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Surface Order in Thin Films of Self-Assembled Columnar Liquid Crystals

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ABSTRACT: The way in which alignment of hexagonal columnar mesophases depends on molecular structure, film thickness, and surface interactions is investigated. Homeotropic orientation of tapered nonpolymeric and polymeric amphiphilic columnar molecules occurs most readily on carbon substrates. The planar alignment of asymmetric dendrimers is favored on a water surface but is not possible for a symmetric dendrimer. For the polymeric material, film thickness has a significant influence on the morphology. Thick films align homeotropically, but films that are only a few column diameters in thickness are planar, and their thickness is quantized. Because they must contain an integral number of layers of cylinders, the resulting morphology is terraced.

Introduction

Various amphiphilic molecules self-assemble into liquid crystalline phases: e.g., lamellar, columnar, and (micellar or bicontinuous) cubic mesophases, depending on the strength of intra- and intermolecular interactions, the relative fractions of different groups within the molecules, and the architecture or shape of the molecules.^{1–6} Among the mesophases, there has been much recent interest in studying the microstructure and properties of columnar materials because of their potential applications as exceptionally selective membranes⁷ and as electrooptic materials, including photoconductive materials^{8–10} with superior charge mobility. In such applications, it is crucial to control column orientation as well as other aspects of morphology in thin films, ranging from molecular to macroscopic dimensions.

Recently, we reported that the orientation of hexagonal columnar phases (Φ_h), comprising a crown ether at one end which forms the center of the column and 3 fluorinated tails at the other supramolecules, could be controlled by surface anchoring, and a high degree of alignment was indicated by transmission electron microscopy (TEM).^{11,12} Homeotropically aligned films in which the column axis is perpendicular to the film surface were achieved on an evaporated amorphous carbon surface, while a planar orientation was obtained on a polar surface such as distilled water.

In this paper, we describe the surface order and morphology in much thinner films of several different dendrimeric molecules forming Φ_h . Most previous ex-

periments in ultrathin films of dendrimers have dealt with disk-shaped molecules.^{13–15} Furthermore, the orientation of columnar molecules aggregated in tapered supramolecular assemblies with respect to surface anchoring is still in open question. Also, we expect that the covalent backbone will affect the columnar alignment of the polymeric materials and that when the total film thickness is less than the polymeric cylindrical length, some perturbations of the homeotropic columnar morphology are likely, due to the strong constraints placed on columnar molecules by the thickness of the sample.

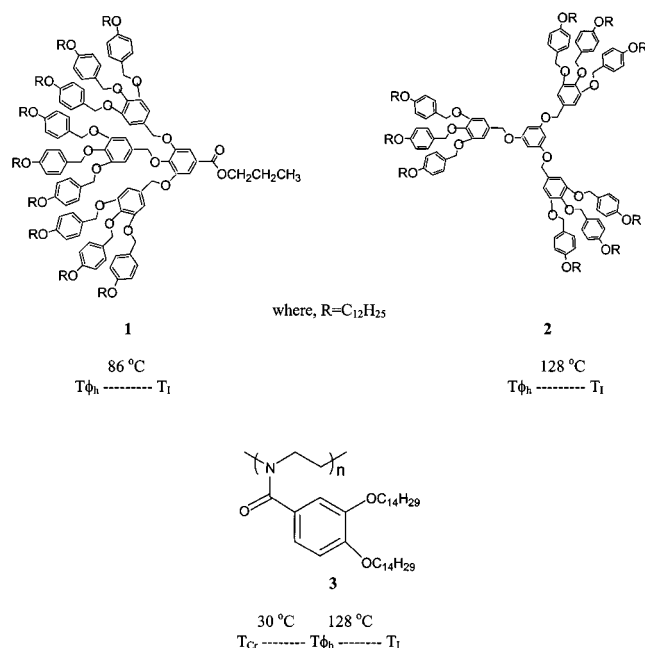
Experimental Section

Insight into the mechanism of surface anchoring of liquid crystalline phases can be gained by studying the alignment of different mesogens on different substrates. To understand surface orientation of the columns, we have employed three different supramolecular architectures forming the hexagonal columnar liquid crystalline mesophase (Scheme 1). Compound **1** is an asymmetric dendrimeric material having tapered molecular architecture,^{16,17} and compound **2** is a symmetric (disk-shaped) dendrimer.^{16,17} The polymeric compound **3** contains a covalent backbone along the cylindrical core, which was obtained by the living cationic polymerization of an oxazoline derivative.¹⁸ The monomer units of the polymer have an aromatic portions which form the hydrophobic core of a column and the tetradecyl tails which form the column periphery. The synthesis of these materials was described in our recent publications.^{16–18}

