Multiarm star-like polydimethylsiloxanes based on dendrimers of the sixth generation

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A series of star-like 128-arm polydimethylsiloxanes was synthesized by the anionic polymerization of hexamethylcyclotrisiloxane using the polylithium initiator, which was obtained from the carbosilane dendrimer of the sixth generation. The measured values of molecular weights and intrinsic viscosity made it possible to characterize the samples prepared as dense globular macromolecules. The behavior of the synthesized multiarm stars at the water—air interface was studied, and the cross-section surface areas of the macromolecules were calculated. A comparison of the obtained sizes with the calculated values suggests some deformation of the dendrite core due to the interaction of the arms with the water surface.

Key words: carbosilane dendrimers, intrinsic viscosity, Langmuir method.

Synthesis and investigation of the properties of nanosized structurally ordered macromolecules is an urgent area of modern chemistry. Studies of star-like polymer forms have been intensified during recent decade. Such polymers characterized by the presence of several linear oligomeric arms connected with one end on the branching center have several specific features compared to linear analogs with the same molecular weight. Polymer stars having three to four arms connected on one center were synthesized and studied rather long ago. At the early stages of studying these polymers, mainly decreased viscosities of melts and solutions compared to linear analogs of the molecular weight attracted attention of researchers. This property allowed their use as the corresponding additives. In addition, they are better processed and useful in composition of coatings to improve a combination of hardness and flexibility characteristics. The study[1] of the rheological properties explained these specific features by the fact that the relaxation time of polymer chains fixed by one end was considerably longer than that of analogous linear polymers. An increase in the number of arms (f) in a star-like structure noticeably changed the behavior of the macromolecule and, beginning from some value of f, the properties changed qualitatively: the transition to so-called "multiarm" structures characterized by high density of units in the branching center was observed. Star-like polymers with the number of arms $f \leq 32$ behave as classical liquids at all concentrations in solutions, whereas with the further increase in the number of arms the behavior of multiarm polymers differs entirely from that of normal liquids and approaches the behavior of solid spheres.[2] In this case, coefficient α in the Mark—Kuhn—Houwink equation[3] changes from 0.6—0.7 corresponding to the ball-like conformation of the polymer to 0.15—0.06, which characterizes polymers as rigid spherical objects.

Thus, there is some critical number of arms and, correspondingly, some density of the structure, at which the properties "jump" from classical polymeric properties. We earlier[4] synthesized a series of star-like polydimethylsiloxanes (PDMS) with 12, 14, 16, and 48 arms. It was shown that already in this range an increase in the number of arms of the star-like macromolecule results in qualitative changes in its properties. The 12—16-arm macromolecules behaved as classical branched polymers, while an increase in the number of arms to 48 changed the organization of the star in solution: the star transformed into a globular object with the whole corresponding complex of properties.[5]

Based on the Daoud—Cotton model[6] assuming three regions of a multiarm star-like polymer structure (the first region is the dense central core; in the second region the density and behavior of the polymer arms are similar to those in a half-dilute solution; and the third region is an external layer in which the polymer chains of the arms take free conformations), one may suggest that an increase in the number of arms results in the predomination of the first and second regions and the corresponding change in the properties of the macromolecule. In the case of the 48-arm polydimethylsiloxane stars, a global structure was observed only in solution. It could be assumed that the further increase in the number of arms should result in qualitative changes in the properties of the macromolecule in block as well. This consecutive change in the properties of the macromolecule, namely, first in

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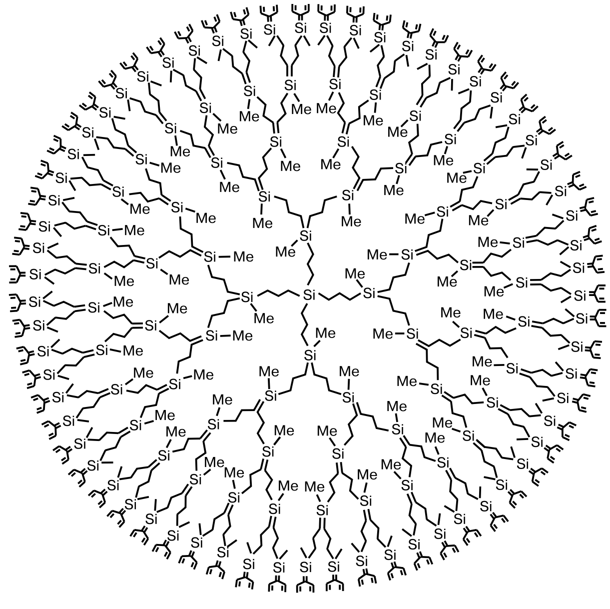
solution and then with further compacting in block, was observed for the carbosilane dendrimers. These molecular nanoobjects behave in solution as specific globular macromolecules already at low generations. A specific effect of structure compacting, which changes the properties of the substance in block, manifests itself on going to higher generations: the second relaxation transition appears in the DSC curves, implying the formation of a physical network.[7] In the case of star-like macromolecules, to manifest the transition of quantitative changes to qualitative ones, it was necessary to obtain such nanoobjected with a higher number of arms. There are many works on the synthesis and study of multiarm macromolecules; however, the number of real compounds with a high and known number of arms of controlled lengths is considerably lower, while there are no such compounds in the chemistry of organosilicon polymers. Thus, real models are needed to evaluate the theoretical model and to check the general tendency for macromolecular nanoobjects, which is the qualitative change in the properties with compacting of the molecular structure. Therefore, the purpose of this work was the synthesis of a series of multiarm polydimethylsiloxane stars with $f > 100$ and different lengths of the arms and the study of their properties.

