Russian Chemical Bulletin, International Edition, Vol. 56, No. 11, pp. 2200—2208, November, 2007

Trimethylsilyl ethers of amphiphilic carbosilane dendrimers of the third–fifths generations. Specific features of hydrolysis at the water—air interface

A. S. Tereshchenko, E. V. Getmanova, A. I. Buzin, G. M. Ignat´eva, E. A. Tatarinova, A. V. Bystrova, V. D. Myakushev, and A. M. Muzafarov★

N. S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences,
70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation.
Fax: +7 (495) 335 9000. E-mail: aziz@ispm.ru

Carbosilane dendrimers from the third to fifth generation with hydroxy groups in the surface layer of the dendrimer were synthesized, as well as their analogs with latent hydroxy groups. The dendrimers differ by the density of the carbosilane core and hydrophilic shell. The amphiphilic nature of the synthesized compounds was manifested already for more hydrophobic trimethylsilyl derivatives of dendrimers. This allowed one to observe the hydrolysis of these objects during compression of their monolayers at the water surface in the Langmuir bath. The parameters of the molecular structure of the dendrimers exert a determining effect on the rate and completeness of the hydrolysis.

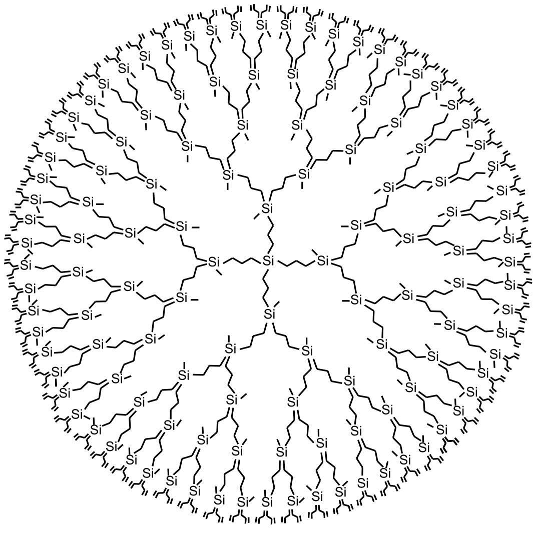
Key words: polyhydroxyl carbosilane dendrimers, amphiphilic dendrimers, monomolecular layers, Langmuir isotherms, monolayer reactions.

Amphiphilic dendrimers are stable monomolecular micelles, unlike multimolecular micelles, which are formed by linear amphiphilic systems.[1—3] This specific feature of molecular organization assumes a basically different behavior of amphiphilic dendrimers at the water—air interface. Common micelle-forming surfactants form classical lamellar monolayers with distinct orientation of each surfactant molecule in the monolayer,[4] whereas for dendrimers this rearrangement is joined with conformational strains.[5—12] From this point of view, investigation of the compression of monolayers of amphiphilic dendrimers with different molecular parameters can provide very important information on the relationship between the molecular structure of the dendrimers and conformational flexibility of their molecules upon a change in the external conditions. To obtain information of this kind, one need representative series of studied objects in which these or other structural factors are varied gradually in order to reveal certain tendencies and monitor their development.

We have earlier[13] synthesized a series of amphiphilic dendrimers of the fifth generation with different densities of the molecular structure of the hydrophobic core of the dendrimer and hydrophilic shell. The purpose of the present work is to synthesize representative series of amphiphilic carbosilane dendrimers of the third—fifth generations with different ratios of the hydrophobic and hydrophilic parts of the molecular structure as the trimethylsiloxy derivatives and to study the hydrolysis process in the monomolecular layers at the water—air interface.

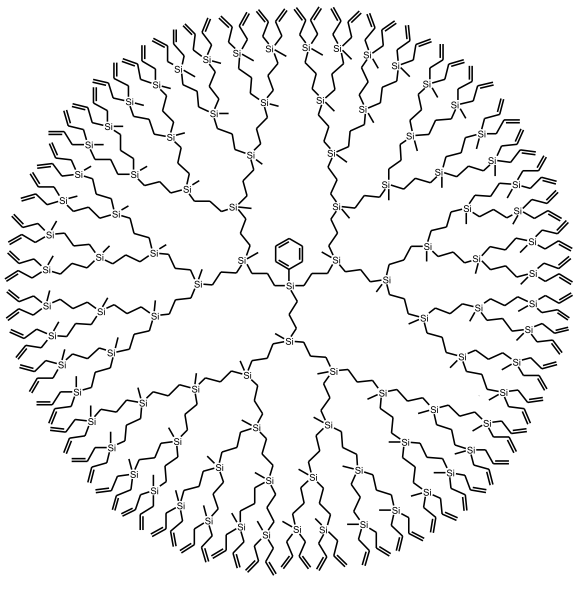
Results and Discussion

Synthesis. Polyallyl carbosilane dendrimers with different densities of the molecular structure were used as



A (hereinafter ⊕—$CH_2CH=CH_2$)

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2125—2133, November, 2007.

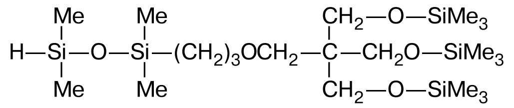


B (hereinafter ⊛—$CH_2CH=CH_2$)

matrices for the synthesis of the amphiphilic dendrimers: the dendrimers of the third—fifth generations with 32, 64, and 128 terminal branches[14] (type **A**) and the dendrimer of the fifth generation with 96 branches[15] (type **B**).

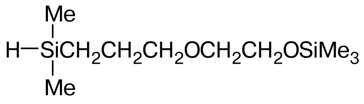
Polyallylcarbosilane dendrimers of types **A** and **B** were hydrosilylated by hydrophilizing agents according to a known procedure.[13] They were thus transformed into amphiphilic carbosilane dendrimers with different ratios of the hydrophobic and hydrophilic parts of the molecular structure.

Siloxane hydride **1** and silane hydride **2** containing three or one latent hydroxy groups, respectively, were used as hydrophilizing agents.



$$H-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-(CH_2)_3OCH_2-\underset{CH_2-O-SiMe_3}{\overset{CH_2-O-SiMe_3}{C}}-CH_2O-SiMe_3$$

1 (hereinafter $HX(OSiMe_3)_3$)



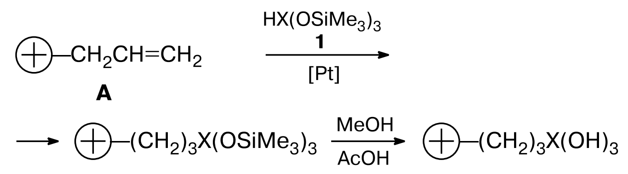
$$H-\underset{Me}{\overset{Me}{Si}}CH_2CH_2CH_2OCH_2CH_2OSiMe_3$$

2 (hereinafter $HZOSiMe_3$)

The general scheme of the synthesis of the amphiphilic dendrimers is exemplified by the dendrimer of type **A** and siloxane hydride **1** (Scheme 1).

