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Synthesis and Properties of Fluorinated Derivatives of Carbosilane Dendrimers of High Generations[1]

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Abstract—Fluorinated derivatives containing different amounts of fluorocarbon groups in the surface layer of the molecular structure have been synthesized by the chemical modification of a polyallylcarbosilane dendrimer of the sixth generation via hydrosilylation and heterofunctional condensation procedures. The fluoro-containing dendrimers are well soluble in organic solvents and supercritical CO_2. Their properties have been studied by DSC, viscometry, dynamic light scattering, and atomic force microscopy.

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INTRODUCTION

Dendritic macromolecules have been intensively studied in the past decade owing to their unique structure and a set of specific characteristics. Methods developed for the chemical modification of the outer surface layer provide a means of controlling the properties of dendrimers in a wide range. Of special interest are fluorinated dendrimers. It is known that the incorporation of fluorocarbon moieties renders dendrite systems hydrophobic and thermally stable [1–4] and improves their lubricating ability compared to the unmodified hydrocarbon analogs. Fluorophenylene dendrimers exhibit good electron-conducting behavior and offer promise as materials for light-emitting diodes [5]. Cooper et al. [6] reported that the fluorinated derivatives of dendrimers based on the polyaminopolyamide core show a high catalytic activity in supercritical CO_2.

Fluorinated derivatives of carbosilane dendrimers are not less promising for practical applications. Owing to combination of the fluorocarbon outer layer and the silicohydrocarbon backbone, the dendrimers of this family may be regarded as core–shell systems and thus offer wide opportunities for the study of dendrimers [7, 8]. In contrast to hydroxyl derivatives of carbosilane dendrimers, their outer shell is even more hydrophobic than the core. Currently available approaches to the synthesis of similar systems suffer from serious drawbacks. These approaches are based on the grafting of long perfluoroalkyl substituents onto the carbosilane backbone [9, 10] via hydrosilylation or radical addition reactions. In both cases, even dendrimers of the third generation are insoluble in organic solvents. As a consequence, potentialities inherent in the study and application of similar systems are limited. Therefore, the development of new synthetic schemes remains an urgent problem.

Recently, we have synthesized fluorinated derivatives of carbosilane dendrimers of high generations [11]. The goal of this study was to develop the above-mentioned approaches and to compare the properties of dendrimers of various modification degrees.

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EXPERIMENTAL

All reactions were carried out under an atmosphere of inert gas. The solvents were dehydrated through distillation over CaH_2. ^1H NMR spectra were recorded with a Bruker WP-200 spectrometer. Dendrimers were purified with a Staier series II chromatograph (Akvilon, Russia) equipped with a refractometric detector and a column of 300 × 21.2 mm. Experiments were performed with Phenogel (10 μm (Phenomenex, US)) as a sorbent and THF as a solvent. Solvents were removed through heating at 50°C under vacuum (1 mmHg).

The glass transition temperatures were estimated from the onset of a step corresponding to the heat capacity jump in the course of devitrification.

The dynamic light scattering study of the dendrimers was performed on an ALV/DLS/SLS-5022F Compact Goniometer System facility (ALV GmbH, Germany) equipped with a He–Ne laser (the wavelength $\lambda = 632.8$ nm and a capacity of 22 mW). All measurements were made at a temperature of 25°C and a scattering angle of 90°. Methyl *tert*-butyl ether and hexafluorobenzene were used as solvents.

The intrinsic viscosity was measured on an Ubbelohde viscometer with a capillary diameter of 0.3 mm. THF, methyl *tert*-butyl ether, and hexafluorobenzene were used as solvents. The temperature regulation was accurate to within 0.1°C.

Dendrimers were applied on substrates from supercritical CO_2 as described in [12, 13]. CO_2 (99.997%) was purchased from OAO Linde Gas Rus. A substrate was exposed in the high-pressure cuvette containing a dendrimer solution in supercritical CO_2 (~0.01 g/l) at a pressure of 65 MPa and a temperature of 65°C for 2 h. The exposure was finished by decompression of the cuvette, the substrate was taken out the cuvette, and the precipitated structures were examined by AFM.