Results and Discussion

Synthesis of 128-arm PDMS based on the carbosilane dendrimer derivative of the sixth generation. The methodical approach to the synthesis of multiarm polydimethylsiloxane systems by the anionic polymerization of hexamethylcyclotrisiloxane (HMCTS) using the dendrite polylithium initiator was developed earlier.[4,5] However, the studies were restricted by 48-arm objects, and dendrimers of higher generations were unavailable. Presently, the development of methods for synthesis of functional dendrimers of higher generations makes it possible to obtain systems with a considerably greater number of arms using the same approaches. The 128-arm polydimethylsiloxane macromolecule was synthesized from the carbosilane dendrimer of the sixth generation.

As it was shown, the possibility of synthesis of an efficient polylithium initiator on the matrix of a dendrite structure is due to the arrangement of lithium atoms in the internal sphere of the carbosilane dendrimer, which prevents their intermolecular aggregation, which is well-known for the carbon—lithium active centers[8] and prevents the formation of soluble polylithium compounds. In this case, the external layer of the dendrimer formed by didodecyl(methyl)silyl groups shields the lithium atoms and prevents their contacts. Thus obtained compound corresponds to all requirements imposed on anionic initiators: an individual character of the polymer support and, correspondingly, the known number of functional groups, as well as their equal activity and high solubility in organic solvents. An increase in the generation of the starting dendrimer over those used in earlier studies did not violate the course of the processes.

The initiator was synthesized from the carbosilane dendrimer of the sixth generation with terminal diallylmethylsilyl groups (**1**).



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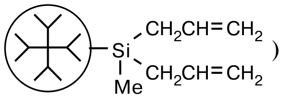
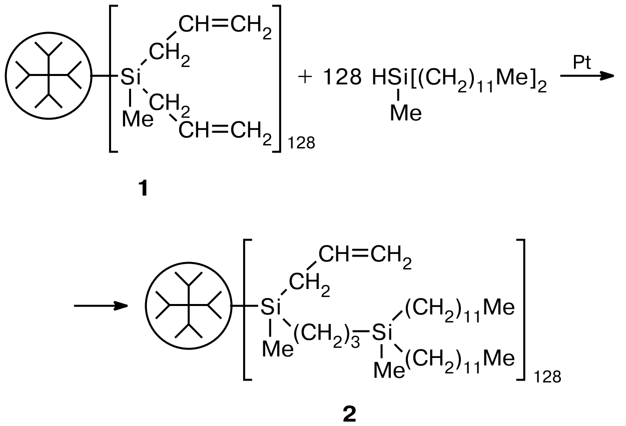
(hereinafter )

The transformation of the external layer of dendrimer **1** by hydrosilylation with didodecyl(methyl)silane gave compound **2** with the shielding hydrocarbon layer and allyl groups in the internal sphere (Scheme 1).

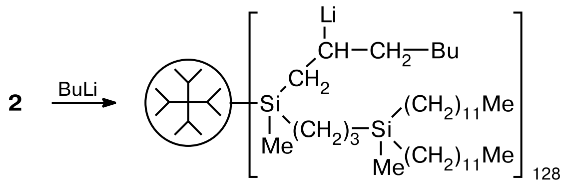
Scheme 1



The amount of didodecyl(methyl)silane necessary for the substitution of 50% allyl groups of the external layer of dendrimer **1** was introduced in the reaction. The selectivity of substitution of each second allyl group on the silicon atom was observed earlier.[5] According to the GPC data, the reaction proceeded without changing the molecular mass distribution (MMD) of the product. The ^{1}H NMR spectroscopy (Fig. 1) showed that the structure of the compound corresponding to that of **2**.

The synthesis of polylithium derivative **3** followed Scheme 2.

Scheme 2



3

The GPC analysis of compound **3** after its neutralization with trimethylchlorosilane showed the complete retention of the MMD of the dendrimer: the signals in the ^{1}H NMR spectrum corresponds to structure **3**.

Thus, we synthesized the multicenter monodisperse initiator containing 128 lithium atoms in the internal sphere of the dendrimer and possessing high solubility in organic solvents, which indicates the absence of intermolecular aggregation at the lithium—carbon centers.

Polydimethylsiloxane multiarm stars **M1**—**M4** were synthesized (Scheme 3) by the anionic polymerization of hexamethylcyclotrisiloxane **4** using the synthesized polylithium derivative of polycarbosilane dendrimer of the sixth generation (compound **3**) by the known two-stage procedure with separation of the initiation stage in the absence of a solvating agent (THF) and the growth stage after addition of the latter.[9]

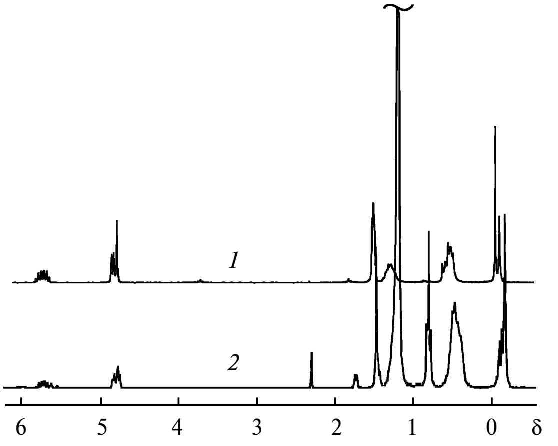
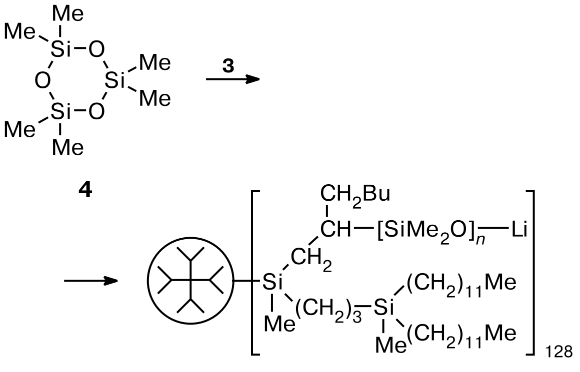


Fig. 1. ^{1}H NMR spectra of the starting dendrimer **1** (*1*) and its didodecyl(methyl)silyl derivative **2** (*2*).

