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Ordered Dendritic Nanorods with a Poly(*p*-phenylene) Backbone

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Abstract: The degree of polymerization (DP_n) of poly(*p*-phenylene) (PPP) **3** with appendant third-generation, Fréchet-type dendrons was determined as 110 after a chemical modification. This DP_n is extraordinarily high and shows that the mechanistically complex Suzuki polycondensation can thus be employed even in the case of sterically highly loaded (dendronized) AA-type monomers, which paves the way to obtain extremely rigid nanorods. A molecular model of **3** was obtained by molecular dynamics simulations which show that the diameter of the rodlike dendrimer fluctuates between approximately 2 and 4 nm in vacuo. Scanning force microscopy (SFM) on **3** adsorbed on graphite indicates the formation of multilayer films made of densely packed nanorods. SFM with molecular resolution reveals highly ordered domains in which the molecules are packed parallel to each other, separated by a lateral periodicity of 4.8 ± 0.5 nm. Lateral and vertical spacings indicate that the (110) plane of the densely packed nanorods is exposed at the film surface. SFM further indicates that different domains exhibit three molecular orientations, reflecting the 3-fold symmetry of the graphite substrate. Chain ends can be resolved at grain boundaries. Time-dependent SFM experiments show reorientation of small domains on a time scale of minutes.

Introduction

Dendrimers have highly branched, compartmentalized structures in the few nanometers range and a defined, large number of functional groups at their surface. Because of these unique features they were investigated, for example, as hosts for drug delivery, carriers for catalytically active sites in flow reactors, and antibody conjugates.[1] Practically all dendrimers known today are believed to attain a more or less spherical structure in solution. Recently dendrimers such as the dendronized poly(*p*-phenylene) (PPP) derivative **3** were synthesized which, by way of construction, should have a cylindrical rather than a spherical shape in solution.[2] Such cylinders would not only be of interest as molecular objects for nanoconstructions on surfaces but also be an important addition to the field of supramolecular chemistry in that suitably constructed and functionalized macrocylinders may act as new constituents for giant micelles, vesicles, membranes, etc. From the elemental composition and an in-depth analysis of its NMR spectra, the structure of the repeat units (ru) of **3** was proven.[2a] Because of the strong tendency of **3** to form aggregates in solution, however, a determination of the number of repeat units per chain, i.e., the molecular weight, turned out to be impossible. Thus, up to now, neither its molecular dimensions nor any information on its shape was available. Here we describe a joint synthetic, polymer analytical, molecular modeling, and microscopical effort into this matter and report (a) on a chemical modification of **3** into the PPP derivative **4** to indirectly obtain the absolute molecular weight of **3** and (b) on molecular dynamic (MD) simulations and scanning force microscopical (SFM) investigations of **3** in order to determine its molecular dimensions and to visualize individual dendrimers in ordered ultrathin films on highly oriented pyrolytic graphite (HOPG). SFM[3,4] is a valuable tool to investigate the morphology and molecular packing of polymers at surfaces with molecular resolution. Important examples include synthetic and biological polymers.[5−9] Also,

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adsorption and aggregation of spherical carbosiloxane dendrimers adsorbed on mica and highly oriented pyrolythic graphite HOPG have been investigated.[10−13]