AFM studies were performed on a MultiMode SPM instrument (Digital Instruments, USA) equipped with a NanoScope-IIIa controller and a preliminarily calibrated D-scanner. Measurements were made in the tapping mode with the use of commercial cantilevers (Lukin State Research Institute of Physical Problems, Russia). The data recording density was 512 × 512 points, and the scan frequency was 1 Hz.

Poly{tris(γ-trifluoropropyl)siloxy}carbosilane dendrimer containing cyclic fragments (G-7.5(F, Si–O–Si)) was synthesized as follows. A mixture composed of tris(γ-trifluoropropyl)silanol (2.6 g, 0.77×10^{-2} mol) and pyridine (0.64 g, 0.81×10^{-2} mol) was added to the stirred solution of the Si_{509}^{256} (Cl) dendrimer (1.55 g, 2.75×10^{-5} mol) in dehydrated toluene (2.4 ml) under an atmosphere of inert gas. The reaction mixture was allowed to stand in a densely closed flask for 24 h and then heated at 40°C for 8 days. The reaction was monitored via measurement of the ^1H NMR spectra of the reaction mixture. Methyl *tert*-butyl ether (100 ml) was added, washed with distilled water, and dried over Na_2SO_4. After reprecipitation, the product (2.18 g, 59%) was isolated.

For $Si_{765}C_{4592}H_{8412}F_{2304}O_{256}$ anal. calcd. (%) (with allowance made for 50% modification): Si, 19.69; C, 45.48; H, 5.64; F, 24.08; O, 3.38

Found (%): Si, 16.81; C, 45.71; H, 7.27; F, 26.28; O, 3.27.

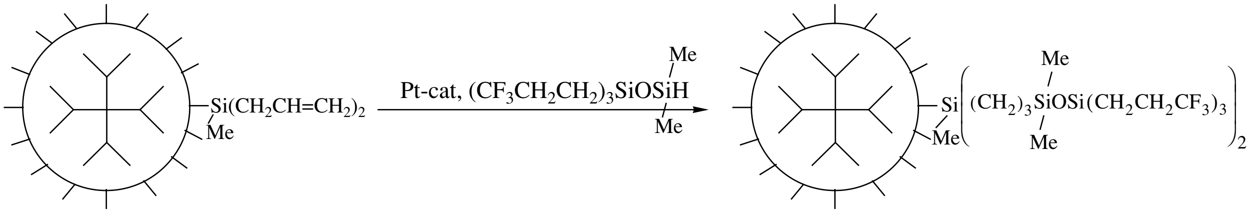
The synthesis of poly{tris(γ-trifluoropropyl)siloxy}carbosilane dendrimer (G-7.5(F)) was described in detail in [11].

The synthesis of tris(γ-trifluoropropyl)silanol was described in [14].