Scheme 3



4

M1—M4

The terminal lithium groups shift from the shielding layer as the siloxane arms grow, and then nothing prevents their aggregation. Under certain polymerization conditions, this process results in the formation of dense gel, being a physical network of the polymer with nodes formed by aggregates of the lithium atoms. A similar effect was observed[4] for the synthesis of less dense star-like PDMS. The assertion that the network is of physical, *i.e.*, reversible, nature follows from the fact of its complete decomposition when the lithium ends are blocked with organochlorosilanes. Naturally, aggregation ceases the polymerization process, *i.e.*, to obtain high molecular weights, it is necessary to find conditions for preventing aggregation or at least its retardation. It was found that an increase in the THF (which solvates the lithium active centers) concentration in the reaction mixture increased the monomer conversion up to the moment of gel formation.

Molecular weights of polymers. The GPC analysis of stars **M1**—**M4** synthesized under optimal conditions was carried out after the terminal active ends were blocked with trimethylchlorosilane and showed the retention of monomodality and a narrow molecular mass distribution M_w/M_n from 1.1 to 1.2 (Table 1; Fig. 2, curves *2*—*4*). The formation of a minor amount of high-molecular-weight admixtures was observed only at high conversions, most probably, due to the chain transfer process (see Fig. 2, curve *5*).

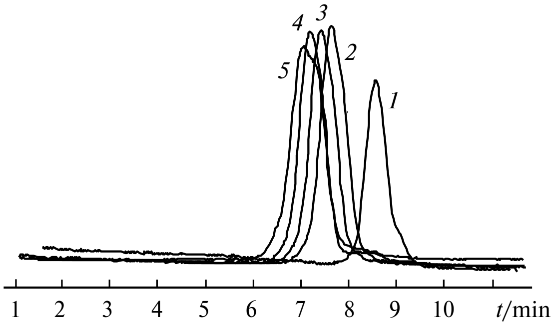


Fig. 2. GPC curves for the starting dendrimer **1** (*1*) and star-like PDMS **M1** (*2*), **M2** (*3*), **M3** (*4*), and **M4** (*5*).

It is well known that the determination of the real molecular mass (MM) of a highly branched macromolecule is a particular problem. Evidently, the MM of a multiarm macromolecule determined by GPC (MM_{GPC}) using linear standards is far from the real value. In our case, as well as in the case of the earlier synthesized PDMS stars with a less number of arms, the true molecular mass of multiarm stars could be calculated by the data of ^{1}H NMR spectroscopy (MM_{NMR}) due to specific features of the structure of dendrite center. In the surface layer of the dendrimer, each silicon atom has one didodecyl(methyl)silyl suibstituent and one linear dimethylsiloxane chain. Therefore, protons of the CH_2 groups of the dodecyl radicals can be used as an independent internal standard in analysis of the structure of the synthesized multiarm PDMS star by ^{1}H NMR spectroscopy (Fig. 3). The arm length (N_{unit}) can be calculated by the ratio of the number of protons to the number of protons of the MeSi groups of the arm. The signal of the protons of the dodecyl groups more than 20 times exceeds the background noise, which provides a sufficient accuracy of integration. Since the number of lithium atoms in the dendrimer initiator and, correspondingly, the number of arms of the PDMS star are known, the total real MM of the macromolecule can be calculated. Using this procedure, it was shown that the best results with the MMD from 1.1 to 1.2 were obtained in a 30% solution of hexane with addition of 20% THF. Under these conditions, 128-arm PDMS **M1—M4** with MM up to ~10^6 (^{1}H NMR spectroscopy data) were obtained corresponding to the arm length about 100 units (see Table 1). Table 1 also contains the data on the molecular weight of the arm of star-like PDMS **M1—M4**. The dendrimer core is rather compact, and its size is constant for the same generation. Thus, the molecular weight of the side arm was calculated as follows:

$$MM_{unit} = (MM_{NMR} - MM_{dendr})/f,$$

where the molecular weight of the dendrimer core (MM_{dendr}) and f were calculated from the chemical structure of the macromolecule.

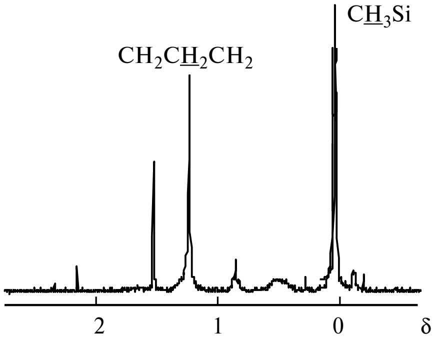


Fig. 3. ^{1}H NMR spectrum of 128-arm PDMS.

During polymerization, the true MM of the star (MM_{NMR}) increases and MM_{GPC} of the star, *i.e.*, its hydrodynamic radius, increases insignificantly (Fig. 4).

