Supramolecular Chemistry

Liquid-Crystalline Assembly from Rigid Wedge–Flexible Coil Diblock Molecules**

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There is a growing interest in the rational design of new self-assembling molecules that possess various chemical or biological functionalities and self-assemble into tunable and predictable supramolecular structures.[1] Among self-assembling molecular systems, a dendritic molecular architecture has proved to be a promising scaffold for nanometer-sized aggregation structures including spheres and cylinders.[2–6] Rod–coil block molecules represent another class of self-assembling systems that are increasingly used for the construction of supramolecular architectures with well-defined shape.[7] The supramolecular structures can be precisely controlled by systematic variation of the type and relative length of the respective blocks.[8,9]

Incorporation of a rigid wedge-shaped building block into a diblock molecular architecture gives rise to a novel class of self-assembling systems consisting of a rigid wedge and a flexible coil because the molecule shares certain general characteristics of both dendrons and block copolymers.

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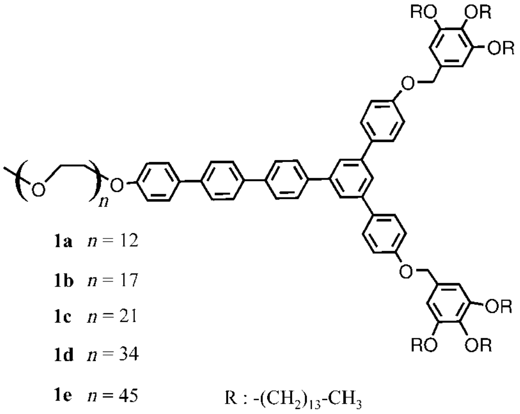
Wedge-shaped molecules based on a short flexible coil should self-assemble into discrete supramolecular structures with a highly curved surface, similar to self-assembling dendron molecules. As the length of the flexible coil increases, however, supramolecular structures with a flatter interface might be formed as a result of the increased effective area of the flexible coil and consequent space-filling requirement. Therefore, a combination of the organizing principles of dendritic wedges and block copolymers may open up new possibilities for the design of unique supramolecular arrangements from wedge-shaped dendritic building blocks.

This work focuses on a novel combination of the above perspectives, in which wedge–coil diblock molecules consisting of a rigid wedge and a flexible poly(ethylene oxide) (PEO) coil were investigated. The self-assembling behavior of these diblock molecules in the melt state was studied by optical polarized microscopy, differential scanning calorimetry (DSC), and X-ray scattering measurements. The molecules self-assembled successively, as the length of the PEO chain increased, into 3D micellar cubic (with *Im*3*m* and *Pm*3*n* lattices), 2D hexagonal columnar, 3D perforated lamellar, and smectic-like lamellar structures in the melt state.



The synthesis of rigid wedge–flexible coil diblock molecules, which consisted of the wedge-shaped rigid aromatic segment containing peripheral tetradecyloxy groups and a flexible PEO chain, started with the preparation of an aromatic scaffold with a tetradecyloxy periphery according to the procedures described previously.[10] The final wedge–coil diblock molecules were synthesized by an etherification reaction of a phenolic precursor with the appropriate tosyl-terminated PEO chains. The resulting block molecules were purified by column chromatography on silica gel with ethyl acetate as the eluent and then further purified by preparative gel-permeation chromatography (prep. GPC, see the Experimental Section). The resulting molecules were characterized by NMR spectroscopy, elemental analysis, GPC, and MALDI-TOF mass spectroscopy, and the data were shown to be in full agreement with the structures presented.

As shown in Table 1, all of the molecules had a thermotropic liquid-crystalline structure after melting. The wide-angle X-ray diffraction patterns of all the molecules in the melt state are characterized by a diffuse scattering, which confirms their liquid-crystalline nature. However, a significant structural variation in the melt state was observed as the length of the PEO segment was varied, as evidenced by optical microscopic textures and small-angle X-ray diffraction scattering (SAXS, Figure 1). Compounds **1a** and **1b**, which are based on a short PEO chain, exhibited a lack of birefringence between crossed polarizers, thus indicating the presence of a 3D cubic liquid-crystalline phase. The SAXS study of **1a** revealed a number of well-resolved reflections corresponding to a body-centered cubic structure with *Im*3*m* symmetry and a lattice parameter of 11.6 nm. However, the SAXS pattern of **1b** appeared to correspond to a 3D cubic structure with a *Pm*3*n* space group symmetry with a lattice constant of 20.3 nm. These results indicate that the symmetry change in the 3D cubic phase, from an *Im*3*m* to a *Pm*3*n* symmetry, occurs with increasing chain length. This symmetry change was also observed for the 3D micellar cubic phase of other dendritic molecules on changing the temperature.[11] The number of molecules per sphere in spherical supramolecular structures is estimated to be 200 and 237 for **1a** and **1b**, respectively.