The hydrosilylation of polyallyl dendrimers of types **A** and **B** by reactants **1** and **2** afforded the polyhydroxyl derivatives with the latent hydroxy group (**3**, **5**, **7**, **9** and **11**, **13**, **15**, **17**). Thus synthesized trimethylsilyl dendrimers were then transformed into the corresponding dendrimers with the free hydroxy group (**4**, **6**, **8**, **10** and **12**, **14**, **16**, **18**) by the elimination of the trimethylsilyl protection using transetherification of the trimethylsiloxy groups with methanol according to a known method.[13]

Scheme 1



⊕—$(CH_2)_3X(OR)_3$ ⊕—$(CH_2)_3ZOR$

3—8 **11—16**

⊛—$(CH_2)_3X(OR)_3$ ⊛—$(CH_2)_3ZOR$

9, **10** **17**, **18**

Dendrimer	Designation	R	Dendrimer	Designation	R
3	$G3(32)(OR)_3$	$SiMe_3$	**11**[16]	G3(32)OR	$SiMe_3$
4	$G3(32)(OR)_3$	H	**12**[16]	G3(32)OR	H
5	$G4(64)(OR)_3$	$SiMe_3$	**13**	G4(64)OR	$SiMe_3$
6	$G4(64)(OR)_3$	H	**14**	G4(64)OR	H
7[13]	$G5(128)(OR)_3$	$SiMe_3$	**15**[13]	G5(128)OR	$SiMe_3$
8[13]	$G5(128)(OR)_3$	H	**16**[13]	G5(128)OR	H
9[13]	$G5(96)(OR)_3$	$SiMe_3$	**17**	G5(96)OR	$SiMe_3$
10[13]	$G5(96)(OR)_3$	H	**18**	G5(96)OR	H

Note. For the description of the dendrimers the designation $Gx(y)(OR)_n$ is used, where x is the generation number; y is the number of allyl groups in the initial dendrimer (equal to the number of terminal branches); R = H and $SiMe_3$ (for the free and latent hydroxy group, respectively); n is the number of hydroxy groups.

Siloxane hydride **1** is more reactive in hydrosilylation than silane hydride **2** due to the hydride group entering the composition of the siloxane rather than carbosilane group. This conclusion can be made from the results of hydrosilylation of the same polyallyl carbosilane dendrimers by each modifying agent. In the case of hydride oligomer **1**, hydrosilylation occurs with the 100% conversion of allyl groups, whereas the hydrosilylation of the polyallyl dendrimers by silane hydride **2** with a considerable elongation of the reaction duration (30 days instead of 14) does not lead to the complete conversion of the allyl groups and is accompanied by side processes of partial isomerization of these groups to vinyl groups (Vin). The data on the conversion of allyl groups obtained from the ratio of integral intensities of protons of the corresponding groups in the ^1H NMR spectra are given in Table 1.

The trimethylsilyl derivatives of dendrimers were purified by preparative GPC and then transformed into polyhydroxyl dendrimers by the elimination of

Table 1. Conversion of allyl groups upon the hydrosilylation of dendrimers

Dendrimer	Conversion (%)	Formed Vin groups (%)	Remained All groups (%)
G3(32)OH	79.7	15.6	4.7
G4(64)OH	82.8	10.9	6.3
G5(96)OH	75.0	14.6	10.4
G5(128)OH	93.8	3.9	2.3
G3(32)(OH)$_3$	100	—	—
G4(64)(OH)$_3$	100	—	—
G5(96)(OH)$_3$	100	—	—
G5(128)(OH)$_3$	100	—	—

the trimethylsilyl protection on reflux in MeOH with glacial AcOH. The chromatograms of the polyhydroxyl dendrimers are presented in Fig. 1.

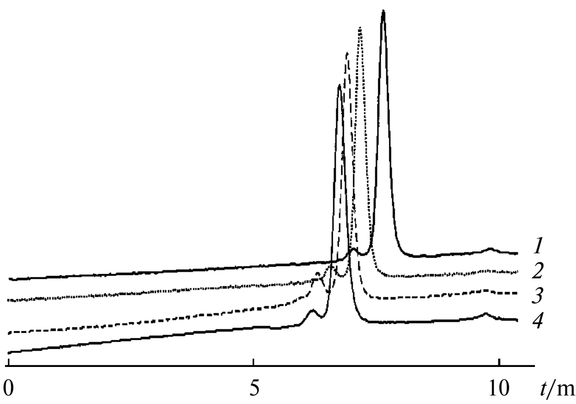
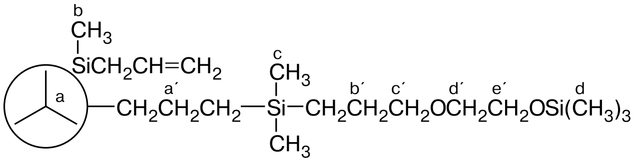


Fig. 1. GPC curves for dendrimers G3(32)OH (*1*), G4(64)OH (*2*), G5(96)OH (*3*), and G5(128)OH (*4*).

The structures of the synthesized compounds were confirmed by the ^{1}H NMR spectra (Tables 2 and 3). After

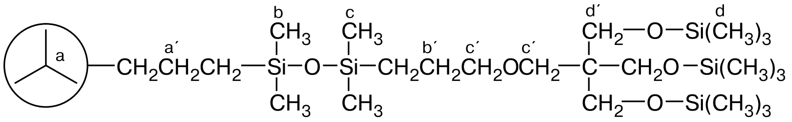
Table 2. ^{1}H NMR spectra (δ, *J*/Hz) of dendrimers G*x*(*y*)OSiMe$_3$ in CDCl$_3$ and G*x*(*y*)OH in DMSO-d$_6$



Dendrimer	SiMe (s)	SiCH$_2$ (m)	CH$_2$ (m)	OCH$_2$ (t)	OH	All (m)	Vin (m)	Ph (m)
G3(32)OSiMe$_3$	−0.09 (74 H, H$_a$); −0.05 (153 H, H$_c$); −0.02 (19 H, H$_b$); 0.11 (230 H, H$_d$)	0.53 (265 H)	1.28 (107 H, H$_{a'}$); 1.52 (51 H, H$_{b'}$)	3.39 (51 H, H$_{d'}$, *J* = 14.0); 3.48 (51 H, H$_{c'}$, *J* = 10.6); 3.71 (51 H, H$_{e'}$, *J* = 10.9)	—	4.80, 5.72 (3 H)	5.57, 5.98 (5 H)	—
G4(64)OSiMe$_3$	−0.09 (163 H, H$_a$); −0.05 (318 H, H$_c$); −0.02 (33 H, H$_b$); 0.11 (477 H, H$_d$)	0.52 (558 H)	1.29 (226 H, H$_{a'}$); 1.53 (106 H, H$_{b'}$)	3.39 (106 H, H$_{d'}$, *J* = 13.9); 3.48 (106 H, H$_{c'}$, *J* = 10.6); 3.71 (106 H, H$_{e'}$, *J* = 10.7)	—	4.78, 5.72 (12 H)	5.57, 5.98 (7 H)	—
G5(96)OSiMe$_3$	−0.09 (243 H, H$_a$); −0.05 (432 H, H$_c$); −0.02 (72 H, H$_b$); 0.11 (648 H, H$_d$)	0.52 (804 H)	1.28 (330 H, H$_{a'}$); 1.52 (144 H, H$_{b'}$)	3.39 (144 H, H$_{d'}$, *J* = 14.0); 3.47 (144 H, H$_{c'}$, *J* = 10.5); 3.71 (144 H, H$_{e'}$, *J* = 10.9)	—	4.80, 5.71 (30 H)	5.58, 6.00 (14 H)	7.34 (5 H)
G5(128)OSiMe$_3$	−0.1 (360 H, H$_a$); −0.06 (720 H, H$_c$); −0.03 (15 H, H$_b$); 0.11 (1081 H, H$_d$)	0.52 (1216 H)	1.29 (488 H, H$_{a'}$); 1.53 (240 H, H$_{b'}$)	3.38 (240 H, H$_{d'}$, *J* = 13.8); 3.47 (240 H, H$_{c'}$, *J* = 11.0); 3.71 (240 H, H$_{e'}$, *J* = 10.6)	—	4.79, 5.72 (9 H)	5.58, 5.96 (10 H)	—
G3(32)OH	−0.13 (74 H, H$_a$); −0.09 (153 H, H$_c$); −0.07 (19 H, H$_b$)	0.50 (265 H)	1.26 (107 H, H$_{a'}$); 1.45 (51 H, H$_{b'}$)	—	4.54 (t, 26 H, *J* = 10.0)	4.75, 5.65 (3 H)	5.53, 5.95 (5 H)	—
G4(64)OH	−0.13 (163 H, H$_a$); −0.09 (318 H, H$_c$); −0.06 (33 H, H$_b$)	0.50 (558 H)	1.27 (226 H, H$_{a'}$); 1.44 (106 H, H$_{b'}$)	—	4.49 (br.s, 53 H)	4.75, 5.66 (12 H)	5.53, 5.92 (7 H)	—
G5(96)OH	−0.13 (243 H, H$_a$); −0.09 (432 H, H$_c$); −0.07 (72 H, H$_b$)	0.50 (804 H)	1.27 (330 H, H$_{a'}$); 1.44 (144 H, H$_{b'}$)	—	4.54 (t, 72 H, *J* = 10.0)	4.74, 5.65 (30 H)	5.52, 5.92 (14 H)	7.34 (5 H)
G5(128)OH	−0.13 (360 H, H$_a$); −0.09 (720 H, H$_c$); −0.06 (15 H, H$_b$)	0.51 (1216 H)	1.27 (488 H, H$_{a'}$); 1.45 (240 H, H$_{b'}$)	—	4.51 (br.s, 120 H)	4.74, 5.64 (9 H)	5.53, 5.94 (10 H)	—