Behavior in solution. The difference observed between MM_{GPC} and MM_{NMR}, as well as the anomalously low viscosity of the star-like polymer compared to the linear analog with the same molecular weight, is a consequence of the dense structure of the multiarm star, and difference increases with an increase in the molecular weight of macromolecules (Fig. 5). It should be mentioned that this property is characteristic of really multiarm stars only. A similar dependence for the 16-arm star is presented in Fig. 5 for comparison and shows its lower viscosity, as well as for any branched polymer, compared to the linear analog. However, the general tendency of increasing viscosity with an increase in the MM is completely manifested in this case as well.

The branching factor g' equal to the ratio of any characteristic parameters of a star-like macromolecule and its linear analog with the same molecular weight is used for the quantitative description of the influence of the star-like polymer structure on its behavior in solution.[10] We used the ratio of intrinsic viscosities $g' = [\eta]_{star}/[\eta]_{lin}$. As can be seen from Fig. 6, factor g' increases with an increase in the molecular weight of stars in the case of 12- and 16-arm dimethylsiloxane star-like macromolecules.[11] The qualitative change in the behavior of macromolecules in solution occurs only with a con-

Table 1. Synthesis and the main characteristics of 128-arm star-like PDMS **M1—M4**

Sample	Time/h	Conversion (%)	Macromolecule			Arm	
			MM_{GPC}	MM_{NMR}	M_w/M_n	MM_{arm}	N_{unit}
M1	4	35	47700	394200	1.11	2390	32
M2	9	59	78700	595423	1.15	3962	54
M3	14	88	96300	753665	1.18	5199	70
M4	19	99	121200	931950	1.23	6592	89

Note. MM_{GPC} and MM_{NMR} are the molecular weights of macromolecules determined by GPC and ^{1}H NMR, respectively; MM_{arm} is the calculated molecular weight of an arm of a star-like macromolecule; and N_{unit} is the number of units in one arm.

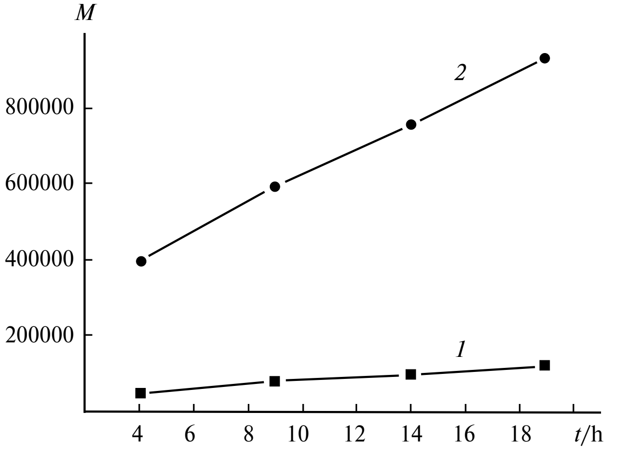


Fig. 4. Changes in the MM_{GPS} (*1*) and MM_{NMR} (*2*) of star-like PDMS during polymerization.

siderable increase in the number of arms; *i.e.*, a loose ball-like macromolecule is transformed into a dense globular structure.

Investigation of the behavior of the synthesized polymers at the water—air interface. Among most important problems of investigation of the properties of multiarm PDMS stars is the study of the processes of organization of these objects on surface of different nature. Interest in these processes is due to two main factors. The first factor is the well known surface activity of classical PDMS, providing the possibility to form monolayers at the water—air interface in addition to other potentialities. The second factor is related to the shape of macromolecules of multiarm stars: it should be revealed whether this form of organization of the molecular structure affects specific features of self-organization processes of macromolecules in the monolayer. The results of studies of specific features of organization of the multiarm PDMS stars by the Langmuir method in monolayers at the water—air interface are presented below. This method makes it possible to determine the sizes (cross-section surface areas) of the macromolecule and to estimate the contribution of its parts to the interaction with the subphase surface.

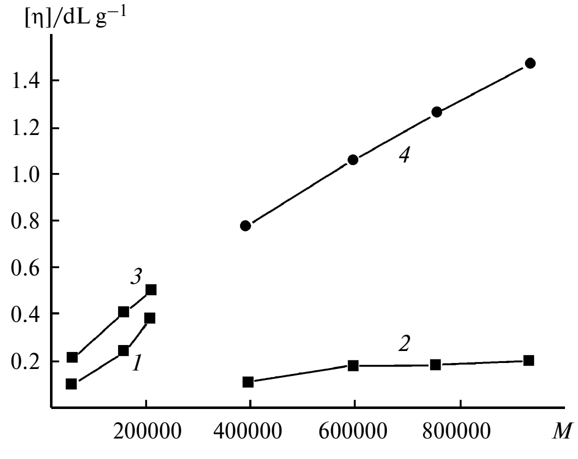


Fig. 5. Intrinsic viscosity [η] of star-like PDMS with 16 (*1*) and 128 arms (*2*) and their linear analogs (*3*, *4*) *vs* molecular weight.

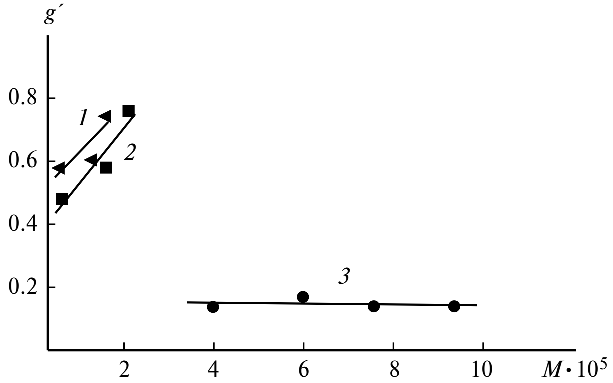


Fig. 6. Branching factor (*g*′) *vs* molecular weight of star-like PDMS with 12 (*1*), 16 (*2*), and 128 arms (*3*).