RESULTS AND DISCUSSION

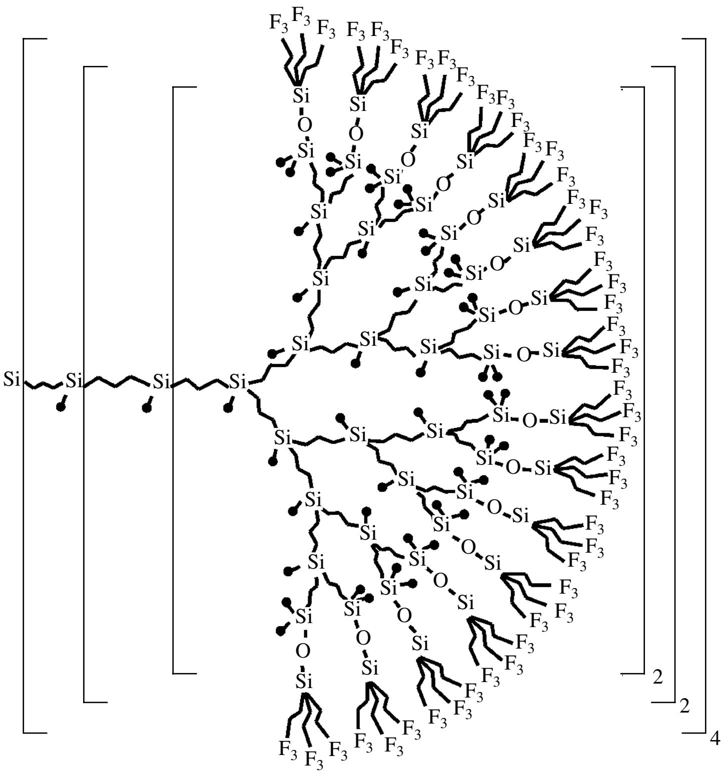
We tested two synthetic schemes that differ in the nature of functional groups of the parent dendrimer and the structure of the modifying agent.

The first synthetic scheme includes the hydrosilylation of allyl groups of the dendrimer with 3,3-dimethyl-1,1,1-tris(γ-trifluoropropyl)disiloxane in the presence of a platinum-containing catalyst in methyl *tert*-butyl ether in accordance with [11].

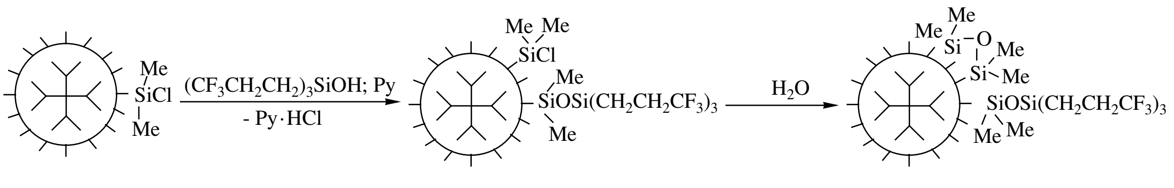


Scheme 1.

On the basis of this approach, we synthesized a fully modified carbosilane dendrimer containing tris(γ-trifluoropropyl) groups in the surface layer of the molecular structure (G-7.5(F)). This dendrimer shows good solubility in various organic solvents. Its structural formula is outlined below.



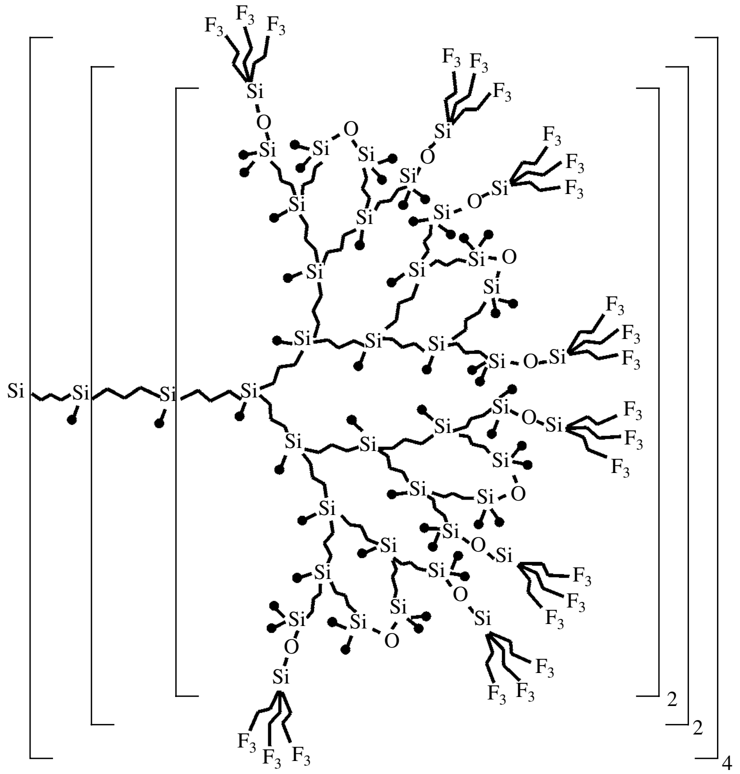
The second variant developed for the synthesis of fluorinated carbosilane dendrimers involved the heterofunctional condensation procedure. The dendrimer bearing chlorosilyl groups in the surface layer (G-6 (Cl)) was used as a parent carbosilane dendrimer, and tris(γ-trifluoropropyl)silanol was used as a modifying agent. The sequence of chemical reactions is illustrated by the following scheme.



