Nanofibers from Functionalized Dendritic Molecules[**]

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Because of their architectural symmetry, the vast majority of dendritic molecules have globular or nearly globular shapes and can form uniform molecular layers on solid surfaces.[1–3] Only dendritic molecules with peculiar architectures were shown to be capable of forming self-assembled one-dimensional supramolecular structures such as rods, fibers, ribbons, and helices, which are of special interest for nanotechnology. These architectures include shape-persistent planar dendrimers, hairy rod and discotic polymers, rod-coils, rod-dendrons, and tapered molecules.[4–10] A proper combination of steric constraints, stacking interactions, and hydrogen bonding is postulated to be critical for precise assembly of these molecules. In contrast, there are very few reports on organized structures from hyperbranched molecules,[11] which, because of their irregular architecture and higher polydispersity, are not expected to form regular structures.[12–15]

It is widely accepted that a precise matching of directional interactions and steric constraints is required to facilitate long-range one-dimensional supramolecular assembly. On the contrary, here we demonstrate that multiple weak interactions among irregular, branched molecules with relatively high molecular weight and high polydispersity can facilitate their assembly into well-ordered one-dimensional supramolecular structures such as long and uniform micro- and nanofibers. To the best of our knowledge, this is the first example of one-dimensional supramolecular structures assembled from irregular, highly branched, dendritic molecules.

Synthesis and comprehensive chemical characterization are described elsewhere.[16] The theoretical chemical structure of the highly branched amphiphilic compound studied here (fourth-generation hyperbranched polyester) with a degree of branching of 40 % and chemical composition determined by NMR spectroscopy is presented in Figure 1. Note that these and other data, as well as the chemical structure, of irregular hyperbranched architectures should be considered only as averages.[17,18] The shell of the modified core after fractiona-

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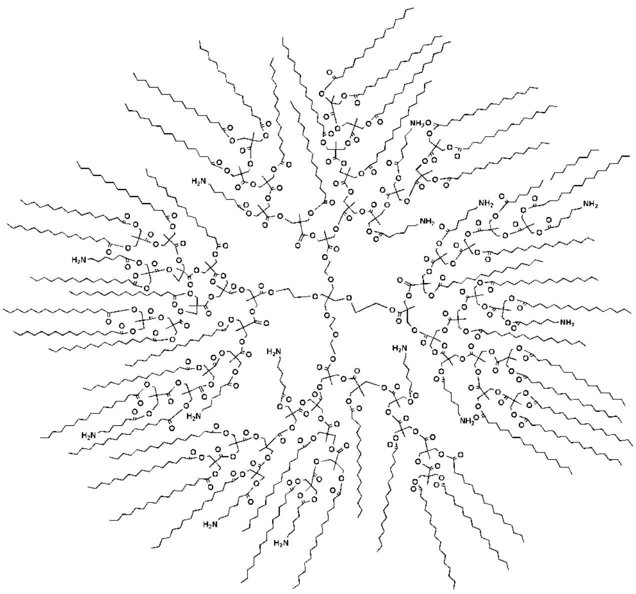

Figure 1. Structural formula of the amphiphilic hyperbranched polyester with a degree of branching of 40%, modified with terminal alkyl and amino groups.

tion was composed of about 50 hydrophobic C_{16} alkyl tails, about 14 amino-terminated groups, and 1–2 hydroxy-terminated branches.

The modified hyperbranched polymer, deposited at an air/water interface, exhibited stable amphiphilic surface behavior with increasing surface pressure during compression to an area per molecule (APM) of less than 12 nm^2.[16] This is in sharp contrast to the "naked" hyperbranched cores, which desorbed in the water subphase during compression.

Remarkably, uniform, stable one-dimensional surface morphologies were formed by these molecules on a silicon surface. At very low surface pressures (APM > 15 nm^2), isolated individual nanofibers became evident all over the surface (Figure 2a). They had an overall height of about 2 nm, lengths of less than 500 nm, and uniform but punctured shapes. The individual nanofibers became more uniform, better defined, and more clearly visible at slightly higher surface pressure (Figure 2b). These longer nanofibers (ca. 1 μm long) were curved and had a low degree of branching with occasional splitting.

