

Synthesis of a Carbosilane Dendrimer with Fluorocarbon Substituents at the Silicon Atoms in the Surface Layer of the Molecular Structure

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The surface layer of a dendrimer molecular structure determines the level and specifics of both intermolecular interactions of dendrimers and their interactions with solvents and other molecular entities and surfaces. One of the basic methods of modifying the surface of dendrimers and, hence, controlling their properties involves chemical transformations with the use of numerous functional groups. The introduction of fluorinated moieties into the surface layer of the dendrimer molecular structure endows such systems with some specific properties: a low surface energy, a combination of hydrophobic and oleophobic interactions, an affinity for supercritical CO₂, and other features [1, 2] determined by the structure of the fluorine atom and the electronic structure of the fluorine–carbon bond [3, 4].

Information on the synthesis of fluorinated derivatives of carbosilane dendrimers is very scarce. The syntheses of dendrimers of the first to third generations with perfluoroalkyl groups at the surface have been described [5, 6]. Similar to the initial carbosilane matrices, they are hydrophobic and thermally stable; in addition, they become oleophobic due to the dense fluorinated layer [6]. However, even the third-generation dendrimer is insoluble in organic solvents. This feature is believed to be due to the high packing density of perfluoroalkyl groups in the surface layer of the dendrimer structure.

The combination of the fluorinated outer layer and the silicon–hydrocarbon core makes it possible to con-

sider these dendrimers as core–shell molecular systems. This accounts for the prospects for their use as molecular containers with the potential to control the barrier layer density [7]. No less important is the possibility of studying the molecular organization of dendrimers by neutron scattering methods [8] and studying monolayer compression isotherms [9]. It should be noted, however, that only readily soluble dendrimers of higher generations are of interest for such applications. Currently, no information on the synthesis of such dendrimers is available.

In this work, we studied different variants of synthetic schemes and, using one of them, pioneered the synthesis of a 7.5-generation carbosilane dendrimer with a fluorinated surface layer, which is readily soluble in organic solvents. The prerequisites were created for further study of fluorine-containing dendrimers, and the most promising ways to improve the synthetic schemes were determined.

To obtain the desired carbosilane dendrimer with a fluorinated surface layer (G-7.5(F)), we tested three synthetic schemes that differ in both the chemical nature of the functional groups of the initial dendrimer and the structure of the fluorine-containing modifying agent. Scheme 1 shows these three variants. Despite the differences in the structures of the reagents and the initial carbosilane dendrimers, all the reaction schemes yield the same target compound, dendrimer G-7.5(F).

Comparison of these synthetic strategies showed that the simplest and most convenient among them is the reaction of hydrosilylation of the allyl groups of a dendrimer with 3,3-dimethyl-1,1,1-tris(γ -trifluoropropyl)disiloxane in the presence of a Pt catalyst (variant I). The reaction course was monitored by observing the disappearance of the ¹H NMR signal of the protons at the double bond.

