Supramolecular Honeycomb by Self-Assembly of Molecular Rods in Rod−Coil Molecule

Myongsoo Lee,*,[†] Byoung-Ki Cho,[†] Kyo Jin Ihn,[‡]
Won-Ki Lee,[‡] Nam-Keun Oh,[§] and Wang-Cheol Zin[§]

Department of Chemistry, Yonsei University
Shinchon 134, Seoul 120-749, Korea
Department of Chemical Engineering
Kangwon National University, Chunchon 200-701, Korea
Department of Materials Science and Engineering
Pohang University of Science and Technology
Pohang 790-784, Korea

Received November 27, 2000

One of the attractive subjects in areas such as materials science, biomimetic chemistry, and molecular electronics is concerned with the creation of supramolecular architectures with well-defined shapes and functions.[1−4] Self-organization of molecules through noncovalent forces including hydrophobic and hydrophilic effects, electrostatic interactions, and hydrogen bonding has the great potential for creating such supramolecular structures.[5,6] An example of the self-assembling systems is provided by rod−coil molecules that have a strong tendency to self-organize into a variety of supramolecular structures in nanoscale dimensions.[7−12] Previously, we have explored a strategy to control the domain structures self-assembled from molecular rods through attachment of flexible coil segments to their ends.[11,13] For a given molecular rod, the relative lengths of the coil segments determine the resulting rod domain structures that include infinitely long cylinders and disklike cylinders. These domains subsequently self-organize into 2-D hexagonal and 3-D body-centered tetragonal symmetries, respectively. We have also shown that hydrophobic force induces the self-assembly of rod−coil molecules into discrete supramolecular spheres with their diameters on the order of 12−14 nm, which aggregate with a lack of long-range order.[14]

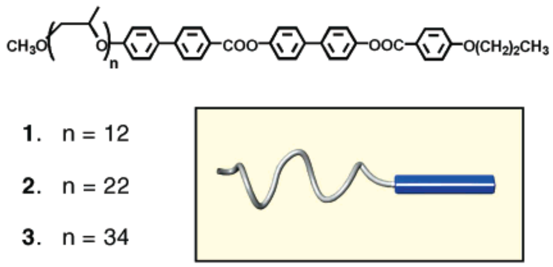

Figure 1. Chemical structure and schematic drawing of rod−coil molecules **1**−**3**.

We present here an unusual example of supramolecular honeycomb formation with in-plane hexagonal arrays of perforations based on the self-assembly of molecular rods in a rod−coil system. The rod−coil molecules consist of two biphenyls and a phenyl group connected through ester linkages as the rod segment and a poly(propylene oxide) (PPO) as the coil segment (Figure 1). Rod-coil molecule **1**, and its analogues with longer PPO coils, **2** and **3**, were synthesized according to conventional procedures, that we used.[11] All of the analytical data are in full agreement with the structures presented. The rod−coil molecules show a narrow molecular weight distribution with polydispersity index in the range of 1.04−1.05, as determined from gel permeation chromatography (GPC) relative to polystyrene standards.

All of the rod−coil molecules show an ordered solid-state structure that is retained up to a melting temperature in the range of 88−122 °C, depending on the molecule. The ordered structure is thermodynamically stable, as evidenced by differential scanning calorimetry (DSC); however, a significant structural variation in the rod-domain is observed as the length of the poly(propylene oxide) block is varied. Small-angle X-ray diffraction revealed that rod−coil molecule **1** has a layered structure in the crystalline state with a primary spacing of 6.8 nm. However, the rod segments of **2** and **3** self-assemble into a supramolecular honeycomblike layered structure, in which perforations are filled by coil segments. These layers, in turn, are stacked spontaneously in ABAB fashion to generate a 3-D order that is stable over a broad temperature range (up to 98 and 88 °C for **2** and **3**, respectively). When cast from dilute chloroform solution onto a carbon support film, honeycomblike supramolecular structure was observed, as revealed by the transmission electron microscopy (TEM) images (Figure 2a). The contrast in these micrographs arises from the aromatic phenyl segments, stained with RuO_4 and thus appearing dark. The image of the film shows a well-ordered array of light PPO perforations in a dark, more stained rod matrix. The light coil perforations are packed on a hexagonal symmetry with the distance between perforations of ∼9.5 and ∼10.0 nm for **2** and **3**, respectively. A selected-area electron diffraction (ED) pattern from an unstained film in Figure 2b shows very well-oriented, single crystal-like, reflections which index to the a*b* reciprocal lattice section of a rectangular lattice (*P2gg* space group) with lattice parameters of 0.81 and 0.56 nm.[15] This result indicates that the rod segments are aligned axially normal to the plane of the micrograph with long-range order extending over areas of 20 μm diameter. Therefore, the shape of the perforation in three dimensions can be readily imagined to be a disklike cylinder with the height corresponding to rod length of 2.6 nm.

