Observation of an unprecedented body centered cubic micellar mesophase from rod–coil molecules†

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We have demonstrated that rod–coil molecules based on a tetra-p-phenylene rod and a poly(propylene oxide) coil self-assemble into an unprecedented body centered cubic micellar structure in the melt, through detailed morphological analysis by X-ray scattering and transmission electron microscopy experiments.

Rod–coil molecules consisting of rigid rod and flexible coil blocks have been focused as a promising molecular candidate for the development of functional nano-materials due to the potential electronic and photonic properties. Unlike conventional coil–coil block copolymers, the conformational asymmetry between rod and coil segments opens a way to novel supramolecular morphologies. Since the early 1990s, the experimental efforts have been made to explore their unique self-assembling behavior. Indeed, unusual morphologies such as supramolecular mushrooms and zigzag lamellar structures have been found, and the associated material functions have been reported.1

For the last decade, we have elaborated amphiphilic rod–coil molecules based on hydrophobic oligophenlenes and hydrophilic poly(propylene oxide) (PPO) or poly(ethylene oxide) (PEO) coils, and focused on the investigation of their mesomorphic (liquid crystalline phase) behavior. As a consequence, we have demonstrated that rod building blocks are self-assembled into a variety of domain structures ranging from 0-D micelle, 1-D columns, 2-D lamellae up to 3-D honeycomb-like lamellar and network channels in the melt.2 Furthermore, we have proved that structural details such as domain size and packing lattice can be engineered by fine-tuning molecular parameters such as volume fraction, rod anisotropy, coil cross-section/architecture etc.3 Among the observed morphologies, cubic mesophases are particularly interesting because of the unique optical and mechanical properties.4 To date, however, all of cubic structural units in rod–coil systems have turned out to be continuous rod channels constituting bicontinuous cubic mesophases.5 In this communication, we report on the first observation of a body centered cubic micellar mesophase from rod–coil molecules in the bulk state. It is interesting to note that so far a few discrete rod–bundle assemblies in rod–coil systems have been reported, but all have shown non-cubic structures such as ordered 3-D tetragonal/hexagonal or disordered mesophases.6 As far as we know, the present result would be the first example of a discrete micellar rod assembly with a body centered cubic (bcc) lattice in the melt.

In this study, we prepared two rod–coil molecules 1 and 2 based on a tetra-p-phenylenes and PPOs (DP = 17 and 34 for 1 and 2) as the rod and coil segments, respectively, and investigated their self-assembly behavior as a function of coil length in the melt (Fig. 1).

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The rod–coil molecules were characterized by 1H NMR spectroscopy and gel permeation chromatography (GPC). All of the analytical data are in full agreement with the designed molecular structures. Molecular weight distributions (Mn/Mw) from GPC were found to be less than 1.04 for both compounds indicative of the high purities.

Their thermal behavior was investigated by a combination of polarized optical microscopy (POM) and differential scanning calorimetry (DSC) as summarized in Fig. 1. On heating, rod–coil molecules 1 and 2 both melt into a mesophase and then convert into a second mesophase which, in turn, undergoes isotropization into the liquid state. On the basis of POM observations, a marked optical difference between 1 and 2 occurs in the lower temperature mesophases. The optical texture of 1 at 130 °C

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Fig. 1 Molecular structure and phase transition temperatures of rod–coil molecules 1 and 2. Temperatures are given in °C; k: crystalline; colh: hexagonal columnar; Mθ-ref: body-centered micellar cubic; Mθ-dis: disordered micellar; i: isotropic liquid phase.
displays a pseudo-focal conic texture typically observed in columnar mesophases, while rod–coil molecule 2 at 80 °C shows no birefringence, strongly suggestive of the existence of a cubic mesophase, see Fig. 1 in ESI.† To characterize the microstructures in the ordered phases, we performed variable temperature small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) experiments. In the crystalline states, SAXS data of both compounds display five reflections characterized as (10), (11), (20), (21) and (30) planes indicative of hexagonal columnar structures, see Fig. 4 in ESI.† On the slow cooling of 1 from the isotropic liquid, the SAXS pattern at 145 °C shows a single primary peak with a moderate intensity together with a broad shoulder (Fig. 2(a)). As demonstrated in previous publications, this data suggests a randomly distributed micelles with a lack of lattice.9 Upon cooling to 135 °C, SAXS data exhibit three well-resolved reflections with q-spacing ratios of 1 : √3 : √4, consistent with a two-dimensional hexagonal structure (Fig. 2(b)). For further TEM analysis, the sample was cryomicrotomed to a thickness of ca. 50–70 nm and stained with RuO4 vapor. In Fig. 3(a), the side view image of 1 reveals columnar arrays of alternating light coil and dark aromatic layers and the top view image in the inset of Fig. 3(a) displays hexagonal patterns of dark aromatic domains surrounded by PPO coil matrix, consistent with the SAXS and POM results.