All studied compounds spread over the water surface to form the Langmuir monolayer. The compression of the monolayer gives the two-step surface pressure isotherm, whose shape is similar to that observed for polydimethylsiloxane.[12,13] In spite of many works devoted to the study of the surface properties of linear PDMS, up to presently there is no single opinion about the nature of the second step of surface pressure in the isotherm. According to the classical point of view,[14,15] the conformational transition ball—helix occurs in PDMS in the region of the first plateau. Thus, at the end of the first plateau the whole surface is covered with PDMS macromolecules in the helical conformation, and the helices begin to detach from the water surface in the region of the second step of surface pressure. However, the data obtained in the later studies[16] prejudice the possibility of this mechanism to occur and suggest the possibility of formation of a PDMS bilayer. The presence of the distinct second jump of surface pressure in the isotherms of all star-like polydimethylsiloxanes studied in this work shows that the terminal PDMS chains are in good contact with the surface of the aqueous subphase and behave independently of the central core of the macromolecule even in the case of the shortest side branches with the length of 32 units (**M1**).

The surface pressure isotherm of star-like PDMS with the longest arms **M4** (see Table 1) is shown in Fig. 7. The compressed sample is decompressed almost without hysteresis. Linear PDMS is also characterized by a similar behavior, which indicates that no stable structures are formed upon the compression of the sample. The isotherm is reproduced after the repeated compression. The behavior of other dendrimers studied in the compression—expansion cycles is analogous.

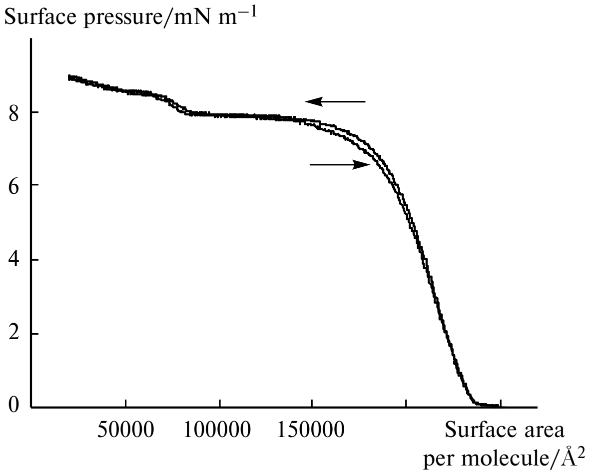


Fig. 7. Surface pressure isotherm of star-like PDMS **M4**.

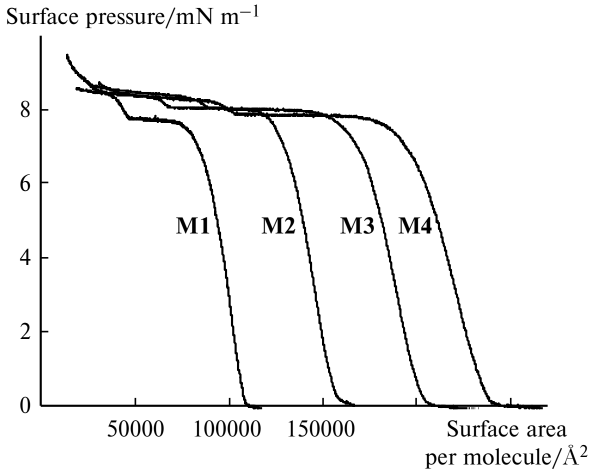


Fig. 8. Surface pressure isotherms of star-like 128-arm PDMS **M1**—**M4**.

The characteristics of the isotherms of star-like 128-arm PDMS **M1**—**M4** are given below.

Sample	A_{star}	A_{unit}	Sample	A_{star}	A_{unit}
	Å			Å	
M1	97 500	23.6	**M3**	186 300	20.7
M2	142 900	20.9	**M4**	217 000	19.0

A_{star} is the surface area per macromolecule in the dense monolayer (surface area in the region of the inflection point of the first step in the surface pressure isotherm); and A_{unit} is the surface area per dimethylsiloxane unit of side arms in the monolayer.

