

Supramolecular Cylinder and Sphere Generating Thermotropic Hexagonal Columnar and Spherical Micellar Liquid Crystalline Assemblies in Coil–Rod–Coil Block Molecules

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Unlike conventional self-assembling materials based on rigid rodlike molecules, rod–coil block systems can provide a variety of supramolecular architectures, which represents one of the most important factors for access to their fascinating physical properties and functions.¹ The unique aggregation behavior of rod–coil systems arises from the competition between microphase separation of the coil and rod blocks into ordered periodic structures and the tendency of the rod block to form anisotropic, orientationally ordered structures.^{2,3} For example, rod–coil molecules based on poly(hexyl isocyanate) have been reported to exhibit various lamellar structures,⁴ while other rod–coil systems have been reported to generate striplike, disklike, or mushroom-like supramolecular objects of nanoscale dimensions, depending on the coil volume fraction in the rod–coil molecules,⁵ although the aggregation behavior of these molecules has not been investigated in the melt states. Recently, our work has shown that rod–coil molecules can self-assemble into various nanostructures^{6,7} with lattice parameters of <10 nm, even in their melt state. These results suggest that a combination of the organizing principles of rodlike mesogens and block copolymers can create novel assembling materials exhibiting a variety of supramolecular nanostructures.

We report herein our results on the thermotropic phase behavior of a series of coil–rod–coil ABC triblock molecules **1**–**6** (Figure 1) which represent different coil volume fractions in the molecules. These molecules, based on a molecular rod, are observed to self-organize into lamellar, cylindrical, and spherical supramolecular architectures in their melt state, generating layered smectic, hexagonal columnar, and novel spherical micellar phases, respectively, depending on the coil volume fraction of the molecules.

The synthesis of coil–rod–coil ABC triblock molecules containing poly(ethylene oxide)s with various degrees of polym-

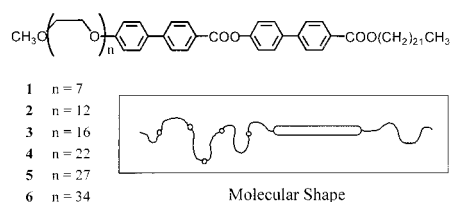


Figure 1. Coil–rod–coil ABC triblock molecules.

erization (DP) as the A block and docosyl alkyl chain as the C block was performed by using a procedure similar to one described previously.⁶ With increasing temperature, all the coil–rod–coil molecules exhibit three different crystalline melting transitions associated with poly(ethylene oxide), docosyl, and rod blocks, respectively. This is also confirmed by wide-angle X-ray diffraction experiments. The flexible hydrophilic poly(ethylene oxide) and hydrophobic docosyl coil blocks and the stiff rod block are believed to be highly incompatible and, therefore, microphase separated between each block, although the molecular weights of each block are very low. Small-angle X-ray diffraction indicates that the microphase-separated supramolecular structure in the crystalline state for all the molecules is a bilayered lamellar structure which is similar to the molecular packing in conventional biological lipid membranes.⁸

In contrast, a significant supramolecular structural change in the liquid crystalline phase is observed as the length of the poly(ethylene oxide) block is varied. **1** exhibits smectic C and smectic A mesophases after melting, corresponding to the rod block, while **2** exhibits only a smectic C mesophase. Optical microscopic observations and X-ray diffraction patterns of these compounds are consistent with this behavior.

3 also exhibits a smectic C mesophase after melting of the rod block, similar to that of **2**. In contrast, at higher temperatures **3** exhibits a hexagonal columnar mesophase which was confirmed by optical microscopic observations, showing characteristic pseudo-focal conic texture. **4**, **5**, and **6**, containing a longer length of poly(ethylene oxide) coils, also exhibit a hexagonal columnar mesophase after melting of the rod block, while they display a lack of layered smectic phase. The small-angle X-ray diffraction pattern of **4** and **5** measured at a birefringent mesophase exhibits three sharp reflections in the ratio of their positions of 1:3^{1/2}:2 (Figure 2), supporting the existence of a hexagonal columnar mesophase with lattice parameters of 122 and 124 Å for **4** and **5**, respectively. These dimensions imply that the rod segments are arranged axially with their preferred direction within a cross-sectional slice of the column.²

A remarkable feature in **4**, **5**, and **6** is the existence of an enantiotropic optically isotropic mesophase at higher temperatures. DSC measurements indicate the presence of an additional phase transition. This transition can also be detected microscopically by a significant increase in the fluidity. These results strongly suggest that **4**, **5**, and **6** exhibit an optically isotropic mesophase in addition to a hexagonal columnar phase. Considering the thermal behavior, which exhibits an intermediate phase between the columnar liquid crystalline and isotropic liquid phases, the optically isotropic phase can be considered as a discrete micellar phase.⁹

The small-angle X-ray diffraction pattern in the optically isotropic phase of these molecules shows a strong primary peak together with a broad peak of weak intensity at about 1.8 relative to the primary peak position, as shown in the representative small-

