Solid-State Scrolls from Hierarchical Self-Assembly of T-Shaped Rod–Coil Molecules**

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One-dimensional nanostructures such as cylinders and tubules are of great interest owing to their unique electro-optical properties and potential applications in areas ranging from nanotechnology to biotechnology, but they are challenging to synthesize.1] Such anisotropic nanostructures with extremely high aspect ratios can be formed when thin crystalline layers roll up under disparate surface stresses on opposite sides of the layers.2,3] Single-crystal nanotubes have also been synthesized using nanowire templates,4] and this method has been extended to prepare polymeric nanotubules with controlled diameters.5] Self-assembly of block copolymers and amphiphilic molecules in solution leads to the formation of tubular structures in a selective solvent that acts as a molecular structure-directing template.6–8] However, the self-assembly of hollow tubules without any template or solvent has not yet been realized, with few exceptions.9,10] Furthermore, we are not aware of any natural or synthetic self-assembling layers that spontaneously form scrolls in the solid state, which is crucial for practical applications in nanotechnology. Herein we report the formation of hollow tubules from the self-assembly of T-shaped rod–coil molecules in the solid state.

Rod–coil molecules are attractive for generating highly defined nanostructures that have physical dimensions as small as a few nanometers.11] The stiff rodlike components of the molecules endow the materials with anisotropic properties arising from their strong tendency to be aligned perpendicular to the direction of rod orientation. In addition to conventional layered structures, the rodlike components of rod–coil building blocks can be made to self-assemble into a wide variety of complex geometries, including perforated layers, ribbons, and bundles, through covalent attachment of long flexible chains to their distal section.12] These nanoscale objects are further organized into two-dimensional (ribbons) and three-dimensional (bundles) structures.12,13] However, the rod segments arrange parallel to each other to form only flat local structures as opposed to radial structures, a prerequisite for nanotubules.14] Herein, we report the formation of filled cylindrical and hollow tubular scrolls from the self-assembly of T-shaped rod–coil molecules in the solid state. The scrolls have a hierarchical structure comprised of alternating rod and coil layers with a narrow distribution of outer scroll diameters.

The rod–coil molecules described herein consist of a penta-2-phenylene conjugated rod connected to a poly(proplylene oxide) (PPO) coil laterally attached through an imidazole linkage (Figure 1a).11] Rod–coil molecules based on lateral chains self-assemble into layered structures in which the rod segments are aligned parallel to the layer planes.15,16] The stiff rod layers are separated by the amorphous layers of the lateral coils. Within the layers, the rods are organized parallel to each other to form sublayers. This special organization of the rod segments into anisotropic 2D layers could be envisioned to roll up into tubules under appropriate conditions.17–19]

Rod–coil molecules 1 and 2, and their analogues 3 and 4 with longer PPO chains, show an ordered state that is retained up to an isotropization transition (Table 1). The ordered structure is thermodynamically stable, as evidenced by differential scanning calorimetry (DSC; Table 1). The solid-state structure was confirmed by X-ray measurements (Figure 1b). Small-angle X-ray scattering (SAXS) reveals that 1 and 2 have a layered structure with a primary spacing of 3.5 and 4.6 nm, respectively. These dimensions correspond roughly to the respective laterally extended molecular lengths, suggesting that the rod segments within the domains are parallel to the layer planes. Notably, both 1 and 2 exhibit an additional sharp reflection at an identical q spacing of 3.57 nm−1 and show similar wide-angle X-ray scattering (WAXS) patterns (Figure S2 in the Supporting Information), indicating that both compounds have an essentially identical crystalline structure within the rod layers. This finding is also reflected in the similar transition temperatures and corresponding enthalpy changes (Table 1). The existence of a sharp peak at an intermediate angle suggests that the rod segments in 1 and
organize into sublayers with a thickness of 1.76 nm within a layer. Considering the calculated rod length of 2.2 nm by the Corey–Pauling–Koltun (CPK) model, this dimension indicates that the rods are tilted relative to the sublayer normal with an angle of 37°. Recent simulations of laterally grafted rod–coil molecules predict the existence of in-plane sublayers with rod tilt.\(^{[10]}\)