Note. No signals of the protons of the CH$_2$O groups in the polyhydroxyl dendrimers are presented, because they are overlapped with the signals of DMSO-d$_6$ at δ 2.5 and 3.3.

Table 3. ^{1}H NMR spectra (δ, J/Hz) of dendrimers Gx(y)(OSiMe$_3$)$_3$ in CDCl$_3$ and Gx(y)(OH)$_3$ in DMSO-d$_6$



Dendrimer	SiMe (s)	SiCH$_2$ (m)	CH$_2$ (m)	OCH$_2$	Ph (m)	OH
G3(32)(OSiMe$_3$)$_3$	−0.1 (84 H, H$_a$); 0.01 (192 H, H$_c$); 0.02 (192 H, H$_b$); 0.05 (864 H, H$_d$)	0.53 (304 H)	1.28 (120 H, H$_{a'}$); 1.52 (64 H, H$_{b'}$)	3.26 (m, 128 H, H$_{c'}$); 3.46 (s, 192 H, H$_{d'}$)	—	—
G4(64)(OSiMe$_3$)$_3$	−0.09 (180 H, H$_a$); 0.02 (384 H, H$_c$); 0.03 (384 H, H$_b$); 0.05 (1728 H, H$_d$)	0.53 (624 H)	1.28 (248 H, H$_{a'}$); 1.51 (128 H, H$_{b'}$)	3.26 (m, 256 H, H$_{c'}$); 3.46 (s, 384 H, H$_{d'}$)	—	—
G5(96)(OSiMe$_3$)$_3$	−0.09 (279 H, H$_a$); 0.02 (576 H, H$_c$); 0.03 (576 H, H$_b$); 0.06 (2592 H, H$_d$)	0.52 (948 H)	1.29 (378 H, H$_{a'}$); 1.52 (192 H, H$_{b'}$)	3.26 (m, 384 H, H$_{c'}$); 3.46 (s, 576 H, H$_{d'}$)	7.34 (5 H)	—
G5(128)(OSiMe$_3$)$_3$	−0.09 (372 H, H$_a$); 0.02 (768 H, H$_c$); 0.03 (768 H, H$_b$); 0.06 (3456 H, H$_d$)	0.53 (1264 H)	1.29 (504 H, H$_{a'}$); 1.52 (256 H, H$_{b'}$)	3.25 (m, 512 H, H$_{c'}$); 3.45 (s, 768 H, H$_{d'}$)	—	—
G3(32)(OH)$_3$	−0.12 (84 H, H$_a$); −0.01 (192 H, H$_c$); 0.0 (192 H, H$_b$)	0.50 (304 H)	1.27 (120 H, H$_{a'}$); 1.44 (64 H, H$_{b'}$)	—	—	4.16 (t, 96 H, J = 10.4)
G4(64)(OH)$_3$	−0.13 (180 H, H$_a$); −0.02 (384 H, H$_c$); 0.0 (384 H, H$_b$)	0.49 (624 H)	1.28 (248 H, H$_{a'}$); 1.44 (128 H, H$_{b'}$)	—	—	4.16 (t, 192 H, J = 10.2)
G5(96)(OH)$_3$	−0.14 (279 H, H$_a$); −0.02 (576 H, H$_c$); −0.01 (576 H, H$_b$)	0.49 (948 H)	1.27 (378 H, H$_{a'}$); 1.44 (192 H, H$_{b'}$)	—	7.34 (5 H)	4.16 (t, 288 H, J = 10.3)
G5(128)(OH)$_3$	−0.14 (372 H, H$_a$); −0.02 (768 H, H$_c$); −0.01 (768 H, H$_b$)	0.50 (1264 H)	1.26 (504 H, H$_{a'}$); 1.45 (256 H, H$_{b'}$)	—	—	4.17 (br.s, 384 H)

the trimethylsilyl protection was eliminated, the signals of protons of the Me$_3$SiO groups at δ 0.05 disappeared and signals of protons of the OH groups at δ 4.16 appeared (for dendrimers **4**, **6**, **8**, and **10** with three functional groups at each branch). Similar situation is observed for the dendrimers with a single functional group at each branch. In this case, the signals of protons at δ 0.11 disappear and signals of protons of the OH groups appear at δ 4.5 (for dendrimers **12**, **14**, **16**, and **18**).

Polyhydroxyl dendrimers are transparent gel-like substances, which, unlike their trimethylsilyl derivatives, are highly soluble in MeOH and EtOH. The contribution of the hydrophilic component in the amphiphilic system hydrophobic core—hydrophilic shell of the dendrimer increases with an increase in the generation, and this contribution increases sharply on going from one to three OH groups at each branch. The G3(32)OH—G5(128)OH dendrimers are soluble in THF, whereas the change in the hydrophilic—hydrophobic balance toward the hydrophilicity increase results in the loss of the solubility in THF due to which the G3(32)(OH)$_3$—G5(128)(OH)$_3$ dendrimers are soluble only in MeOH and EtOH.

Langmuir isotherms. A stimulus for the creation of the "library" of polyhydroxyl carbosilane dendrimers was hope of obtaining additional information on the behavior of dendrimers of different structure under external factors by the study of monolayers of these objects on the water surface using the Langmuir method. In fact, even basically hydrophobic trimethylsilyl dendrimer derivatives formed monolayers on the water surface due to polar ether groups in their molecules. This specific feature of the trimethylsilyl dendrimer derivatives makes it possible to determine the sizes (surface areas of the cross-section) of the dendrimers under study and monitor the regularities of their hydrolysis.