Scheme 2.

The ratio of reagents in the first reaction was selected so as to prepare the dendrimer containing half the amount of tris(γ-trifluoropropyl) groups on the surface of that of the dendrimer synthesized in accordance with Scheme 1. In other words, after completion of condensation, the as-modified dendrimer should contain almost equal proportions of dimethyl(chloro)silyl and tris(γ-trifluoropropyl)siloxane groups.

When the reaction was completed, the product was washed with water and the hydrolysis of remaining chlorosilyl groups gave rise to cyclic moieties. Under milder hydrolysis conditions, the process could be stopped at the stage of hydroxyl derivatives by analogy with [15]. The synthesis illustrated by Scheme 2 produced the carbosilane dendrimer containing cyclic siloxane moieties in the surface layer along with tris(γ-trifluoropropyl) groups. The structural formula of the dendrimer (G-7.5(F, Si–O–Si)) is depicted below.



The target product was isolated by preparative gel chromatography. Its structure was established by IR and ^{1}H NMR spectroscopy and elemental analysis. The two latter methods are extremely sensitive to the completeness of modification. According to the elemental analysis data, the content of fluorine atoms in the dendrimer G-7.5(F, Si–O–Si) is 26.28% and markedly differs from the content of fluorine in the G-7.5(F) dendrimer (32.89%). According to IR spectroscopy, hydroxyl groups are absent in dendrimers G-7.5(F) and G-7.5(F, Si–O–Si).

Naturally, a question arises as to the distribution of modifying units between dendrimer molecules prepared through the partial modification procedure. In this case, regular and irregular distributions of modifying units are feasible. With due regard for the fact that tris(γ-trifluoropropyl) units are sufficiently bulky substituents, it may be expected that the distribution of substituents will be regular by analogy with methylbidecylsilyl substituents [16]. Such a distribution of substituents is confirmed by the GPC analysis of the G-7.5(F, Si–O–Si) dendrimer carried out immediately after completion of the reaction (Fig. 1).

The chromatographic curve presented in Fig. 1 shows that, despite the presence of high-molecular-mass fractions that result from side intermolecular reactions occurring in the course of hydrolysis, the target product is characterized by a narrow peak typical of dendrimers. If the distribution were irregular (this would lead to the nonuniform distribution of substituents in the dendrimers), the basic peak would appear as a widened asymmetric maximum.

The assumption that the distribution is regular is confirmed by the NMR studies as well.

A comparison of the spectra obtained for the fully modified dendrimer G-7.5(F) and the dendrimer with

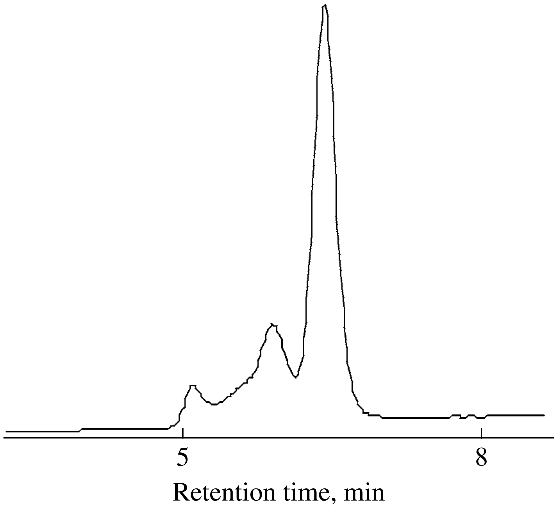


Fig. 1. GPC traces of the G-7.5(F, Si-O–Si) dendrimer after completion of the reaction.

