Self-Assembly of Dendron Rodcoil Molecules into Nanoribbons

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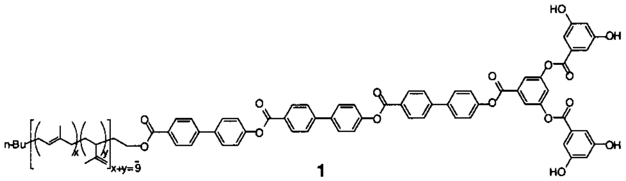
Received February 9, 2001

One of the expectations in science is the discovery of materials with surprising properties or functionality based on designed molecules that self-order or fold. The focus on self-assembly throughout the 90s has generated very useful knowledge toward this expectation and many prospects are on the horizon.[1−6] Learning how to control the dimensionality and shape of self-assembled structures through molecular design remains a challenge.

We report here on the self-assembly of molecules **1** which we refer to as dendron rodcoils (DRC) because of their blocked covalent architecture consisting of coil-like, rodlike, and dendritic segments. These molecules are synthesized in 15 steps with an overall yield of 40% (see Supporting Information). Extremely dilute solutions (as low as 0.2 wt %) of **1** in various organic solvents undergo spontaneous gelation, producing birefringent soft solids with a blue-violet hue. Formation of a birefringent gel strongly suggests self-assembling behavior of molecules **1** in organic solvents.



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The bulky geometry of the dendron relative to the rod could frustrate the formation of two-dimensional assemblies. Nonetheless, the identical aromatic rod-dendron segments of molecules **1** should be strongly driven to aggregate in one dimension through noncovalent interactions. These could involve hydrogen bonding among hydroxyl groups in the periphery of the dendron as well as aromatic $\pi-\pi$ stacking of biphenyl units. We used transmission electron microscopy (TEM) to study self-assembly of molecules **1** in organic solvents. Figure 1 shows a micrograph obtained from a 0.004 wt % solution of the DRC in dichloromethane cast onto a TEM grid. The unstained sample clearly shows one-dimensional objects with a strikingly uniform width of 10 nm. Most of the strands shown in Figure 1 have lengths on the order of micrometers. We also observed isolated strands as long as 10 μm, and thus their aspect ratio can be as high as 1000. The fully extended length of an average-size DRC molecule is ~6.5 nm, and thus the 10 nm width is consistent with a bimolecular packing of DRC molecules. A head-to-head packing of molecules could generate the narrow structures observed by TEM. Examination of the one-dimensional structures by atomic force microscopy (AFM) reveals their uniform thickness of 2 nm, clearly indicating a ribbonlike shape (see Supporting Information). Therefore, the self-assembly of DRC molecules results in the formation of nanoribbons 10 × 2 nm and several μm long, which we conclude lie flat on the carbon substrates used for imaging. Small-angle X-ray scattering (SAXS) experiments on the gels did not reveal peaks even when a synchrotron source was used, suggesting that the gels contain one-dimensional structures that are not highly aggregated and therefore lack the necessary structural coherence to generate X-ray diffraction.

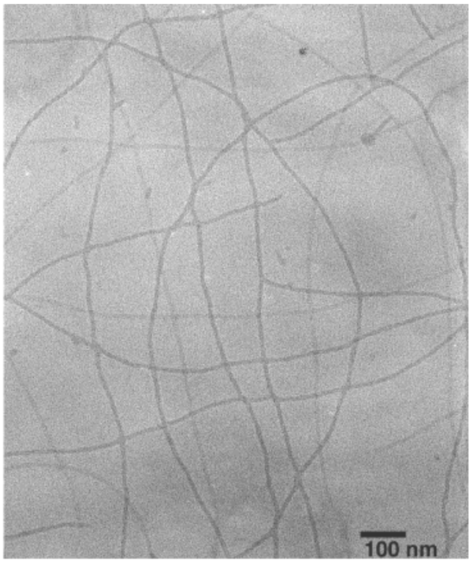

Figure 1. Bright-field TEM micrograph of unstained DRC nanoribbons formed in dichloromethane.

