

Structural inversion in 3-D hexagonal organization of coil–rod–coil molecule†

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We report an unusual example of supramolecular structural inversion in coil–rod–coil molecules, from organized coil perforations in a rod layers to organized discrete rod-bundles in a coil matrix, while maintaining a 3-D hexagonal superlattice.

The self-assembly of specific molecules based on a rigid rod segment into supramolecular structures is attracting a growing interest in areas ranging from materials science to biological science.¹ Rod–coil molecules, consisting of a flexible and a rigid block, represent a unique class of self-assembly systems, where the anisotropic orientation of the rod segments and repulsion between the covalently connected segments lead to self-organization into a wide variety of aggregation structures.² The supramolecular structures can be tuned by careful selection of the type and relative length of the respective blocks. Previous publications from our laboratory reported synthesis and structural analysis of rod–coil block systems that self-assemble into lamellar, cylindrical, and discrete nanostructures depending on the relative volume fraction of the rod segments.³ In addition, we have shown that rod–coil systems with an elongated rod block self-assemble into discrete bundles or perforated layers that organize into 3-D tetragonal or 3-D hexagonal superlattices, respectively.⁴ These results imply that the length of the rod building blocks as well as volume ratio between the blocks in rod–coil systems has a strong influence on the shape of the supramolecular structure.

A strategy to manipulate the aggregation structure assembled from a rod building block may be accessible by incorporation of side groups into a rod block.⁵ The side groups could lead to loose packing of the extended rod segments, which may modify the resulting supramolecular structure. In this context, we have synthesized coil–rod–coil molecules consisting of a rod block with methyl side groups in the center and poly(propylene oxide) (PPO) coils (Scheme 1).

In this communication, we report an unusual example of supramolecular structural inversion from coil–rod–coil molecules, from perforated layers to discrete bundles, while maintaining a 3-D hexagonal superlattice (Fig. 1). A coil–rod–coil molecule showing phase inversion consists of five biphenyl units connected through ether linkages as a rod block containing methyl side groups in its center and poly(propylene oxide) (PPO) coils with the number of repeating units of 17. For comparison, we have also prepared an analogous molecule based on a rod segment with a lack of methyl side groups. Coil–rod–coil molecules were synthesized using

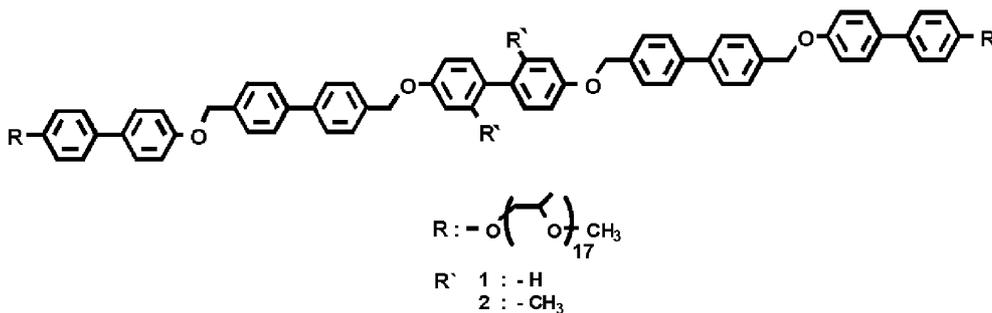
4,4'-biphenol and 2,2'-dimethyl-4,4'-biphenol as starting materials for **1** and **2**, respectively. The resulting coil–rod–coil molecules were characterized by ¹H NMR spectroscopy, elemental analysis and gel permeation chromatography (GPC), and shown to be in full agreement with the structures presented.

The structural behavior of the molecules was investigated by means of differential scanning calorimetry (DSC), thermal optical polarized microscopy and X-ray scatterings. The molecules appeared to be opaque waxy solid that melts into a liquid crystalline phase, followed by an isotropic liquid at 183 and 159 °C for **1** and **2**, respectively. On slow cooling from the isotropic state, a spherulitic texture with arched striations for both molecules was observed on optical polarized microscope, indicating the presence of a 3-D hexagonally ordered liquid crystalline phase.^{4,6} To corroborate the detailed structures of the coil–rod–coil molecules, small-angle X-ray scattering experiments were performed (Fig. 2). The small-angle X-ray diffraction pattern of **1** in the melt showed a number of well-resolved reflections, which can be indexed as a 3-D hexagonal order (*P6₃/mmc* space group symmetry) with lattice constants $a = 8.2$ nm and $c = 14.4$ nm (Fig. 2a),^{4,6} indicating that **1** exhibits a 3-D perforated lamellar mesophase. When cryo-microtomed films of **1** after annealing at 145 °C (stained with RuO₄) were characterized by transmission electron microscopy (TEM), a honeycomb-like supramolecular structure with a hexagonally ordered array of light coil perforations in a dark, more stained rod matrix could be observed (see Supporting Information).† On the basis of the optical and transmission electron microscopies and X-ray diffractions, **1** can be considered to self-assemble into hexagonal perforated layers stacked in ABAB order in the melt.⁴