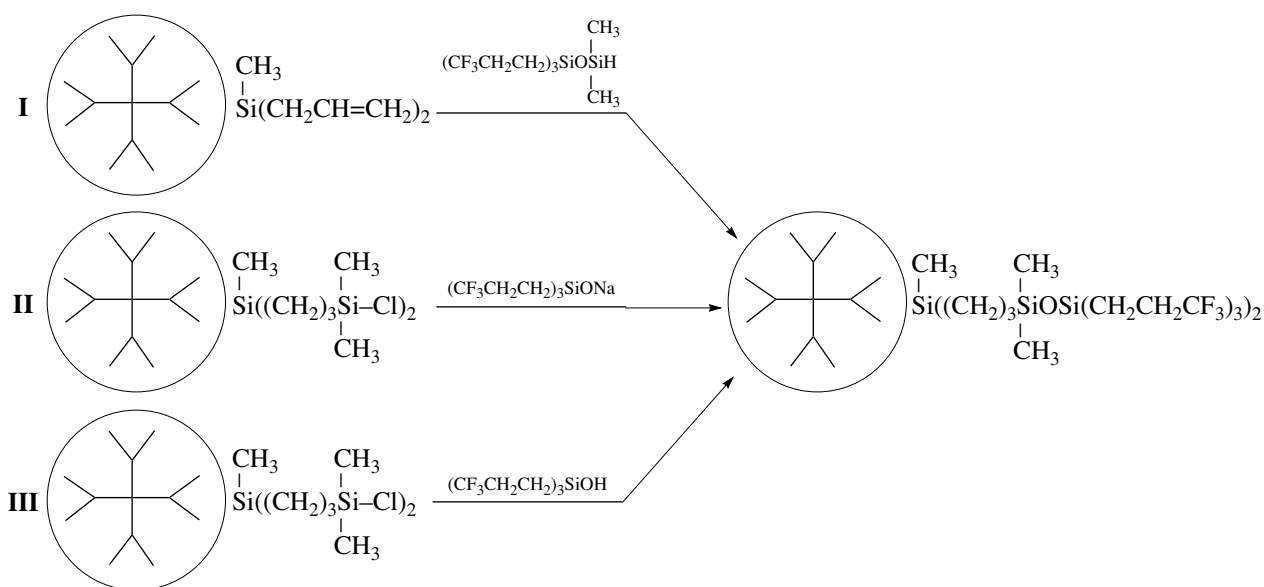
The other two methods also resulted in the fluorinated derivative of the dendrimer but involved difficulties. The reaction with sodium tris(γ -trifluoropropyl)silanolate requires the maintenance of definite temperature conditions and exactly stoichiometric amounts of the fluorine-containing silanolate. Deviation from these

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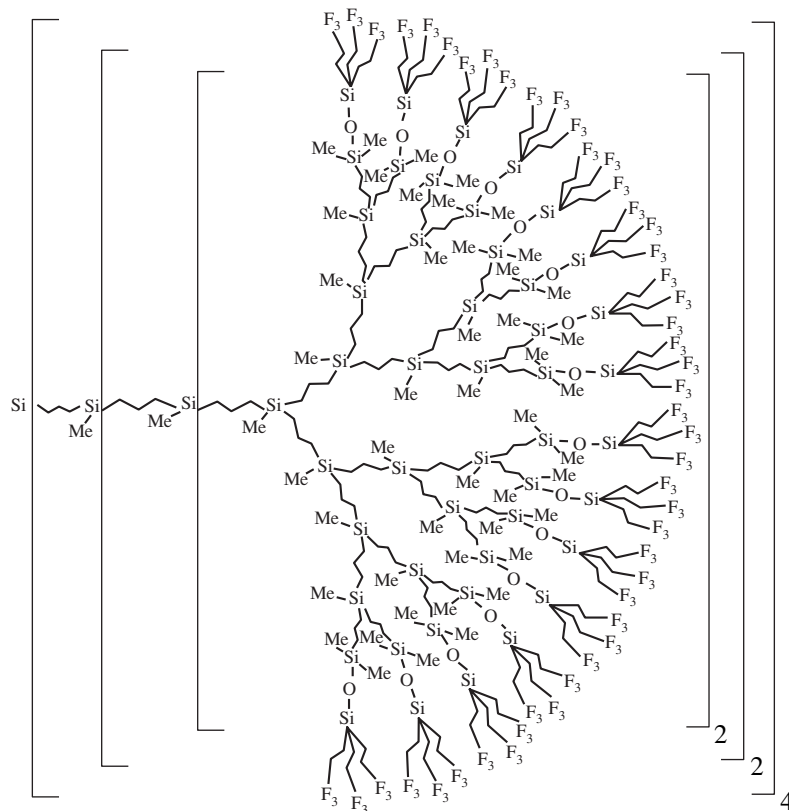


Scheme 1.

conditions leads to splitting of the siloxane bond in the dendrimer to form by-products. Using tris(γ -trifluoropropyl)silanol as the fluorinated modifying reagent also led to the formation of by-products, which was caused by water traces resulting from homocondensation of silanol. These difficulties can hardly be obviated taking

into account the high functionality and sensitivity of the chlorosilyl dendrimer derivative with respect to hydroxyl-containing reagents.

