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COMMUNICATIONS

Published on Web 10/09/2008

Stepped Strips from Self-Organization of Oligo(*p*-phenylene) Rods with Lateral Dendritic Chains

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The design of novel self-assembling molecules offers an opportunity to extend our understanding how to create unique supramolecular structures with desired functions.[1] Diverse self-assembling molecules including dendrimers,[2] liquid crystals,[3] and block copolymers[4] are being created as a means of manipulating aggregation structure. Incorporation of a stiff rodlike building block into a block molecular architecture is particularly attractive for generating highly defined self-assembled structures that have physical dimensions as small as a few nanometers.[5] In addition to the conventional layered structures, the rod building blocks self-assemble into a wide variety of complex geometries, including perforated layers, columns, and bundles, through covalent attachment of long flexible chains to their distal part.[6] Increasing volume fraction of coil segments drives the layers to break up into smaller domains including columns in which the rods are arranged perpendicular to the column axis. Previously, we have shown that the macrocyclic attachment of a flexible chain into both ends of a rod frustrates the formation of two-dimensional layers commonly observed for linear rod−coil molecules.[7] Instead, the rod segments are driven to aggregate in one dimension to form flat ribbons in which the rod segments are arranged again perpendicular to the ribbon axis.

We present here the formation of stepped strips from the self-assembly of molecular rods with laterally attached flexible chains. The rod segments within the strips are aligned parallel to each other to form discrete sheets which subsequently stack together with a partial overlap to form a stepped 1D structure. The self-assembling rod molecules that form these aggregates consist of an oligo(*p*-phenylene) rod and penta(ethylene oxide) branched chains that are grafted together at the mid part of the rod (Figure 1).[8,9]

The melting temperature of **1** based on an octa(*p*-phenylene) rod determined from differential scanning calorimetry (DSC) heating was observed to be 55 °C, whereas that of **2** based on a dodeca(*p*-phenylene) rod is 207 °C. The small-angle X-ray scattering (SAXS) of **1** in the solid state shows a number of well-resolved reflections that correspond to a 2-D oblique structure with lattice constants of $a = 2.8$ nm and $b = 2.0$ nm and a characteristic angle of 73° (Figure 2a).

The wide-angle X-ray scattering (WAXS) shows a reflection centered at a q spacing of 14.3 nm^{-1}, which is due to crystal packing of the rod segments within the aromatic domains with an inter-rod distance of 4.4 Å (See Supporting Information, Figure S2). When microtomed films of **1** stained with RuO_4 were characterized by transmission electron microscopy (TEM), the images showed a 2-dimensional array of dark aromatic domains in a matrix of light-colored dendritic chains as well as views in the direction of the strip (Figure 2b). The interdomain distances are approximately 2.5 nm which is well matched with those obtained from the SAXS data.

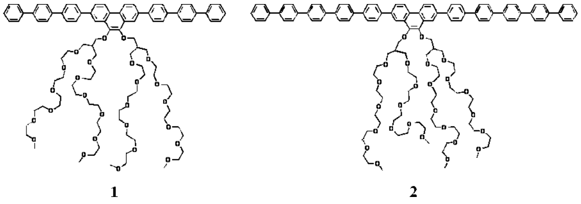

Figure 1. Molecular structure of **1** and **2**.

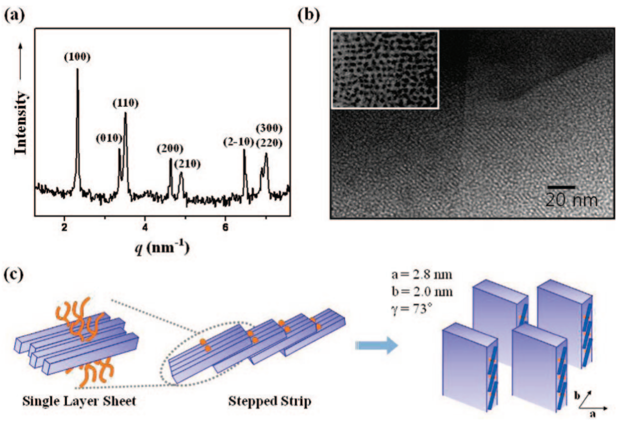

Figure 2. (a) SAXS pattern of **1**, (b) TEM image of ultramicrotomed film of **1** revealing 2-D oblique columnar array of aromatic stepped core, and (c) schematic representation of the stepped strip from **1**.