At even higher surface pressure, the uniform nanofibers formed densely packed bundles weaving across large surface areas with overall lengths exceeding several micrometers (Figure 2c,d). At higher pressures the height of these structures increased slightly to 3–4 nm. In this condensed state they formed a dense interwoven network with a texture typical of nematic liquid-crystalline phases with characteristic topological defects.[19] Remarkably, the nanofibers preserved their identity without merging into thicker fibers, even at high packing density. These surface structures were exceptionally stable under normal scanning conditions and resisted higher shear forces even in the hard tapping mode.

High-resolution imaging in the tapping mode at low forces revealed a dilated shape of the nanofibers, which is a typical artifact produced by the AFM tip (Figure 2). We carefully analyzed the shape of these nanostructures with a very sharp carbon nanotube tip with a calibrated radius of less than 8 nm to deconvolute the tip shape and estimate the true lateral dimensions. We used a hemispherical approximation to account for tip dilation, in accordance with a known approach.[20] Considering the very small height of the one-dimensional structures of 2–4 nm (analysis of 30 randomly selected cross sections), tip dilation generally contributed less than 50% of the apparent width, which makes this correction quite reliable. These results led us to the conclusion that the observed one-dimensional structures are indeed nanofibers with a height of 3–4 nm and lateral dimensions of 4–8 nm, that is, close to molecular dimensions estimated from molecular models.

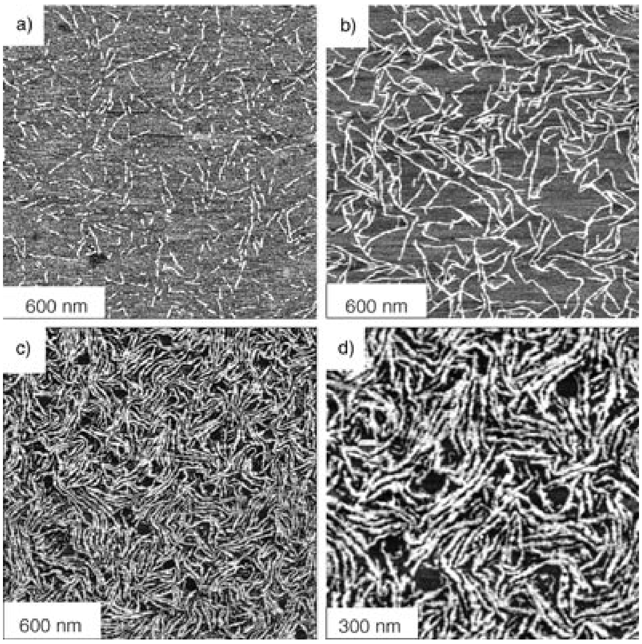

Figure 2. AFM phase images of nanofibrillar structures formed from dendritic molecules at different surface pressures. a) 0.2 mN m^{-1}; b) 5 mN m^{-1}; c, d) 30 mN m^{-1}, different scales.

We considered possible molecular conformations of amphiphilic hyperbranched molecules on a hydrophilic surface, including edge-on packing and flattened cores.[21] However, X-ray reflectivity studies on the molecules at the air/water interface demonstrated that the alkyl tails are predominantly oriented upwards with a certain tilt and a total monolayer thickness of about 3 nm.[18] From the analysis of the combined AFM and X-ray data on nanofiber dimensions, Langmuir isotherm data of molecular areas, X-ray data on tail orientation, and molecular dimensions from minimized molecular models, we suggest asymmetric molecular packing of these nanofibers (Figure 3). In this model, the molecules adopt a hemispherical conformation in which hydrophilic cores are squashed against the solid surface, as was suggested for amphiphilic dendrimers.[13] A number of important observations support this model. First, the proposed conformation maximizes interactions between terminal amino groups and surface silanol groups and thus makes this structure energetically favorable.[22] Second, this conforma-