The structural formula of the target dendrimer is shown in Scheme 2. Dendrimer G-7.5(F) was isolated from a reaction mixture by preparative chromatogra-



Scheme 2.

phy, and its chemical structure was established based on gel permeation chromatography (GPC), elemental analysis, and ^1H NMR data.

The chromatograms of the initial sixth-generation carbosilane dendrimer G-6(All) and the modified product G-7.5(F) are shown in Fig. 1.

Despite the fact that modification leads to a fourfold increase in the molecular weight of the product compared to the initial compound, the increase in the hydrodynamic radius is insignificant, which is typical of solutions of dendrimers, dense globular molecular entities.

Dendrimer G-7.5(F) is a transparent, colorless, and odorless resinous noncrystalline substance soluble in organic solvents, such as THF, hexafluorobenzene, and ether.

Figure 2 shows the DSC curve for dendrimer G-7.5(F). The heat capacity jump at -50°C should be assigned to the glass transition temperature. The introduction of fluorocarbon moieties considerably elevates the glass transition temperature of the dendrimer as compared to the initial carbosilane analogue, for which the glass transition is observed in the range from -80 to -90°C [10].

Figure 3 shows the TGA curves obtained in air and in an argon atmosphere. The thermal behavior of G-7.5(F) in an inert atmosphere is analogous to the behavior of un-cross-linked hyperbranched carbosilane polymers [11]. The thermal degradation of G-7.5(F) starts at about 400°C and comes to an end in a narrow temperature range. In an oxidative atmosphere, the behavior is different from that in an inert atmosphere: the degradation takes place in two stages and thermal oxidative processes start even at about 200°C . We may assume that, at these temperatures, the fluorocarbon moieties of the surface layer are oxidized. At the second stage (about 330°C), the process is sharply accelerated, which is evidence of the degradation of the core structure accompanied by detachment of large structural fragments. Our findings show that the upper limit of the thermal stability of dendrimer G-7.5(F) is 350°C in an inert atmosphere and 180°C in an oxidative atmosphere.

It was previously shown that dendrimers of higher generations have a sufficiently dense molecular structure to hold their three-dimensional geometric shape not only in solutions but also in the bulk. Figure 4 shows the AFM images of the polycarbosilane dendrimer with tris(γ -trifluoropropyl) groups G-7.5(F) applied from a solution in hexafluorobenzene ($c = 0.001$ mg/mL) to a pyrolytic graphite substrate. Decreasing the scale of the scanned area to 300 nm makes it possible to distinguish separate dendrimer molecules.

Analysis of the AFM images showed that the measured height of the dendrimer monolayer over the substrate surface is 3.0–4.5 nm. The scatter of the values obtained is caused by deformations of layers under an AFM probe tip; the power action of the latter is hard to

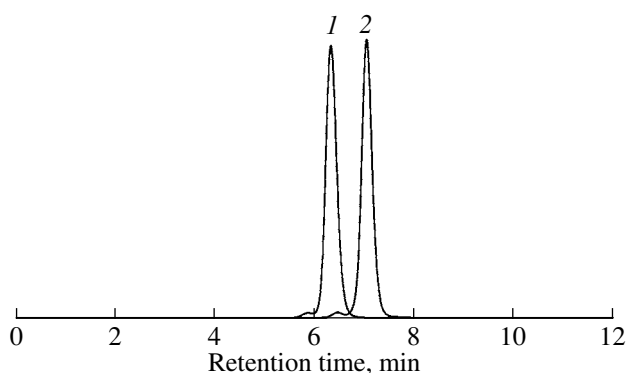


Fig. 1. GPC curves for (1) G-7.5(F) and (2) G-6(All).