The compression isotherms of the smallest dendrimer of the dendrimers with a single OSiMe$_3$ group at each branch are shown in Fig. 2, *a*. The initial isotherm (blue-colored) has two steps (the first step is observed at 900—1100 Å^2, and the second one lies at 250—450 Å^2), which correspond, most likely, to the detachment of the ether groups of two types from the water surface. The compressed sample is decompressed virtually without hysteresis, indicating that no stable structures are formed during sample compression. The repeated compression slightly shifts the isotherm with a decrease in the surface area per one molecule, and the series of these repetitions results in a qualitative change in the isotherm shape. The first step disappears gradually but a new one appears at a higher pressure and smaller surface area (in a region of 450—600 Å^2). The position of the second step changes insignificantly. The measurements were finished when the subsequent repeated compressions induced no changes in the isotherm shape. The resulting isotherm almost completely coincided with the compression isotherm of the hydroxyl derivative preliminarily prepared in macroquantities by the reaction in solution.

The character of changes in the compression isotherm of the trimethylsilyl derivative in time and coincidence of the resulting compression isotherm with an analogous curve for the hydroxyl derivative suggest that gradual changes in the compression isotherm reflect, in essence, the hydrolysis of the trimethylsilyl derivative in the monolayer on the water surface. Based on the decrease in the surface area of the first step during hydrolysis, we can assume that the first step is related to the detachment of the OSiMe or OH groups from the water surface, because it reflects a smaller surface area occupied by the OH groups compared to that of the $OSiMe_3$ groups. Then the second step, whose position remains virtually unchanged upon hydrolysis, concerns the beginning of detachment of the internal C—O—C bond. The height of the second step for the hydrolyzed samples is higher than that for the initial trimethylsilyl samples. In addition, the second step of the hydrolyzed samples is virtually horizontal, whereas the second step of the initial samples has a considerable slope. This is related, most likely, to the enhancement of the degree of perfection of the Langmuir layer due to a decrease in the volume of the terminal fragments. Thus, the surface pressure of the second step for the hydrolyzed samples with the terminal OH groups, being 32 mN m^{-1} for all four samples, should be close to the equilibrium value.

The fact that the reaction occurs in the monolayer on the water surface directly in the Langmuir bath is well known[17,18] unless trivial. It is more surprising that hydrolysis occurs in the monolayer rather easily, whereas this process could not be carried out in solution even at

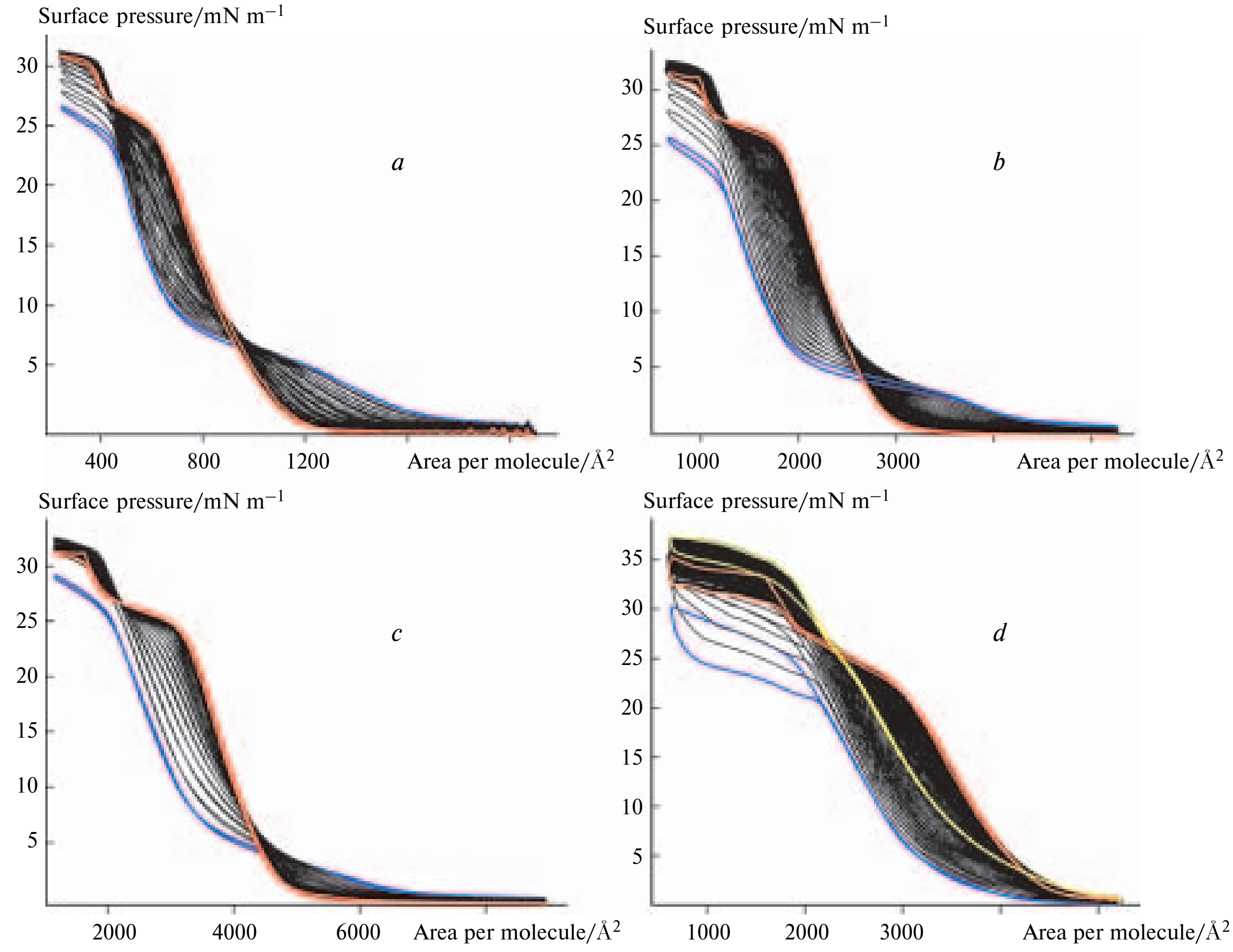


Fig. 2. Surface pressure isotherms of dendrimers $G3(32)OSiMe_3$ (*a*), $G4(64)OSiMe_3$ (*b*), $G5(96)OSiMe_3$ (*c*), and $G5(128)OSiMe_3$ (*d*) ($T = 22$ °C): blue-colored initial isotherm, black-colored changes in the isotherm during the hydrolysis of the dendrimers under study, red-colored equilibrium isotherm (complete hydrolysis), and yellow-colored surface pressure isotherm with the maximum value of the second-step pressure.

Note. Fig. 2 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

elevated temperatures and the use of the catalyst.[13] This phenomenon can be explained by the specific character of contacts of the alkoxy groups with water in the monolayer: this is almost a molecular contact, whereas these contacts are strongly hindered for the bulk reaction even in the presence of a homogenizing solvent.[19] In fact, the kinetics of this reaction can be monitored by the change in the isotherm, which was not a task of our work. However, the consecutive and reproducible changes in the compression isotherms in the monolayer for various objects confirm completely this possibility.

In the framework of the present study it seemed more actual to investigate specific features of hydrolysis in the monolayer for the trimethylsilyl dendrimer derivatives with different molecular parameters. The successive increase in the generation number with the unchanged structure of the surface groups revealed no basic differences. The changes in the compression isotherms in time for the G4(64)OSiMe$_3$, G5(96)OSiMe$_3$, and G5(128)OSiMe$_3$ samples are shown in Fig. 2, *b—d*. In all cases, the compression isotherms become stable in time, indicating that the hydrolysis process ceases.