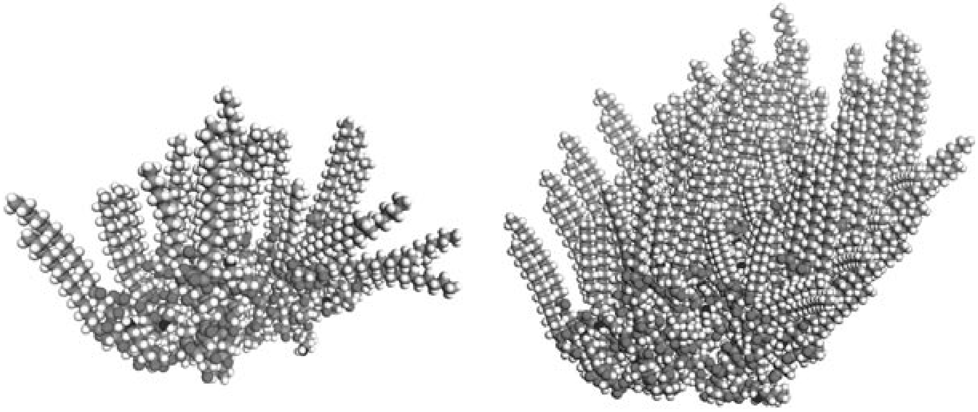

Figure 3. Molecular graphics representation of the suggested conformation of a single amphiphilic hyperbranched molecule on a solid hydrophilic surface (left) and their aggregation in the one-dimensional supramolecular structure (right).

tion results in the the overall height of the molecules of 2–4 nm and the lateral dimensions of 4–8 nm, depending upon the degree of tail orientation and core conformation, and closely corresponds to both X-ray and AFM data. Third, the hydrophobic alkyl tails that dominate in the shell are oriented upwards, tilted, cover most of the core, and thus define the surface APM of about 11 nm^2, which is close to the results of Langmuir isotherms of condensed monolayers. Finally, the proposed molecular arrangement should result in a modestly hydrophobic surface, which was confirmed by measurement of the contact angle (60–80°). All other known conformations that were examined (edge-on, face-on, and face-on flattened orientations) could not satisfy the whole set of experimental data.

Dense lateral stacking is suggested as a way of assembling these branched molecules in one-dimensional continuous rows resembling hemicylindrical micelles. Although the nature of the driving forces behind this one-dimensional assembly is not clear, we suggest that directional crystallization of alkyl tails could play a significant role. The less disturbed alkyl tails oriented vertically in the central portion of the molecules could be involved in local ordering, while more distorted, tilted alkyl tails along the edges could prevent crystallization in the lateral direction. X-ray scattering showed highly disturbed (paracrystalline) packing of alkyl chains in this material.[23] On the other hand, the proposed stacking provides the best chance for the amino, hydroxy, ester, and carboxy groups of the cores and inner shells of neighboring molecules to form a saturated network of hydrogen bonds and polar interactions without significant interference with the packed alkyl tails.[24] This would be impossible in a symmetrical face-on conformation. The critical role of these interactions is supported by the fact that similar molecules without amino groups do not form nanofibrillar structures.[16]

Cylindrical and hemicylindrical micellar structures similar to those reported here were observed for conventional ionic surfactants.[25,26] A fine balance of weak intermolecular interactions was considered to be crucial for the formation of these surface micellar structures. However, the core–shell architecture of the amphiphilic hyperbranched molecules studied here makes these one-dimensional nanofibrillar supramolecular structures unique. The multiple intermolecular hydrogen bonding and polar interactions between flexible cores stabilize these nanofibers and make them robust but flexible, unlike unstable hemicylindrical micelles from conventional surfactants, which are easily disrupted by drying and rarely form microscopically continuous fibers.

The peculiar internal organization of these nanofibrils with hydrophilic inner core and hydrophobic shell makes them an intriguing candidate for templating inorganic wired nanostructures, as already demonstrated for rigid molecules.[4] However, we believe that these flexible branched molecules could be much more versatile because of their straightforward one-pot synthesis.[27] Moreover, our findings question the current paradigm calling for well-defined, shape-persistent, and rigid molecules with precisely placed functional groups as building blocks for one-dimensional supramolecular nanostructures, and extend the known concept of steric balance and intermolecular interactions beyond well-defined shape-persistent (e.g., rod-dendron) architectures. Our results show the critical role of a highly branched chemical structure with multiple specific intermolecular interactions in the assembly of organized supramolecular structures. The amplification of weak, directional interactions facilitated by the presence of multiple peripheral branches of irregular, flexible molecules can lead to their efficient self-assembly into stable nanofibrillar structures. This example demonstrates that one-dimensional supramolecular assembly can be achieved without tedious multistep synthesis of shape-persistent molecules.

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