The mesomorphic phase behavior was characterized by a combination of techniques comprising differential scanning calorimetry (DSC), polarized optical microscopy, X-ray diffraction, and transmission electron microscopy (TEM). Thermal transition temperatures were determined by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7) at scanning

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Scheme 1. Chemical Structure and Phase Transition Temperatures of the Thermotropic Amphiphilic Compounds Investigated: Asymmetric Tapered Molecule 1, Symmetric Disk-Shaped Molecule 2, and a Polymeric Amphiphilic Molecule 3 (Poly(oxazoline))^a



^a Transition temperatures were obtained from DSC (heating scan, $10^\circ\text{C}/\text{min}$). Cr, ϕ_h , and I represent crystal, hexagonal columnar, and isotropic, respectively.

rates of $10^\circ\text{C}/\text{min}$. A polarized optical microscope (Olympus BX-60) equipped with hot stage (Mettler FP 82) was used to analyze columnar phase textures and determine T_{ϕ_h} (the hexagonal-to-isotropic transition temperature).

The orientation of the hexagonal columnar phase was controlled by surface anchoring conditions. For planar alignment of the columnar materials, thin films suitable for TEM examination were cast from solution onto distilled water, held at a temperature at which the columnar phase is stable, and retrieved on carbon-coated copper grids. The sample film thickness was controlled by the solution concentration, with the thinnest films being cast from solutions of 0.01 wt %. Ultrathin films were also cast from solution onto freshly cleaved mica that had been coated with carbon. Homeotropically aligned columnar specimens were obtained by heat-treating thin films that had been prepared by either of these two methods and were supported on highly uniform (~ 100 Å thick) vacuum-evaporated carbon films. These supported films were heated to the isotropic phase and cooled at a rate of $5^\circ\text{C}/\text{min}$ to a temperature well below T_{ϕ_h} , before final quenching to room temperature. This melting and cooling procedure was used to generate homeotropically aligned films.

These films were examined at 100 kV using a JEOL 100CX TEM. ED and bright field phase contrast TEM micrographs were obtained by low-dose procedures¹⁹ before and after sample staining with RuO_4 vapors (solutions of 0.5 wt % aqueous RuO_4). Electron images were recorded on SO-163 plates at appropriate under-focus conditions to obtain lattice images.

Results and Discussion

Based on the polarized optical texture, all three materials exhibited a texture with fan-shaped domains, which is one of the characteristic textures of columnar mesophases. The fan texture of compound 1 was formed a few degrees below the isotropic temperature on slow cooling at the rate of $0.1^\circ\text{C}/\text{min}$ from the isotropic phase within glass slide (Figure 1). This type of fan texture is

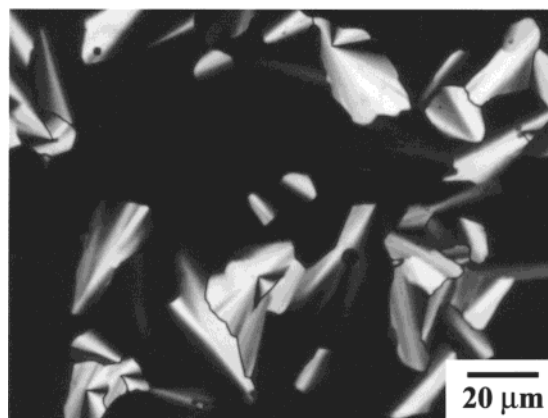


Figure 1. Polarized optical microscopy texture of the hexagonal columnar mesophase of compound 1.

