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# Atomic Force Microscopy Study of Structural Organization of Carbosilane Liquid Crystalline Dendrimer

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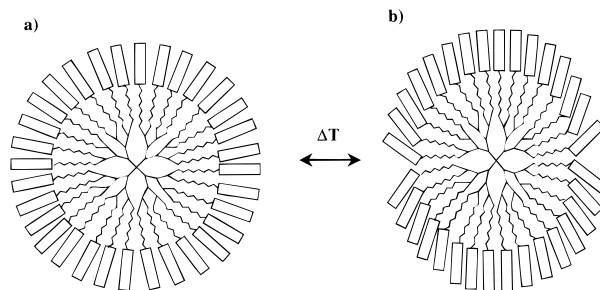
Structural organization of a carbosilane liquid crystalline dendrimer of fifth generation with cyanobiphenyl mesogenic groups in the 25–130 °C range was examined by atomic force microscopy (AFM). Studies were performed on the dendrimer films of different thicknesses, from single macromolecular layers to films several micrometers thick. Packing motifs of spherical macromolecules (5.5 nm in diameter) were revealed in submicrometer AFM images of the dendrimer films. Rectangular and hexagonal lattices were found in the single layers on different substrates. With an increase of film thickness, first smectic layers are formed, and then domains consisting of aggregates of flat-on lying and edge-on standing smectic layers were found. In thick films, the domains exhibit layered structures of different thicknesses and with different orientations. AFM images recorded at different temperatures demonstrated height changes of different domains caused by anisotropic changes of lattices of the smectic layers.

## 1. Introduction

In recent years dendrimers have attracted increased attention of researchers owing to their unique starburst molecular architecture and possibilities for their use in novel materials. Contemporary synthetic techniques allow creating dendritic molecules with a well-defined molecular size and shape, which approaches a sphere at high generations.<sup>1</sup> Terminal groups of the dendrimers play an important role by defining their properties.

Carbosilane dendrimers have been synthesized and examined by several research groups. These macromolecules can be prepared with different branching extents as well as with different peripheral groups.<sup>2</sup> Modification of them with mesogenic groups produces liquid crystalline (LC) carbosilane dendrimers (Scheme 1). LC dendrimers could be useful for optical switching and electrooptical applications. Smectic-type structures were found in the carbosilane LC dendrimers<sup>3</sup> and in some other dendrimers with mesogenic groups.<sup>4</sup> Dendrimers with a different chemistry of core and shell groups also exhibit columnar<sup>5</sup> and cubic<sup>6</sup> mesophases.

**Scheme 1 Schematic 2D Representation of the Molecular Structure of Carbosilane LC Dendrimer: (a) Spherical Shape in Solution or Isotropic Phase and (b) Distortion of Its Shape in the Anisotropic Mesophases**



Molecules of LC dendrimers join two completely opposite tendencies. On one hand, dendrimers are a class of synthetic macromolecules, in which well-defined branches radiate from a central core, becoming more branched and crowded as they extend out to the periphery. As a result they have spherical symmetry; i.e., all branches in the dendritic molecules tend to be isotropically distributed in the space because of entropic gain (Scheme 1a). On the other hand, mesogenic groups are rigid and sticklike, and have strong mutual orienting interactions. That leads to a distortion of the molecular shape of LC dendrimer from spherical to elongated (Scheme 1b) owing to large enthalpic gain in a certain temperature region (below clearing point). That is why such molecular structure of LC dendrimers is favorable to formation of anisotropic mesophases. To facilitate LC mesophase formation, mesogenic groups are

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(1) (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 9, 138. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concept, Synthesis, Perspectives*; VCH: Weinheim, 1996.

(2) Frey, H.; Lach, C.; Lorenz, K. *Adv. Mater.* **1998**, *10*, 279 and references therein.

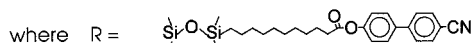
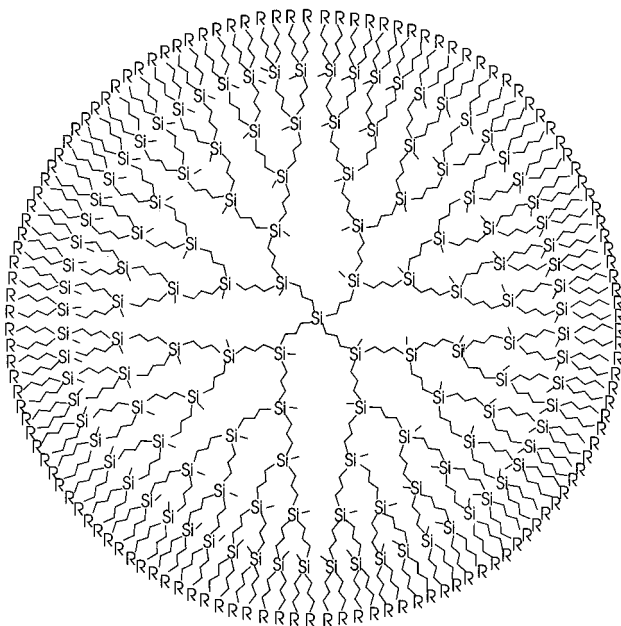
(3) (a) Ponomarenko, S. A.; Rebrov, E. A.; Bobrovsky, A. Yu.; Boiko, N. I.; Muzafarov, A. M.; Shibaev, V. P. *Liq. Cryst.* **1996**, *21*, 1. (b) Lorenz, K.; Höltzer, D.; Stühn, B.; Mülhaupt, R.; Frey, H. *Adv. Mater.* **1996**, *8*, 414. (c) Terunuma, D.; Kato, T.; Nishio, R.; Matsuoka, K.; Kuzuhara, H.; Aoki, Y.; Nohira, H. *Chem. Lett.* **1998**, 59. (d) Ponomarenko, S. A.; Boiko, N. I.; Rebrov, E. A.; Muzafarov, A. M.; Whitehouse, I. J.; Richardson, R. M.; Shibaev, V. P. *Mol. Cryst. Liq. Cryst.* **1999**, *330*, 1411.