We synthesized a series of molecules analogous to **1** to probe the role played by hydrogen bonding in self-assembly. In addition to **1**, three other structures were synthesized that differed only in the number of hydroxyl groups present in the dendron segment. Molecules **2** do not contain hydroxyls at all, whereas **3** and **4** contain two and six hydroxyl groups, respectively (Table 1). Molecules **2** form isotropic solutions when dissolved in organic solvents, and gelation was never observed in this system (see Supporting Information). When only two hydroxyl groups are present (material **3**), gelation is still not observed when molecules are dissolved at elevated temperature. Once these solutions are cooled to room-temperature precipitation occurs. Therefore, the presence of at least four hydroxyl groups per molecule is necessary for solvent gelation by the network of self-assembled nanoribbons. As expected, the same gelation behavior described for **1** was observed for molecules **4** which contain six hydroxyl groups in their dendron. A second series of molecules (**5**−**7**) was synthesized in order to probe the role of aromatic interactions in self-assembly. In this series all of the molecules have identical dendron segments with four hydroxyl groups and therefore retain the same capacity to form hydrogen bonds. However, the molecules differ in the number of biphenyl ester units forming their rod segment. Interestingly, results from these studies indicate that aromatic interactions play an important synergistic role together with hydrogen bonds in triggering self-assembly. As shown in Table 1, molecules **5** (with one biphenyl-ester unit) do not gel organic

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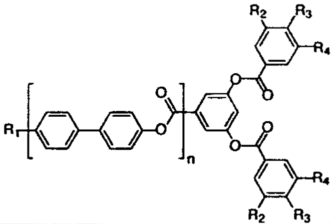
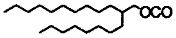
10.1021/ja015653+ CCC: $20.00 © 2001 American Chemical Society
Published on Web 04/04/2001

Table 1. Structure and Behavior in Dichloromethane of DRC Analogs and Model Compounds



molecules	R_1	*n*	R_2	R_3	R_4	behavior in CH_2Cl_2
2	PI9–$(CH_2)_2$–OCO	3	H	H	H	solution
3	PI9–$(CH_2)_2$–OCO	3	H	H	OH	insoluble material
4	PI9–$(CH_2)_2$–OCO	3	OH	OH	OH	gel
5	PI9–$(CH_2)_2$–OCO	1	OH	H	OH	solution
6	PI9–$(CH_2)_2$–OCO	2	OH	H	OH	weak gel
7	PI9–$(CH_2)_2$–OCO	4	OH	H	OH	gel
8	PB9–$(CH_2)_2$–OCO	3	OH	H	OH	gel
9	PS9–PI9–$(CH_2)_2$–OCO	3	OH	H	OH	solution
10	PS9–PB9–$(CH_2)_2$–OCO	3	OH	H	OH	solution
11		3	OH	H	OH	gel
12		3	OH	H	OH	insoluble material
13	H	3	OH	H	OH	insoluble material
14	H	1	OH	H	OH	solution

solvents or produce the characteristic blue-violet hue. In contrast, the addition of a second biphenyl-ester unit in molecules **6** results in the formation of a gel but one that is mechanically weak relative to that formed by **1**. Self-assembly is enhanced in molecules **7** containing 4 biphenyl ester units (in comparison with DRC **1**), as indicated by the fact that gelation is now observed in a larger variety of solvents. For example, birefringent gels are obtained when molecules **7** are dissolved in the monomeric polar solvents methyl methacrylate and butyl methacrylate at 1 wt %, whereas molecules **1** only form clear solutions in these same solvents at this concentration.

We have also synthesized DRC molecules containing the same rod-dendron part, but different coils. The presence of a diblock coil in molecules **9** and **10** significantly increases their solubility and gelation does not occur. On the other hand, the absence of a coil (compound **13**) resulted in formation of highly insoluble material. Compound **12** containing a fairly short dodecanyl coil was still insoluble, whereas molecule **11** with a larger coil segment (2-octyl-1-dodecanyl) was found to form gels similar to those of DRC **1**. Finally, molecules **15**−**18** (see Supporting Information) containing the same coil and rod as those in DRC **1** but different dendrons (generation 2, 3, 4, and 5) were prepared in order to understand the influence of the dendron's size. These four molecules were soluble in organic solvents, and none of them led to the formation of gels. Thus, at least three biphenyl-ester units in the rod and four hydroxyls in the dendron segment are required to form a robust gel, which is a signature of extensive self-assembly given the large number of molecules in one nanoribbon. Also the dendritic block must be of generation 1, and a coil of length comparable to the rod must be present in the structure (see Supporting Information). On the basis of these findings, and also the disappearance of all aromatic and hydroxyl peaks in the NMR spectra of gels, we conclude that self-assembly involves the aggregation of DRC molecules **1** through hydrogen bonding and aromatic interactions. The oligoisoprene segments, on the other hand, are found by NMR to retain their rotational freedom after gelation (see Supporting Information).