At the same time, a comparison of the presented data shows substantial changes in the character of the initial isotherms with an increasing density of the structure of the dendrimers under study. The first step, attributed by us to the elimination of the terminal groups from water during compression, was not virtually manifested for the most dense G5(128)OSiMe$_3$ sample of this series based on the tetrafunctional branching center, unlike other dendrimers of this series with the trifunctional central branching fragment. However, the second step appears for the considered sample during hydrolysis and is similar to those observed for other three samples. This is related, most likely, to the fact that this dendrimer can optimally be arranged on the surface due to a decrease in the volume of the terminal groups.

The time necessary for the complete hydrolysis of the samples increased regularly on going from G3(32)OSiMe$_3$ (30 min) to the G4(64)OSiMe$_3$ and G5(96)OSiMe$_3$ samples (90 min) and reached 150 min for the G5(128)OSiMe$_3$ sample.

The compression isotherms of the second series of the samples with the tris(trimethylsilyl) fragments in the surface layer shown in Fig. 3 differ noticeably from those described above. In these cases, even allusions to the step at low degrees of compression completely disappear and the stabilization of the isotherm in time does not imply the completion of the hydrolysis process. This conclusion follows from a comparison of the isotherm of the trimethylsilyl derivative after the stabilization was achieved and that of the hydroxyl derivative synthesized in the flask: these isotherms do not coincide. Finer distinctions can also be observed. For example, a noticeable hysteresis appears upon decompression.

The qualitatively different behavior of the dendrimers with a denser external layer can be explained, most likely, as follows. In the dendrimers with a less dense structure of the external layer, all terminal trimethylsilyl fragments can interact with water (Fig. 4, *a*). In addition, each structural fragment of the external layer, including the spacer, can contact with water. This explains two steps in the isotherms of the dendrimers of the first series. The samples with a denser surface layer contact with water in different manner. Only a part of the dendrimer macromolecule enters into the contact (Fig. 4, *b*). It seems that other regions of the surface would gradually get a possibility of similar contacts due to rotation. However, it should be kept in mind that on contact with water the hydrolysis of the Me$_3$Si—O—CH$_2$ groups starts to form trimethylsilanol and alcohol groups in the surface layer of the dendrimer and, hence, the affinity to water of this part of the dendrimer structure increases sharply, the molecule transforms into a distinctly oriented surfactant, and the further hydrolysis does not occur because the remaining trimethylsilyl groups do not contact with water. That is, differences between the dendrimers in density of the surface layer structure are determined just by the possibility or impossibility to contact of all trimethylsiloxy groups simultaneously with the water surface. A denser molecular structure restricts similar contacts in the initial step and makes them impossible after the hydrolysis of at least several Me$_3$Si—O—CH$_2$ groups.

It is interesting that for the samples with a less dense surface layer the maximum surface pressure of the second step is observed for some intermediate compound (see Fig. 2, *d*, yellow lines) rather than for the final, completely hydrolyzed dendrimer. The reason for this phenomenon remains unclear. For the further hydrolysis, the pressure of the second step decreases to the equilibrium value. In the case of G5(128)OSiMe$_3$ (see Fig. 2, *d*), it is distinctly seen that the isotherm of its intermediate compound contains no first step. However, with time the isotherm gains the same two-step shape, which is characteristic of other three samples. For the four samples with a dense surface layer, the surface pressure necessary for the decomposition of the hydrolysis product layer ranges from 40 to 47.5 mN m^{-1}, whereas for the specially prepared corresponding polyhydroxyl derivatives this value is 37—40 mN m^{-1}. This confirms that the trimethylsiloxy groups in these compounds were incompletely hydrolyzed. In this connection, the densest one of the "monohydroxyl" dendrimer (G5(128)OH) also contains, most likely, a number of the nonhydrolyzed trimethylsiloxy groups, because the surface pressure of the product of its hydrolysis is somewhat higher, in this case, than that for the polyhydroxyl analog.

Monodispersity of the studied objects makes it possible to calculate the sizes of the molecules (more exactly, surface areas of their cross-sections) from the results of

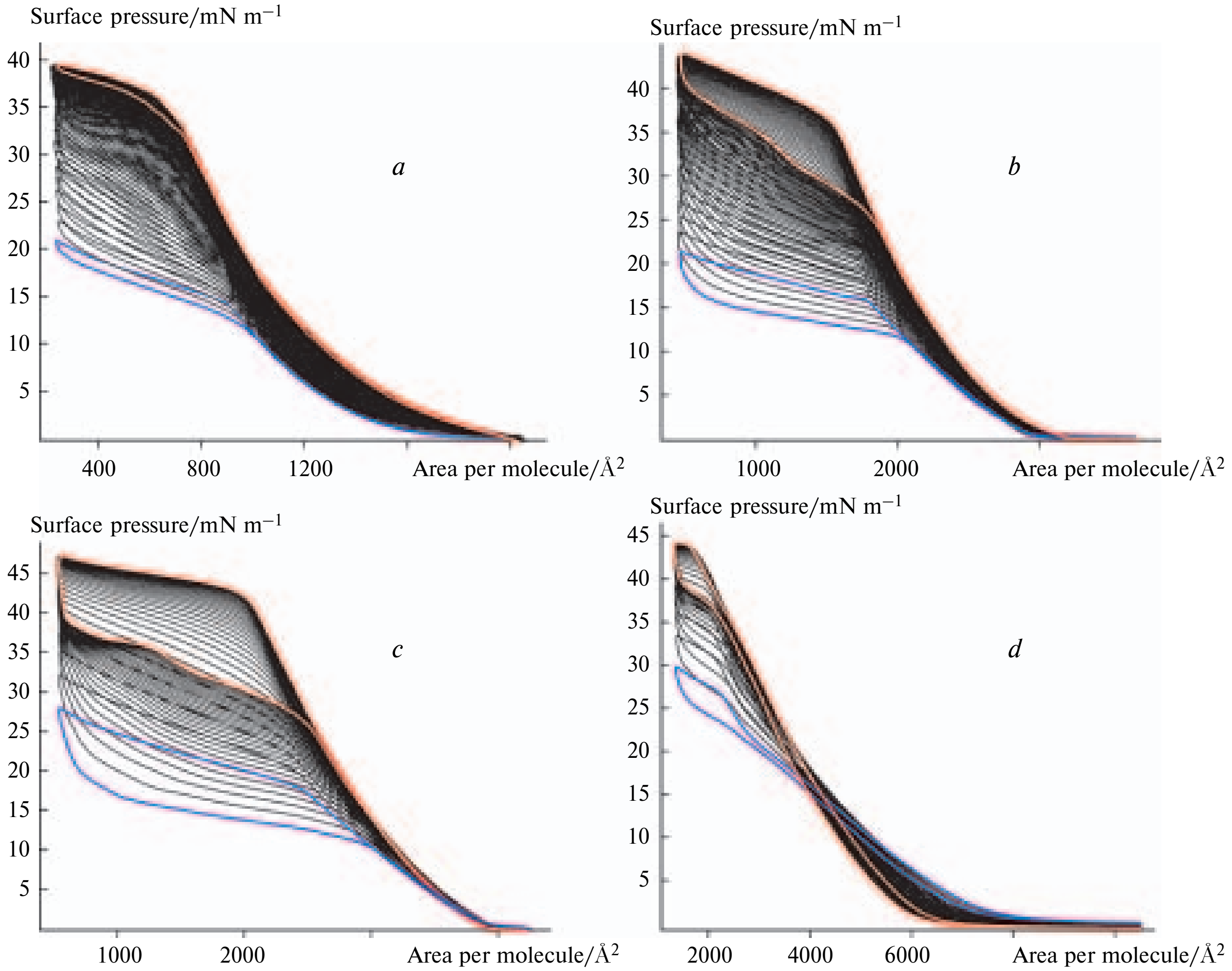


Fig. 3. Surface pressure isotherms of dendrimers G3(32)$(OSiMe_3)_3$ (*a*), G4(64)$(OSiMe_3)_3$ (*b*), G5(96)$(OSiMe_3)_3$ (*c*), and G5(128)$(OSiMe_3)_3$ (*d*) (*T* = 22 °C).