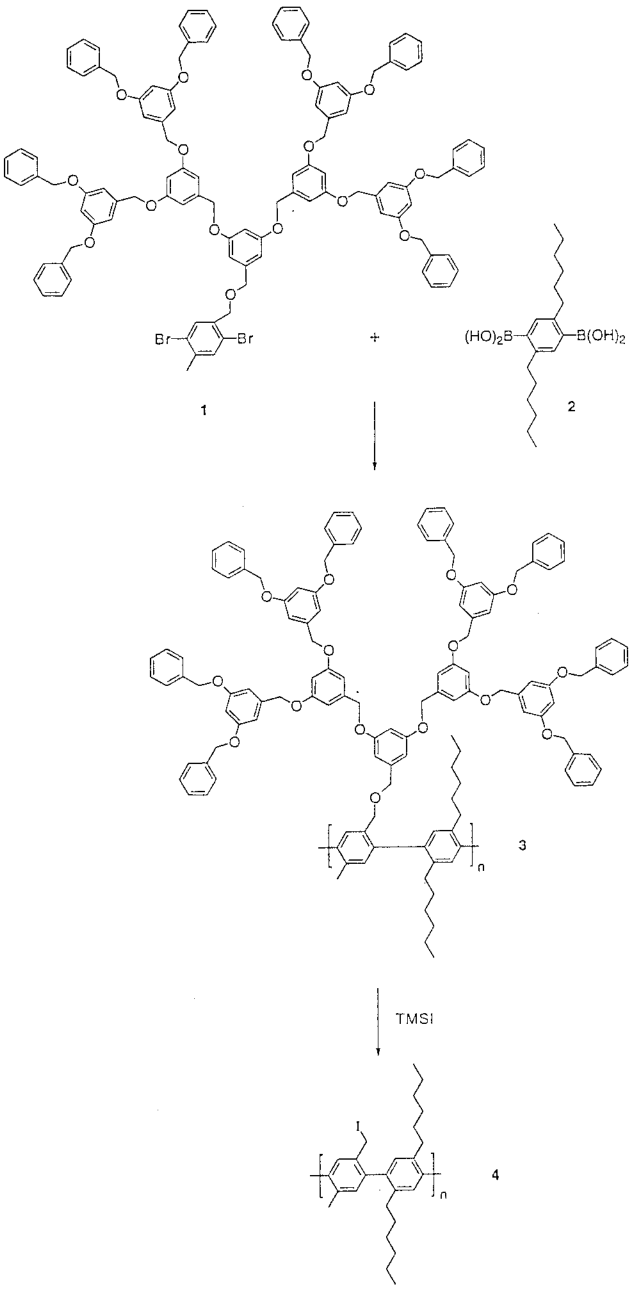
Experimental Section

Scanning Force Microscopy. SFM was carried out with a Nanoscope III (Digital Instruments, Inc., Santa Barbara, CA) in the tapping mode,[4] where the cantilever is oscillated close to its resonance. The change of the vertical cantilever oscillation amplitude is detected, which is caused by the interaction of the tip with the sample surface. Silicon cantilevers (length 125 μm, width 30 μm, thickness $3-5$ μm) with a spring constant between 17 and 64 N/m and a resonance frequency in the range of $240-400$ kHz were used. The measurements were carried out in air under normal conditions. For distance calibration of the piezo controller, images of mica and gold calibration gratings were employed. Imaging was performed by displaying the height signal (output of the feedback system) and the phase signal (phase shift of the cantilever oscillation relative to the driver). No filtering techniques were applied. Multilayer films of **3** were prepared from chloroform solution (0.001% w/v). Two microliters of a solution which had been treated under ultrasonic stirring for 1 h was dropped onto a freshly cleaved graphite surface. Evaporation of the solvent (25 °C/24 h) gave a sample whose film thickness was in the range $40-50$ nm. The film thickness was determined by scratching a hole in the film until the dendrimer was removed and the graphite substrate was exposed. The hole was created by scanning a 20×20 nm^2 area at high forces in the SFM contact mode. The resulting square was visualized by SFM in the tapping mode, and the resulting height difference between the graphite and the dendrimer film was then analyzed in the cross sectional profile. This method allowed us to determine a film thickness of about 45 nm with an uncertainty of ± 5 nm.

Molecular Dynamic Simulations. As starting structure a molecular chain consisting of 40 repeat units of **3** was created. The chain was then energy minimized by the molecular mechanics and molecular dynamics method implemented in the Discover code of Biosym Inc.[14] The force field parameters for the intramolecular interactions were taken from the Biosym polymer package (pcff).[14] MD was performed in vacuo at a temperature $T = 300$ K using the loose coupling algorithm of Berendsen.[15] The cutoff distance for the nonbonded interactions was chosen to be 0.95 nm.