In contrast to conventional layered structures, these layers form scrolls with a nearly uniform diameter, as revealed by the transmission electron microscopy (TEM) images in Figure 2. The side-view image of cryomicrotomed films of 2 Stained with RuO\(_4\) shows a layered structure with a primary spacing of 4.6 nm, consistent with that obtained from SAXS. Views of the cross-section, however, reveal the formation of scrolls with a spiral arrangement of alternating light coil and dark rod layers with scroll diameters ranging from 80 to 100 nm (Figure 2b). Additional information on the structural dimensionality was obtained by 2D X-ray diffraction with an annealed sample of 2 exhibiting macroscopic orientation. As shown in Figure 2c, the X-ray beam was directed perpendicular to the principle axes of the scrolls. At small angles, two pairs of strong (100) and (200) reflections are diffracted along the equator. At an intermediate angle, the additional repeat distance associated with the sublayer thickness in each rod layer occurs at the same direction relative to the layer reflections, demonstrating that the scroll axis is parallel to the sublayer direction. At wide angles, two pairs of reflections

![Figure 1](image1.png)  
**Figure 1.** a) Molecular structures of 1–4. b) 1D SAXS patterns of 1–4 plotted against \(q = 4\pi \sin \theta \lambda^{-1}\). Black arrows indicate an intermediate-angle reflection for each molecule.

![Figure 2](image2.png)  
**Figure 2.** a) TEM image of a layered structure confined in the scrolls, revealing an ordered array of alternating light-colored PPO layers and dark aromatic layers. b) Cross-sectional image along the rolled lamellar sheet axis. Scale bars 50 nm. c) 2D SAXS pattern obtained from 2 at 25 °C. d) 2D WAXS pattern of 2. The diffraction pattern shows \{010\}, \{110\} reflections of the rolled lamellar structure. e) Schematic representation of the filled scrolls from 2.

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[a] Transition temperature estimated from differential scanning calorimetry. [b] Enthalpy change \((\Delta H)\) estimated from differential scanning calorimetry. [c] Layer thicknesses \((d)\) measured from \(q\) values of 1D X-ray profiles.
associated with the inter-rod distance are diffracted along the meridian (Figure 2d), indicative of crystallization of the rod segments within the sublayers. This result demonstrates that the repeat distance associated with π–π stacking interactions is perpendicular to the rolling axis.

The electron microscopy observations together with the X-ray results lead to the structural model of the scrolls of 2 as shown in Figure 2e. The bulk layers are formed parallel to the molecular long axes with a thickness of 4.6 nm, and the rod segments within the layers are organized parallel to each other to form sublayers with rod tilt with respect to the sublayer normal at an angle of 37°. Subsequently, the layers roll up along the direction of the sublayers to form scrolls with diameters ranging from 80 to 100 nm. As evidenced in the simulations described below, the rod tilt with respect to the sublayer normal leads to helical scrolls, because the rolling axis is parallel to the sublayer direction.

Rod–coil molecules 3 and 4, based on longer PPO chains, also self-organize into layered structures. Each small-angle X-ray diffraction pattern shows three sharp equidistant reflections, indicative of layer-like structures that are consistent with the lattice constant determined from small-angle X-ray scattering experiments performed on a 3D WAXS pattern of 3. The diffraction pattern shows {100}, {200}, and {300} reflections. The sharp intermediate-angle peak suggests that the rod segments in the two compounds organize into sublayers with a thickness of 1.52 nm. Considering the calculated rod length of 2.2 nm by the CPK model, this dimension indicates that the rods are tilted with an angle of 47° relative to the sublayer normal.

When cryomicrotomed films of 3 stained with RuO4 were characterized by TEM, stacks of long cylindrical objects with nearly uniform diameters of (90 ± 10) nm and lengths up to several tenths of micrometers were observed (Figure 3). The magnified images reveal that the elongated objects consist of an inner core of approximately 30 nm separated by multilayer walls of about 30 nm, demonstrating that the 1D objects are multiwall tubules. The image of the cross-section of the tubules shows that the walls consist of layers rolled into a spiral in which the layer thickness is 6.2 nm (Figure 3c), consistent with the lattice constant determined from small-angle X-ray diffraction. These results suggest that the formation of a tubular structure arises from a rolling up of the layers. When thin films of 3 were cast from dilute methanol solutions and negatively stained with uranyl acetate solution, which is able to fill the empty space by capillary action, the image showed a dark interior in the elongated objects (Figure 3d), clearly indicating a hollow cavity along the scroll axis.

To investigate the molecular orientation within the rolled tubules, 2D X-ray scattering experiments were performed with an annealed sample of 3. The diffraction pattern shows two pairs of strong (100) and (200) reflections that are diffracted along the equator at small angles (Figure 3e). At intermediate angles, two pairs of strong arcs corresponding to a sublayer thickness are found in the cross directions at an angle of approximately 90°, implying that the rods are packed into a smectic C liquid-crystal-like structure with a tilt angle of approximately 45° relative to the sublayer normal. At wide angles, a diffuse scattering centered at 0.45 nm is diffracted in a circular pattern (Figure 3f), characteristic of liquid-crystalline order between the rod segments.

