

## Organized Monolayers of Carbosilane Dendrimers with Mesogenic Terminal Groups

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**ABSTRACT:** The structural ordering of mesogenic-terminated carbosilane dendrimers within surface monolayers was studied. We have shown that despite their symmetrical spherical shape layering with average spacing close to 6 nm is observed for dendrimers with butoxyphenylbenzoate terminal groups deposited on hydrophilic silicon substrates. The molecular layered packing is formed by flattened dendritic molecules with terminal groups stacking into bilayers. This layered ordering is controlled by strong interactions between the polar mesogenic groups and the hydrophilic surface and by microphase separation of the dendritic core and terminal groups. The dilution of the outer mesogenic shell with a nonmesogenic component partially disturbs the layered packing within the monolayer. Complete disruption of the regular lamellar ordering is observed if butoxyphenylbenzoate terminal groups are replaced with shorter and more polar cyanbiphenyl groups. For all dendrimers studied here the replacement of the hydrophilic support with hydrophobic one prevents the formation of dense surface layers due to antagonistic interactions between polar terminal groups and a methyl-terminated surface. However, the presence of the nonmesogenic hydrophobic terminal groups stimulates the formation of two-dimensional circular molecular structures which are characteristic of columnar LC dendrimer phases.

### Introduction

The assembly and ordering of branched molecules is dependent on the molecular architecture with major factors being the degree of branching, the core shape, the flexibility of the branches, the generation number, and the terminal functionality.<sup>1</sup> Tailoring the chemical and physical properties of dendritic polymers, facilitated by the stepwise synthesis methodologies, has been the driving force in the exploration of different molecular architectures and chemical composition of dendrimers.<sup>2,3</sup> Although the vast majority of dendrimers synthesized to date are carbon-based materials, several examples of inorganic-based molecules (such as silicon or phosphorus-containing dendrimers) have been reported.<sup>4,5</sup> The exploration of heteroatom dendrimer architecture offers greater possibilities in catalysis and organic–inorganic hybrid material applications, especially for the stable dispersion of metal nanoparticles. Additionally, the inclusion of silicon in the inner repeat units of the dendritic core offers favorable synthetic routes for ideal dendrimers as well as thermodynamically and kinetically stable molecules.<sup>6–8</sup> Carbosilane dendrimers are favorable for further functionalization because the low polarity and high energy of the Si–C bonds creates a chemically stable core. The exceptional flexibility of the carbosilane dendrimers also makes them easily adaptable with an overall shape dictated by interactions among terminal groups and terminal groups with supporting surfaces in cases of their adsorption on solid substrates.<sup>9</sup> Depending upon interfacial interactions and molecular flexibility, a variety of diverse organized nanostructures (compressed nanoparticles, uniform monolayers, nanofibers, individual cylinders, and lay-

ered, rectangular, and hexagonal lattices) have been observed for functional dendritic molecules.<sup>10,11</sup>

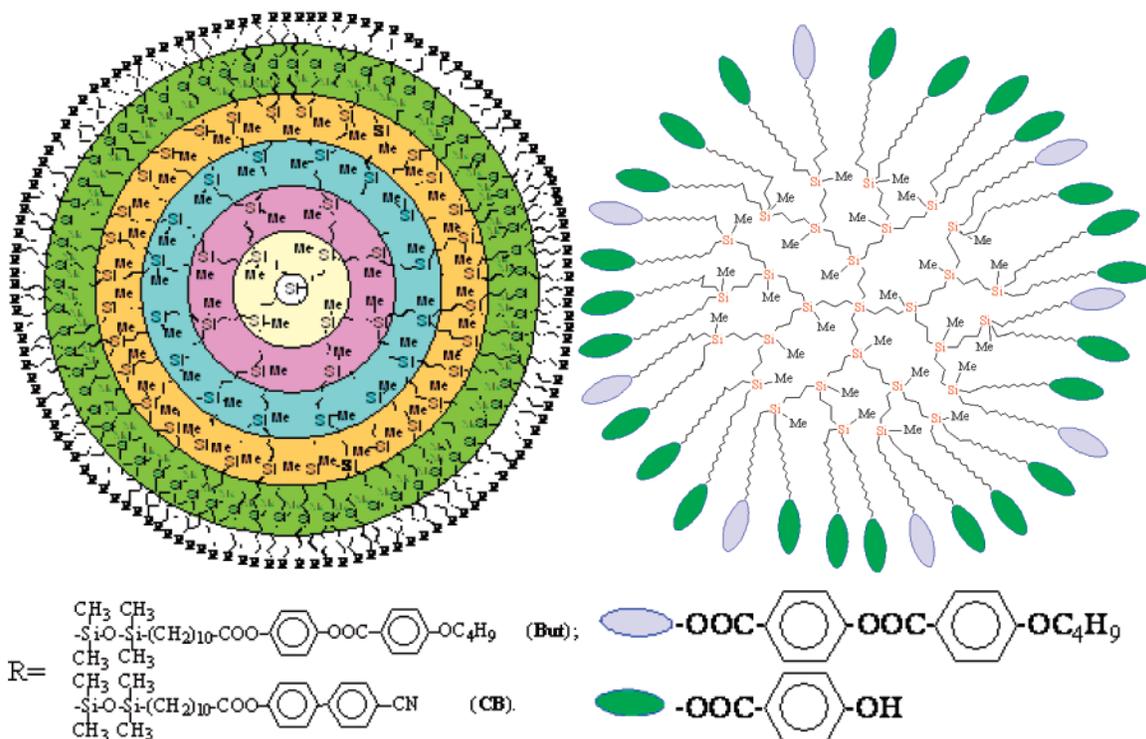
The incorporation of liquid crystalline (LC) fragments in dendritic architecture is an intriguing design approach which can result in fabrication of hybrid structures combining LC properties and dendritic functionalities and shapes.<sup>12</sup> Competing trends of mesogenic fragments to arrange in highly ordered structures and dendritic cores to form symmetrical shapes can fuse into a multitude of amalgam structures. Indeed, the alternating mesogenic fragments and aliphatic spacers within the dendritic architecture compel the molecules to form an onion-type column largely different from the mesophases typical for end functionalized LC dendrimers.<sup>13</sup> The controlled synthetic methodology allows for the preparation of dendrimers with alternating mesogenic fragments for each generation.<sup>14–16</sup> The ellipsoidal shape of the dendritic core has been shown to adversely affect the order of the mesogenic fragments attached to higher generation dendrimers.<sup>17</sup> Similarly, properties such as dielectric relaxation have been influenced by the shape and flexibility of the dendritic core affecting the ordering and mobility of the mesogenic fragments.<sup>18</sup>