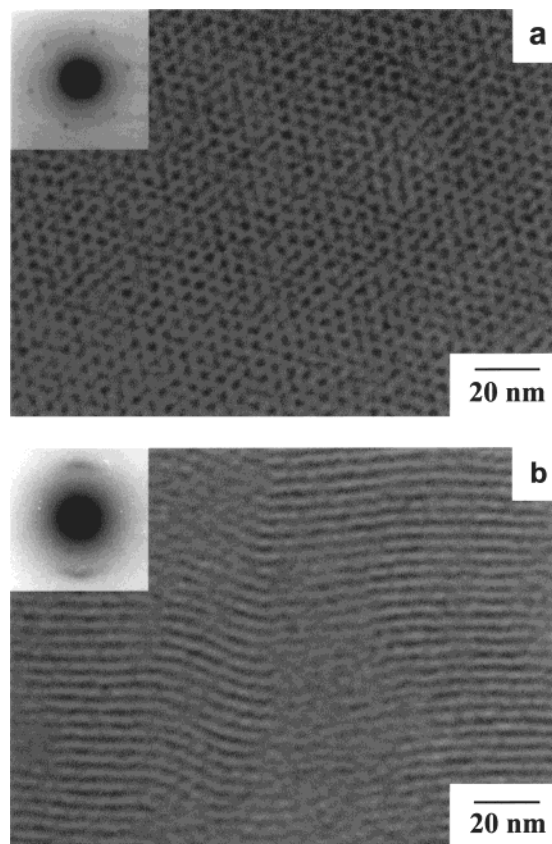


Figure 2. TEM micrographs of (a) homeotropically and (b) planar aligned Φ_h LC assembly generated by supramolecular cylinders self-assembled from 1. Insets are electron diffraction patterns obtained from these specimens.

typical of discotic liquid crystals, smectic and columnar phase, and is a consequence of the high viscosity and birefringence.²⁰ Over large areas of the sample, the columns are well-aligned, and there are few disclinations where abrupt changes of orientation around disclinations of columns are observed.

Further identification of the hexagonal columnar phase was obtained from TEM examination of the columns in oriented samples (Figure 2). The electron image of a homeotropically aligned columnar specimen 1 shows a regular hexagonal lattice (Figure 2a). There is a high degree of perfection in the packing of the cylinders. ED patterns (inset) exhibit six sharp (10) reflections at small angles, corresponding to Φ_h order. At wide angles, only a diffuse scattering maximum at

5.6 Å is observed, indicating that the structure at this resolution is disordered. The d spacings from ED were determined by calibrating each pattern to a Au crystal standard, and the column diameter was determined to be 61 Å.

In the formed image, the column cores appear dark. The contrast may be reversed, however, if the image is overfocused rather than underfocused. When the image is underfocused (as in Figure 2a), the darker regions of the image correspond to regions of higher density, i.e., where the RuO₄ stain has preferentially associated. Since this agent preferentially stains aromatic and ether portions of the molecules,²¹ these can be identified as forming the core of a column, consistent with the expected molecular shape. Staining was found to enhance image contrast and to increase the beam resistance of this and other nonpolymeric materials. Diffraction patterns obtained from unstained specimens confirm that negligible change in structure (both symmetry and dimension) results from staining. When the specimen is not stained with RuO₄, the specimen is much more sensitive to the electron beam, and the low-angle reflections disappear as the specimen is irradiated; i.e., the electron beam induces structural rearrangements that destroy the hexagonal packing of columns. Although this was the usual effect of staining, it was not universal for all materials tested. For example, some other polymeric hexagonal columnar materials^{22,23} have been found to disorder as a function of increased time of exposure to the stain. It was therefore important to control staining time to avoid structural changes. One polymeric material containing a polystyrene backbone^{22,23} was especially sensitive and disordered immediately upon exposure to either RuO₄ or OsO₄ staining agents, as revealed by a diffuse ring at small angles. Perhaps staining of aromatic moieties directly attached to the polymeric backbone causes conformational changes that disrupt the hexagonal packing. It is also worth mentioning that these stains are not appropriate for the investigation of the more highly ordered phases of these nonpolymeric or polymeric materials. The existence of crystals in appropriately annealed materials is identified by additional sharp reflections at wide angles, e.g., at ~5 Å. Those peaks are destroyed rapidly by staining with RuO₄.