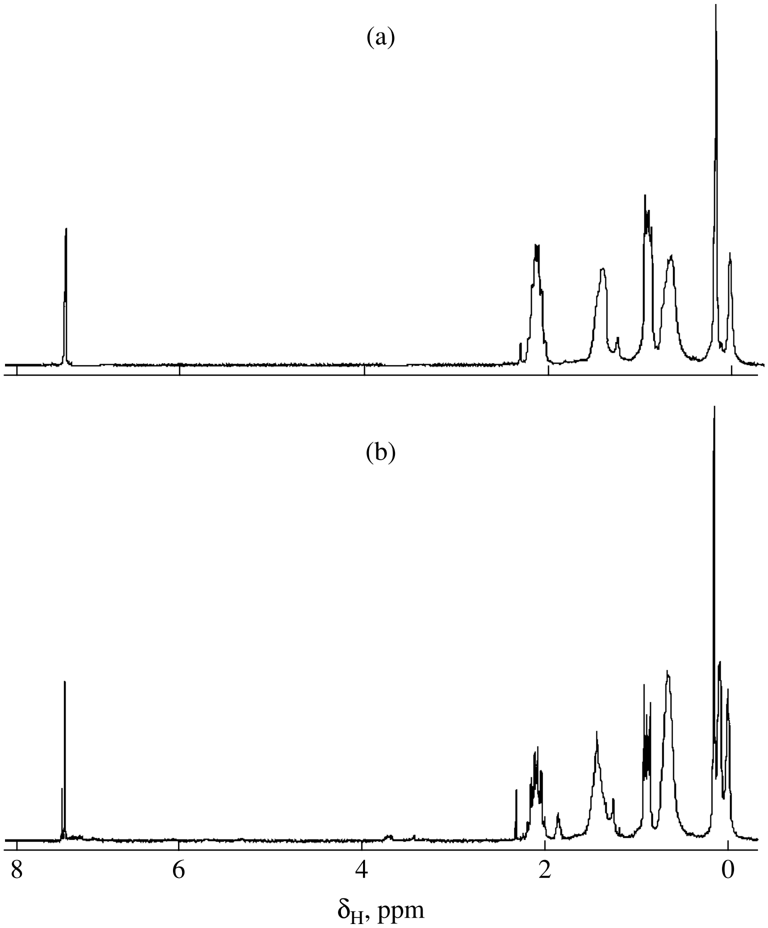


Fig. 2. ^{1}H NMR (CDCl$_3$) spectra of dendrimers (a) G-7.5(F) and (b) G-7.5(F, Si–O–Si).

the partial addition of fluorohydrocarbon moieties G-7.5(F, Si–O–Si) (Fig. 2) reveals that, in the latter case, signals due to methyl protons of silicon atoms of the dendrimer are represented by two singlets (0 and 0.09 ppm), in contrast to the single singlet observed in the case of G-7.5(F). If modification were irregular, three signals would be observed since an additional variant of silicon atoms incorporated into two cyclosiloxane groups would appear, but this is not the case. Thus, if the reagent is in shortage, only one group of each two chlorosilyl groups on the branching silicon atom is replaced in the course of modification.

Both products are transparent colorless resinlike noncrystalline substances that are well soluble in organic solvents, for example, THF, methyl *tert*-butyl ether, and hexafluorobenzene.