The functionality of the terminal groups might exert ultimate control on the molecular packing of dendrimer cores.<sup>19–21</sup> The combination of flexible dendritic cores and mesogenic groups creates novel LC behavior.<sup>22</sup> The attachment of mesogenic groups to PAMAM dendritic cores has been observed to force the molecules to adopt a cylindrical shape, forming lamellae structures with influence of the generation number on the ordering.<sup>23</sup> The inclusion of mesogenic groups at the periphery forced a transition to a disk shape facilitating a columnar ordering.<sup>23c</sup> Similarly, the grafting of mesogenic groups to a PAMAM core produced a transition from smectic ordering to columnar ordering as the molecular cross-section increased.<sup>24</sup> A fifth generation carbosilane

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**Figure 1.** Chemical formulas of G-3(Und-PH-But-70%), G-5(Und-But)<sub>128</sub>, and G-5(Und-CB)<sub>128</sub> LC carbosilane dendrimers.

dendrimer with 128 cyanobiphenyl groups was shown to have significant peculiarities in the LC behavior upon heating unlike the lower generations dendrimers of the same type.<sup>25</sup> The first four generations were observed to form conventional lamellar (smectic A and C) mesophases while the fifth generation transitioned from lamellar ordering at 40 °C to elliptical columns at moderate temperature to hexagonal ordering of rounded columns at 130 °C. Surface studies of the fifth generation dendrimer showed that the film thickness and the substrate controlled the molecular packing.<sup>26</sup>

Here we focus on the elucidation of the molecular packing in the LC carbosilane dendrimers with 128 polar cyanobiphenyl groups and polar butoxyphenylbenzoate groups. These mesogenic groups have been chosen because their well-known LC behavior and similar dendrimers displayed peculiar structural ordering in the bulk state as will be discussed below. We observed that dendrimers with 128 butoxyphenylbenzoate terminal groups and hydrophobic tails form organized layering caused by phase separation of the flexible cores and mesogenic groups and the strong trend of the latest to form bilayer packing. The dilution of the outer mesogenic shell with a nonmesogenic component partially disrupts the layered packing. Complete disappearance of the regular layer ordering in molecular surface layers is observed if butoxyphenylbenzoate terminal groups are replaced with shorter and more polar cyanobiphenyl groups, despite the fact that these molecules formed smectic phases in the bulk state. The replacement of the hydrophilic silicon surface with hydrophobic substrates prevents the formation of dense surface films for all dendrimers studied here due to antagonistic interactions between polar terminal groups and a methyl-terminated surface of the hydrophobic substrate.

## Experimental Section

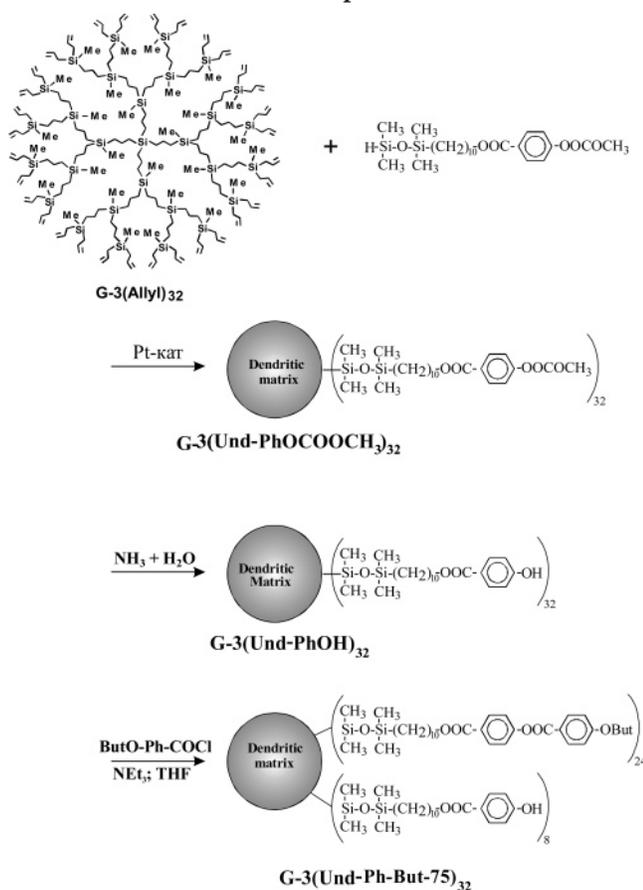
**Synthesis.** The fifth generations of the carbosilane LC dendrimers with a complete shell (100% substitution of