(4) (a) Ponomarenko, S. A.; Rebrov, E. A.; Boiko, N. I.; Vasilenko, N. G.; Muzafarov, A. M.; Freidzon, Ya. S.; Shibaev, V. P. *Vysokomol. Soedin., Ser. A* **1994**, *36*, 1086; *Polym. Sci., Ser. A* **1994**, *36*, 896. (b) Percec, V.; Chu, P.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1995**, *117*, 11441. (c) Deschenaux, R.; Serrano, E.; Levelut, A.-M. *Chem. Commun.* **1997**, 1577. (d) Busson, P.; Ihre, H.; Hult, A. *J. Am. Chem. Soc.* **1998**, *120*, 9070. (e) Saez, I. M.; Goodby, J. W. *Liq. Cryst.* **1999**, *26*, 1101. (f) Yonetake, K.; Masuko, T.; Morishita, T.; Suzuki, K.; Ueda, M.; Nagahata, R. *Macromolecules* **1999**, *32*, 6578.

(5) (a) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855. (b) Cameron, J. H.; Facher, A.; Lattermann, G.; Diele, S. *Adv. Mater.* **1997**, *9*, 398. (c) Percec, V.; Schlueter, D.; Ungar, G.; Cheng, S. Z. D.; Zang, A. *Macromolecules* **1998**, *31*, 1745. (d) Pesak, D. J.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1636. (e) Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 643. (6) Balagurusami, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539.

usually linked to dendritic matrixes through a flexible aliphatic spacer.<sup>3,4</sup>

Recently we have synthesized a series of carbosilane LC dendrimers with cyanobiphenyl (CB) terminal groups.<sup>7</sup> The fifth generation dendrimer, G5(Und-CB)<sub>128</sub>, shows the most unusual phase behavior.<sup>8</sup> At room temperature these macromolecules form a lamellar (smectic A) phase,



which develops in-plane ordering above 40 °C. This was tentatively explained by a tendency to form columns of molecules which are perpendicular to the layers. Above 121 °C the material transforms into another more disordered mesophase that was defined as a disordered hexagonal columnar phase. Structural models were suggested for molecular packing in these different mesophases.<sup>18</sup>

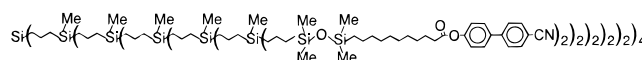
So far, analyses of structure and thermal behavior of this and other LC dendrimers have been performed with X-ray diffraction, optical microscopy, and DSC, which are commonly used for characterization of LC polymers. However, the structural characterization of the architecture of complex materials such as LC dendrimers with diffraction techniques requires the use of structural models, whose validity needed to be justified by high-resolution microscopic techniques such as TEM<sup>9</sup> or atomic force microscopy (AFM).<sup>10</sup> We believe that AFM visualization of structures on different scales (from a few nanometers to hundreds of micrometers) will substantially complement the structural analysis of dendrimer architecture. AFM has been successfully used for characterization of large molecules of tecto-dendrimers<sup>11</sup> and dendritic polymers of spherical and columnar shapes formed by self-assembly.<sup>12</sup> Several efforts have been made to characterize

carbosilane dendrimers by AFM that was applied to ultrathin layers<sup>13</sup> and aggregates of single molecules on a solid substrate.<sup>14</sup> However, the nanostructure of these layers and the following steps of mesophase formation have yet to be seen.

The present work describes the characterization of the structural organization of LC dendrimer G5(Und-CB)<sub>128</sub> with AFM. In this study we achieved visualization of individual macromolecules and their packing in single molecular layers on different substrates and characterization of multilayer and domain organization in thick dendrimer films. AFM imaging at elevated temperatures allowed monitoring of structural changes at dendrimer thermal transitions.

## 2. Experimental Section

**Materials.** Synthesis of the carbosilane LC dendrimer G5(Und-CB)<sub>128</sub> was described previously.<sup>7</sup> It has 128 terminal cyanobiphenyl (CB) mesogenic groups linked to the carbosilane dendritic matrix of the fifth generation through an undecylenic (Und) spacer:



A pure monodisperse compound was isolated by preparative GPC. Its structure and purity was checked by FTIR, <sup>1</sup>H NMR, and GPC methods.<sup>7</sup>

**Sample Preparation.** Ultrathin layers were obtained by spin-coating chloroform solutions (10<sup>−3</sup> and 10<sup>−4</sup> wt %) of the dendrimer on Si wafers and freshly cleaved mica substrates. The spinning rate was 3000 rpm. Thin and thick LC films (several hundreds nanometers and several micrometers in thickness, respectively) were prepared by rubbing the LC dendrimer on glass and Si wafers. Before AFM studies, the samples were heated to  $T = 130$  °C and slowly cooled to room temperature.

