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Chain Length-Dependent Three-Dimensional Organization of Molecular Rods with Flexible Coils

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Self-assembly of molecular rod building blocks into organized structures is a fascinating phenomenon that has attracted great interest in supramolecular and nanoscale chemistry.[1] Rod shaped molecular architectures containing flexible coils have proven to self-assemble into a rich variety of organized structures of nanoscale dimensions through the combination of shape complementarity and repulsive interaction of rigid and flexible parts as an organizing force.[2,3] Previous experiments from our laboratory have demonstrated that the self-assembled structure based on rod building blocks in rod-coil diblock systems can be manipulated through systematic variation of the length of flexible part, from lamellar to hexagonal columnar structures with a bicontinuous cubic structure as the intermediate regime.[4] These results suggest that one of the important factors that determines the supramolecular structure of the rod-coil systems is the rod to coil volume ratio.

Recently, we have shown that the rod building blocks in coil-rod-coil triblock molecules based on an elongated rod self-assemble into discrete cylinders that organize into a 3-D tetragonal superlattice above a certain coil volume fraction.[5] More recently, we have also demonstrated that rod-coil diblock molecules based on an elongated rod can self-assemble into 3-D honeycomblike supramolecular structure.[6] Our results imply that the length of the rod building block has a strong influence on the shape of the supramolecular structure. Consequently, systematic variation in the rod length would provide a novel strategy to manipulate the supramolecular structure. With this idea in mind, we have synthesized rod-coil triblock molecules with variation in the rod length at the identical rod to coil volume ratio and investigated their structural behavior.

We present here the significant 3-D supramolecular structural change with simple variation in the chain length of the rod-coil molecule or temperature, from organized discrete rod-bundles in a coil matrix (tetragonal structure) to organized coil perforations in rod layers (3-D honeycomb structure) (Figure 1). The synthesis of rod-coil molecule **1** has been reported[5] and its longer analogues **2** and **3** with the same rod to coil volume ratio have been synthesized in a similar stepwise fashion. All products were characterized by ^{1}H NMR and elemental analysis. Purity was accessed by gel permeation chromatography (GPC), which showed a narrow molecular weight distribution with polydispersity index in the range 1.04−1.05. Since the molecules have an identical rod to coil volume ratio ($f_{\mathrm{rod}} = 0.22$), the shape change of the supramolecular structure may mainly be attributed to the variation in the chain length of the molecule.

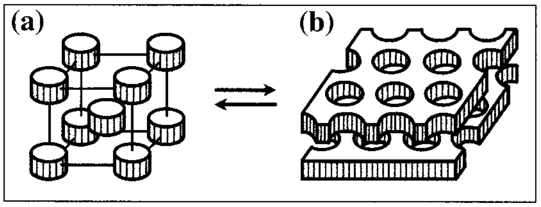
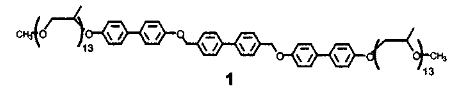


Figure 1. Schematic representation of self-assembly of rod-coil molecules into (a) organized bundles (3-D body centered tetragonal structure) and (b) organized honeycombs (3-D hexagonal structure).



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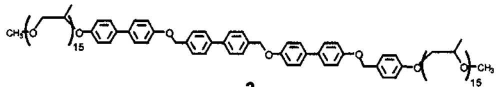

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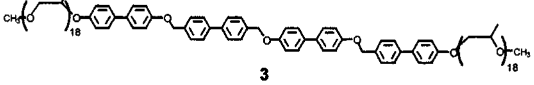

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Previously, X-ray diffraction studies of **1** have demonstrated a three-dimensional tetragonal lattice with a body centered symmetry with lattice parameters $a = 8.32$ nm and $c = 7.65$ nm with $c/a = 0.92$.[5] The lattice constants and density measurements indicated that the rod segments of the molecule crystallize into discrete bundles that organize into a 3-D body centered tetragonal superlattice. This molecule also exhibits a 3-D body centered tetragonal liquid crystalline phase. In great contrast, the rod segments of **2** based on longer chain length than **1** self-assemble into a supramolecular honeycomblike layered structure in the bulk state, in which perforations are filled by coil segments.[7] These layers, in turn, are stacked spontaneously in ABAB fashion to generate a 3-dimensional hexagonal order. A DSC heating trace of **2** shows a crystalline melting transition at 136 °C, followed by a birefringent liquid crystalline phase that undergoes transformation into another liquid crystalline phase at 157 °C on heating (see Supporting Information). The SAXS pattern in its solid state shows a number of well-resolved reflections, which can be indexed as a 3-dimensional hexagonal order ($P6_3/mmc$ space group symmetry) with lattice parameters $a = 7.02$ nm and $c = 12.92$ nm (Figure 2a). The diameter of a perforation determined from the lattice constants and measured density appears to be 5.7 nm. The wide-angle X-ray diffraction patterns in the solid state show sharp reflections at *q*-spacings of 13.8, 15.7, and 19.4 nm^{-1}, which are due to crystal packing of the rod segments within the aromatic domain. This result indicates that the rod segments pack in a rectangular lattice ($P2gg$ space group) with unit cell dimensions of $a = 0.80$ nm and $b = 0.55$ nm.

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[7] The transmission electron microscopy (TEM) image of a carbon-supported film of **2** (stained with RuO_4) shows a honeycomblike supramolecular structure with an hexagonally ordered array of light PPO perforations in a dark, more stained rod matrix.