To corroborate the 3-D order of these films, we investigated **2** and **3** in their solid state by small-angle X-ray scattering (SAXS) techniques. The SAXS patterns in their solid state show a number of well-resolved reflections (Figure 3), which indicate the existence of a highly ordered nanoscopic structure. These reflections can be indexed as a 3-D hexagonal structure (*P6₃/mmc* space group symmetry) with lattice parameters $a = 9.7$ nm, $c = 14.8$ nm with $c/a = 1.52$ for **2** and $a = 10.1$ nm, $c = 17.0$ nm with

---

* To whom all correspondence should be addressed. Fax: 82-2-364-7050. E-mail: mslee@yonsei.ac.kr.
[†] Yonsei University.
[‡] Kangwon National University.
[§] Pohang University of Science and Technology.

[1] Lehn, J. M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995.

[2] Stupp, S. I.; Braun, P. V. *Science* **1997**, *277*, 1242.

[3] Sleytr, U. B.; Messner, P.; Pum, D.; Sara, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1034.

[4] Oesterbacka, R.; An, C. P.; Jiang, X. M.; Vardeny, Z. V. *Science* **2000**, *287*, 839.

[5] Whitesides, G. M.; Mathias, J. P.; Seto, C. P. *Science* **1991**, *254*, 1312.

[6] Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161.

[7] Chen, J. T.; Thomas, E. L.; Ober, C. K.; Mao, G.-P. *Science* **1996**, *273*, 343.

[8] Loss, K.; Munoz-Guerra, S. In *Supramolecular Polymers*; Ciferri, A., Ed.; Marcel Dekker: New York, 2000; pp 263−321.

[9] (a) Radzilowski, L. H.; Stupp, S. I. *Macromolecules* **1994**, *27*, 7747. (b) Radzilowski, L. H.; Carragher, B. O.; Stupp, S. I. *Macromolecules* **1997**, *30*, 2110.

[10] Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Kesser, M.; Amstutz, A. *Science* **1997**, *276*, 384.

[11] Lee, M.; Cho, B.-K.; Kim, H.; Yoon, J.-Y.; Zin, W.-C. *J. Am. Chem. Soc.* **1998**, *120*, 9168.

[12] Jenekhe, S. A.; Chen, X. L. *Science* **1999**, *283*, 372.

[13] Lee, M.; Cho, B.-K.; Jang, Y.-G.; Zin, W.-C. *J. Am. Chem. Soc.* **2000**, *122*, 7449.

[14] Lee, M.; Lee, D.-W.; Cho, B.-K.; Yoon, J.-Y.; Zin, W.-C. *J. Am. Chem. Soc.* **1998**, *120*, 13258.

[15] This diffraction pattern underwent no change irrespective of the sample places, but only rotation of the pattern occurred. The angle between diagonal axes of the ED pattern appears to be 69.3°.

10.1021/ja004071+ CCC: $20.00

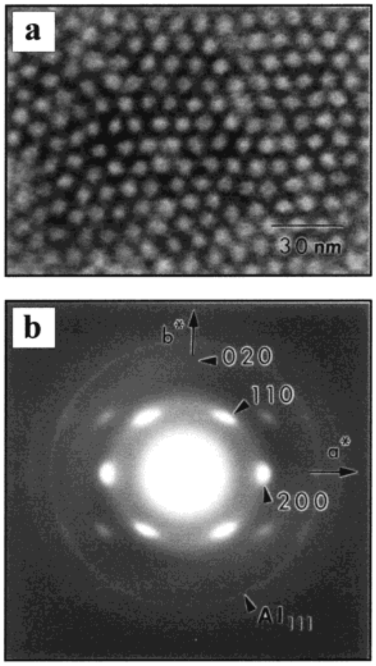

Figure 2. (a) Transmission electron micrograph of solution-cast thin film of rod−coil molecule **3** stained with RuO_4, revealing the formation of a well-ordered hexagonal structure with nanoscale dimensions. The light regions correspond to the coil domains, the dark regions to the rod matrix. (b) Selected-area ED pattern of an unstained film of rod−coil molecule **3** using an objective aperture of 20 μm, indicating a high degree of crystalline order.