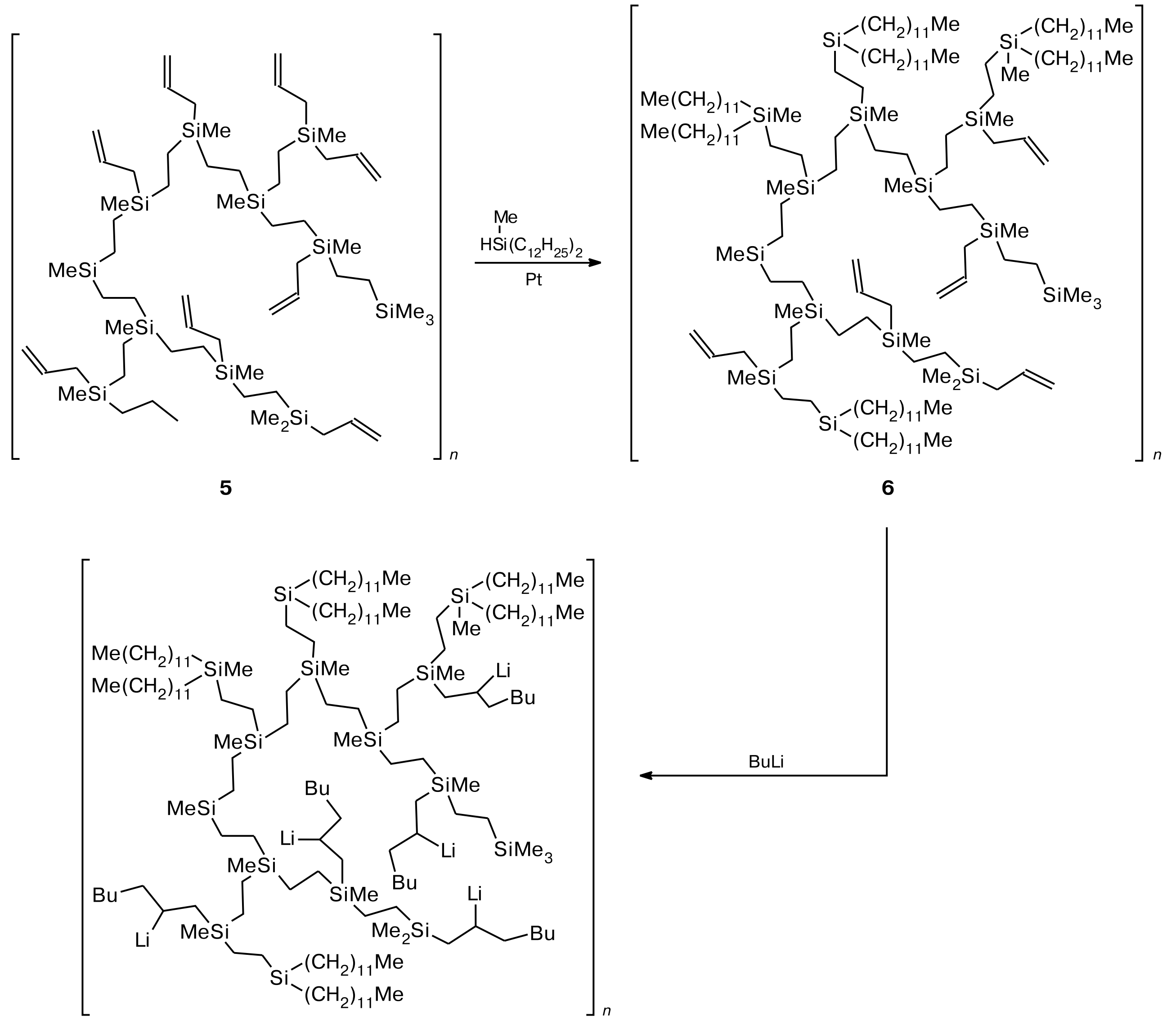
The obtained values of surface area per dimethylsiloxane (DMS) unit (A_{unit}) are slightly overestimated, because the surface area of the dendrimer core on the subphase surface was ignored in the calculations. This surface area is unknown; however, based on the published data,[17] it can be estimated approximately as <1000 Å^2 for a dendrimer of the third generation and as ~3000 Å^2 for dendrimers of the sixth generation.

The surface pressure isotherms of studied star-like 128-arm PDMS **M1**—**M4** are shown in Fig. 8. The surface area per molecule in the monolayer in the series **M1**—**M4** increases as the molecular weight of the corresponding star increases. The surface area per DMS unit in the monolayer for macromolecule **M1** is 23.6 Å^2. As the side chain elongates, the surface area decreases and gradually reaches the values characteristic of pure PDMS (18—20 Å^2). Probably, this is due to the presence of bulky didodecyl(methyl)silyl side groups in the macromolecule composition. In spite of hydrophobicity, they should occupy some place in the bulky dendrimer structure due to a considerable volume, but their contribution to the total surface area of the macromolecule becomes insignificant with the elongation of the side arms of PDMS.

The data obtained on the surface area occupied by a star-like macromolecule on the surface turned out unexpectedly high. If starting from the simplified concepts and considering a carbosilane dendrimer (core of a multiarm star) as rather dense spherical particle, it should be expected that some DMS units would be incapable of reaching the subphase surface. This should be expressed as a smaller value of the averaged surface area per DMS unit of the side chain of the star in the Langmuir monolayer compared to the surface area of the undisturbed unit of linear PDMS. However, the data obtained by us for the surface area occupied by a dendrimer molecule on the surface of the liquid subphase show that this is not true: in most cases, the DMS units of the side chains interact with the surface of the liquid and occupy place on it. This fact suggests that the dendrimer core on the subphase surface is flattened. The assumption does not contradict the common concepts on the conformational flexibility of the molecular structure of the carbosilane core. However, it should be taken into account that this phenomenon was not observed for the same core but with hydroxyl functions, having considerably higher affinity to water. Thus, long siloxane arms exert much more significant effect on the core than hydroxyl ends.

Synthesis of star-like PDMS based on hyperbranched polyallylcarbosilane. The possibility of using the above discussed approach for the synthesis of soluble polylithium compound was also accomplished on the basis of hyperbranched polyallylcarbosilane (Scheme 4). Unlike dendrimers, such compounds are not core—shell systems, and the possibility to create a shielding layer did not seem evident because of the random distribution of functional groups over the molecular structure. Grafting of didodecyl(methyl)silyl groups to 50% unsaturated substituents did not warrant the formation of an external layer capable of preventing aggregation of carbon—lithium centers during subsequent stages. However, the exhaustive lithiation of the remained allyl groups of compound **6** afforded solu-

Схема 4



ble product **7**. According to the data of ^{1}H NMR spectroscopy of the polymer after it was treated with trimethylchlorosilane, the number of trimethylsilyl groups corresponding to the amount of lithium centers introduced was well consistent with the calculated data.