In contrast, compound **1c** displayed a birefringent mesophase upon melting of the crystalline phase. SAXS studies confirmed the formation of a 2D hexagonal columnar structure with a lattice constant $a = 10.3$ nm, which is in accordance with the phase assignment made by optical microscopy (Figure 2a). Remarkably, further cooling from the hexagonal structure gave rise to a metastable perforated lamellar structure. On cooling from the hexagonal columnar mesophase, arc-shaped striations appeared on the pseudo-focal conic domains at 45 °C (see Supporting Information), which was indicative of transformation into a 3D hexagonal structure. This finding was confirmed by SAXS experiments that showed a number of reflections with low intensity in addition to a strong reflection at a lower angle, which can be

Table 1: Thermal transitions of **1a–e** (data from heating and cooling scans).

	M_w/M_n[b]	Phase transition[a] [°C] and corresponding enthalpy changes [kJ mol^{-1}]	
		Heating	Cooling
1a	1.08	cr 60.8 (31.5) cub(*Im*3*m*) 78.4 (0.14) i	i 74.5 (0.08) cub(*Im*3*m*) 18.5 (12.5) cr
1b	1.04	cr 60.2 (32.0) cub(*Pm*3*n*) 88.4 (0.80) i	i 83.9 (0.09) cub(*Pm*3n) 22.4 (14.9) cr
1c	1.04	cr 56.5 (18.1) col 93.2 (0.99) i	i 91.5 (0.34) col 50.7 (0.23) L_{hex} 21.0 (36.3) cr
1d	1.05	cr 57.5 (29.6) L_{hex} 115.6 (1.90) i	i 112.9 (0.26) L_{hex} 36.1 (3.65) cr 28.8 (13.5) cr
1e	1.05	cr 48.0 (49.6) s_A 143.7 (0.36) i	i 142.1 (0.38) s_A 32.4 (4.07) cr 24.0 (1.75) cr 10.3 (49.0) k

[a] cr: crystalline phase, cub: cubic phase, col: hexagonal columnar phase, L_{hex}: hexagonal perforated lamellar phase, s_A: smectic A phase, i: isotropic phase. [b] Determined by GPC.

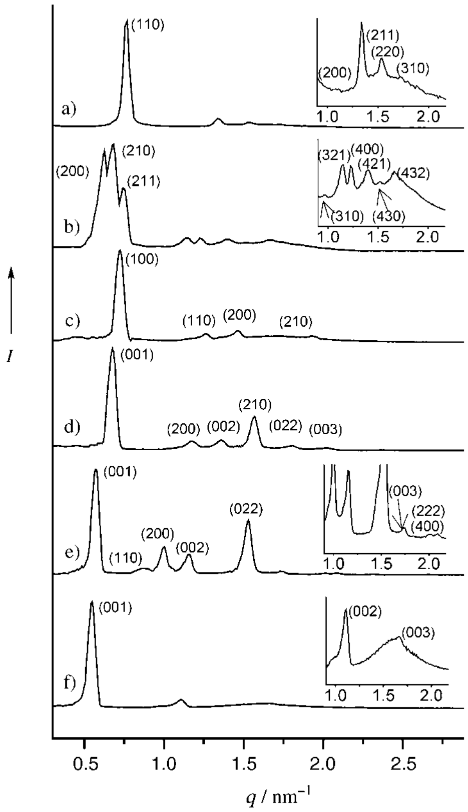


Figure 1. Small-angle X-ray diffraction patterns of **1 a–e** plotted against *q*. a) The *Im*3*m* cubic lattice exhibited by **1 a** at 65 °C; b) the *Pm*3*n* cubic lattice exhibited by **1 b** at 65 °C; c) the hexagonal columnar lattice exhibited by **1 c** at 70 °C; d) the hexagonal perforated layer lattice exhibited by **1 c** at 40 °C; e) the hexagonal perforated layer lattice exhibited by **1 d** at 70 °C; and f) the lamellar lattice exhibited by **1 e** at 70 °C.