Note. Fig. 3 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

measurement of the compression isotherms of the dendrimer monolayers. The surface area per one macromolecule in the monolayer increases regularly with an increase in the generation number. The data on the surface areas of the macromolecules are given in Table 4. Comparing the surface area values calculated under the assumption that the dendrimers are rigid spheres with the density equal to unity and surface areas calculated by the processing of the compression isotherms of the dendrimers, we can monitor the character of qualitative changes in the dendrimer shape with an increase in the generation number. The experimental values of the surface areas for the dendrimers with the dense surface layer coincide with the theoretical ones, taking into account

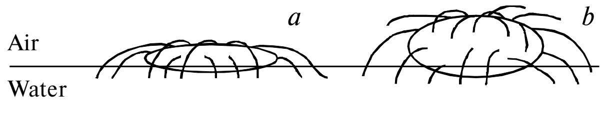


Fig. 4. Schematic structures of dendrimers G*x*(*y*)$OSiMe_3$ (*a*) and G*x*(*y*)$(OSiMe_3)_3$ (*b*) on the water surface.

Table 4. Parameters of the dendrimer molecules (cross-section surface area (*S*) and radius (*R*)) calculated from the compression isotherms

Dendrimer	S_1 /Å²	R_1 /Å	S_2 /Å²	R_2 /Å	S_{theor} /Å²	R_{theor} /Å
G3(32)$OSiMe_3$	1215	19.7	450	12.0	771	15.7
G4(64)$OSiMe_3$	3550	33.6	1215	19.7	1257	20.0
G5(96)$OSiMe_3$	4550	38.1	1685	23.2	1595	22.5
G5(128)$OSiMe_3$	—	—	1915	24.7	2113	25.9
G3(32)$(OSiMe_3)_3$	910	17.0	—	—	1274	20.1
G4(64)$(OSiMe_3)_3$	1780	23.8	—	—	2032	25.4
G5(96)$(OSiMe_3)_3$	2450	27.9	—	—	2672	29.2
G5(128)$(OSiMe_3)_3$	2310	27.1	—	—	3234	32.1

Note. Indices "1" and "2" mark the values corresponding to the onset of the first and second steps.

the assumptions for the density of the dendrimers made in the calculation.

Thus, it was shown for the polyhydroxyl derivatives of carbosilane dendrimers and their trimethylsilyl precursors that the consecutive change in the sizes and density of the carbosilane core and the density of the external layer of the molecular structure is an efficient tool for controlling the properties of molecular particles of the core—shell type.

Experimental

^{1}H NMR spectra were measured on a Bruker WP-250 SY instrument (250.13 MHz) using Me_4Si as the internal standard. IR spectra were recorded on a Bruker Equinox 55/S instrument. GLC analysis was carried out on a 3700 chromatograph (Russia) using a katharometer as the detector, helium as the carrier gas, and columns 2 m × 3 mm (SE-30 (5%) stationary phase supported on Chromaton-H-AW). GPC analysis was carried on a Laboratorni pristroje liquid chromatograph (Czechia) using a RIDK-102 refractometer as the detector and a column 300×7.8 mm (sorbent Phenogel 10×4 E (5 μm, Phenomenex, USA) and THF as the eluent). The preparative chromatographic system consisted of a high-pressure isocratic pump (Akvilon), a RIDK-102 refractometer, and a preparative column 300×20.2 mm (sorbent Phenogel 10×3 E (10 μm, Phenomenex, USA), THF as the eluent).

Surface pressure isotherms were obtained using the Langmuir trough (612D, Nima, England). The Teflon bath was 20×30 cm in size, and distilled water deionized on an Akvilon D-301 installation (resistance 18 MOhm cm^{-1}) was used; the temperature of water was 22 °C. Dendrimers were dissolved in chloroform (concentration 1 mg mL^{-1}). The rate of barrier movement was 300 cm^2 min^{-1}.

All reactions were carried out in an inert atmosphere and anhydrous solvents. (Divinyltetramethyldisiloxane)platinum(0)$^{\mathbf{20}}$ was used as the catalyst in the form of a solution (2.1—2.4% Pt) in xylene (Aldrich). Commercial reagents were used.

Dendrimer G3(32)($OSiMe_3$)$_3$ (3). A mixture of dendrimer of type **A** of the third generation (0.3728 g, 0.1 mmol), compound **1** (1.6867 g, 3.2 mmol), anhydrous toluene (7 mL), and the catalyst (9 μL) was stored for 15 days at 35—40 °C in a tightly closed flask blown with argon (until the signals of protons at the double bond almost completely disappeared in the ^{1}H NMR spectra of samples of the reaction mixture). The solvents were evaporated to dryness. Compound **3** was first purified from the catalyst by chromatography on silica gel (Merck, toluene as eluent) and then from high-molecular-weight admixtures using preparative GPC (THF as eluent). ^{1}H NMR ($CDCl_3$), δ: −0.10 (s, SiMe); 0.01, 0.02 (both s, $SiMe_2$); 0.05 (s, $SiMe_3$); 0.53 (m, $SiCH_2$); 1.28 (m, $SiCH_2C\underline{H}_2CH_2Si$); 1.52 (m, $C\underline{H}_2CH_2O$); 3.26 (m, $C\underline{H}_2OC\underline{H}_2$); 3.46 (s, CH_2OSi) in the ratio ~7.4 (SiMe) : : 1.7 ($SiCH_2$) : 0.76 (CH_2) : 0.7 (CH_2O) : 1 (CH_2OSi), which agrees with the calculated ratio (84 H + 192 H + 192 H + + 864 H) : 304 H : (120 H + 64 H) : 128 H : 192 H.

Dendrimer G3(32)(OH)$_3$ (4) was synthesized by heating of compound **3** (0.15 g, 0.007 mmol), toluene (4 mL), MeOH (2 mL), and glacial AcOH (1 mL) for 48 h at 70 °C with stirring. The solvents were evaporated to dryness, and the dendrimer was dried *in vacuo* (1 Torr). ^{1}H NMR (DMSO-d$_6$), δ: −0.12 (s, 84 H, SiMe); −0.01, 0.0 (both s, 192 H each, $SiMe_2$); 0.50 (m, 304 H, $SiCH_2$); 1.27 (m, 120 H, $SiCH_2C\underline{H}_2CH_2Si$); 1.44 (m, 64 H, $C\underline{H}_2CH_2O$); 4.16 (t, 96 H, OH, *J* = 10.4 Hz)* (no signals of protons of the CH_2O groups are presented, because they are overlapped with the signals of DMSO-d$_6$ at δ 2.5 and 3.3).

Dendrimer G4(64)($OSiMe_3$)$_3$ (5) was synthesized similarly to compound **3** from dendrimer of type **A** of the fourth generation (0.1 mmol) and compound **1** (6.4 mmol). ^{1}H NMR ($CDCl_3$), δ: −0.09 (s, 180 H, SiMe); 0.02, 0.03 (both s, 384 H each, $SiMe_2$); 0.05 (s, 1728 H, $SiMe_3$); 0.53 (m, 624 H, $SiCH_2$); 1.28 (m, 248 H, $SiCH_2C\underline{H}_2CH_2Si$); 1.51 (m, 128 H, $C\underline{H}_2CH_2O$); 3.26 (m, 256 H, $C\underline{H}_2OC\underline{H}_2$); 3.46 (s, 384 H, CH_2OSi).