Dendrimers G-7.5(F) and G-7.5(F, Si-O–Si) were isolated from the reaction mixture via preparative chromatography. Figure 3 shows the chromatograms for the dendrimers subjected to preparative purification.

Thus, two fluorinated carbosilane dendrimers were synthesized that differ in the amount of tris(γ-trifluoropropyl) groups in the surface layer and the presence or absence of cyclic moieties between dendrimer branches. The occurrence of cyclic moieties in G-7.5(F, Si–O–Si) should formally enhance the rigidity of its

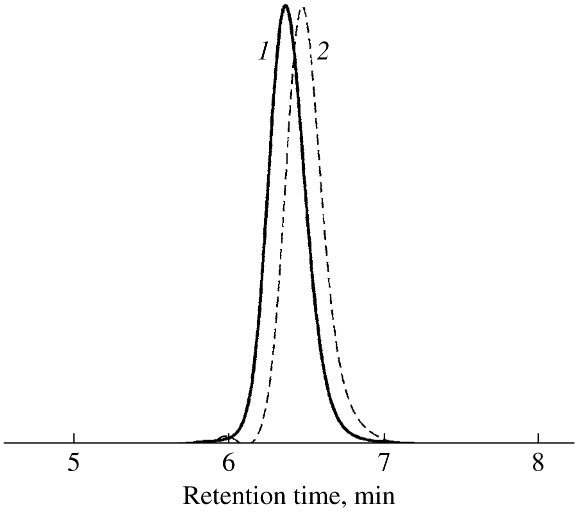


Fig. 3. GPC traces of dendrimers (*1*) G-7.5(F) and (*2*) G-7.5(F, Si–O–Si) after preparative purification.

molecular structure, as should be reflected by its physical properties.

Figure 4 displays the DSC curves of G-7.5(F) and G-7.5(F, Si–O–Si) dendrimers. The heat capacity jumps observed at –50°C for G-7.5(F) and −44°C for G-7.5(F, Si-O–Si) should be assigned to their glass transition temperatures. A comparison of these data with the results of DSC studies available for the parent carbosilane analog (T_g = –90°C) [17] leads us to infer that the glass transition temperature significantly increases owing to incorporation of fluorocarbon substituents into the surface layer of the molecular structure of dendrimers.

The amount of fluorohydrocarbon moieties in the G-7.5(F, Si–O–Si) dendrimer is half that in the dendrimer with the fully fluorohydrocarbon surface layer G-7.5(F). Therefore, it is expected that the devitrification of the dendrimer with a smaller amount of fluorohydrocarbon groups would take place in the range from –90°C (the T_g of the carbosilane analog) to –50°C (the T_g of the fully substituted G-7.5(F)). However, the glass transition temperature of the G-7.5(F, Si–O–Si) dendrimer is 6° higher than that of G-7.5(F). This difference in the glass transition temperatures should be attributed to a significant reduction in the molecular mobility of the system containing cyclic fragments.

The solution behavior of the test samples is different also (table). In the case of the G-7.5(F) dendrimer, a change in the size of the molecular globule is evident from the viscometry data. The intrinsic viscosity of this dendrimer in THF is lower than those in hexafluorobenzene and methyl *tert*-butyl ether. This finding is indicative of a more compact molecular organization of the dendrimer in this solvent. The maximum size of the molecular globule is detected in the case of methyl *tert*-butyl ether.

The nature of solvent has almost no effect on the intrinsic viscosity of the G-7.5(F, Si–O–Si) dendrimer. It appears that cyclic moieties decrease the conformational mobility of separate branches and thus restrain the possibility of responding to a change in the quality of the solvent. In other words, there is detectable difference between the systems under comparison; however, both dendrimers are sufficiently dense globular objects. In addition to the viscometry data, this conclusion is confirmed by the dynamic light scattering measurements of hydrodynamic radii of dendrimers in various solvents (Fig. 5).