Gel Permeation Chromatography (GPC)/Light Scattering/Viscosimetry. The measurements were done with a GPC setup of Thermo Separation, equipped with a Wyatt Dawn DSP laser photometer, an Optilab 903 refraction increment detector, and a Viscotek H 902 B viscometry detector. The data were obtained by measuring the polymer concentration every 1 s and the connected light intensity at 16 different angles from 12.3° to 159.7° and extrapolation to zero scattering angle. The angular dependence of the scattered light was successfully linearized in all chromatographic slices using a Zimm plot. Measurements were carried out on a derivative of **3** whose dendritic substituents have been removed. For de-dendronization a solution of **3** (500 mg, 0.26 mmol) and TMSI (5.0 g, 24 mmol) in chloroform (150 mL) was heated to reflux for 24 h. The volume of the resulting solution was reduced to 15 mL and the polymer precipitated by pouring this solution into methanol (300 mL). The polymeric material was recovered, lyophilized (benzene), and identified as **4** by comparison with authentic material[2a] (mass recovery regarding backbone 90%).

Scheme 1. Synthetic Sequence for the PPP-Derived Dendrimer **3** and Its De-dendronized Counterpart **4**



Results and Discussion

Molecular Weight Determination. Dendrimer **3** was synthesized from AA-type monomers **1** and **2** according to the Suzuki polycondensation protocol[16,17] (Scheme 1) which leads to a PPP with third-generation Fréchet-type[18] dendrons at every other benzene ring.[2a] If both the rigidity of the backbone and the space demand of the dendrons is high enough, dendrimer **3** should attain a stretched conformation and its envelope is ideally a cylinder, the dimensions of which are determined by the degree of polymerization (DP$_n$) and the diameter of the dendritic "layer" around the backbone. The difficulty to measure the DP$_n$ of **3**