Considering the calculated rod length of 3.8 nm, these dimensions are too small to be interpreted as a perpendicular arrangement of the rods to strip axis. Therefore, parallel arrangements of the rods along the strip axis would be an appropriate model. On the basis of the lattice constants and measured densities, the average number of rod units per cross section of the strip is calculated to be ∼7. Considering that the ratio of the lattice parameters a and b is deviated from unity ($a/b = 1.4$), this number of molecules suggests that the rods are packed parallel to each other into stacks of four rods to produce monolayer sheets with a width of 1.43 nm (Figure 2c). The individual monolayer sheets subsequently stack together with an overlap of half of the rod length to form stepped strips that self-organize into a 2-D oblique lattice.

Molecule **2** based on a dodeca(*p*-phenylene) rod also self-organizes into a 2D structure. The small-angle X-ray diffraction shows a number of reflections which can be indexed as a 2D oblique

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10.1021/ja807035j CCC: $40.75 © 2008 American Chemical Society

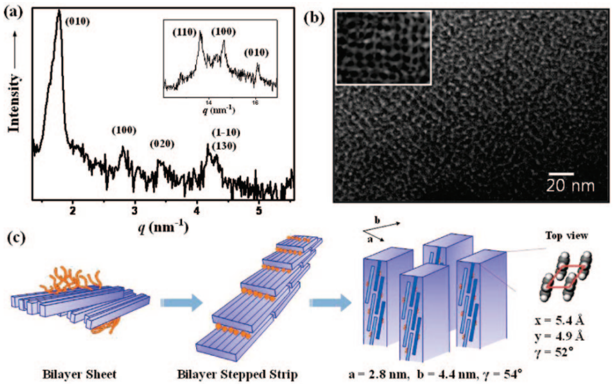

Figure 3. (a) X-ray diffraction pattern of **2**, (b) TEM image of ultramicrotomed film of **2** revealing 2-D oblique columnar array of aromatic stepped core, and (c) schematic representation of stepped ribbon from **2**.

structure with lattice constants of $a = 2.8$ nm and $b = 4.4$ nm and a characteristic angle of 54° (Figure 3a). The TEM image stained with RuO_4 shows an oblique array of dark spots in a matrix of light-colored branched chains (Figure 3b). The image reveals that the interdomain distances are roughly 3 nm, which is comparable to that the lattice parameters obtained from SAXS. Considering the rod length (5.6 nm by CPK), these dimensions suggest again that the rods are arranged parallel to the strip axis.

The WAXS pattern shows several sharp reflections that can be indexed as (110), (100), and (010) planes of a 2D oblique lattice with lattice parameters of $x = 0.54$ nm and $y = 0.49$ nm and a characteristic angle of 52° (Inset in Figure 3a). From the lattice constants and the densities, the number of molecules in a cross-section of the strip can be calculated to be approximately 18. The aggregation of 18 rods in a cross-section and both oblique lattices as seen in the X-ray results suggest that the cross-section consists of 6 × 3 rods to give rise to bilayer sheets in which six rods are arranged parallel to each other to form single layers which, in turn, face each other through aromatic stacking interactions to produce bilayer sheets. Subsequently, two adjacent bilayers are half-overlapped due to laterally attached chains to form stepped strips that self-organize again into a 2D oblique structure (Figure 3c).

To gain further insight into the strip structure of **2**, we performed molecular dynamic simulations using Brownian dynamics (BD).[11,12] To mimic molecular characteristics of **2**, we constructed coarse-grained models which consist of hydrophobic rigid rod segment and hydrophilic side chains that are tightly bound to the center beads of the rod (Figure S3). As shown in Figure S4, the simulation results clearly support the stepped strip structure as depicted in Figure 3.

The results described above demonstrate that the elongated rods with lateral chains self-assemble into a strip structure, where the rod segments are arranged parallel to the strip axis with a stepped fashion. Subsequently, the resulting stepped strips self-organize into a 2D oblique lattice. Compared to other self-assembling rod systems that form columnar structures in which the rods are aligned perpendicular to column long axis,[6,10] it is remarkable that the rod segments self-assemble into flat stepped strips in which the rods pack parallel to strip long axis.[13] This special organization of the rod segments arises from a balance between the energetic gain of a parallel arrangement of the rods and the resulting entropic penalty associated with stretching of the lateral flexible chains.[12]

Another interesting point to be noted is that **1** molecules based on a short rod self-assemble into monolayer sheets, whereas **2** molecules based on a long rod self-assemble into bilayer sheets. This notable contrast in sheet structure with small variation in rod length of the molecule could be understood by considering the similar way monolayers are formed in preference to a bilayer lamellar structure to reduce chain stretching in smectic liquid crystals.[14] Such packing arrangements of conjugated rods may offer intriguing potentials for nanowires and organic semiconductors.