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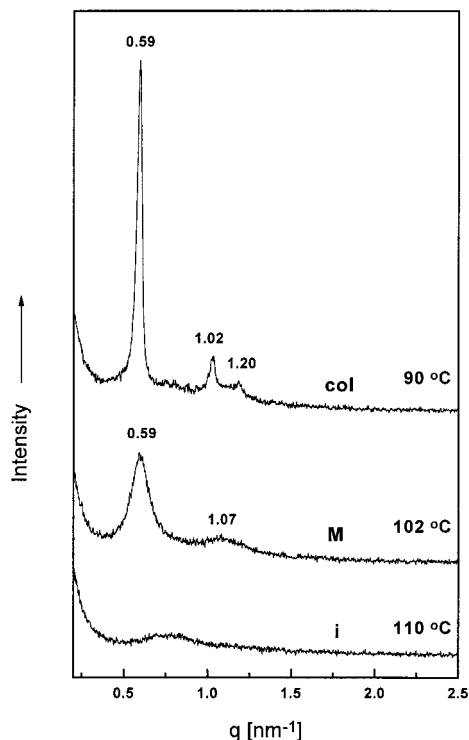


Figure 2. Small-angle X-ray diffraction patterns of **5** plotted against q ($=4\pi \sin \theta/\lambda$) at various temperatures. col, hexagonal columnar phase; M, spherical micellar phase; i, isotropic phase.

angle X-ray diffraction patterns of **5** (Figure 2).¹⁰ The existence of a broad, higher order peak is significantly different from conventional cubic phases of both thermotropic^{7,11,12} and lyotropic⁹ systems, which show well-defined higher order reflections. This indicates that the spatial distribution of centers of the spherical micelles has only liquidlike short-range order, most probably due to random thermal motion of spherical micelles. Therefore, the optically isotropic phase can be best described as a novel discrete spherical micellar phase with a lack of cubic symmetry.¹³ From the observed primary peak, the diameter (d) of spheres can be estimated to be 123, 130, and 138 Å for **4**, **5**, and **6**, respectively,^{14,16} in reasonable agreement with twice the length of the single coil-rod-coil molecules with melted coils. On the basis of the experimental results, the schematic representation for the organization of supramolecular cylinders and spheres into the

(10) This diffraction characteristic persists for a prolonged annealing time, indicative of equilibrium state.

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(14) Assuming liquidlike spherical micelles, an approximate diameter (d) of the sphere was calculated from $d = 1.23(2\pi/q)$, where q is a scattering vector obtained from the primary peak of the X-ray diffraction pattern measured at optically isotropic phase.¹⁵

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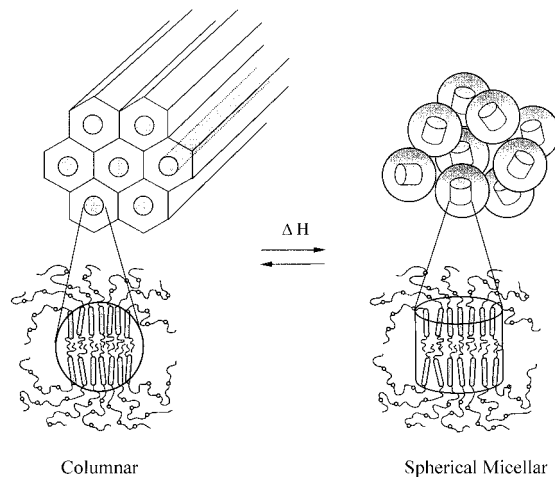


Figure 3. Schematic representation for the formation of the hexagonal columnar and spherical micellar phases of **5**.

hexagonal columnar and spherical micellar mesophases, respectively, can be constructed as shown in Figure 3.

The formation of spherical micelles in the melt state of mesogenic molecules is very rare and has been observed in only a few systems, such as carbohydrate derivatives¹¹ and dendritic molecules,¹² of which the molecular shape can easily adopt spherical aggregation, generating cubic phases. Thus, the formation of spherical micelles from the melt of the rodlike molecules and the aggregation of the spheres into a micellar phase with a lack of cubic symmetry are notable. This unique phase behavior in the coil-rod-coil block molecules is believed to originate from the anisotropic orientation of rods within microphase-separated aromatic domains and the resulting entropic penalties associated with coil stretching.^{2,3} Consequently, the molecular organization of the rods in each spherical micelle favoring anisotropic orientation with their long axes would give rise to the micellar core with a more square cross section rather than a circular cross section (Figure 3). The results described in this study demonstrate that molecular rod systems can give rise to supramolecular spheres in addition to supramolecular cylinders upon introduction of long flexible coils, generating a novel thermotropic spherical micellar phase.

In summary, the coil-rod-coil ABC triblock molecules, which can be considered as large smectogens, were observed to organize into successively layered smectic, cylindrical, and spherical micelles which generate the hexagonal columnar and spherical micellar liquid crystalline assemblies as a function of relative coil length-to-rod ratio or temperature. These results suggest that introduction of flexible coils in molecular rod systems might provide access to a novel strategy to construct one-, two-, and three-dimensional supramolecular nanostructures.

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Supporting Information Available: Tables of analytical data, thermal transitions and SAXS data, and DSC curves for all of the molecules reported, XRD curves of **2** and **5**, 2-D SAXS patterns of **5**, representative optical micrographs for **1**, **3**, and **5**, and a plot of diameter of sphere as a function of molar volume of the molecule (15 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.