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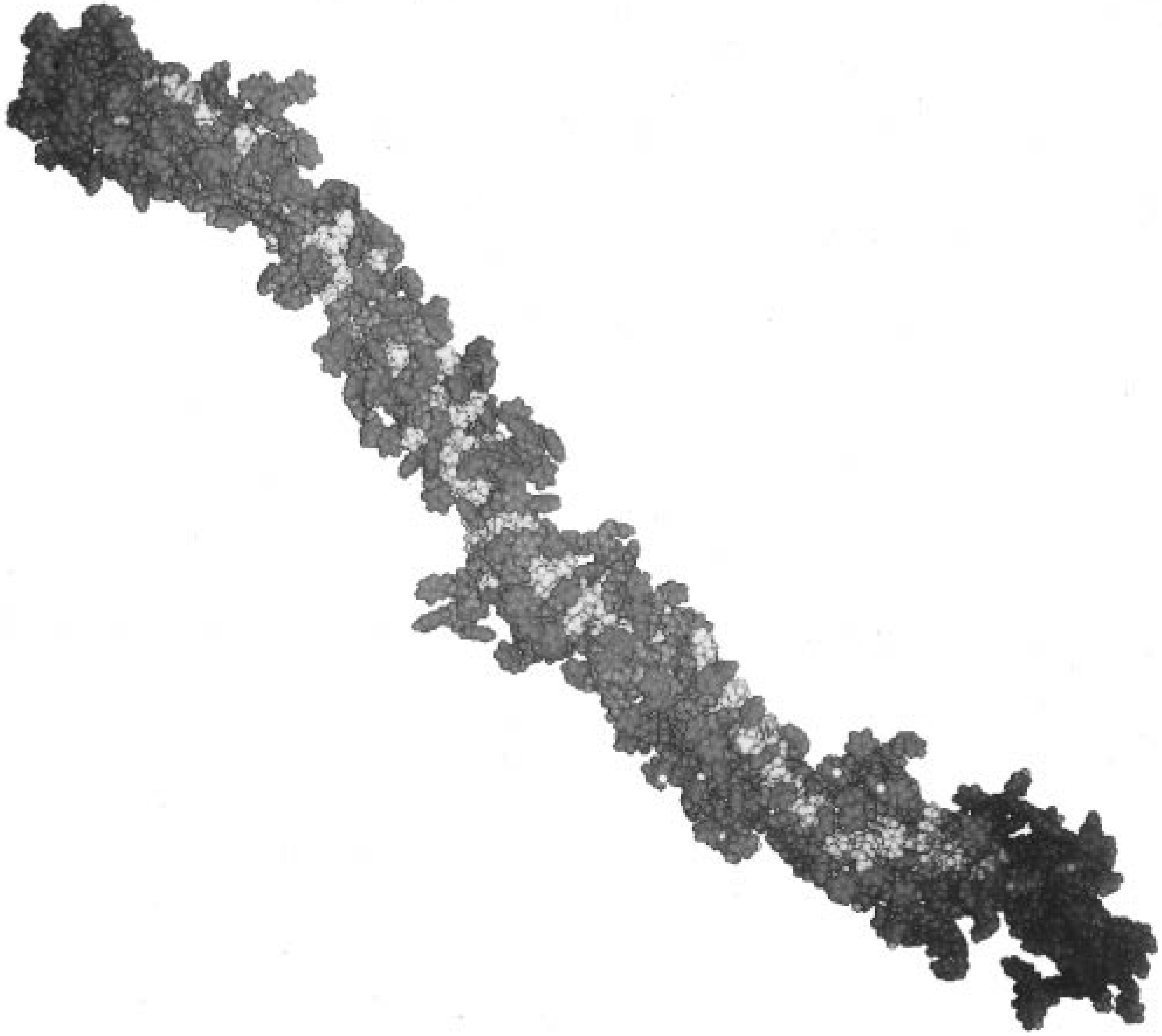

Figure 1. MD simulations for a dendrimer **3** with 40 repeat units (contour length 33 nm). The backbone and the hexyl chains are in yellow, the terminal benzene rings in red, and all other atoms in green. The diameter of the molecule fluctuates between approximately 2 and 4 nm.