**AFM Measurements.** AFM studies were performed with a scanning probe microscope MultiMode Nanoscope IIIa (Digital Instruments/Veeco Metrology Group, Santa Barbara, CA). The microscope was equipped with a heating accessory, which includes a modified vertical J-scanner, and an optical control system. Optical polarization measurements in reflection mode were applied for the control of thermal phase transitions in thick dendrimer samples, which were examined with AFM at different temperatures in the 25–130 °C range.

All AFM images were obtained in tapping mode. Etched Si probes with a stiffness of 40 N/m and resonant frequency in the 150–200 kHz range were used in the experiments. The driving frequency was chosen at the resonant frequency of the probe in the immediate vicinity of the sample surface. Height and phase images were recorded simultaneously. Using a relatively small amplitude of the free-oscillating probe,  $A_0 \sim 10$  nm, the tip-sample force interactions were minimized to avoid sample damage and to achieve high-resolution in submicrometer scans. For more correct measurements of surface steps (or layer thickness), the set-point amplitude,  $A_{sp}$ , was chosen close to  $A_0$ , which further lowers the tip force. However, a slight force increase (drop in  $A_{sp}$  or increase of  $A_0$ ) was required for visualization of single dendrimer macromolecules.

## 3. Results

AFM images of dendrimer samples prepared on different substrates from the most diluted solution (10<sup>−4</sup> wt %) showed that owing to a shortage of material the dendrimer

(7) Ponomarenko, S. A.; Rebrov, E. A.; Boiko, N. I.; Muzafarov, A. M.; Shibaev, V. P. *Vysokomol. Soedin., Ser. A* **1998**, *40*, 1253; *Polym. Sci., Ser. A* **1998**, *40*, 763.

(8) Richardson, R. M.; Ponomarenko, S. A.; Boiko, N. I.; Shibaev, V. P. *Liq. Cryst.* **1999**, *26*, 101.

(9) Hudson, S. D.; Jung, H.-T.; Kewsuwan, P.; Percec, V.; Cho, W.-D. *Liq. Cryst.* **1999**, *26*, 1493.

(10) (a) Magonov, S. N.; Reneker, D. *Annu. Rev. Mater. Sci.* **1997**, *27*, 175. (b) Sheiko, S. S. *Adv. Polym. Sci.* **2000**, *151*, 61.

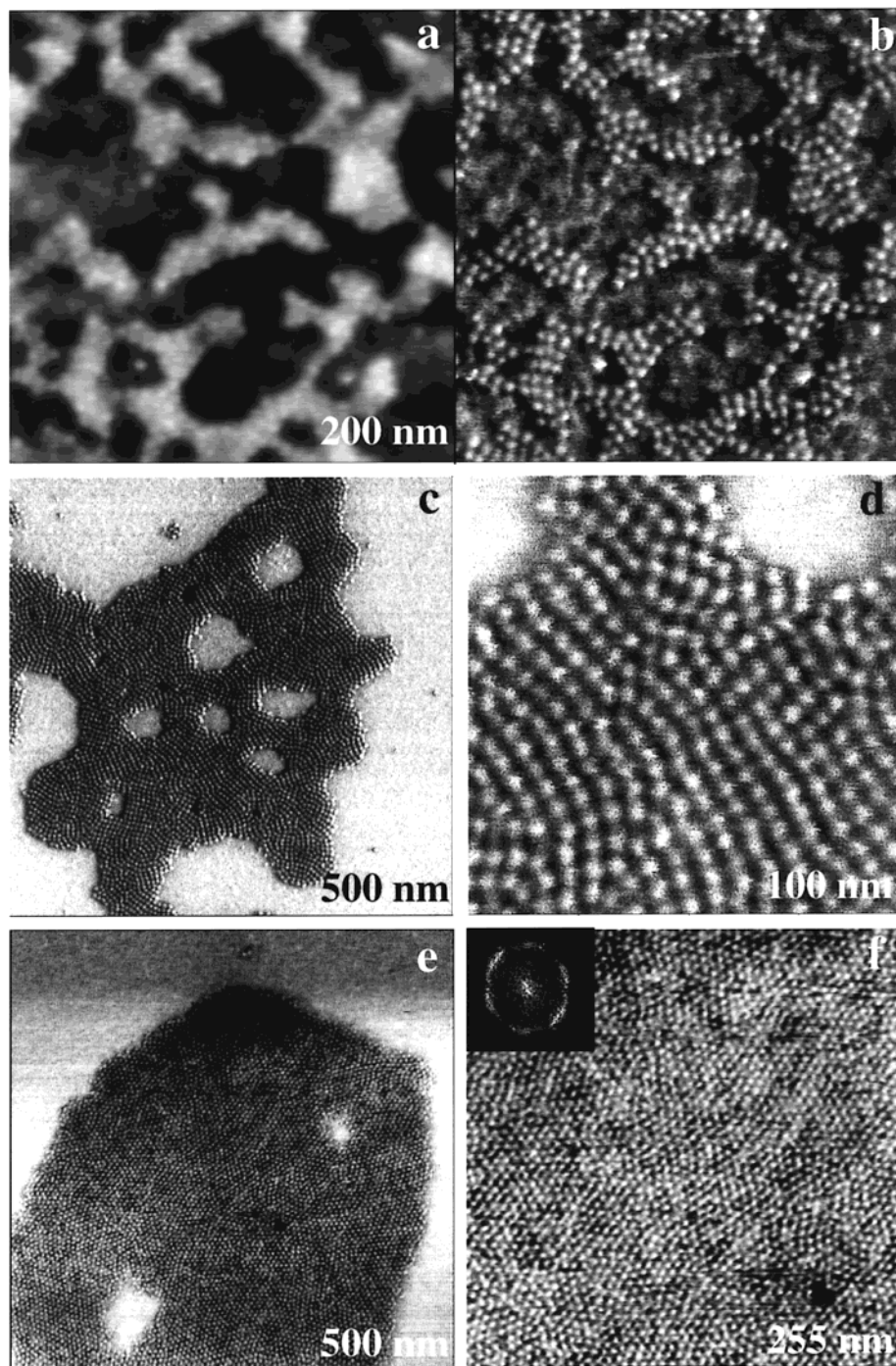
(11) Li, J.; Swanson, D. R.; Qin, D.; Brothers, H. M.; Piehler, L. T.; Tomalia, D.; Meijer, D. J. *Langmuir* **1999**, *15*, 7347.