Similar to that of **1**, the small-angle X-ray diffraction pattern of **2** in the solid state showed reflections corresponding to a 3-D hexagonal perforated lamellar structure with lattice constants $a = 9.5$ nm and $c = 16.5$ nm. Interestingly, the small-angle X-ray diffraction pattern in the melt recorded at 145 °C showed more separated two strong reflections, together with several reflections with low intensity at higher angles. Indeed, this can also be assigned as a 3-D hexagonal structure with lattice constants $a = 8.8$ nm and $c = 15.0$ nm (Fig. 2c). However, the peak intensities indexed as 101 and 102 reflections appeared to be very strong, as opposed to those of a hexagonally perforated lamellar structure.⁴ This result suggests that the fundamental structure of the 3-D hexagonal structure in the melt is based on discrete bundles rather than perforated layers.^{6,7}

To further confirm the 3-D hexagonal structures, we investigated **2** in its solid and molten states by TEM. The TEM image of a microtomed film (stained with RuO₄) showed a honeycomb supramolecular structure with a hexagonal array of light coil

† Electronic Supplementary Information (ESI) available: Experimental procedures. See <http://www.rsc.org/suppdata/cc/b4/b416089d/>
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Scheme 1 Structure of 1 and 2.

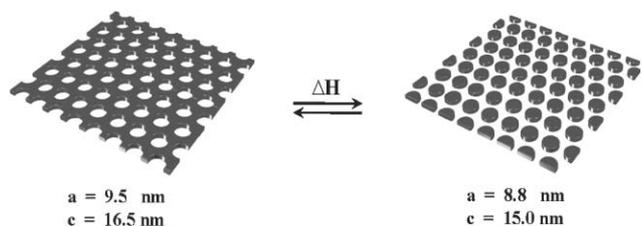


Fig. 1 Schematic representation of self assembly of coil-rod-coil molecule **2** into the hexagonal perforated layer crystalline phase and subsequent conversion to hexagonal close-packed bundles.

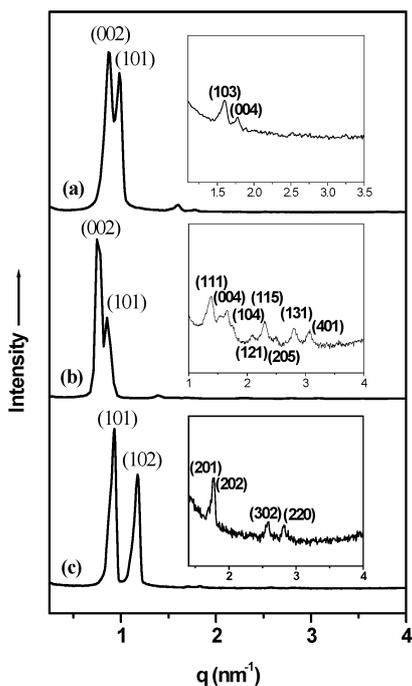


Fig. 2 Representative SAXS spectra of: (a) the hexagonal perforated layer structure of **1** at 160 °C; (b) the hexagonal perforated layer structure of **2** at 72 °C; and (c) the hexagonal close-packed micellar structure of **2** at 145 °C.

perforations in a dark rod matrix (Fig. 3a).⁴ In contrast, the image of a cryo-ultramicrotomed film after annealing at 145 °C showed a hexagonal array of dark rod domains in a light coil matrix (Fig. 3b).⁶ These results together with the small-angle X-ray scatterings demonstrate that **2** self-organizes into hexagonally

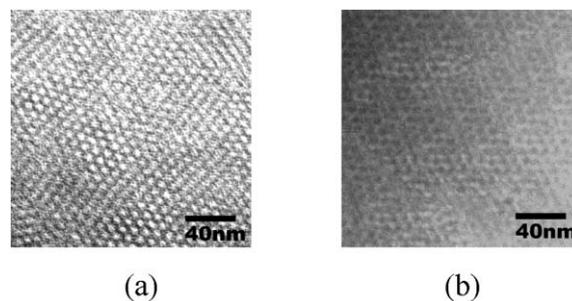


Fig. 3 Transmission electron micrographs of ultramicrotomed thin films of **2** stained with RuO_4 , revealing the formation of a well-ordered (a) hexagonal perforated layer structure with nanoscale dimensions, the light regions correspond to the coil domains, the dark regions to the rod matrix; (b) hexagonal close-packed structure, the light regions correspond to the coil matrix, the dark regions to the rod domains.

perforated layers stacked in ABAB order in the solid state and a 3-D hexagonally ordered discrete bundle structure in the melt. This phase transition on heating is most probably due to larger entropic contribution to the free energy associated with coil stretching.^{8,9} In comparison with the mesophase structure of **1**, this indicates that the introduction of methyl side groups into a rod segment leads to the transformation of a 3-D hexagonal perforated lamellar structure into a 3-D hexagonally organized discrete bundles.

The notable feature described here is that the incorporation of alkyl side groups into the center of a rod segment generates the structural inversion from organized coil perforations in rod layers to organized discrete rod-bundles in a coil matrix, while maintaining a 3-D hexagonal superlattice. It is also remarkable that this structural inversion, retaining a 3-D hexagonal superlattice, occurs directly without passing through any intermediate structures in a reversible way by changing temperature, as evidenced by structural behavior of **2**. This abrupt structural change in rod-assembly may offer an attractive potential for use in supramolecular switch and thermal sensor.

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