Meanwhile, after melting rod–coil molecule 2 with the longer PPO coil show two kinds of optically isotropic mesophases with temperature. As appeared in 1, the observed mesophase from 95.0 to 115.7 °C is a disordered micellar mesophase, confirmed by SAXS analysis. In marked contrast, SAXS data of another optically isotropic mesophase at 80 °C show a considerable number of well-resolved reflections with q-spacing ratios of √2 : √4 : √6 : √8 : √14 (Fig. 2(c)). By fitting to probable cubic lattices, these peaks can be indexed as the (110), (200), (211), (220) and (321) planes of a body-centered cubic lattice (space group Im3m),10 see Table 1 in ESI.† From the dimension of the (110) reflection, the cubic lattice parameter can be estimated as a = 11.7 nm. By considering the phase sequence as a function of PPO coil length, the cubic mesophase of 2 might consist of micelles not continuous cylinders because 1 with the shorter PPO coil exhibited the columnar mesophase.3 To verify this argument, TEM experiments were performed with a thin-film of 2 (stained with RuO4) in three different projections such as [110], [111] and [010] directions. The bright field TEM image along the [110] direction shows a strip-like array of dark aromatic domains (Fig. 3(b)). By rotation of the viewing axis into [111] and [010], the dark aromatic spots are arrayed in hexagonal and tetragonal symmetries, respectively (Fig. 3(c) and (d)).11 The symmetry assignment of each lattice plane was corroborated via Fourier transform powder spectra (FTPS) of the images. In the insets of Fig. 3(b), (c) and (d), the two-, six- and four-fold reflections of the FTPS are clearly shown for the [110], [111] and [010] lattice planes, respectively. The lattice constant from the TEM images was estimated to 10.7 nm which is smaller than that (11.7 nm) from SAXS. This might be due to the convex bending of liquid-like PPO coil matrix in order to decrease the surface free energy of PPO coils on the ultrathin film.12 On the basis of the POM, SAXS and TEM data, it can be concluded that

![Fig. 2 Small angle X-ray scattering patterns plotted against q (= 4π sin θ/λ) of 1 (a, b) and 2 (c). (a) The random micellar mesophase at 140 °C, (b) the hexagonal columnar mesophase at 130 °C, and (c) the body-centered cubic mesophase at 80 °C.](Image)

![Fig. 3 TEM images revealing the formation of (a) alternating light coil and dark rod stripes in the columnar mesophase of 1 (the inset at a perpendicular beam incidence shows a hexagonal array of dark rod domains in a light coil matrix); (b, c and d) stripe-like, hexagonal and tetragonal arrays of dark rod domains in a light coil matrix in the cubic mesophase of 2 along the [110], [111] and [010] directions, respectively. The insets of (b), (c) and (d) represent Fourier transform powder spectra of the TEM images of 2.](Image)
the cubic mesophase of 2 reveals a body centered lattice composed of discrete micelles. As noted earlier, the notable feature of this study, to the best of our knowledge, is the first observation of a micellar cubic mesophase with Im3m symmetry. Compared to the previously reported rod–coil molecule based on a similar rod length that shows a 3-D anisotropic mesophase,9 a large increment in the volume fraction of PPO segments seems to be responsible for the formation of this unique micellar cubic phase.

In summary, we have prepared rod–coil molecules containing a tetra-p-phenylene rod, and investigated their mesomorphic behavior as a function of PPO coil length and temperature. Upon heating rod–coil molecule 1 with a shorter PPO coil shows hexagonal columnar and disordered micellar mesophase. In contrast, after melting rod–coil molecule 2 with a longer PPO coil exhibits an unprecedented body centered cubic micellar mesophase which transforms into a disordered micellar mesophase.

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Notes and references