(12) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161.

(13) Coen, M. C.; Lorenz, K.; Kressler, J.; Frey, H.; Mülhaupt, R. *Macromolecules* **1996**, *29*, 8069.

(14) Sheiko, S. S.; Eckert, G.; Ignat'eva, G.; Muzafarov, A. M.; Spickermann, J.; Räder, H. J.; Möller, M. *Macromol. Rapid Commun.* **1996**, *17*, 283.





**Figure 1.** AFM images of LC dendrimer samples prepared by spin-coating  $10^{-4}$  wt % chloroform solution on different substrates. (a, b) Simultaneously recorded height and phase images of a G5(Und-CB)<sub>128</sub> layer on Si substrate, respectively; (c) phase image of a not-annealed G5(Und-CB)<sub>128</sub> layer on mica; (d) phase image of a part of the layer shown in (c); (e) phase image of an annealed G5(Und-CB)<sub>128</sub> layer on mica; (f) part of the phase image in (e) with an inset (left top corner), which shows 2D FFT spectra. In the height image in (a), the contrast covers height variations in the 0–4 nm range.

layer does not cover the substrate completely. Dendrimer patches with a thickness of  $\sim 3$  nm exhibit a networklike morphology on Si substrate. In the submicron images, Figure 1a,b, one sees that these patches consist of individual particles. The distance between the particles is close to the estimated size of G5(Und-CB)<sub>128</sub> macromolecules, which equals 5.5 nm according to X-ray diffraction data.<sup>8</sup> Therefore these particles represent individual macromolecules, which are most resolved in the phase image in Figure 1b. Reversible tip-induced deformation, which is common for AFM of soft materials, leads to the reduced height of the single layer seen in the

height images. With a slight increase of tip–sample force interaction, which was required for the visualization of single macromolecules, the layer height decreases from 3 to 2 nm. These results are in agreement with the earlier AFM studies of dendritic molecules.<sup>11</sup>

The possibility to distinguish individual macromolecules allows analyzing their packing in the single layer. Strings of single molecules and their aggregates with traces of rectangular and hexagonal packing motifs are seen in the phase image in Figure 1b. More compact separate domains were found in the samples prepared on mica which can be related to an atomic-scale smoothness of this substrate.

One of such a domain is shown in the phase image in Figure 1c. Actually, the darker contrast of the dendrimer domain in this image, most likely, reflects the relative softness of this layer as compared to the substrate.<sup>10</sup> Within the dendrimer domain on mica surface, individual macromolecules are packed in a more ordered fashion than within the dendrimer patches on Si surfaces. In a large number of locations, one can distinguish rectangular packing with different repeat distances in the orthogonal directions. One such region is shown in Figure 1d. Rows or columns of macromolecules, which are oriented from the lower right corner toward the top left corner, are characterized by a repeat distance of  $4.7 \pm 0.2$  nm. The distance between the neighboring rows is larger,  $5.7 \pm 0.3$  nm.