Acknowledgment. This work was supported by the Creative Research Initiative Program of the Ministry of Education, Science and Technology of the Korean Government and the Korea Science and Engineering Foundation (KOSEF-R01-2007-000-11831-0, ES). D.H, E.L, and M.H. thank a fellowship of the BK21 program of the Ministry of Education, Science and Technology of the Korean Government.

Supporting Information Available: Details of the synthesis, analysis, structural characterizations, and property measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Ryu, J.-H.; Hong, D.-J.; Lee, M. *Chem. Commun.* **2008**, 1043–1054. (b) Hill, J. P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N; Aida, T. *Science* **2004**, *304*, 1481–1483. (c) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546.

(2) (a) Percec, V.; Dulcey, A. E.; Peterca, M.; Ilies, M.; Sienkowska, M. J.; Heiney, P. A. *J. Am. Chem. Soc.* **2005**, *127*, 17902–17909. (b) Bury, I.; Heinrich, B.; Bourgogne, C.; Guillon, D.; Donnio, B. *Chem.—Eur. J.* **2006**, *12*, 8396–8413. (c) Kato, T.; Matsuoka, T.; Nishii, M.; Kamikawa, Y.; Kanie, K.; Nishimura, T.; Yashima, E.; Ujiie, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1969–1972.

(3) (a) Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 38–68. (b) Tschierske, C. *Chem. Soc. Rev.* **2007**, *12*, 1930–1970. (c) Saez, I. M.; Goodby, J. W. *Struct. Bonding (Berlin)* **2008**, *128*, 1–62.

(4) Förster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 688–714.

(5) (a) Lee, M.; Cho, B.-K.; Zin, W.-C. *Chem. Rev.* **2001**, *101*, 3869–3892. (b) Ryu, J.-H.; Cho, B.-K.; Lee, M. *Bull. Korean Chem. Soc.* **2006**, *27*, 1270–1282. (c) Klok, H.-A.; Lecommandoux, S. *Adv. Mater.* **2001**, *13*, 1217–1229.

(6) (a) Ryu, J.-H.; Oh, N.-K.; Zin, W.-C.; Lee, M. *J. Am. Chem. Soc.* **2004**, *126*, 3551–3558. (b) Lee, M.; Cho, B.-K.; Jang, Y.-G.; Zin, W.-C. *J. Am. Chem. Soc.* **2000**, *122*, 7449–7455.

(7) (a) Yang, W.-Y.; Ahn, J.- H.; Yoo, Y.-S.; Oh, N.-K.; Lee, M. *Nat. Mater.* **2005**, *4*, 399. (b) Yang, W.-Y.; Lee, E.; Lee, M. *J. Am. Chem. Soc.* **2006**, *128*, 3484–3485.

(8) Ciszek, J. W.; Tour, J. M. *Tetrahedron Lett.* **2004**, *45*, 2801–2803.

(9) Yoo, Y.-S.; Choi, J.-H.; Song, J.-H.; Oh, N.-K.; Zin, W.-C.; Park, S.; Chang, T.; Lee, M. *J. Am. Chem. Soc.* **2004**, *126*, 6294–6300.

(10) (a) Radzilowski, L. H.; Carragher, B. O.; Stupp, S. I. *Macromolecules* **1997**, *30*, 2110–2119. (b) Huang, Z.-G.; Ryu, J.-H.; Lee, E.; Lee, M. *Chem. Mater.* **2007**, *19*, 6569–6574.

(11) Lin, S.; Numasawa, N.; Nose, T.; Lin, J. *Macromolecules* **2007**, *40*, 1684–1692.

(12) Horsch, M. A.; Zhang, Z.; Glotzer, S. C. *Nano Lett.* **2006**, *6*, 2406–2413.

(13) It should be mentioned that rod−coil molecules based on lateral chains self-assemble into various honeycomb-like liquid crystal structures in which the walls consist of rod stackings. (a) Chen, B.; Baumeister, U.; Pelzl, G.; Das, M. K.; Zeng, X.; Ungar, G.; Tschierske, C. *J. Am. Chem. Soc.* **2005**, *127*, 16578–16591. (b) Chen, B.; Zeng, X.; Baumeister, U.; Ungar, G.; Tschierske, C. *Science* **2005**, *307*, 96–99.

(14) (a) Semenov, A. N.; Vasilenko, S. V. *Sov. Phys.—JEPT (Engl. Transl.)* **1986**, *63*, 70–79. (b) Semenov, A. N. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 191–199.

JA807035J