terminal groups) of cyanobiphenyl (G-5(Und-CB)<sub>128</sub>) and butoxyphenylbenzoate (G-5(Und-But)<sub>128</sub>) groups were synthesized as previously described (Figure 1).<sup>25</sup> The third generation of LC co-dendrimer (G-3(Und-PH-But-70%)) with butoxyphenylbenzoate and phenolic terminal groups was synthesized from a dendrimer with terminal phenolic groups according to Scheme 1.<sup>27</sup> The LC co-dendrimer was isolated in the individual state by preparative gel-permeation chromatography (GPC). The co-dendrimer composition was calculated by analyzing of an <sup>1</sup>H NMR spectrum taken from its CDCl<sub>3</sub> solution (Scheme 2).<sup>23d</sup> The integral intensities ratio of the proton signals corresponding to substituted an unsubstituted phenolic terminal groups gave a calculated composition result as 70% substituted *p*-butoxybenzolic groups over phenolic groups. The calculated method error was 3%, which is less than one substituted/unsubstituted group.

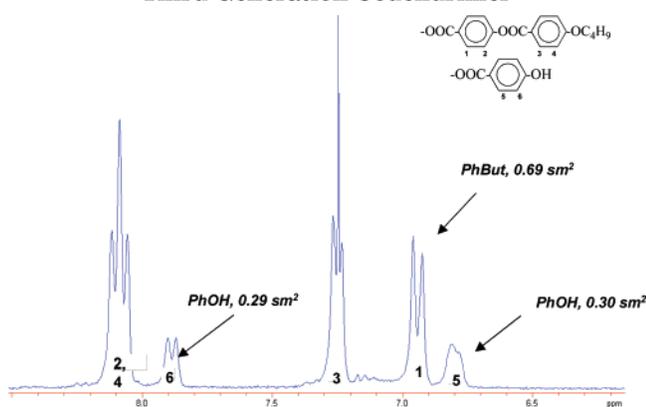
Atomically smooth silicon wafers of the {100} orientation with one side polished were used as substrates (Semiconductor Processing Co.). Silicon wafers were treated in "piranha" solution (30% hydrogen peroxide: 94% sulfuric acid, 1:3. **Caution:** chemical hazard!) according to the standard procedure.<sup>28</sup> The silicon substrates were used as cleaned bare substrates or as modified substrates with a self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS, Aldrich).<sup>29</sup> Toluene (Fisher) solutions of 0.03–0.08 wt % were spin cast at 3000 rpm and rinsed with toluene. The sample rinsing and the volume of solution deposited were varied to optimize the surface film formation. The thickness of the films was varied by the rinsing or adding additional droplets.

Ellipsometric measurements of monolayer thickness were carried out with a COMPEL Automatic ellipsometer (In-OmTech, Inc.). Imaging of the monolayers was performed with AFM microscopes, Dimension-3000 and Multimode (Digital Instruments), in the light tapping mode according to an experimental procedure described elsewhere.<sup>30</sup> Surfaces of the monomolecular layers were probed at several random locations with widely varying scan sizes from 0.1 to 30 μm. The geometrical parameters of all molecules were estimated from molecular models built with the Materials Studio 3.0 software package using the PCFF force field.<sup>31</sup> The combination of molecular dynamics and energy minimization was used to generate molecular models.<sup>32</sup>

**Scheme 1. Synthesis of Carbosilane Codendrimers of the Third Generation with Statistical Distribution of Butoxyphenylbenzoate and Phenolic Terminal Groups**



**Scheme 2. High-Resolution  $^1\text{H}$  NMR Spectrum of the Third Generation Codendrimer**



## Results and Discussion

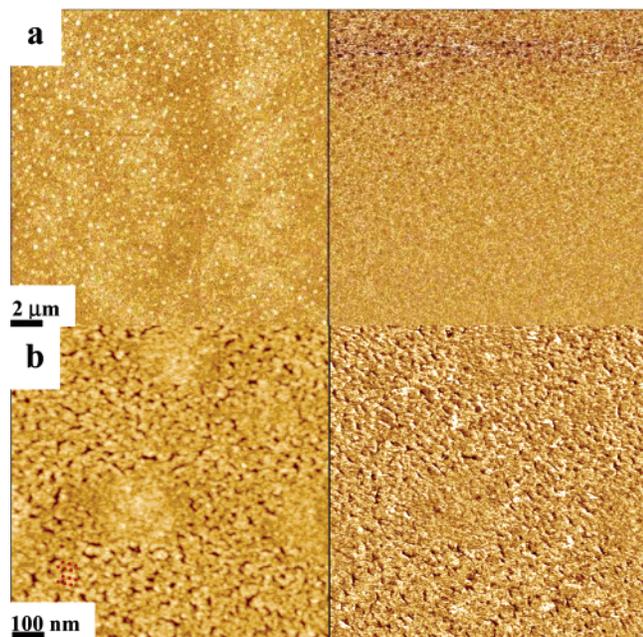
**Surface Films on Hydrophilic Substrates.** The measured effective thickness of the three monolayer samples for all three molecules was considerably lower than the diameter of the molecules determined by molecular models (around 12.9 nm for fifth generation molecules, see below) (Table 1). The effective thickness of the surface layer of G-5(Und-But)<sub>128</sub> varied from 2.1 to 6.1 nm depending upon deposition conditions with a similar trend in film thickness observed for G-3(Und-PH-But-70%) molecules (Table 1). Dissimilarly, G-5(Und-CB)<sub>128</sub> molecules formed the thinnest layers (1.7 nm to 3.0 nm), lacking a discernible trend in film thickness. The uniformity of these films and their internal micro-