Thus, in spite of the irregular and less dense structure of the starting polymer matrix, the soluble polylithium initiator based on hyperbranched polyallylcarbosilane can also be obtained. The chemical composition of the polylithium initiator based on hyperbranched polyallylcarbosilane (**7**) is identical to that of regular analog **3** and, hence, it is an important object of comparison for regular PDMS stars. The further study of these polylithium derivatives would allow one to evaluate distinctions in reactivity of carbon—lithium centers differed by their position in the structure of the multicenter initiator. Star-like PDMS were synthesized from obtained macroinitiator **7** using the standard procedure (see Experimental). The properties of these PDMS will be studied elsewhere.

In the present work, we synthesized for the first time a series of 128-arm star-like PDMS with different molecular weights. The properties of the synthesized polymers were studied in solution and at the water—air interface by the capillary viscosimetry and Langmuir methods. The results of viscosimetric studies suggest the unusual behavior of macromolecules in solution, which manifests itself, in particular, as a low intrinsic viscosity. Using the developed methodology, we synthesized for the first time the polylithium initiator of polymerization from hyperbranched polyallylcarbosilane. Further, star-like PDMS were synthesized on the basis of this initiator. In future we are planning to study the thermal properties of the multiarm stars in block and compared them with those of classical linear analogs.

Experimental

Didodecyl(methyl)silane was synthesized by the known procedure.[7] Samples of carbosilane dendrimers of the sixth generation with allyl groups (M = 32013.7) were prepared at the N. S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences using the known procedure.[18] The Pt catalyst PC072 (Aldrich) was used. All reactions were carried out under argon.

^{1}H NMR spectra were recorded on a Bruker WR-250 (250.13 MHz) spectrometer in $CDCl_3$ using Me_4Si as an internal standard.

GPC analysis was carried out on a GPC liquid chromatograph (Czechoslovakia) in toluene or THF on LiChrosphere 100, LiChrosphere 300, Silasorb 600 (4×250 mm), Phenogel-75 KD, and Phenogel-500 KD columns (particle size 7.5 μm). The molecular weight was determined from the ratio to linear polystyrene standards. A RIDK-102 differential refractometer was used as a detector, a DAWN-F instrument with λ = 633 nm served as a detector for laser light scattering, and the sorbent was Phenogel with the pore size 10^4 Å and the grain size 10 μm.

The intrinsic viscosity was measured on an automated Ubbelohde viscosimeter (Schott ViscoSystem AVS 470) with a capillary diameter of 0.53 mm using toluene as a solvent. The accuracy of temperature maintenance was 0.1 °C. To determine the intrinsic viscosity, 2, 1.7, 1.5, 1.3, 1, and 0.5% working solutions were used. The measurements were carried out at 25 °C.

Surface pressure isotherms were obtained using a Teflon Langmuir bath (612D, Nima, England) 20×30 cm in size. The subphase was distilled water deionized on an Akvilon D-301 setup (specific resistance 18.2 MOhm cm^{-1}). The solvent was chloroform, the solution concentration was 1 mg mL^{-1}, the rate of barrier movement was 50 cm^2 min^{-1}, and the accuracy of surface pressure determination was 0.1 mN m^{-1}.

Didodecyl(methyl)silyl derivative of carbosilane dendrimer 2. The dry platinum catalyst PC072 (14 μL) was added to a mixture of carbosilane dendrimer of the sixth generation **1** (1.243 g, 0.00178 mol) and didodecyl(methyl)silane (2.731 g, 0.00713 mol) in anhydrous toluene (10 mL). The mixture was stirred for 42 h at 45 °C. GPC gave the monomodal distribution, M_n = 20 238 (PSS), and M_w/M_n = 1.03. ^{1}H NMR ($CDCl_3$), δ: –0.05 (m, 1123.44, CH_3Si); 0.55 (m, 1933.36, CH_2Si); 0.85 (m, 768, $CH_2C\underline{H}_3$); 1.31 (s, 5268.07, $CH_2CH_2CH_2$); 1.55 (s, 464.36, $CH_2CH_2CH_2$); 4.82 (m, 231.99, CH_2=); 5.75 (m, 147.70, CH=).

Lithium-functional derivative of carbosilane dendrimer 3. A 1.6 *M* solution of *n*-butyllithium in hexane (0.099 mL, 0.158 mmol) and tetramethylethylenediamine (0.025 mL, 0.158 mmol) were added to a solution of dendrimer **2** (0.1 g, 1.23 μmol) in toluene. The mixture was stirred for 42 h at 25 °C. The completeness of the reaction was determined by the disappearance of signals for the protons of allyl groups in the ^{1}H NMR spectra. ^{1}H NMR of the compound blocked with trimethylchlorosilane ($CDCl_3$), δ: –0.05 (m, 2147.70, CH_3Si); 0.55 (m, 1960.44, $-CH_2Si$); 0.85 (m, 1007.26, $CH_2C\underline{H}_3$); 1.31 (s, 5700.00, $CH_2CH_2CH_2$); 1.55 (s, 301.91, $CH_2CH_2CH_2$). GPC: monomodal distribution, M_n = 20 240 (PSS).

Didodecyl(methyl)silyl derivative of carbosilane hyperbranched polymer 5. The platinum catalyst PC072 (10 μL) was added to a mixture of hyperbranched polymer **5** (1.02 g, 0.11 mmol) and didodecyl(methyl)silane (1.8 g, 4.7 mmol) in anhydrous toluene (10 mL). The mixture was stirred for 24 h at 55 °C. ^{1}H NMR ($CDCl_3$), δ: –0.05 (m, 9.00, $C\underline{H}_3Si$); 0.52 (m, 14.86, CH_2Si); 0.80 (m, 5.55, $CH_2C\underline{H}_3$); 1.29 (s, 41.63, $CH_2CH_2CH_2$); 1.52 (s, 2.55, $CH_2CH_2CH_2$); 4.82 (m, 1.81, $C\underline{H}_2$=); 5.75 (m, 1.46, CH=).