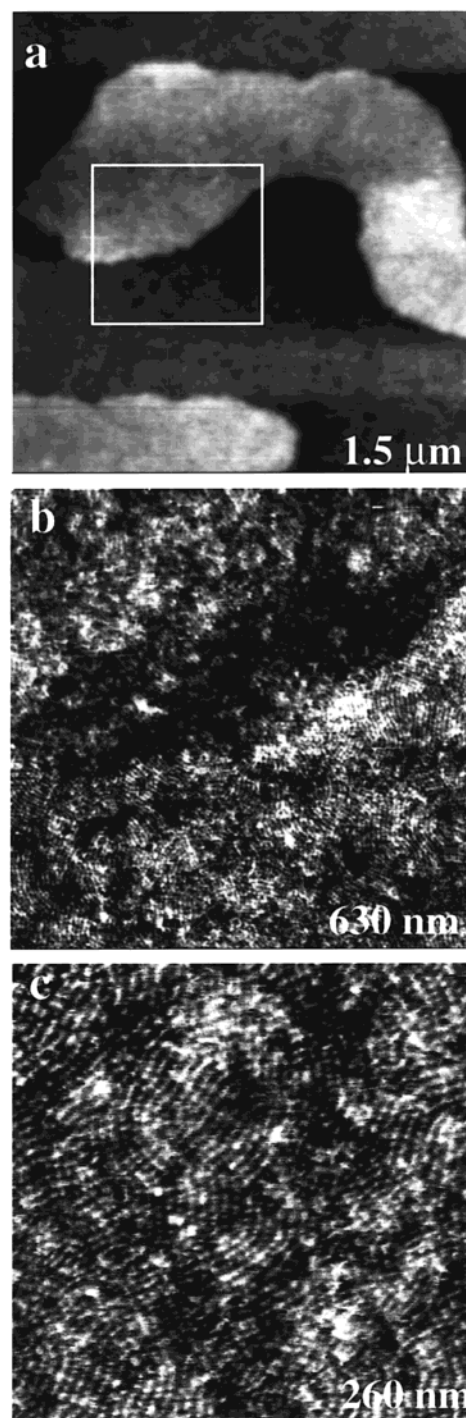
Thermal annealing of the dendrimer domains on mica led to a transition from the rectangular to hexagonal packing. This is clearly seen from the phase images in Figure 1e,f. A FFT power spectrum, which is shown in the inset in Figure 1f, confirms the preferential hexagonal packing of dendrimer macromolecules in this domain. Quantitative estimates showed that the repeat distance of this hexagon is  $\sim 4.9$  nm.

Spin-coating a  $10^{-3}$  wt % solution formed dendrimer films consisting of 2–3 molecular layers. This result was obtained from the height measurements of the film thickness, which were performed by scratching a part of the film with an AFM tip scanning in high-force contact regime. This procedure is often applied for evaluation of the thickness of organic layers. A part of the G5(Und-CB)<sub>128</sub> film consisting of two complete molecular layers is shown in Figure 2a. Bright “islands” of the top third layer exhibit a thickness of  $\sim 5$  nm. A part of this area, which includes areas of the second and the third layers (marked by a “white border”), is shown in the phase image in Figure 2b. Traces of individual molecules are distinguished on both layers; however, their packing motif is best resolved on the bottom layer, Figure 2c. In this image, one sees rows of individual macromolecules, which in some places are linear and in other places are bent. The distance between these rows is slightly larger than the separation between the neighboring macromolecules within the rows. This is similar to the macromolecular packing seen in Figure 1d.

AFM images of dendrimer films, which are 200 nm thick, reveal their domain morphology. Two domains of several tens of micrometers in size, which exhibit differently oriented linear features, are seen in the right part of the height image in Figure 3a. The angle between the linear structures of the neighboring domains is  $\sim 60^\circ$ . Bright patterns, which are seen in the left part of this image, present smaller regular domains of the top layer, and they are  $\sim 55$  nm in height. The fact that the top domains have their structures aligned along the main direction of the underlying layer indicates their homoepitaxy.

In the composite AFM image (Figure 3b), the lower part (height) shows top “islands” with layered structures parallel to the surface and the upper part (phase) emphasizes the linear structure of the lower layer. Steps of  $\sim 5.5$  nm in height, which are seen on the elevated domains, suggest the multilayer architecture (single layers are stacked on each other) of these domains. The linear features, which are seen in the lower layer (see the upper part of Figure 3b), are tens of nanometers wide, and they can be assigned to edge-on-oriented macromolecular layers.

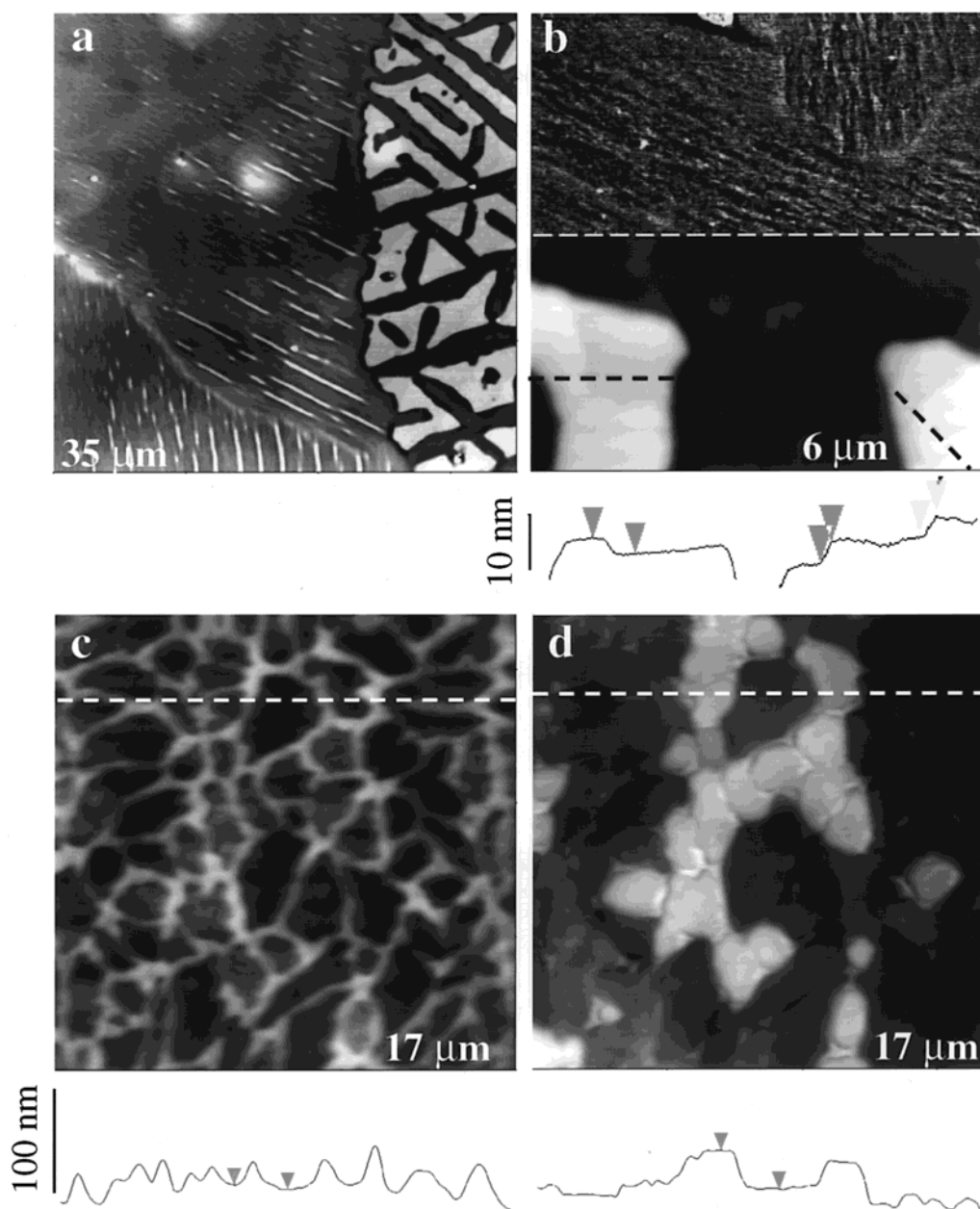
Heating of this dendrimer film allowed us to find that the height of the steps on the elevated domains changes from 5.5–6.0 nm at room temperature to 4.0–4.5 nm at