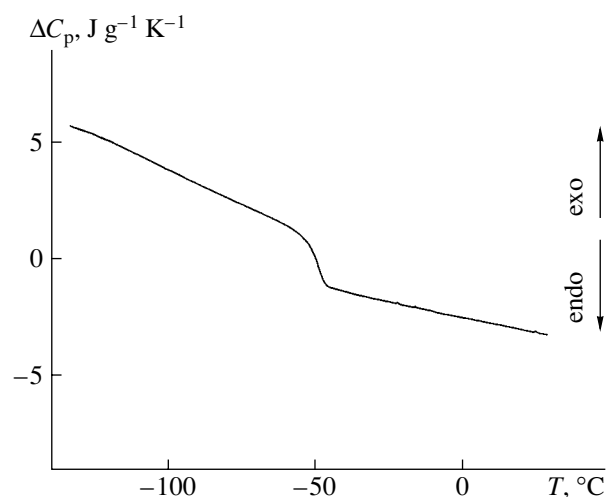


Fig. 2. DSC curve for dendrimer G-7.5(F) at a heating rate of 10 K/min.

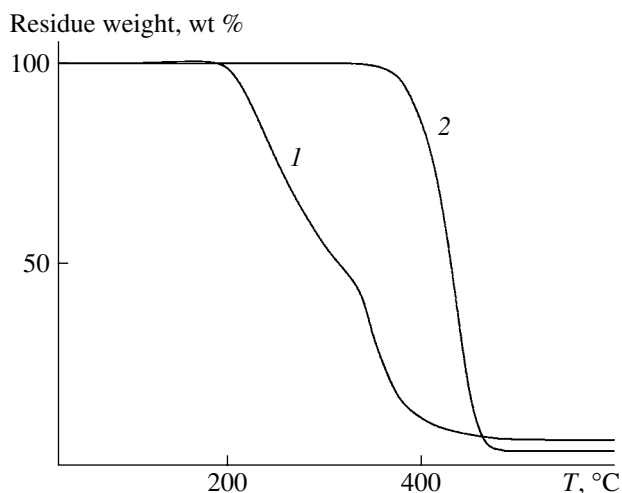


Fig. 3. TGA curves for dendrimer G-7.5(F) in (1) air and (2) argon at a heating rate of 5 K/min.