**Table 1. Effective Thickness,  $t$ , of the Surface Films of LC Carbosilane Dendrimers and the Corresponding  $d$  Spacings**

sample no.	substrate	$t$ , nm	$d$ , nm
G-5(Und-But) <sub>128</sub>			
1	Si	2.2 ± 0.2	5.7 ± 0.4
2	Si	3.5 ± 0.1	5.4 ± 0.1
3	Si	6.1 ± 0.2	5.9 ± 0.4
4	OTS	0.3 ± 0.2	
G-3(Und-PH-But-70%)			
1	Si	2.5 ± 0.2	6.2 ± 0.4
2	Si	3.8 ± 0.1	5.2 ± 0.5
3	Si	5.5 ± 0.4	NA
4	OTS	0.4 ± 0.1	NA
G-5(Und-CB) <sub>128</sub>			
1	Si	1.7 ± 0.5	NA
2	Si	3.0 ± 0.1	NA
3	Si	1.6 ± 0.2	NA
4	OTS	0.2 ± 0.1	NA

structure were probed with AFM. The thickness of surface layers well below the unperturbed, symmetrical diameter of molecules indicated their pancake conformation after deposition on the hydrophilic silicon substrate. Here and below, we compare the experimentally obtained data on the film thickness with unperturbed molecular dimensions assuming extended conformation of the molecular fragment, a standard practice in similar studies. This approach can verify if the possibility of the extended conformation exists if the molecules are densely packed within the surface layers. In the case where actual molecular dimensions (such as a thickness of the layers in our case) are much smaller than the expected extended conformation, the only conclusion can be made that the actual conformation is much more compact than a simple fully extended conformation. Thus, this difference may justify making changes in actual conformation by, e.g., compressing molecular fragments and generating different conformations with combined bond twisting, molecular dynamic relaxation, and energy minimization which will satisfy the experimentally measured dimensions (film thickness and lateral spacing in our case) and can be used for illustration of the molecular packing proposed. This approach is important to verify if the proposed molecular packing with particular spacings does not contradict the possible (although one of many) conformation of the molecules in the energy minimized and relaxed state (local minimum). The value of this approach is in an exclusion of the unrealistic molecular packings disallowed by the internal molecular architecture and dimensions of the molecular fragments (there are limits on how much arms can be twisted without breaking them).

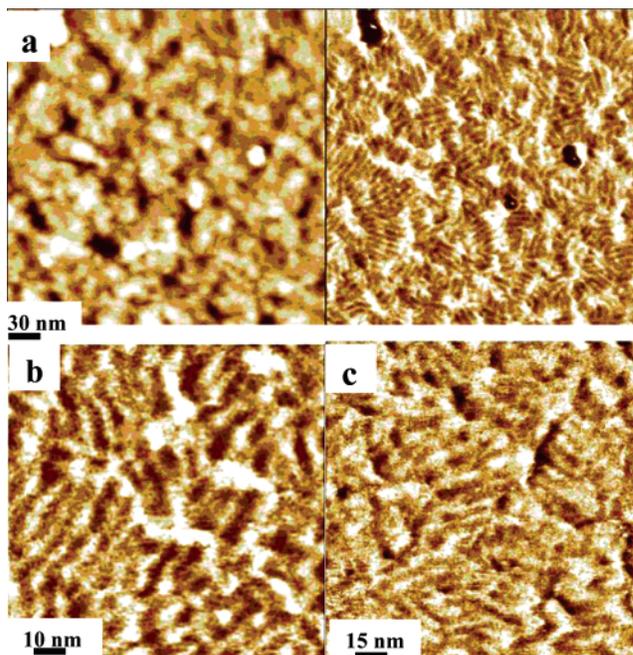
The G-5(Und-But)<sub>128</sub> films had a peculiar microscopic surface texture with regularly spaced circular surface areas with elevated height (0.3 nm above surrounding film) and an average diameter of 350 nm occupying 17% of the monolayer surface (Figure 2a). 2D Fourier transform indicated a very weak, short-range ordering of these circular elevations. The small height of the circular domains conflict with the idea of a thicker film expected with the molecular dimensions but signify more condensed packing of the molecules. Closer examination of the surface film surrounding these areas revealed an internal lamellae structure with poor but still visible periodicity limited only to a very few adjacent layers (see dotted lines for several layers in Figure 2b). The interlamellar spacings calculated from cross sections of the AFM images were within 5.4–5.9



**Figure 2.** Irregular ordering of the condensed areas for the surface films of G-5(Und-But)<sub>128</sub> on hydrophilic silicon substrate. Topographical image shown on left and phase image shown right. Z range: (a) 5 nm (topography), 20° (phase); (b) 5 nm (topography), 5° (phase). White dotted lines show an example of poor layered morphology.

nm for films prepared under different conditions (Table 1). These periodicities are well below the overall molecular diameter determined from the models (12.9 nm) but slightly larger than the diameter of the G5 carbosilane core itself (5.3 nm) (Figure 3).