**Figure 2.** AFM images of a LC dendrimer sample prepared by spin-coating  $10^{-3}$  wt % chloroform solution on Si substrate. (a) Height image, (b) phase image of a part of the sample shown in (a), see the marked area; (c) phase image of a part of the lower layer seen in (a). In the height image in (a), the contrast covers height variations in the 0–20 nm range.

100 °C. It is consistent with the tendency of decreasing interlayer distance with temperature found by SAXS measurements.<sup>8</sup> Heating to the higher temperature caused isotropization of this film, and a new polydomain structure, with individual domains of a few micrometers in size, was formed when this sample was cooled to 100 °C, Figure 3c. Further cooling led to an appearance and gradual growth of the height difference between domains of two types. Figure 3d shows the topography of the same location as in Figure 3c after cooling to 80 °C. A number of domains



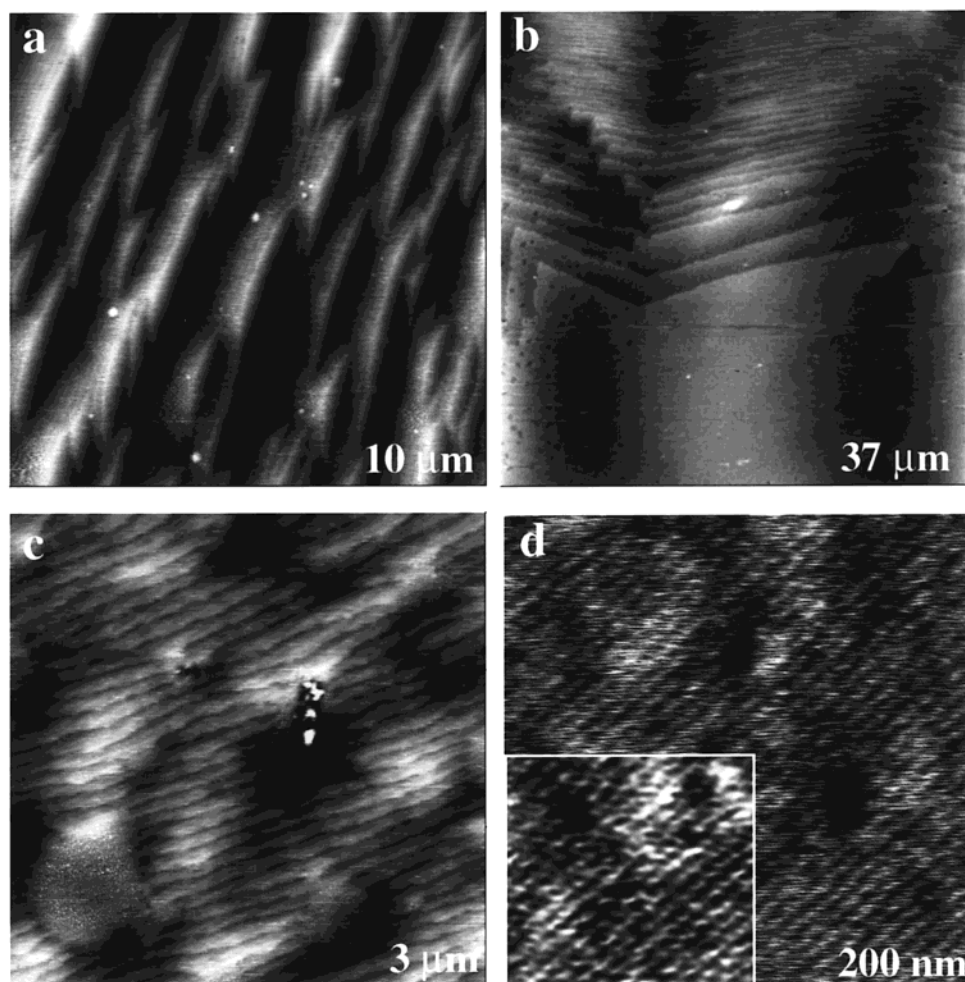


**Figure 3.** AFM images of a LC dendrimer sample prepared by rubbing a thin layer (ca. 200 nm in thickness) on Si substrate. (a) Height image, which shows domains with differently oriented linear features (left part) and regular “islands” of the top layer (right part). (b) Image of the sample area, which includes the bottom part shown as height image and the top part shown as phase image. Height profiles across surface locations, which are indicated in the image with dotted lines, are shown underneath the image. Arrows indicate surface steps  $\sim 5.5$  nm in height. The images in (a) and (b) were obtained at room temperature. The contrast covers height variations in the 0–250 nm range in (a) and in the 0–120 nm in the bottom part of (b). (c, d) Height images of the same area of the thick dendrimer layer after its isotropization and cooling to 100 and 70 °C, respectively. In (c) and (d) the contrast covers height variations in the 0–300 nm range. Height profiles across surface locations, which are indicated in the images c and d with dotted lines, are shown underneath the images. Vertical distances between the same locations, which are indicated in the profiles with arrows, are 5 nm (left profile) and 40 nm (right profile).

in the central part of the area became elevated as compared to their neighbors. The height difference for the sample at 80 °C became  $\sim 55$  nm, and it increased to 120 nm when the sample was cooled to 30 °C. The differences of the thermal behavior of the domains are directly related to the orientation of their multilayer structures. The elevated domains exhibit layers oriented parallel to the surface, whereas the lower domains show linear structures similar to those seen in the upper part of Figure 3b.

Analysis of thick dendrimer layers (several micrometers in thickness) was assisted by optical polarizing microscopy, which helps in the monitoring of the thermal phase transitions in these samples. Cooling the sample from

isotropic melt leads to formation of a polydomain structure. The size of the domains depends on the cooling conditions: fast cooling leads to large domains, slow cooling, to smaller domains. The domains formed in G5(Und-CB)<sub>128</sub> film exhibit well-defined mosaic texture with domains seen in different colors in a polarizing optical microscope. This is, possibly, due to the different orientation of smectic layers in each of the domains.<sup>8</sup> Morphology of three different domains, which were formed after fast cooling of the thick film to 105 °C, are shown in Figure 4a–c. It is clearly seen that they have different orientation of layers. Edge-on-oriented layers of  $\sim 130$  nm in thickness are seen in Figure 4a. Their edges exhibit a hexagonal