Dendrimer G4(64)(OH)$_3$ (6) was synthesized similarly to compound **4**. ^{1}H NMR (DMSO-d$_6$), δ: −0.13 (s, 180 H, SiMe); −0.02, 0.0 (both s, 384 H each, $SiMe_2$); 0.49 (m, 624 H, $SiCH_2$); 1.28 (m, 248 H, $SiCH_2C\underline{H}_2CH_2Si$); 1.44 (m, 128 H, $C\underline{H}_2CH_2O$); 4.16 (t, 192 H, OH, *J* = 10.2 Hz).

Dendrimer G5(128)($OSiMe_3$)$_3$ (7) was synthesized similarly from dendrimer of type **A** of the fifth generation using a known procedure.$^{\mathbf{13}}$ ^{1}H NMR ($CDCl_3$), δ: −0.09 (s, 372 H, SiMe); 0.02, 0.03 (both s, 768 H each, $SiMe_2$); 0.06 (s, 3456 H, $SiMe_3$); 0.53 (m, 1264 H, $SiCH_2$); 1.29 (m, 504 H, $SiCH_2C\underline{H}_2CH_2Si$); 1.52 (m, 256 H, $C\underline{H}_2CH_2O$); 3.25 (m, 512 H, $C\underline{H}_2OC\underline{H}_2$); 3.45 (s, 768 H, CH_2OSi).

Dendrimer G5(128)(OH)$_3$ (8) was synthesized according to a known procedure.$^{\mathbf{13}}$ ^{1}H NMR (DMSO-d$_6$), δ: −0.14 (s, 372 H, SiMe); −0.02, −0.01 (both s, 768 H each, $SiMe_2$); 0.50 (m, 1264 H, $SiCH_2$); 1.26 (m, 504 H, $SiCH_2C\underline{H}_2CH_2Si$); 1.45 (m, 256 H, $C\underline{H}_2CH_2O$); 4.17 (br.s, 384 H, OH).

Dendrimer G5(96)($OSiMe_3$)$_3$ (9) from dendrimer of type **B** using a known procedure.$^{\mathbf{13}}$ ^{1}H NMR ($CDCl_3$), δ: −0.09 (s, 279 H, SiMe); 0.02, 0.03 (both s, 576 H each, $SiMe_2$); 0.06 (s, 2592 H, $SiMe_3$); 0.52 (m, 948 H, $SiCH_2$); 1.29 (m, 378 H, $SiCH_2C\underline{H}_2CH_2Si$); 1.52 (m, 192 H, $C\underline{H}_2CH_2O$); 3.26 (m, 384 H, $C\underline{H}_2OC\underline{H}_2$); 3.46 (s, 576 H, CH_2OSi); 7.34 (m, 5 H, Ph).

Dendrimer G5(96)(OH)$_3$ (10) was synthesized according to a known procedure.$^{\mathbf{13}}$ ^{1}H NMR (DMSO-d$_6$), δ: −0.14 (s, 279 H, SiMe); −0.02, −0.01 (both s, 576 H each, $SiMe_2$); 0.49 (m, 948 H, $SiCH_2$); 1.27 (m, 378 H, $SiCH_2C\underline{H}_2CH_2Si$); 1.44 (m, 192 H, $C\underline{H}_2CH_2O$); 4.16 (t, 288 H, OH, *J* = 10.2 Hz); 7.34 (m, 5 H, Ph).

Dendrimer G3(32)$OSiMe_3$ (11) was synthesized according to a known procedure$^{\mathbf{16}}$ from dendrimer of type **A** of the third generation and compound **2**. ^{1}H NMR ($CDCl_3$), δ: −0.09 (s, 74 H, SiMe); −0.05 (s, 153 H, $SiMe_2$); −0.02 (s, 19 H, SiMeAll); 0.11 (s, 230 H, $SiMe_3$); 0.53 (m, 265 H, $SiCH_2$); 1.28 (m, 107 H, $SiCH_2C\underline{H}_2CH_2Si$); 1.52 (m, 51 H, $C\underline{H}_2CH_2O$); 3.39 (t, 51 H, $CH_2OC\underline{H}_2$, *J* = 14.0 Hz); 3.48 (t, 51 H, $C\underline{H}_2OCH_2$, *J* = 10.6 Hz); 3.71 (t, 51 H, CH_2OSi, *J* = 10.9 Hz); 4.80, 5.72 (m, 3 H, All); 5.57, 5.98 (m, 5 H, Vin).

Dendrimer G3(32)OH (12) was synthesized similarly to compound **4**. ^{1}H NMR (DMSO-d$_6$), δ: −0.13 (s, 74 H, SiMe);

---

* Hereinafter the calculated numbers of protons consistent with the results of integrating with respect to the groups of signals, as shown above for dendrimer **3**, are presented for the description of the ^{1}H NMR spectra.

−0.09 (s, 153 H, $\mathrm{SiMe_2}$); −0.07 (s, 19 H, SiMeAll); 0.50 (m, 265 H, $\mathrm{SiCH_2}$); 1.26 (m, 107 H, $\mathrm{SiCH_2C\underline{H}_2CH_2Si}$); 1.45 (m, 51 H, $\mathrm{C\underline{H}_2CH_2O}$); 4.54 (t, 26 H, OH, $J = 10.0$ Hz); 4.75, 5.65 (m, 3 H, All); 5.53, 5.95 (m, 5 H, Vin).

Dendrimer G4(64)OSiMe$_3$ (13) was synthesized similarly to compound **3** from dendrimer of type **A** of the fourth generation (0.1 mmol) and compound **2** (6.4 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: −0.09 (s, 163 H, SiMe); −0.05 (s, 318 H, $\mathrm{SiMe_2}$); −0.02 (s, 33 H, SiMeAll); 0.11 (s, 477 H, $\mathrm{SiMe_3}$); 0.52 (m, 558 H, $\mathrm{SiCH_2}$); 1.29 (m, 226 H, $\mathrm{SiCH_2C\underline{H}_2CH_2Si}$); 1.53 (m, 106 H, $\mathrm{C\underline{H}_2CH_2O}$); 3.39 (t, 106 H, $\mathrm{CH_2OC\underline{H}_2}$, $J = 13.9$ Hz); 3.48 (t, 106 H, $\mathrm{C\underline{H}_2OCH_2}$, $J = 10.6$ Hz); 3.71 (t, 106 H, $\mathrm{CH_2OSi}$, $J = 10.7$ Hz); 4.78, 5.72 (m, 12 H, All); 5.57, 5.98 (m, 7 H, Vin).

Dendrimer G4(64)OH (14) was synthesized similarly to compound **4**. ^{1}H NMR (DMSO-d$_6$), δ: −0.13 (s, 163 H, SiMe); −0.09 (s, 318 H, $\mathrm{SiMe_2}$); −0.06 (s, 33 H, SiMeAll); 0.50 (m, 558 H, $\mathrm{SiCH_2}$); 1.27 (m, 226 H, $\mathrm{SiCH_2C\underline{H}_2CH_2Si}$); 1.44 (m, 106 H, $\mathrm{C\underline{H}_2CH_2O}$); 4.49 (br.s, 53 H, OH); 4.75, 5.66 (m, 12 H, All); 5.53, 5.92 (m, 7 H, Vin).