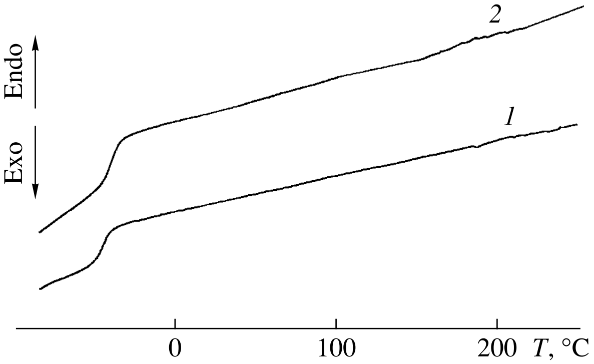


Fig. 4. DSC traces of dendrimers (*1*) G-7.5(F) and (*2*) G-7.5(F, Si–O–Si) recorded at a heating rate of 20 K/min under argon.

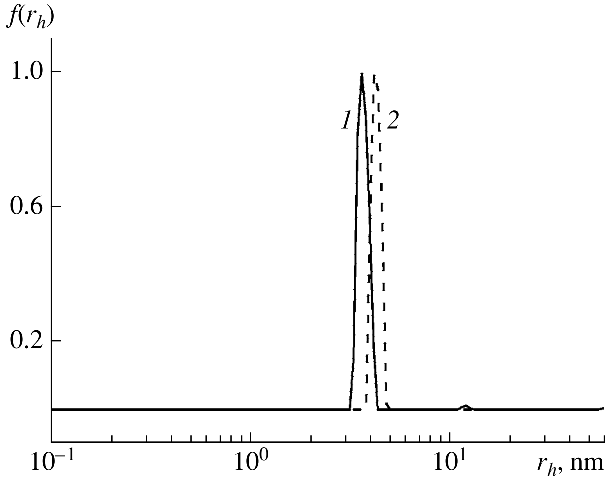


Fig. 5. The hydrodynamic radius distribution function for dendrimers in hexafluorobenzene: (*1*) G-7.5(F, Si–O–Si) and (*2*) G-7.5(F).

One of the important distinguishing features of fluoro-containing polymer systems, among them dendrimers, consists in their solubility in supercritical CO_2. In the case of dendrimers, this specific feature is of significance owing to a substantially large size of the dendrimer and, hence, its larger capacity as a potential

Intrinsic viscosity and hydrodynamic radii estimated by viscometry and dynamic light scattering

Solvent	[η], dl/g		$r_{[\eta]}$, nm		r_{DLS}, nm	
	G-7.5(F)	G-7.5 (F, Si–O–Si)	G-7.5(F)	G-7.5 (F, Si–O–Si)	G-7.5(F)	G-7.5 (F, Si–O–Si)
Tetrahydrofurane	0.02	0.03	3.65	3.47	–	–
Methyl *tert*-butyl ether	0.03	0.03	4.03	3.5	4.05	3.7
Hexafluorobenzene	0.03	0.03	3.9	3.4	4.2	3.9