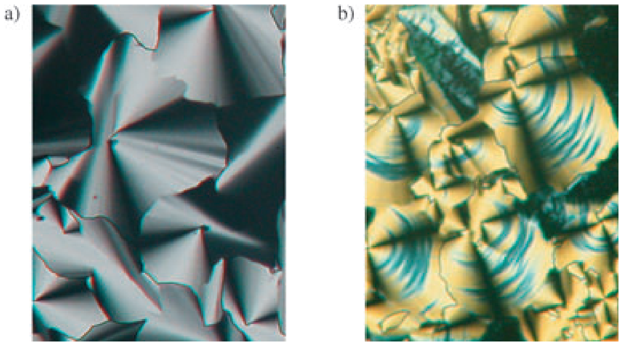


Figure 2. Representative optical micrographs (100×) of: a) the texture exhibited by the hexagonal columnar mesophase of **1 c** at 80 °C in the cooling scan; and b) the texture exhibited by the hexagonal perforated lamellar mesophase of **1 d** at 90 °C in the cooling scan.

indexed as a 3D hexagonal close-packed structure with lattice constants of $a = 12.3$ nm and $c = 9.2$ nm (Figure 1 d). The peak intensity associated with the (001) reflection appeared to be the most intense, which suggests that the fundamental structure is lamellar, similar to that of the perforated lamellar structure reported previously.[9,12] Thus, this 3D hexagonal structure can be considered as a system of perforated aromatic layers with in-plane hexagonal packing of coil perforations. The consequent layers are stacked in a bilayer AB–AB arrangement to generate 3D order. The tendency of a hexagonal columnar phase to transform into a perforated lamellar phase on cooling is consistent with the results from rod–coil systems described previously.[9c,13]

Compound **1d** displayed a stable perforated lamellar mesophase. Small-angle X-ray scattering revealed a similar diffraction pattern to that of the lower-temperature mesophase of **1c**, which indicates the presence of a bilayer lamellar structure with in-plane hexagonally ordered coil perforations ($a = 14.5$ nm and $c = 11.0$ nm). This phase identification is further supported by transmission electron microscopy (TEM) and optical microscopic observations. The TEM images stained with RuO_4 showed a layered structure with in-plane light-colored coil domains in a matrix of dark rod segments (Figure 3 a). An arc-shaped pseudofocal conic texture was observed on an optical polarized microscope (Figure 2 b) on cooling from the isotropic liquid, which supports the formation of a 3D hexagonal structure.[9b] In contrast, compound **1e** exhibited a smectic A phase, as confirmed by optical microscopic texture and X-ray diffraction studies. The layer thickness obtained from the X-ray diffraction pattern appeared to be 11.5 nm, that is, much smaller than the estimated molecular length (17.1 nm by CPK models), and suggests that the molecules are packed with a monolayer lamellar structure in which the rigid wedge segments are interdigitated. This result is further supported by TEM experiments that showed much thinner dark aromatic layers compared to those of **1d** (Figure 3 b). These findings indicate that increasing coil length leads to transformation of a bilayer to an interdigitated monolayer structure.

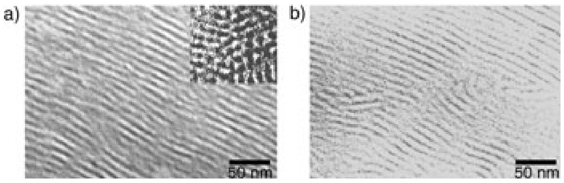


Figure 3. Representative TEM images of a) an ultramicrotomed film of **1 d** stained with RuO_4 revealing an ordered array of alternating light-colored PEO layers and dark aromatic layers. The inset shows an in-plane hexagonally ordered array of PEO perforations. b) An ultramicrotomed film of **1 e** stained with RuO_4 exhibiting alternating dark aromatic layers and light PEO layers.

