).

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