To gain insight into the internal structure of the nanoribbons, we synthesized model compound **14** containing a dendron identical to that present in DRC **1** but covalently attached to only one biphenyl. Figure 2 shows side and top views of the crystal structure of this compound revealing the presence of a ribbonlike structure composed of tetrameric cycles (upper and middle right).[7] The tetramers are formed by hydrogen bonds among dendritic segments and are stacked on top of each other along the *a* axis of the crystal. The crystal structure reveals eight hydrogen bonds that stitch the tetramers along the axis of the ribbon. Two OH- -OH and two OH- -O═C hydrogen bonds form the cyclic tetramer, whereas four OH- -OH and four OH- -O═C hydrogen bonds connect adjacent tetramers along the ribbon axis (hydrogen bonds are shown in yellow). The biphenyl units are stacked 4.93 Å apart, a distance that should allow for $\pi-\pi$ stacking interactions among them. The thickness of the tetrameric cycles from the crystal structure is about 2 nm, which is in excellent agreement with the thickness of the DRC nanoribbons, as determined by AFM. Twisting of the nanoribbons into helical structures has also been observed by TEM (see Supporting Information). Thus, on the basis of these data as well as the crystal structure of the model compound **14**, we envision the structure of the ribbons as depicted in Figure 2 (bottom right, and left).

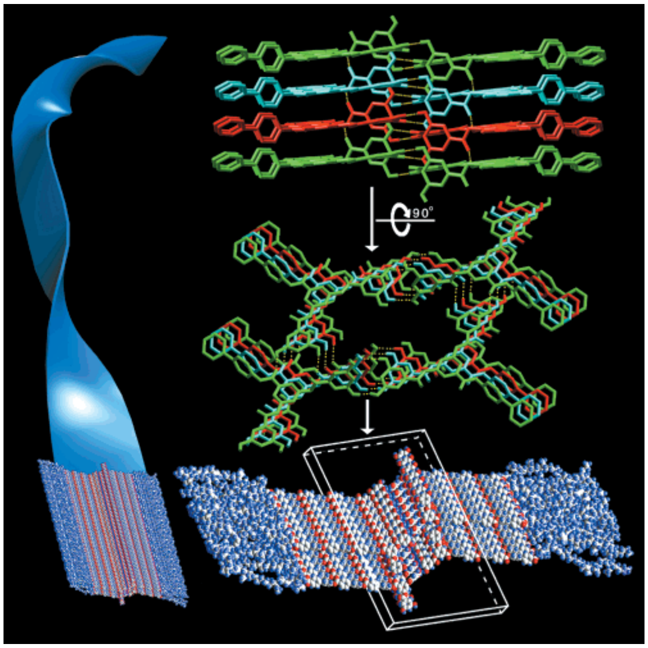


Figure 2. Side view of the ribbonlike structure taken directly from the crystal structure of **14** shows color-coded hydrogen-bonded tetramers (upper right) stacked on top of each other along the [100] direction of the crystal (top view is shown in the middle right). Schematic (left and bottom right) representation of the proposed structure for a DRC nanoribbon.

We have demonstrated that dendron rodcoil molecules **1** self-assemble via hydrogen bonding and $\pi-\pi$ stacking interactions into well-defined nanoribbons with uniform width and thickness (10 × 2 nm) and lengths that can be 1000 times greater. These structures can build networks that cause solvents to gel at self-assembler contents as low as 0.2 wt %. The type of self-assembly described here offers a synthetic route to well-defined one-dimensional organic nanostructures.

Acknowledgment. This work was supported by the U.S. Army Research Office, the National Science Foundation, and the Department of Energy. E.D.S. thanks NSERC of Canada for a graduate scholarship.

Supporting Information Available: Synthesis of **1**, AFM image and height profiles of ribbons, NMR of DRC gel and solution, TEM of twisted nanoribbons (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[7] Crystal data for compound **14**: $C_{33}H_{22}O_{10}$, M = 578.51, triclinic, $P\bar{1}$, a = 4.9341 (5) Å, b = 19.219 (2) Å, c = 33.022 (3) Å, α = 85.805 (2)°, β = 88.850 (2)°, γ = 88.669 (2)°, V = 3121.6 (6) $Å^3$, Z = 4.