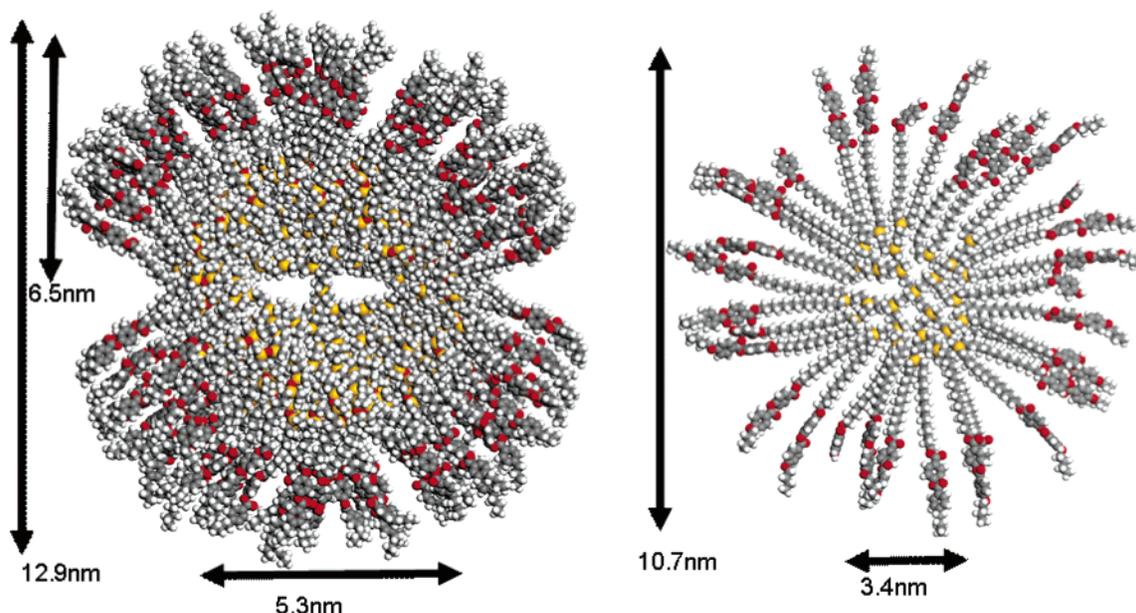
High resolution AFM imaging revealed that the surface areas of condensed packing had similar nanostructure with internal lamellae as the more loosely packed monolayer surrounding them for G-5(Und-But)<sub>128</sub> films (Figure 4). Although the layered ordering appears to be slightly denser than the layer outside the circular domains with increased height the interlamellar spacing remains within the margin of error (Table 1). The grain nanostructures are packed with stacks of



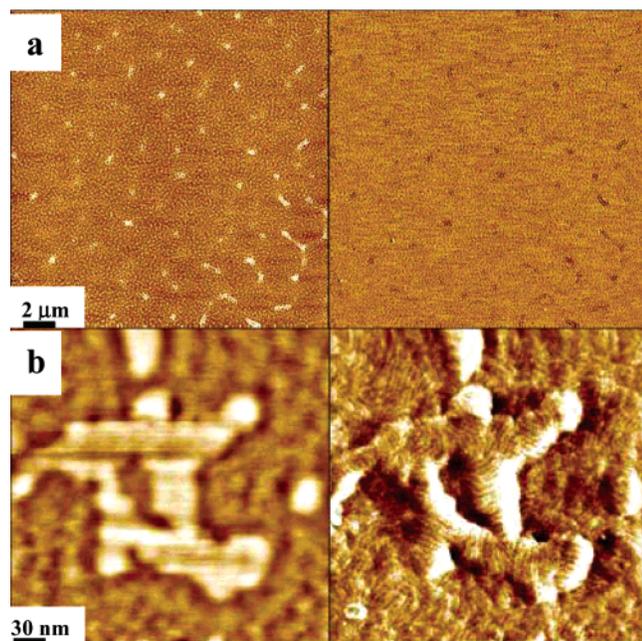
**Figure 4.** Grain nanostructure with internal lamellae of 2.2 nm surface films of the G-5(Und-But)<sub>128</sub> molecules is easily discerned from the high-resolution AFM image (a) within the condensed area, and (b and c) phase images demonstrating the short range ordering observed at highest resolution. Z range for images: topography 5 nm (left), phase 10° (right).

3–6 correlated lamellae with spacings of 5.4–5.9 nm. An abrupt change of orientation for lamellar stacks with correlated defects propagating across multiple lamellae (Figure 4b,c). Cross-sectional analysis of the lamellae structure revealed an undulating height along the lamella with weakly defined modulation of 10 nm.