Lithium-functional derivative of carbosilane hyperbranched polymer 7. A 1.6 *M* solution of *n*-butyllithium in hexane (0.268 mL, 0.43 mmol) and tetramethylethylenediamine (64 μL, 0.43 mmol) was added to a solution of compound **6** (0.254 g, 0.72 μmol) in hexane. The mixture was stirred for 62 h at 25 °C. ^{1}H NMR of the reaction product blocked with trimethylchlorosilane ($CDCl_3$), δ: –0.05 (m, 18.30, CH_3Si); 0.53 (m, 14.49, $-CH_2Si$); 0.82 (m, 9.00, $CH_2C\underline{H}_3$); 1.29 (s, 57.60, $CH_2CH_2CH_2$); 1.54 (s, 1.58, $CH_2CH_2CH_2$).

Synthesis of 128-arm PDMS M1—M4 (general procedure). A solution of polylithium initiator **3** (0.0012 mmol) in anhydrous hexane (1.5 mL) was added to a solution of HMCTC **4** (4.5 mmol) in anhydrous hexane (27.3 mL) at room temperature. The mixture was stirred for 1.5 h. Then anhydrous THF (10 mL) was added, and stirring was continued (the polymerization duration is indicated in Table 1). Polymerization was stopped by the addition of a trimethylchlorosilane excess followed by stirring for 2 h. The solution was diluted with hexane, washed with water to the neutral pH, and dried with Na_2SO_4. Volatile admixtures were removed *in vacuo*. The samples obtained were analyzed by GPC and ^{1}H NMR spectroscopy.

Synthesis of star-like PDMS based on hyperbranched polylithium initiator 7. A solution of polylithium derivative of hyperbranched polymer **7** (0.35 μmol) in anhydrous hexane (1.5 mL) was added to a solution of HMCTC **4** (13.5 mmol) in anhydrous hexane (22.5 mL). The mixture was stirred for 1.5 h. Then anhydrous THF (8 mL) was added, and the solution was stirred for 18 h. Polymerization was stopped by the addition of a trimethylchlorosilane excess, and the polymer obtained was isolated as described above.

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References

1. P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, 1979.
2. M. Watzlawek, H. Loven, C. N. Likos, *J. Phys. Condens. Matter*, 1998, **10**, 8189.
3. K. Ito, Y. Tomi, S. Kawaguchi, *Macromolecules*, 1992, **25**, 1534.
4. N. G. Vasilenko, E. V. Getmanova, V. D. Myakushev, E. A. Rebrov, M. Meller, A. M. Muzafarov, *Vysokomol. Soedin.*,

Ser. A, 1997, **39**, 1449 [*Polym. Sci.*, *Ser. A* (*Engl. Transl.*), 1997, **39**, 977].

5. N. G. Vasilenko, E. A. Rebrov, A. M. Muzafarov, B. Eschwein, B. Striegel, M. Moeller, *Macromol. Chem. Phys.*, 1998, **199**, 889.
6. M. Daoud, J. P. Cotton, *J. Phys.-Paris*, 1982, **43**, 531.
7. A. S. Tereshchenko, G. S. Tupitsina, E. A. Tatarinova, A. V. Bystrova, A. M. Muzafarov, N. N. Smirnova, A. V. Markin, *Vysokomol. Soedin.*, *Ser. B*, 2010, **52**, 132 [*Polym. Sci.*, *Ser. B* (*Engl. Transl.*), 2010, **52**, 41].
8. J. Stellbrink, L. Willner, O. Jucknischke, D. Richter, P. Lindner, L. J. Fetters, J. S. Huang, *Macromolecules*, 1998, **31**, 4189.
9. S. Boileau, *Macromol. Chem.*, *Macromol. Symp.*, 1993, **73**, 177.
10. J. Roovers, L.-L. Zhou, P. M. Toporowski, M. van der Zvan, H. Iatrou, N. Hadjichristidis, *Macromolecules*, 1993, **26**, 4324.
11. N. G. Vasilenko, E. A. Rebrov, A. M. Muzafarov, S. S. Sheiko, M. Moller, *Polym. Prepr.*, 1998, **39**, 479.
12. V. V. Arslanov, *Usp. Khim.*, 1994, **63**, 1 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1994, 63].
13. S. I. Belousov, A. I. Buzin, Yu. K. Godovskii, *Vysokomol. Soedin.*, *Ser. B*, 1999, **41**, 1687 [*Polym. Sci*, *Ser. B* (*Engl. Transl.*), 1999, **41**, 303].
14. W. Noll, H. Steinbach, C. Sucker, *J. Polym. Sci.*, *Part C*, 1971, **34**, 123.
15. H. W. Fox, P. W. Taylor, W. A. Zisman, *Ind. Eng. Chem.,* 1947, **39**, 1401.
16. S. Granick, S. J. Clarson, T. R. Formoy, J. A. Semlyen, *Polymer*, 1985, **26**, 925.
17. A. S. Tereshchenko, E. V. Getmanova, A. I. Buzin, G. M. Ignat´eva, E. A. Tatarinova, A. V. Bystrova, V. D. Myakushev, A. M. Muzafarov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 2125 [*Russ. Chem. Bull.*, *Int. Ed.*, 2007, **56**, 2200].
18. E. A. Tatarinova, E. A. Rebrov, V. D. Myakushev, I. B. Meshkov, N. V. Demchenko, A. V. Bystrova, O. V. Lebedeva, A. M. Muzafarov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 2484 [*Russ. Chem. Bull.*, *Int. Ed.*, 2004, **53**, 2591].

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