The alignment of the columns of compound **1**, parallel to the water surface, is shown in Figure 2b. The image represents a projection, through a film, with a thickness equal to approximately 14 column diameters. The columns are aligned coherently, and the [21] direction is normal to the film. Interestingly, this orientation indicates that the surface planes are not close packed. This unexpected orientation is probably dictated by the structure of the surface layer in contact with the water substrate. Obviously, the hydrophobic tails orient away from the water, and the more hydrophilic core is in contact with the water. Additional characteristics of the structure of this layer depend on the wedge shape of the molecules and the strength of inter- and intramolecular interactions. For example, a dense monolayer of wedge-shaped molecules on water may consist of fractional columns (Figure 3b). In contrast, planar alignment was not possible for the symmetric compound **2**. Instead, only homeotropic alignment was observed on water. Thus, planar ordering of the symmetric compound on a water surface was not achieved, apparently because a monolayer with all tails oriented from

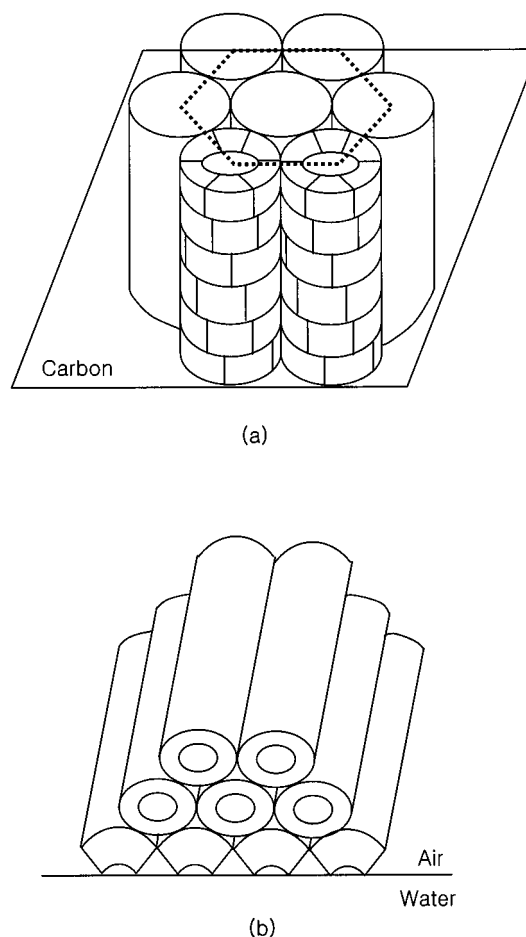


Figure 3. Schematic representation of (a) homeotropically and (b) planar aligned Φ_h LC assembly generated by tapered amphiphilic liquid crystals.

the water surface is energetically unfavorable (Figure 3b). Additional experiments on the surface structure in LB films of those materials are in progress to gain further understanding of the present phenomena. Our preliminary experiment shows that the molecule **1** spread on a water surface and formed a monolayer upon compression, and the shape of the surface pressure vs area (π - A) isotherms is similar to that of the oligo-functionalized monodendrons²⁴ which form edge-on-oriented monolayers at the water interface, suggesting fractional cylindrical configuration at the water interface.

Homeotropic anchoring also depends on molecular shape and interactions. Perhaps this configuration is preferred on flat, rigid, and relatively noninteracting substrates, because it accommodates the flat equilibrium molecular conformation, or face-on configuration, as is described in other studies.^{13,14,24-26} The carbon surface is relatively flat on the scale of the column diameter, and it may not interact strongly with either the core or the tails (Figure 3a). Planar alignment on such a surface may require significant distortion of the tails: they must stretch to reach the surface between neighboring surface cylinders. Indeed, homeotropic alignment of columns on smooth carbon substrates has been found for all thermotropic hexagonal mesophases that we have examined thus far.^{6,11,12,16-18}

A high degree of homeotropic (Figure 4a) and planar alignment (not shown) is also obtained in relatively thick films (≥ 600 Å) of the poly(oxazoline) columnar