For the thicker surface films of the G-5(Und-But)<sub>128</sub> molecules on the hydrophilic silicon substrate the formation of smaller pointlike domains of considerable height was observed (Figure 5a). The 4.4 nm thick domains with the average diameter of 100 nm were



**Figure 3.** Molecular model of G-3(Und-PH-But-70%) and G-5(Und-But)<sub>128</sub> in symmetrical conformation.

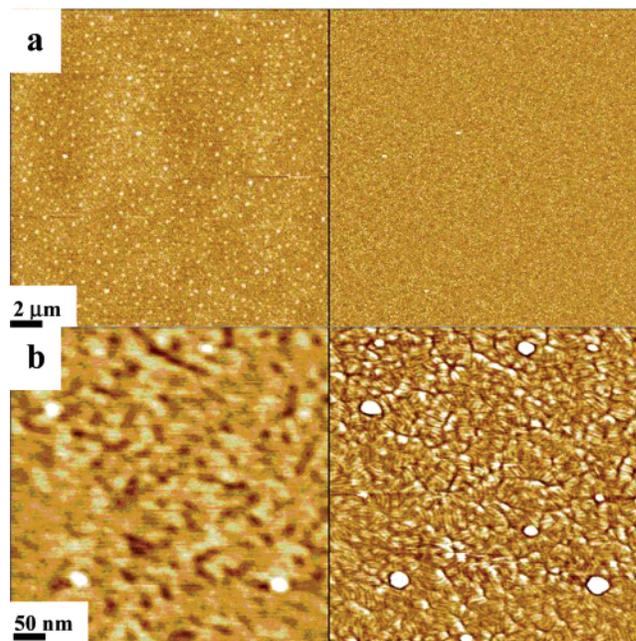


**Figure 5.** (a) Bilayer formation of G-5(Und-But)<sub>128</sub> observed as small point like domains for 3.8 nm thick surface films. (b) High-resolution AFM revealed the internal structure of the domains to be similar to the underlying monolayer. Topography image (left) and phase image (right) with Z range of (a) 20 nm (topography), 20° (phase), and (b) 20 nm (topography), 15° (phase).

composed of several irregular regions with lamellar ordering which was better defined than for surrounding surface areas (Figure 5b). The interlamellar spacing for these surface areas was 5.1–5.7 nm, closely resembling that observed for thinner surface films (Table 1). The spacings observed here were comparable with the intermolecular spacings calculated from X-ray diffraction.<sup>33</sup>

Similarly, the surface films for the G-3(Und-PH-But-70%) molecules showed a microscopic surface texture with the circular surface areas of a similar height as seen for the larger molecule (Figures 6a). Upon further scrutiny, a comparable nanostructure of small grains composed of poorly ordered internal lamellae was observed (Figure 6b). The interlamellar spacings for the G-3(Und-PH-But-70%) monolayers were within 5.2–6.4 nm (Table 1). The comparison of the overall molecular diameter (10.7 nm) and the core diameter (3.4 nm) suggest deviation from simple symmetrical shape as will be discussed below. The fabrication of thicker surface films from G-3(Und-PH-But-70%) molecules made the film surface more uniform (not shown).

Comparison of the molecular models with the film thickness and the  $d$  spacings of the lamellae structure indicates that a simple spherical model with symmetrical extension of the branches does not fit the experimental facts. The compression of the dendrimer molecules into a flattened oblate shape is required to agree with the experimental data. The in-plane lamellar structure observed with  $d$  spacing equal to approximately half of the molecular diameter can be formed if the laterally compressed molecules are staggered in an alternating manner as demonstrated in Figure 7. Such molecular arrangement creates running ridges of the densely packed terminal groups separated by grooves with spacing between neighboring grooves formed by depleted densities of the central cores of about 6 nm