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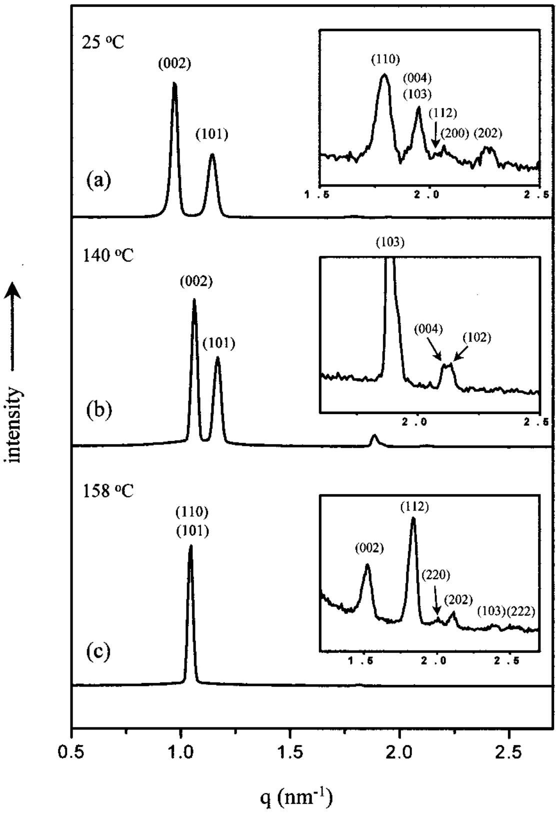

Figure 2. Small-angle X-ray diffraction patterns measured at different temperatures plotted against q ($=4\pi \sin \theta/\lambda$) in (a) the honeycomb crystalline phase at 25 °C, (b) the honeycomb mesophase at 140 °C, and (c) the body centered tetragonal mesophase at 158 °C for **2**.

The small-angle X-ray diffraction pattern of **2** in the melt state recorded at 140 °C shows two strong reflections together with several reflections with low intensity, corresponding to a 3-D perforated honeycomb structure with the lattice constants a = 6.97 nm and c = 11.86 nm (Figure 2b), whereas only a diffuse halo could be observed in the wide-angle region, indicating a liquid crystalline order. Polarized optical microscopy reveals an arced pseudofocal conic texture, indicative of a lamellar phase with in-plane hexagonal order.[8] In contrast, the small-angle X-ray diffraction pattern in the higher temperature mesophase recorded at 158 °C shows only a strong reflection together with a number of reflections with low intensity (Figure 2c), corresponding to a 3-D body centered tetragonal superlattice with the lattice constants a = 8.66 nm and c = 8.14 nm.[9] On slow cooling from the isotropic liquid, the formation of fern-like domains growing in four directions with an angle of approximately 90°, which coalesce into a mosaic texture could be easily observed on the polarized optical microscope, further supporting the presence of a 3-D tetragonal mesophase (Figure 3a).[5,10] These results together with optical microscopic observations indicate that the 3-D honeycomb supramolecular structure of **2** transforms directly into the 3-D body centered tetragonal supramolecular structure in a reversible way by changing temperature.[11]

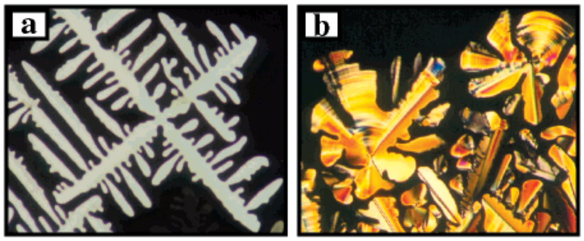

Figure 3. Representative optical polarized micrographs (100×) of the textures exhibited by (a) the body centered tetragonal mesophase of **2** at 156 °C and (b) the honeycomb mesophase of **3** at 195 °C on the cooling scan.

Rod-coil molecule **3** based on the longest rod length displays a honeycomblike crystalline structure. On heating to 151 °C, this molecule melts into a layered liquid crystalline phase that transforms into an isotropic liquid at 204 °C. Small-angle X-ray diffraction patterns in the crystalline state show reflections corresponding to a 3-D honeycomb supramolecular structure with the lattice constants of a = 8.04 nm and c = 14.71 nm. The diameter of a perforation is determined to be 6.14 nm, which is slightly larger than that of **2**. The reflections in the wide-angle region are very close to those observed from the crystalline phase of **2**, suggesting that the rod segments of the molecule crystallize into a rectangular lattice. In the melt state, the small-angle X-ray scattering reveals a similar diffraction pattern to that observed from the crystalline state, indicating that **3** exhibits a 3-D honeycomb mesophase. This phase identification is further supported by optical microscopic observations. On slow cooling from the liquid state, dendritic domains with striations that merge into an arced pseudofocal conic texture, similar to that of the lower temperature mesophase of **2** (Figure 3b), are observed.

The results described here demonstrate that, as the chain length of the molecule increases at the fixed rod to coil volume ratio, the self-assembled 3-D structure changes significantly from organized rod-bundles in a coil matrix (tetragonal structure) to organized coil perforations in rod layers (honeycomb structure). This supramolecular structural change is also accompanied by decreasing temperature as in the case of **2**. Therefore, changing temperature produces an effect similar to varying the chain length of the rod-coil molecule. It is remarkable that this complicated 3-D structural change takes place directly without passing through intermediate structures such as bicontinuous cubic and 2-D hexagonal columnar structures in a reversible way as evidenced by the thermal behavior of **2**. Although the definitive driving forces responsible for this complicated structural change are not clear at present, the strong tendency of the elongated rods to be aligned with their long axes seems to play an important role in this unique behavior.

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

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