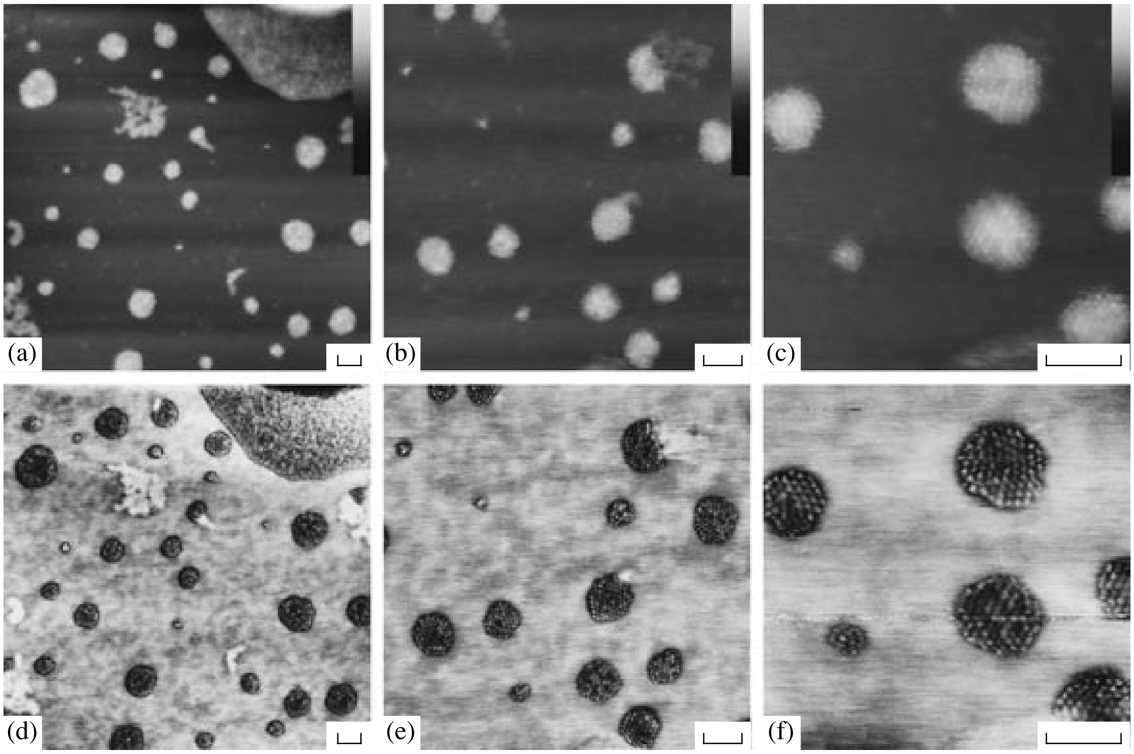


Fig. 6. (a–c) Topographic and (d–f) corresponding AFM images of islands of the monolayer of dendrimers with the fluorohydrocarbon layer (G-7.5(F)) after precipitation on the mica surface from supercritical CO_2 solution. Magnification increases from right to left: the microimage sizes are (a, d) 750 × 750, (b, e) 500 × 500 and (c, f) 250 × 250 nm. The reference scale is 50 nm, and the height scale is 10 nm.

container for reactions in supercritical CO_2. Under the selected experimental conditions, we managed to dissolve the dendrimer sample in supercritical CO_2 and to deposit the material thus obtained on a mica substrate. Figure 6 shows the AFM images of the dendrimer with the fluorohydrocarbon layer (G-7.5(F)) on the surface of mica.

Separate islands of the dendrimer monolayer of 3.6 ± 5 nm in height are well seen above the substrate surface. It is pertinent to note that, as in the case of the AFM data reported for the pyrographite substrate [11], the AFM images exhibit individual dendrimers packed to a regular two-dimensional lattice close to the hexagonal lattice with a unit-cell period of 6.1 ± 0.4 nm. The measured values of the packing period of the dendrimers and of the monolayer thickness are consistent with the data from [11].

It appears that the method of dendrimer deposition and the nature of the substrate insignificantly affect the packing of macromolecules into the two-dimensional regular structure.

CONCLUSIONS

Thus, the grafting of the outer fluorohydrocarbon layer onto the carbosilane dendrimer leads to the densification of this layer, while the incorporation of crosslinks between the branches transforms the dendrimer into a hydrodynamically rigid object insensitive to the quality of solvent. The glass transition temperatures of the modified dendrimers are determined by the nature of the outer layer, whereas restriction of the mobility of separate branches of the dendrimer affects its glass transition temperature. The solubility of the carbosilane dendrimer with the fluorohydrocarbon outer layer of the molecular structure in supercritical CO_2 lends support for the above suggestion and facilitates studies concerning the use of amphiphilic dendrimers as active additives for processes carried out in supercritical CO_2.

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