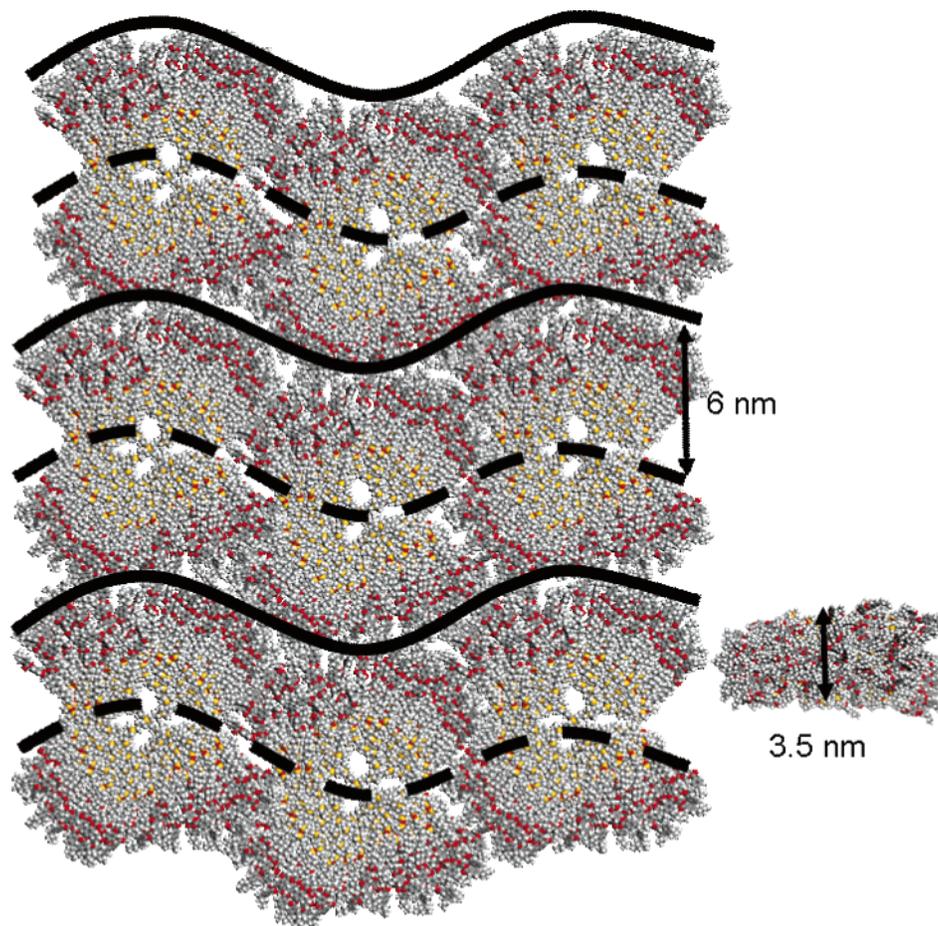


**Figure 6.** Microscopic surface texture of surface films of G-3(Und-PH-But-70%) molecules on hydrophilic silicon substrate with irregularly ordering areas of condensed packing. Topography image (left) and phase image (right) with Z range of (a) 5 nm (topography), 20° (phase), and (b) 5 nm (topography), 5° (phase).

wide. In addition, a modulation along the ridges with a periodicity of about 10 nm is formed. The layered structure with these molecular dimensions suggests a highly compressed dendrimer core and layered packing of polar terminal groups in close contact with the hydrophilic silicon surface. Very flat arrangement of dendrimer molecules makes them incommensurate with lamellar spacing observed in the bulk state, thus suggesting a more complicated layered packing (Figure 7).

The molecular model which can fit to the experimental data collected here should include lateral compression of the molecule in addition to the oblate conformation of the molecules. We suggest that the terminal LC groups form dense layered structures that exerted constraints upon the core perpendicular to the ordering direction. The flexible core rearranged from a flattened radial shape to a compressed elliptical orientation with the terminal groups aligned in the major axis direction (Figure 7). The dominant polar interactions between the terminal groups and the substrate reduced the influence of the dendrimer cores making them flat with the effective thickness of the molecules about 3 nm.

The divergence in chemical composition of the fifth generation molecules caused by replacing the butoxyphenylbenzoate terminal groups with more polar but shorter cyanbiphenyl terminal groups disrupted completely the lamellar ordering within the surface films. In contrast, the G-5(Und-CB)<sub>128</sub> molecules formed uniform surface films with no indication of internal ordering and much lower surface microroughness (not shown). The thickness varied within 1.6–3.0 nm (Table 1). Here, we suggest that lower tendency to form stable bilayer packing of cyanbiphenyl groups shifts the balance and prevents the layering of the terminal groups confined by the radially symmetrical dendritic cores. In fact, independent studies suggested although both mesogenic terminal groups have tendencies to form smectic structures the shorter cyanbiphenyl groups are more prone

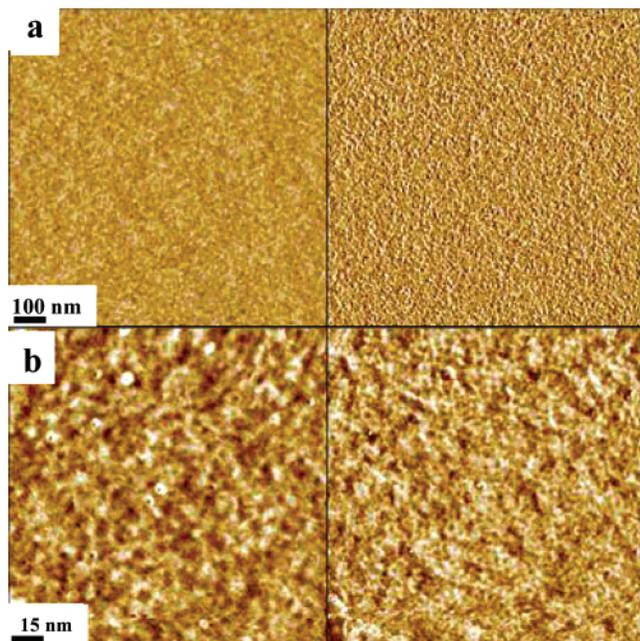


**Figure 7.** Molecular model of staggered layered ordering of flattened G-5(Und-But)<sub>128</sub> molecules (top view) and a side view of an individual molecule (right).