Dendrimer G5(128)OSiMe$_3$ (15) was synthesized according to a known procedure[13] from dendrimer of type **A** of the fifth generation and compound **2**. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: −0.1 (s, 360 H, SiMe); −0.06 (s, 720 H, $\mathrm{SiMe_2}$); −0.03 (s, 15 H, SiMeAll); 0.11 (s, 1081 H, $\mathrm{SiMe_3}$); 0.52 (m, 1216 H, $\mathrm{SiCH_2}$); 1.29 (m, 488 H, $\mathrm{SiCH_2C\underline{H}_2CH_2Si}$); 1.53 (m, 240 H, $\mathrm{C\underline{H}_2CH_2O}$); 3.38 (t, 240 H, $\mathrm{CH_2OC\underline{H}_2}$, $J = 13.8$ Hz); 3.47 (t, 240 H, $\mathrm{C\underline{H}_2OCH_2}$, $J = 11.0$ Hz); 3.71 (t, 240 H, $\mathrm{CH_2OSi}$, $J = 10.6$ Hz); 4.79, 5.72 (m, 9 H, All); 5.58, 5.96 (m, 10 H, Vin).

Dendrimer G5(128)OH (16) was synthesized similarly to compound **4**. ^{1}H NMR (DMSO-d$_6$), δ: −0.13 (s, 360 H, SiMe); −0.09 (s, 720 H, $\mathrm{SiMe_2}$); −0.06 (s, 15 H, SiMeAll); 0.51 (m, 1216 H, $\mathrm{SiCH_2}$); 1.27 (m, 488 H, $\mathrm{SiCH_2C\underline{H}_2CH_2Si}$); 1.45 (m, 240 H, $\mathrm{C\underline{H}_2CH_2O}$); 4.51 (br.s, 120 H, OH); 4.74, 5.64 (m, 9 H, All); 5.53, 5.94 (m, 10 H, Vin).

Dendrimer G5(96)OSiMe$_3$ (17) was synthesized similarly to compound **3** from dendrimer of type **B** (0.1 mmol) and compound **2** (9.6 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: −0.09 (s, 243 H, SiMe); −0.05 (s, 432 H, $\mathrm{SiMe_2}$); −0.02 (s, 72 H, SiMeAll); 0.11 (s, 648 H, $\mathrm{SiMe_3}$); 0.52 (m, 804 H, $\mathrm{SiCH_2}$); 1.28 (m, 330 H, $\mathrm{SiCH_2C\underline{H}_2CH_2Si}$); 1.52 (m, 144 H, $\mathrm{C\underline{H}_2CH_2O}$); 3.39 (t, 144 H, $\mathrm{CH_2OC\underline{H}_2}$, $J = 14.0$ Hz); 3.47 (t, 144 H, $\mathrm{C\underline{H}_2OCH_2}$, $J = 10.5$ Hz); 3.71 (t, 144 H, $\mathrm{CH_2OSi}$, $J = 10.9$ Hz); 4.80, 5.71 (m, 30 H, All); 5.58, 6.00 (m, 14 H, Vin); 7.34 (m, 5 H, Ph).

Dendrimer G5(96)OH (18) was synthesized similarly to compound **4**. ^{1}H NMR (DMSO-d$_6$), δ: −0.13 (s, 243 H, SiMe); −0.09 (s, 432 H, $\mathrm{SiMe_2}$); −0.07 (s, 72 H, SiMeAll); 0.50 (m, 804 H, $\mathrm{SiCH_2}$); 1.27 (m, 330 H, $\mathrm{SiCH_2C\underline{H}_2CH_2Si}$); 1.44 (m, 144 H, $\mathrm{C\underline{H}_2CH_2O}$); 4.54 (t, 72 H, OH, $J = 10.0$ Hz); 4.74, 5.65 (m, 30 H, All); 5.52, 5.92 (m, 14 H, Vin); 7.34 (m, 5 H, Ph).

Dendrimers **4**, **6**, **8**, **10**, **12**, **14**, **16**, and **18** have a broad band in the IR spectrum at 3400 cm^{-1} (OH).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 06-03-32683), the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Program "Chemistry and Physical Chemistry of Supramolecular Systems and Atomic Clusters") and the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-4439.2006.3)

References

1. Y. H. Kim and O. W. Webster, *J. Am. Chem. Soc.*, 1990, **112**, 4592.
2. G. R. Newkome, C. N. Moorefield, G. R. Baker, A. L. Johnson, and R. K. Behera, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1176.
3. G. R. Newkome, C. N. Moorefield, G. R. Baker, M. J. Saunders, and S. H. Grossman, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1178.
4. I. Langmuir, *J. Am. Chem. Soc.*, 1917, **39**, 1848.
5. P. M. Saville, P. A. Reynolds, J. W. White, C. J. Hawker, J. M. J. Frechet, K. L. Wooley, J. Penfold, and J. R. P. Webster, *J. Phys. Chem.*, 1995, **99**, 8283.
6. J. P. Kampf, C. W. Frank, E. E. Malmstrom, and C. J. Hawker, *Langmuir*, 1999, **15**, 227.
7. Y. Sayed-Sweet, D. M. Hedstrand, R. Spinder, and D. A. Tomalia, *J. Mater. Chem.*, 1997, **7**, 1199.
8. A. P. H. J. Schenning, C. Elissen-Roman, J.-W. Weener, M. W. P. L. Baars, S. J. van der Gaast, and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **120**, 8199.
9. C. M. Lee, J.-W. Kim, S. Peleshanko, K. Larson, Y.-S. Yoo, D. Vaknin, S. Markutsya, and V. V. Tsukruk, *J. Am. Chem. Soc.*, 2002, **124**, 9121.
10. S.-B. Jung, C. Kim, and Y.-S. Kwon, *Thin Solid Films*, 2003, **438—439**, 27.
11. S. S. Sheiko, A. I. Buzin, A. M. Muzafarov, E. A. Rebrov, and E. V. Getmanova, *Langmuir*, 1998, **14**, 7468.
12. S. S. Sheiko and M. Möller, *Top. Curr. Chem.*, 2001, **212**, 137.
13. E. V. Getmanova, A. S. Tereshchenko, G. M. Ignat´eva, E. A. Tatarinova, V. D. Myakushev, and A. M. Muzafarov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 134 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 137].
14. S. A. Ponomarenko, E. A. Rebrov, N. I. Boiko, A. M. Muzafarov, and V. P. Shibaev, *Vysokomol. Soedin., Ser. A*, 1998, **40**, 1253 [*Polym. Sci., Ser. A*, 1998, **40**, 763 (Engl. Transl.)].
15. D. K. Polyakov, G. M. Ignat´eva, E. A. Rebrov, N. G. Vasilenko, S. S. Sheiko, M. Möller, and A. M. Muzafarov, *Vysokomol. Soedin., Ser. A*, 1998, **40**, 1421 [*Polym. Sci., Ser. A*, 1998, **40**, 876 (Engl. Transl.)].
16. E. V. Getmanova, T. B. Chenskaya, O. B. Gorbatsevich, E. A. Rebrov, N. G. Vasilenko, and A. M. Muzafarov, *React. Func. Polym.*, 1997, **33**, 289.
17. V. V. Arslanov, L. S. Sheinina, R. A. Bulgakova, and A. V. Belomestnykh, *Langmuir*, 1995, **11**, 3953.
18. J. Sjoblom, G. Stakkestad, H. Ebeltoft, S. E. Friberg, and P. Claesson, *Langmuir*, 1995, **11**, 2652.
19. E. A. Chernyshev, P. V. Ivanov, and D. N. Golubykh, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 1909 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1998].
20. B. D. Karstedt, US Pat. 3419593; *Chem. Abstrs*, 1967, **66**, 115791p.

Received January 24, 2007;
in revised form October 11, 2007