**Figure 4.** (a–c) AFM height images of different domains in thick film of the LC dendrimer prepared by rubbing on Si substrate. The images were recorded at 105 °C on the sample, which was cooled to this temperature after isotropization. The contrast covers height variations in the 0–25 nm range in (a), in the 0–60 nm range in (b), and in the 0–12 nm range in (c). (d) Molecular-scale AFM height image of the thick dendrimer layer, which was obtained at room temperature. The left lower quarter of the image is shown after filtering. The contrast covers height variations in the 0–2 nm range.

shape that indicates the similar packing of macromolecules within these layers. Packs of ultrathin layers ( $\sim 5$  nm in thickness) have been found in another domain, Figure 4b. The shape of these layers is characterized by edges oriented at different angles to each other. The variety of the orientations can be interpreted by the presence of different packing motifs in these layers. A layered morphology with multiple edges separated by 100–150 nm in height is found on the third domain, Figure 4c. The different orientation of layered structures in these domains is consistent with their different colors in optical polarizing micrographs.

At elevated temperatures, the dendrimer material becomes softer, and this limits the capabilities of AFM imaging at submicrometer scales. Therefore, we did not succeed in high-resolution imaging of thick G5(Und-CB)<sub>128</sub> films. The room-temperature experiments have been more successful, and the height image, which reveals macromolecular order in one of dendrimer domains, is shown in Figure 4d. Linear striations separated by 5 nm distances, which are seen in this image, could be assigned to linear sequences of individual macromolecules. This order is more similar to the rectangular packing seen in Figures 1d and 2c than to the hexagonal packing.

#### 4. Discussion

Relatively small cantilever amplitudes applied in AFM imaging of the LC dendrimer films help to optimize tip–

sample force interactions for visualization of individual G5(Und-CB)<sub>128</sub> macromolecules  $\sim 5$  nm in size and of their packing in these samples. In other words, small tip–sample forces did not damage the soft LC dendrimer and led to a small tip–sample contact area that is equal or less than 5 nm, thus allowing high-resolution imaging. In previous AFM studies of carbosilane dendrimers, individual macromolecules in their aggregates or in a single layer were not seen.<sup>13,14</sup> Visualization of individual macromolecules and polymer chains was demonstrated on PS-*b*-PMMA block copolymer on mica<sup>15</sup> and on a number of other polymers, including monodendron-jacketed PS<sup>16</sup> and self-assembling dendrimers.<sup>12</sup>

The size of G5(Und-CB)<sub>128</sub> macromolecules was estimated from the AFM phase images as the distance between centers of neighboring particles. According to the chemical structure, the LC dendrimer macromolecule is a microphase-separated particle with a nonpolar aliphatic carbosilane core and an exterior of polar aromatic cyanobiphenyl groups. The microphase separation in polymer systems leads to different local tip–sample force interactions that are responsible for the different contrasts

(15) Kumaki, J.; Nishikawa, T.; Hashimoto, T. *J. Am. Chem. Soc.* **1996**, *118*, 3321.