To determine whether the tubules form directly from the melt or by spontaneous rolling up of planar sheets, we
investigated cryomicrotomed films of 3 with different annealing times (Figure 4a–d). When the melt was quickly quenched by blowing cold argon onto it, the TEM images showed loosely curved layers together with uncurved layers. However, when the films were cooled slowly from the melt to ambient temperature, we observed closely packed scrolls throughout the image area (Figure 4d). This result implies that the molecules first assemble into a layered structure that subsequently forms scrolls. On the basis of these results, we hypothesize that the hollow tubules are formed by rolling up along an axis parallel to the rod direction of the bulk layers in which the laterally grafted rod segments are arranged parallel to each other to form sublayers with a rod tilt of approximately 45° relative to the sublayer normal (Figure 4e). These scrolls have external diameters ranging from 80–100 nm and a hollow interior with a diameter of approximately 30 nm.

To gain further insight into the rolling behavior of the layers of T-shaped rod-coil molecules, we performed Brownian dynamics simulations (for details, see the Supporting Information) of individual preformed bilayer sheets of molecules 1 or 2 and 3 or 4. Our previous simulations demonstrated that the molecules first assemble into a layered structure that subsequently forms scrolls. On the basis of these results, we hypothesize that the hollow tubules are formed by rolling up along an axis parallel to the rod direction of the bulk layers in which the laterally grafted rod segments are arranged parallel to each other to form sublayers with a rod tilt of approximately 45° relative to the sublayer normal (Figure 4e). These scrolls have external diameters ranging from 80–100 nm and a hollow interior with a diameter of approximately 30 nm.

Top-view snapshots of the simulated bilayer sheets for which the rod packing is as proposed in Figure 2e for 1 and 2 with different aspect ratios (measured in pairs of rods), rod tilt angles, and short and long coil lengths, corresponding to 1 (“short” coil) and 2 (“long” coil). Upper row: (48:12, 37°, short coil), (60:8, 37°, long coil), and (48:8, 37°, long coil). Lower row: (60:12, 37°, short coil), (48:12, 0°, short coil), and (48:12, 0°, long coil). Side-view snapshots of the simulated structures (Figure 5b) indicate that the scrolls are helical for nonzero tilt angles in which the rod packing is as proposed in Figure 2e for 2 (coils removed for clarity). Left: (48:12, 37°, long coil). Right: (48:12, 0°, long coil).

c) Snapshots of scrolls formed by sheets for which the rod packing is as proposed for 3 and 4 in Figure 4e. The first two images from the left are the top view and side view (with coils removed) of a 6:80 sheet with short coils corresponding to compound 3. The third image shows the top view of a scroll formed from a 6:90 sheet with long coils corresponding to compound 4.
rod direction in every case, consistent with the model proposed in Figure 4c. The simulated structures (Figure 5c, left) show excellent agreement with the hollow tubules formed by compounds 3 and 4. We observe that the loose packing of the rods in interdigitated sublayers is maintained under rolling (Figure 5c, middle). Furthermore, our simulations reveal that the radius of the hollow core increases with the coil length (Figure 5c, right), presumably because of the limited compression of the coils and the increasing thickness (and thus decreasing bending elasticity) of the bilayer sheets. The results described herein demonstrate that T-shaped rod–coil molecules self-assemble into layered structures in which the long axis of the rod segment is parallel to the layer plane. The layers, in turn, unexpectedly roll up to form scrolls in the solid state. Rolling of the layers can be understood by considering the grafting density at the rod–coil interface and the resulting space-filling requirements. Lamellar ordering of rod–coil molecules self-assemble into layered structures in the solid state. Rolling of the layers can be understood by considering the grafting density at the rod–coil interface and the resulting space-filling requirements. Lamellar ordering of rods would confine rod–coil junctions to a flat interface. However, the large mismatch between the cross-sectional areas of the coil segments and the side face of the rod results in a strong energetic penalty associated with low grafting densities of the coils and the increasing thickness (and thus decreasing bending elasticity) of the bilayer sheets.

The most notable feature of the structurally simple rod–coil molecules investigated herein is their ability to hierarchically and reversibly self-assemble into scrolls in the solid state. It is also remarkable that the core structure of the scrolls, from filled cylindrical to hollow tubular, can be controlled by only a small variation of coil length of the T-shaped rod–coil molecule. Such solid-state scrolls with controlled interior hold outstanding potential for a broad range of applications in nanoscience.

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