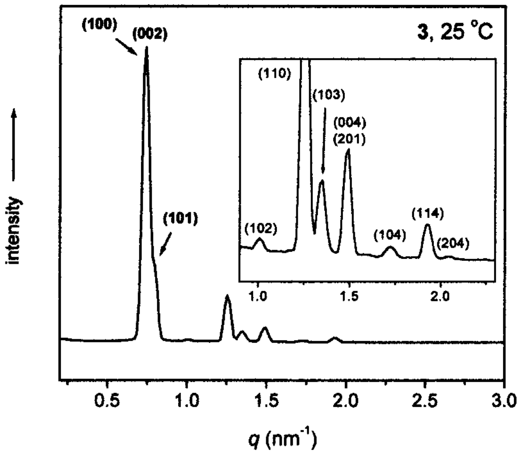

Figure 3. Small-angle X-ray diffraction pattern of rod−coil molecule **3**. Inset, SAXS reflections for $q = 0.8{-}2.7$ with an intensity (counts per second) scale expansion of ×10.

$c/a = 1.69$ for **3**.[16] These results indicate that the dimensions of **2** and **3** corresponding to a layer thickness are 7.4 and 8.5 nm, respectively, less than the extended molecular lengths (11.3 nm for **2** and 15.8 nm for **3**), suggesting a monolayer packing arrangement.

On the basis of the TEM images, ED patterns, and X-ray diffraction data described above, the supramolecular structure can be described as a honeycomblike crystalline layer of the rod segments with in-plane hexagonal packing of coil perforations. The consequent layers are stacked in ABAB arrangement to generate 3-D order. The shape of the perforation can be considered as a disklike cylinder since the stiff rod segments are aligned axially with respect to the layer normal as revealed by ED patterns (Figure 2b). From the lattice parameters determined from the X-ray diffraction patterns and the densities of each segment, the perforation sizes in diameter are estimated to be 6.0 and 7.2 nm for **2** and **3**, respectively, which are consistent with those determined from TEM images. This result suggests that the diameter of a perforation can be controlled through the variation of coil length in our rod−coil system. On the basis of the data presented so far, the schematic representation of the honeycomblike layered structure can be illustrated as shown in Figure 4.

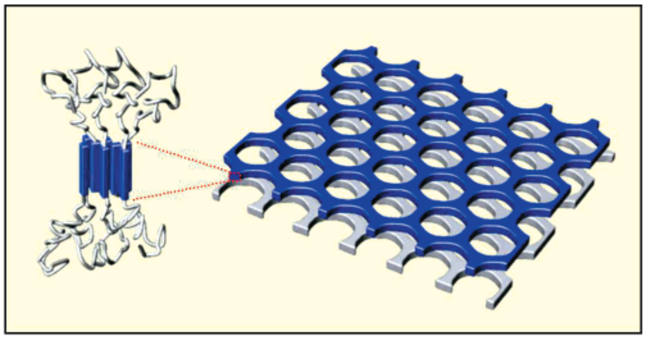

Figure 4. Schematic representation of supramolecular honeycomb structure formed by rod−coil molecules. The honeycomb layers are stacked in ABAB arrangement to give rise to 3-D order. The rod segments are aligned axially perpendicular to the layer plane with a herringbone arrangement.

Formation of the honeycomblike supramolecular structure from the rod−coil system is believed to arise from the tendency of rod blocks to form anisotropic arrangement and consequent space-filling requirements. A rod−coil molecular architecture comprising a stiff rodlike segment and a flexible coillike segment drives a microphase separation into alternating layers of rod and coil segments due to large chemical differences between each segment. However, lamellar ordering of rods would confine rod−coil junctions to a flat interface with a relatively high density of grafting sites. With increasing volume fraction of coil segments, space crowding in the coil domains would be larger, which forces a strong stretching of the coils away from the interface. To minimize coil deformation and fill space efficiently, the sheetlike rod-domains would be perforated by splaying the coil segments.

The notable feature of the structurally simple rod building blocks investigated here is their ability to self-assemble into a supramolecular honeycomb, through the combination of shape complementarity and phase separation of rod and coil segments as an organizing force. It is also remarkable that the supramolecular honeycomblike structure is thermodynamically stable as evidenced by DSC. The tendency of the rod segments to be arranged into anisotropic crystalline order along their axes seems to play an important role in the stability of the supramolecular structure. These results demonstrate that this approach to controlling supramolecular structure allows a novel highly ordered nanostructure to be produced, which potentially has applications as diverse as biomimetic transport membrane,[17,18] periodic porous materials,[16,19] and nanopatterning.[20]

Acknowledgment. This work was supported by CRM-KOSEF, the Korea Science and Engineering Foundation, and Pohang Accelerator Laboratory. B.K.C. acknowledges the BK 21 fellowship from the Ministry of Education, Korea.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA004071+

---

[16] Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.

[17] Gu, L.-Q.; Braha, O.; Conlan, S.; Cheley, S.; Bayley, H. *Nature* **1999**, *389*, 686.

[18] Weiss, L. A.; Sakai, N.; Ghebremariam, B.; Ni, C.; Matile, S. *J. Am. Chem. Soc.* **1997**, *119*, 12142.

[19] Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 56.

[20] Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.