(16) Prokhorova, S. A.; Sheiko, S. S.; Ahn, C.-H.; Percec, V.; Möller, M. *Macromolecules* **1999**, *32*, 2653.

in the phase images.<sup>17</sup> However, the small size of the macromolecules (each macromolecule appears as a bright spot of 3–4 nm in the phase image), which is comparable with a part of the tip radius, makes it difficult to judge unambiguously about differences of tip force interactions with the core and the periphery.

The microphase separation in G5(Und-CB)<sub>128</sub> plays an important role in packing of the macromolecules that leads to lattices of hexagonal and rectangular types as predicted in our first work on the LC dendrimers.<sup>4a</sup> The microphase separation on the larger scales of tens of nanometers is common block- and graft-copolymers and routinely observed in AFM images.<sup>10</sup> The rectangular macromolecular packing or a formation of columns seen in Figure 1d means that interaction between mesogens (cyanobiphenyls) of neighboring macromolecules is different; probably it is stronger between the macromolecules of the same column and it is weaker between the macromolecules of the neighboring columns. The observation of macromolecular lattices of two types in the two-dimensional patches of the LC dendrimer could be attributed to the initial step of the formation of smectic layers with different orientation (parallel and perpendicular to the substrate) that was actually observed in AFM images of thin layers, Figure 3a,b. This suggestion is supported by the fact that the distance between columns in rectangular ordering (~5.5 nm) agrees with X-ray data, showing the same distance between smectic layers at room temperature.

According to X-ray diffraction measurements of G5-(Und-CB)<sub>128</sub> bulk samples, smectic mesophase, which exists at room temperature, does not exhibit an order within smectic layers. Rectangular and hexagonal columnar mesophases were found only at elevated temperatures.<sup>8</sup> Therefore, we assume that the rectangular and hexagonal packing observed in single dendrimer layers on different substrates was induced by the presence of the substrate. However, it could not be totally excluded that a poor SAXS sensitivity to local order is the reason that the local packing within the layers was not found in the bulk samples at room temperature.<sup>8</sup> AFM images obtained on thin and thick films (Figures 3 and 4) confirmed a strong influence of the substrate on the structural organization of LC dendrimers. In thin films, smectic layers within the structural domains were oriented either parallel or perpendicular to the substrate. A variety of orientation patterns was found in the dendrimer domains of the thick films. Also in the thick films, in addition to smectic layers, 50 nm thick layers were observed. This indicates a more sophisticated structural hierarchy in bulk dendrimer samples.

As it was mentioned, SAXS studies of G5(Und-CB)<sub>128</sub> revealed the additional structural ordering at elevated temperatures and, particularly, an appearance of macromolecular order within the smectic layers.<sup>8</sup> Further-

more, with an increase in temperature the interlayer distance gradually decreases and the in-layer intermolecular distance increases. Heating of the dendrimer sample from 40 °C to 110 °C leads to ~10% decrease of the smectic layer's thickness and to ~10% increase of the in-plane repeat distance. Measurements of the surface steps in AFM images of the domains in thin films at elevated temperatures confirmed that those smectic layers become thinner with an increase of temperature. An anisotropy of structural changes with temperature, which were observed in AFM images recorded during cooling of the thin dendrimer film (Figure 3c,d), was most remarkable. The domains with the flat-on-lying smectic layers become substantially higher than their neighbors with edge-on-lying smectic layers. The height difference of 120 nm was found upon cooling from 100 to 30 °C. Though this effect is very pronounced, there is some controversy. The height difference of 120 nm corresponds to 60 nm changes in the height of each domain, and if one follows the expected 10% change of lattice parameters in this temperature range then the thickness of the neighboring domains under consideration should be around 600 nm. This estimate contradicts the thickness of this film, which was found to be ca. 200 nm. Tentatively, we suggest that the mobility of liquid crystals that can move material from one domain to the other is responsible for this effect.

## 5. Conclusions

AFM studies of the LC dendrimer films with different thicknesses substantially supplements results of optical microscopy and SAXS in the characterization of the structural architecture of this material. A whole spectrum of structural elements, from individual macromolecules to smectic layers and domains of tens of micrometers in size, was documented in AFM images. The visualization of individual macromolecules in the dendrimer films enabled us to analyze the macromolecular packing in smectic layers. It has been shown that the substrate and the film thickness of LC dendrimer both influence the structural organization of LC dendrimer. Imaging of the LC dendrimer at elevated temperatures allows the monitoring of anisotropic changes of dimensions of smectic layers and their aggregates in correspondence with temperature-dependent lattice variations revealed previously by SAXS.

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(17) Magonov, S. N.; Cleveland, J.; Elings, V.; Denley, R.; Whangbo, M.-H. *Surf. Sci.* **1997**, *85*, 201.