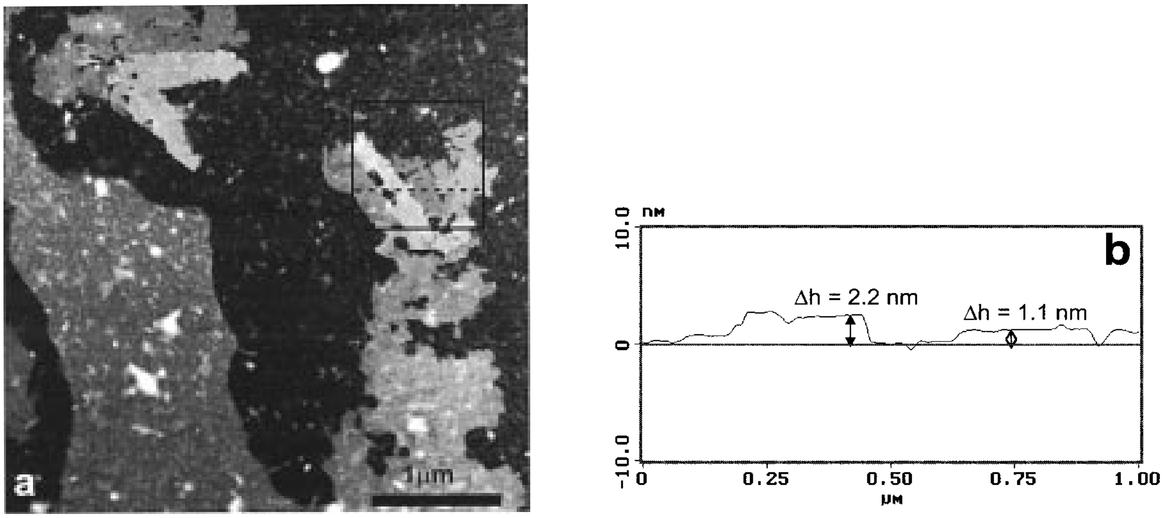

Figure 2. (a) Large-scale SFM image (4 × 4 μm^2, height image) of a multilayer film of dendrimer **3** on graphite (height image, *z*-scale 5 nm). (b) Height profile of a zoomed region as indicated by the dashed line in the upper right square of panel a. The smallest height difference between two successive monolayers is 1.1 ± 0.2 nm.