to form less ordered states such as nematics with lower thermal stability.<sup>25</sup> Cyanbiphenyl groups are known for their tendency to form nematic phases and weak layered phases due to strong dipole–dipole interactions but very short rodlike shape. Despite this fact, the chemical attachment of the CB mesogenic groups to the dendritic cores resulted in the formation of smectic phases with well-defined layering due to microphase separation of flexible cores and mesogenic enriched shell.<sup>25</sup> Here, we can speculate that by adding a new player in the game, namely, strong interactions with hydrophilic substrates and the CB groups, disrupts the layered packing formed in the bulk state. Unlike polar and short CB groups, phenylbenzoate groups form very strong bilayer packing due to both stronger steric effects (longer rod shape) and additional enthalpic contributions caused by microphase separation between polar central fragments of these groups and hydrophobic alkyl tails.<sup>34</sup> We suggest that, in this case, the preferable interfacial interactions between polar cores and the hydrophilic substrate are strong enough to compress the adsorbed molecules but not strong enough to disturb the layered packing of these groups, thus resulting in the preservation of the two-dimensional version of the layered ordering in the molecular surface films resembling that observed for the bulk ordering and for other columnar LC dendrimers.<sup>24,25</sup>

The molecular ordering of the G-5(Und-CB)<sub>128</sub> on hydrophilic silicon oxide (amorphous) and mica (crystalline) substrates was previously studied by Pomarenko et al.<sup>26</sup> The film thickness in this study varied from very

thin comparable to surface films studied here (3 nm) to very thick films with 100 nm thickness. The authors observed that the spin-cast films on silicon formed a network-like morphology that nonuniformly covered the surface as a result of intensive dewetting of hydrophobic material on the hydrophilic substrate. Individual molecules with a diameter of 5.5 nm were observed forming short-range rectangular and hexagonal ordering within the 3 nm thick domains. The molecular ordering was found to be much more pronounced on the mica substrate with 4.7 nm spacing between molecules inside the columns and 5.7 nm spacing between neighboring columns. The ordering transitioned from rectangular to hexagonal ordering upon annealing of the macromolecular layers on the mica. Thus, similar dendrimer molecules deposited on highly crystalline mica substrates formed lamellae nanostructures with short range ordering similar to that observed for the G-5(Und-But)<sub>128</sub> molecules on the hydrophilic silicon substrates.<sup>25</sup> This difference in surface organization points out a critical role of the crystalline and charged mica surface in the ordering of highly polar terminal groups of the LC dendrimers. Apparently, the replacement of this highly ordered substrate studied before with the amorphous silicon dioxide in this study shifts the interfacial balance toward a less organized surface structure of the CB-containing dendrimers. The G-5(Und-CB)<sub>128</sub> molecule lacked similar ordering in bulk structures at room temperature, supporting the suggestion that the layered ordering seen for the surface films was initiated by the crystalline ordering of the supporting substrate.<sup>12</sup>



**Figure 8.** Surface films on a hydrophobic surface: (a) Uniform microscopic texture of the G-5(Und-But)<sub>128</sub> molecules, (b) finer grainy texture of the G-3(Und-PH-But-70%) surface films with circular molecular shapes. Topography image (left) and phase image (right) with Z range of (a) 5 nm (topography), 5° (phase), and (b) 2 nm (topography), 5° (phase).

**Surface Films on Hydrophobic Substrates.** Unlike the films discussed above, the surface films on the hydrophobic surfaces with very small effective thicknesses lacked indications of layered ordering for all dendrimers studied here (Table 1, Figure 8a). However, co-dendrimers G-3(Und-PH-But-70%) showed grainy texture and round doughnut nanoscale features were revealed at higher resolution images (Figure 8b). These round features possess a diameter of  $10 \pm 2$  nm, which is fairly close to that expected for G-3(Und-PH-But-70%) molecules in completely flattened conformation, indicating that we observed individual dendrimer molecules forming two-dimensional surface structures resembling those for columnar phases of LC dendrimers (Figure 3).<sup>23,25</sup> The elevated rim is formed by the bulky terminal groups and the dendrimer core formed a thinner central area of the circular surface structures.

**Conclusions.** In conclusion, we revealed different molecular packing in the LC carbosilane dendrimers with 128 polar cyanbiphenyl groups and polar butoxyphenylbenzoate groups within molecularly thin surface films. We observed that dendrimers with 128 butoxyphenylbenzoate terminal groups formed two-dimensional organized layered packing caused by the microphase separation of the flexible cores and mesogenic terminal groups. This type of ordering observed for truly monomolecular surface films is similar to that observed for the bulk materials. The dilution of the outer mesogenic shell with a nonmesogenic component partially disturbed the layered packing within the surface monolayer adsorbed on the hydrophilic substrate. However, the circular shape of these dendrimer molecules with binary composition of terminal groups adsorbed on the hydrophobic substrates demonstrated that the dendritic core dominated molecular ordering in the case when the interfacial interaction between polar mesogenic groups and the hydrophobic substrate diminished making symmetrical round ordering preferable for dendrimer

molecules with highly hydrophobic cores and mesogenic shells significantly diluted with hydrophobic nonmesogenic units.

Complete disruption of the regular lamellar ordering was observed if butoxyphenylbenzoate terminal groups were replaced with shorter and more polar cyanbiphenyl groups with a weaker trend toward layered (smectic) ordering due to microphase separation of core and shell fragments. Obviously the tendency of the terminal cyanbiphenyl groups to layering is overpowered by favorable interactions with the hydrophilic substrate accompanied by a core trend to induce the arrangement avoiding hydrophobic–hydrophobic interfacial interactions. The adsorption on these CB-containing dendrimers on the hydrophobic surface does not result in the formation of dense surface layers due to antagonistic interactions between highly polar terminal groups and a methyl-terminated hydrophobic surface.

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