The results described above demonstrate the capability of manipulating the supramolecular structure by grafting flexible PEO chains of different lengths to the apex of the same wedge-shaped rigid building block (Figure 4). The variation in the supramolecular structure can be rationalized by considering the microphase separation between the dissimilar parts of the molecule and the space-filling requirement of the flexible PEO chains. The molecules based on a short PEO chain can be packed with a radial arrangement to fill the space efficiently, which results in a spherical supramolecular

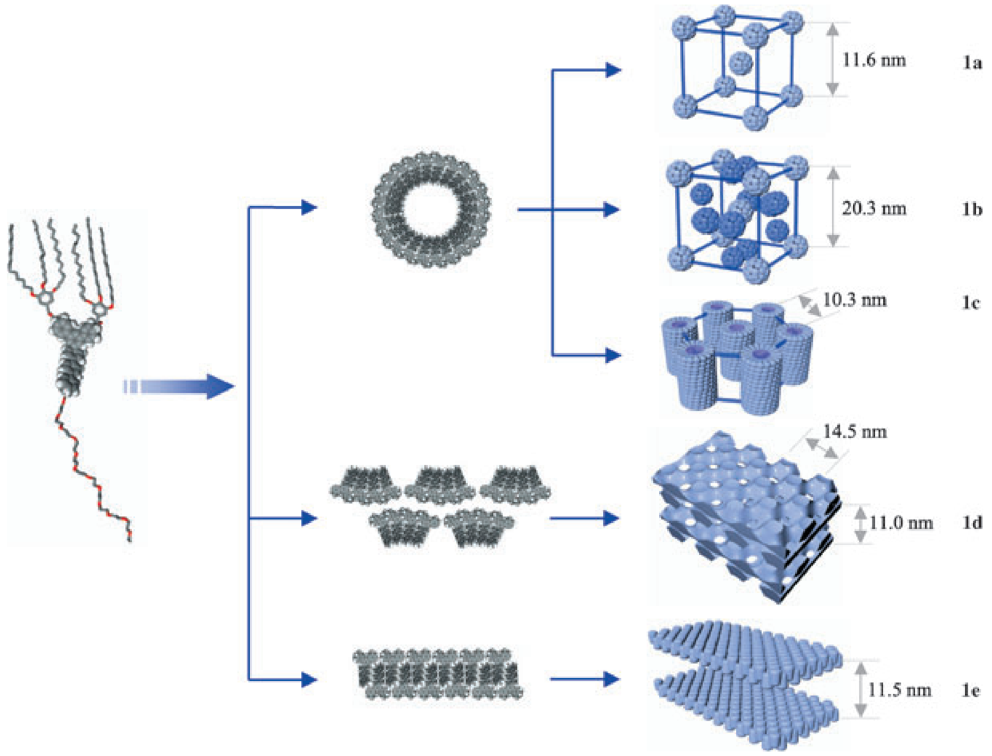


Figure 4. Schematic representation of supramolecular structures formed by wedge-shaped molecules.

structure. Increasing the length of the PEO chain results in more space for the chains being required while maintaining the radial arrangement of the rigid segments. Consequently, the discrete PEO domains will be extended to an infinitely long cylindrical domain in which the coils are less confined, which results in the formation of a 2D hexagonal columnar structure. Further increasing the length results in the rigid wedge-shaped segments assembling into a perforated lamellar structure with a radial arrangement of rigid segments, which allows a greater volume for the PEO chains to explore compared to that of the columnar structure. The radial arrangement of the wedge-shaped rigid segments eventually transforms into a parallel arrangement with interdigitation, to produce a flat interface while maintaining a constant density of the rigid hydrophobic domain. This transformation results in a monolayer lamellar structure as in the case of **1e**.

The self-organization phenomena of the series of rigid wedge–flexible coil diblock molecules demonstrate that systematic variation in the coil length can regulate the supramolecular structure, from 3D micellar cubic with different lattices, 2D hexagonal columnar, and perforated lamellar to smectic-like liquid crystalline assemblies. The primary force responsible for this structural change is believed to be the combination of shape complementarity and microphase separation between rigid and flexible segments. Compared to other self-assembling systems based on dendritic molecules,[2–6,11,14] the remarkable feature of the wedge-shaped building blocks investigated here is their ability to self-assemble not only into spherical cubic and columnar structures, but also into an unusual bilayer lamellar structure with in-plane hexagonally ordered coil perforations. These results demonstrate that this approach of controlling supramolecular structures using wedge-shaped building blocks and only a small variation in the length of grafted coils allows unexpectedly complex superstructures to be produced.

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