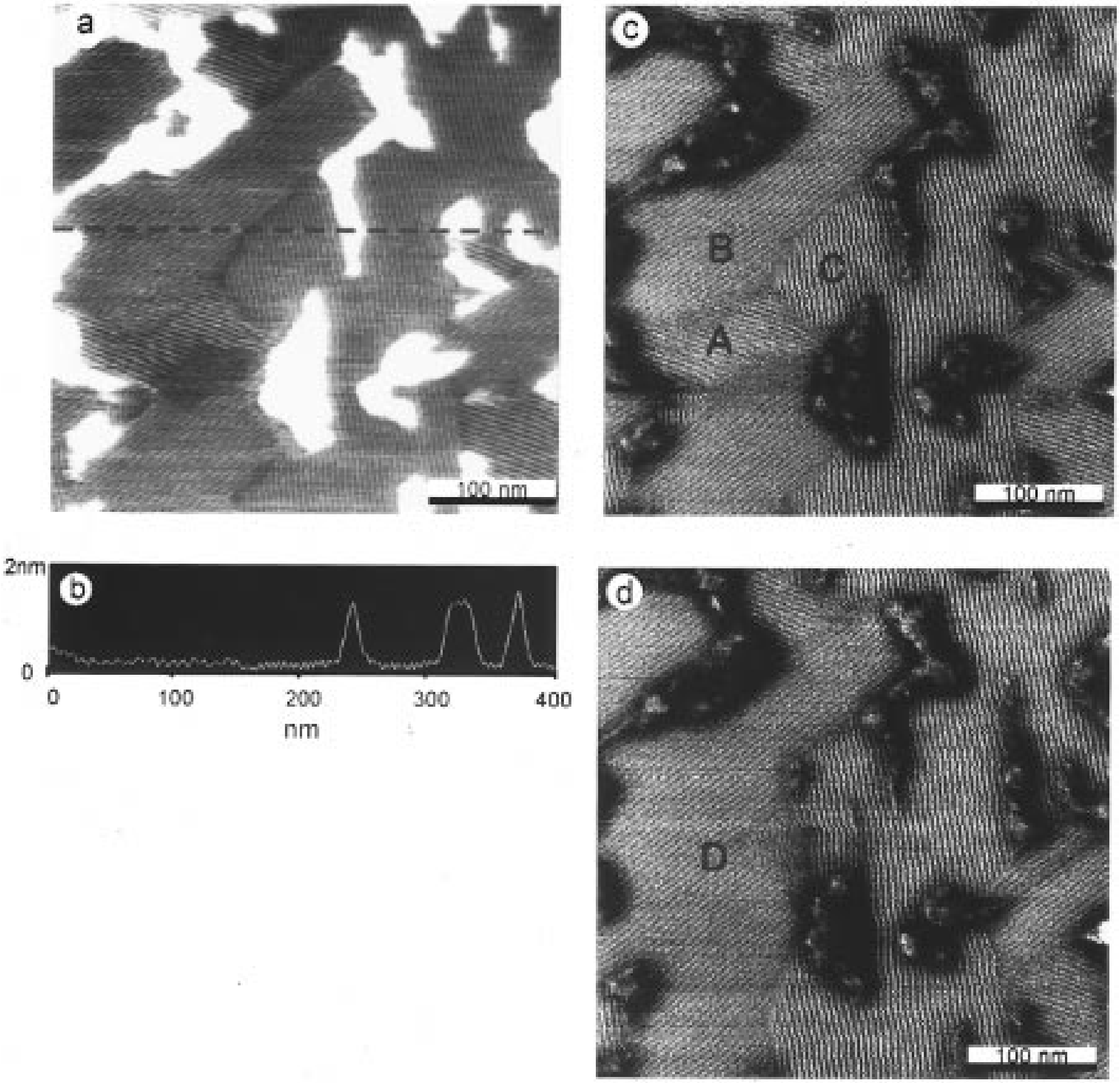

Figure 3. (a) Height and (c, d) phase contrast SFM images (400 nm × 400 nm) of a multilayer film of dendrimer **3** on HOPG. The dendrimers are grouped in domains. Within the domains they are packed parallel to each other, separated by a periodicity of 4.8 ± 0.5 nm. Note the three molecular orientations as indicated by A, B, and C in panel c. (b) Cross sectional profile along the horizontal line indicated in panel a. The thickness of outermost terraces on the film surface (bright areas in a) is about 1 nm. Images c and d have been recorded subsequently at the same position at an interval of 10 min. Domain A reorients in the same direction as domain B, resulting in a new domain D.

has been overcome by a chemical trick: De-dendronization of **3** with a large excess of trimethylsilyl iodide (TMSI), a very potent reagent for ether cleavages,[19] afforded polymer **4**. In contrast to its dendronized precursor and practically all other rodlike polymers, PPP **4** does not form aggregates and thus was amenable to an in-depth molecular weight determination. State-of-the-art combined gel permeation chromatography/light scattering (LS)/viscometry measurements gave $M_n = 54.000$, $M_w = 139.000$, and $M_w/M_n = 2.6$. This M_n value translates into an average $DP_n = 110$ of **4** which, in turn, corresponds to an average length of 90 nm (825 pm/ru) for the individual chain. Since the treatment of **3** with TMSI should leave the backbone intact, the individual chains of dendrimer **3** must also have a DP_n of 110 and, therefore, a contour length of 90 nm. According to Carother's equation[20] this DP_n results when each coupling step proceeds with a conversion of 99.1%. From a synthetic point of view this result is truly remarkable. It tells that the Suzuki cross-coupling, despite its considerable mechanistic complexity, is rather insensitive to monomers with high steric demand.

Molecular Dynamics Simulations. To estimate the cross section of dendrimer **3**, MD simulations[14−15] in vacuo were carried out for a dendrimer with 40 repeat units (contour length: 33 nm). They showed that (a) dendronized PPP attains an almost stretched conformation with an end-to-end distance between 28 and 32 nm, (b) the dendritic layer around the PPP backbone is quite dense but not fully compact, and, as a result, (c) the diameter fluctuates between approximately 2 and 4 nm. A molecular model of dendrimer **3** was obtained by MD simulations (Figure 1).

Scanning Force Microscopy. For SFM investigation, **3** was adsorbed on graphite from chloroform solution. Figure 2a represents a large-scale SFM image over an area of 4 × 4 μm^2. It should be mentioned that the whole surface area in Figure 2 is covered with dendrimer. Terraces (bright regions in Figure 2a) are visible on the film surface. A cross sectional profile of

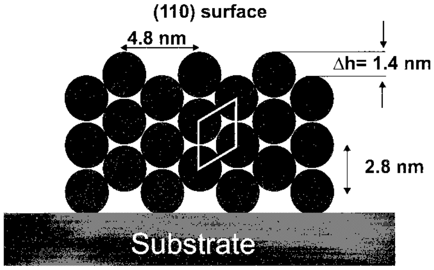

Figure 4. Schematic model of densely packed nanorods of **3** on graphite. The average diameter of the nanorods is aproximately 2.8 nm, resulting in a lateral periodicity of 4.8 nm at the (110) surface. The smallest height difference between two successive layers is about 1.4 nm.