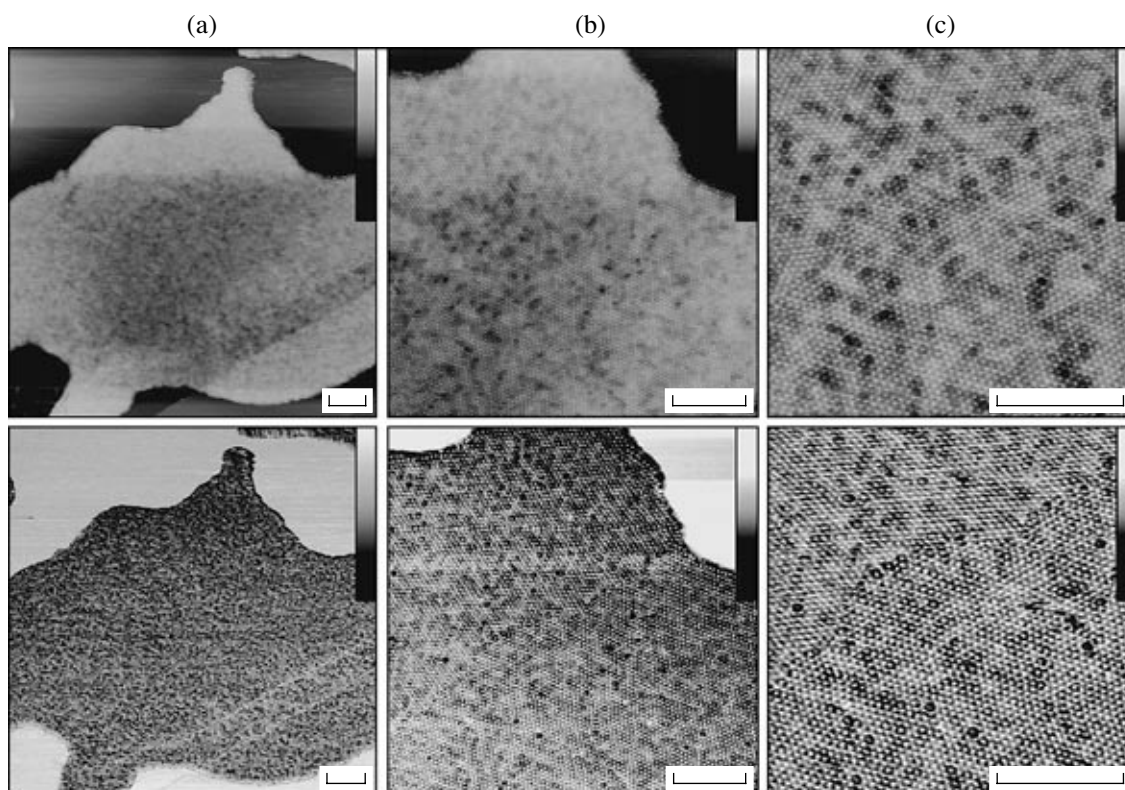


Fig. 4. Topographic (height scale, 10 nm) (top) and phase (scale, 50°) AFM images of dendrimer G-7.5(F) applied to a pyrolytic graphite surface. The magnetization increases from left to right; frame size: (a) 1×1 , (b) 0.5×0.5 , and (c) 0.3×0.3 μm . Bars represent 100 nm.

control in tapping-mode AFM studies. The monolayer reveals a regular molecular arrangement with a period of 5.6–6.5 nm. Here, the scatter is caused by distortions due to mutual temperature-induced drift of the probe and the sample, which are especially significant for the tapping mode since the scan rate is limited. Thus, the AFM data (taking into account that the measured heights are underestimated because of deformations) allow us to conclude that the dendrimer size is about 6 nm.

Thus, the successful synthesis of the target dendrimer with a fluorohydrocarbon surface layer created necessary prerequisites for study of the structure–property relationship in carbosilane dendrimers.

EXPERIMENTAL

Synthesis of G-7.5(F) was performed in two stages. In an inert gas atmosphere, 10 μL of Pt catalyst PC-072 was added to a solution of 0.99 g (0.31×10^{-4} mol) of Si_{256}^{253} (All) in 4 mL of absolute diethyl ether and an excess (3.44 g, 0.87×10^{-2} mol) of 3,3-dimethyl-1,1,1-tris(γ -trifluoropropyl)disiloxane was added to the stirred mixture. The resulting reaction mixture was kept in a sealed vessel for 72 h. The conversion was 80% as probed by ^1H NMR. After that, the solvent was removed by evaporation, 2.4 g (0.61×10^{-2} mol) of 3,3-

dimethyl-1,1,1-tris(γ -trifluoropropyl)disiloxane and 5 μL of PC-072 were added to the dry residue, and the mixture was allowed to stand at 110°C. After the exhaustive conversion of the allyl groups of the dendrimer was achieved, the product was reprecipitated. The yield was 3.06 g (75%) of the product.

For $\text{Si}_{765}\text{C}_{4592}\text{H}_{8412}\text{F}_{2304}\text{O}_{256}$ anal. calcd. (wt %): Si, 16.15; C, 41.47; H, 6.38; F, 32.91; O, 3.09.

Found (wt %): Si, 15.90; C, 41.58; H, 6.36; F, 32.89; O, 3.27.

^1H NMR (δ , ppm): 0.05 (m, 756H, SiCH_3); 0.20 (m, 1536H, $\text{Si}(\text{CH}_3)_2$); 0.70 (m, 2032H, SiCH_2), 0.90 (m, 1536H, $\text{CH}_2\text{CH}_2\text{CF}_3$), 1.45 (m, 1016H, CH_2), 2.10 (m, 1536H, $\text{CH}_2\text{CH}_2\text{CF}_3$).

Tapping-mode AFM images were taken on a Digital Instruments Nanoscope-IIIa instrument with a preliminarily calibrated D-scanner and commercially available silicon cantilevers (NIIFP, Russia). Frames of 512×512 pixels were recorded at a scan frequency of 1 Hz.

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