a zoomed region is shown in Figure 2b. SFM indicates the formation of multilayer films. The smallest height difference Δh between successive layers is (1.1 ± 0.2) nm. Molecular steps of about 1.1, 2.2, and 3.3 nm height can be observed by SFM, corresponding to one, two, and three molecular layers. High-resolution SFM images, which can be obtained in every region of Figure 2a, show a remarkably high degree of order (Figure 3). Domains are observed whose size varies between 25×25 nm^2 and 100×200 nm^2 and which consist of periodical arrays of linear rows with a periodicity of 4.8 ± 0.5 nm. Since the average length and diameter of a dendrimer are 90 nm (LS) and 2−4 nm (MD), respectively, the SFM features are attributed to the molecular level. Within these domains, the dendrimers are packed parallel to each other in a multilayer film. The periodicity perpendicular to the chains is larger by a factor of approximately 1.7 (or $3^{1/2}$) than the average molecular diameter of **3** obtained by MD (3 nm). The vertical dimensions of the bright terraces in Figure 3a are shown in Figure 3b. Both, the lateral and vertical spacings can be explained if the (110) plane of densely packed nanorods of 2.8-nm diameter is exposed at the film surface. A schematic model is shown in Figure 4. For the given model one would expect a step height between successive layers of about 1.4 nm (Figure 4). The small differences between the expected and measured smallest height differences may be explained by assuming that the nanorods form ellipsoidal flattened cylinders at the interface. To obtain a compact multilayer with a typical density of about 1 g/cm^3, one would expect a monolayer thickness of about 1 nm. This value agrees well with the smallest height differences of 1.1 and 2.2 nm for mono- and bimolecular terraces (Figure 2b).

A reliable correlation of individual chain lengths with domain size cannot be done with the present data. This would require detection of all chain ends with certainty. However, despite the excellent resolution, only the chain ends at the grain boundaries can be identified without doubt, while those in the interior may be obscured if two dendrimers with the same director axis are in tight contact and oscillate somewhat along this axis.

SFM further indicates that different domains exhibit three molecular orientations, reflecting the 3-fold symmetry of the graphite substrate. Figure 3c shows three domains, marked A, B, and C, which are separated by grain boundaries. Individual chain ends can be identified at these boundaries. Different domains exhibit three molecular orientations at 60° ± 8° to each other, indicating that, despite the layer thickness of about 40−50 nm, the top layer “feels” the 3-fold symmetry of the graphite surface. From this it is concluded that the molecules in the first monolayer exhibit a high degree of order which enables them to recognize lattice axes of graphite.

Time-dependent SFM experiments show reorientations of small domains on a time scale of minutes. The images in Figure 3c,d have been recorded subsequently at the same position at an interval of 10 min. The small domain A in which the dendrimers are oriented from upper left to lower right (Figure 3c) disappears, while the neighboring, larger domain B grows into the new domain D (Figure 3d) where the dendrimers are aligned from lower left to upper right. This phenomenon can be described by an Ostwald ripening process, during which the interfacial energy is minimized similarly to the strictly two-dimensional case.[21] The direct observation of Ostwald ripening under ambient conditions suggests a rather high mobility of the nanorods in the smallest domains of the films. This effect may be influenced by the SFM tip. However, a correlation between the scan direction and the resulting orientation of domains cannot be observed. It should be mentioned that Ostwald ripening could not be observed in previous studies on cylindrical dendrimers with a poly(styrene) backbone,[22] whereas different samples of PPP films show this effect repeatedly at room temperature. The rather remarkable reorientation of small domains is beyond the scope of this paper and is still the subject of ongoing research.

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