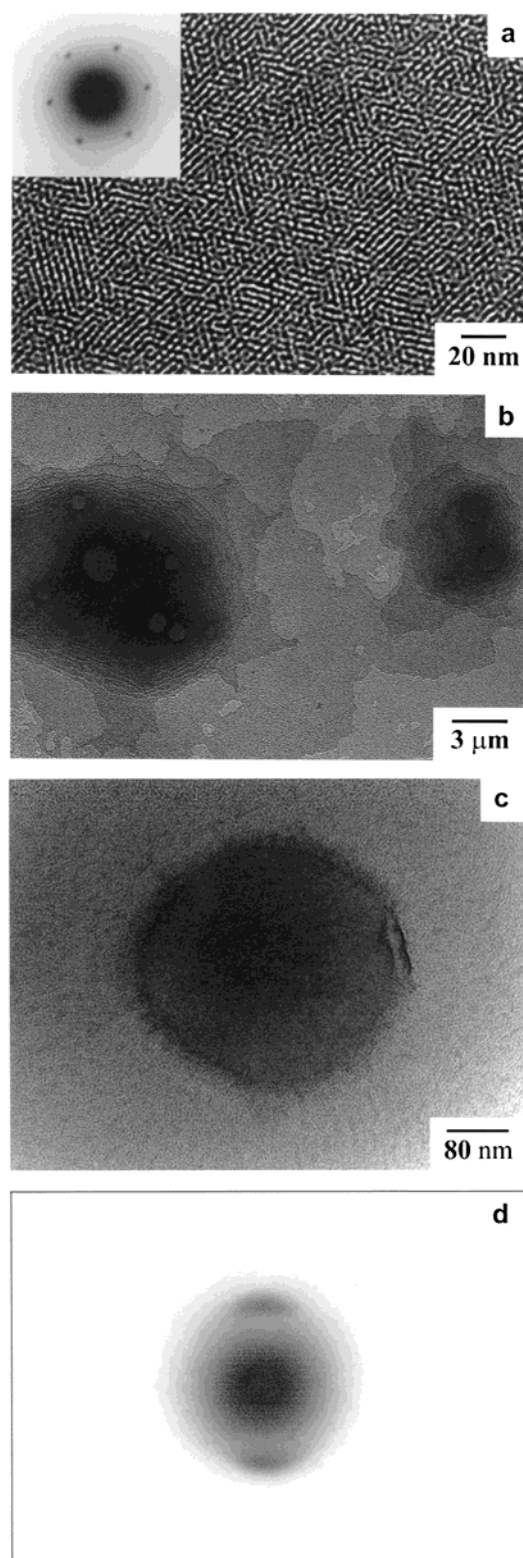


Figure 4. TEM micrograph of the hexagonal columnar mesophase formed from compound **3**: (a) A relatively thick, homeotropically aligned specimen. (b) A thinner film showing a terraced planar morphology. The contrast of the steps in the image was enhanced by platinum shadowing. (c) A higher magnification image of the planar texture visible in the terraced morphology. In the majority of the field of view, the film is the thickness of three layers of columns. A disclination defect is present on the right-hand side of the image. (d) Electron diffraction pattern of a region of (b). The polyoxazoline used in this study, **3**, had a number-average degree of polymerization equal to 200 ($M_n \sim 114\,000$) and a polydispersity $M_w/M_n = 1.1$.¹⁸

material, **3**, which contains a covalent backbone as the headgroup. In thinner films (40–500 Å), cast from solution onto carbon-coated mica and then heat-treated (as described above), however, a different orientation of the columns and morphology is observed. The most striking difference is visible at low magnification (Figure 4b), because the film thickness is quantized. The image intensity is darker, as the film thickness increases step by step. The edges of the steps are made more distinct by shadowing the heat-treated specimen with Pt–C (Figure 4b). The origin of these steps is made clear by examination at higher magnification, which reveals planar alignment and typical fingerprint textures that include disclinations (Figure 4c). Another piece of evidence is given by the electron diffraction pattern taken from a region of Figure 4b, indicating a planar morphology (Figure 4d).

When the alignment is homeotropic, the hexagonal periodicity of the columnar phase has little effect on the surface morphology of the film, because the two-dimensional periodicity is contained within the film. However, when the columns are aligned in the plane of the film, the periodicity of the material selects discrete film thicknesses (Figure 4b). This phenomenon has been reported previously in studies involving the orientation and morphology in ultrathin films of symmetric block copolymers²⁷ and smectic liquid crystals.²⁸ In these examples,^{27,28} relative surface energies determine the orientation of lamellae within ultrathin films. If the thickness matches the periodicity of the ordered phase, the free surface of the film is flat. Otherwise, either islands or holes are formed on the surface after annealing.²⁹ Similar behavior was also observed for the surface morphology of block copolymers with a cylindrical microphase.^{30,31} It was also shown that the orientation of the cylinders also depends on the film thickness. For films thinner than two repeat distances, the cylinders were oriented homeotropically, while planar ordering was observed for thicker films. That result is the opposite of the results reported here. In the previous cases,^{30,31} there was no polymer backbone extended along the column axis, as there is in the present instance for polymer **3**.

The existence of a polymer backbone, **3**, along the center of a column implies a minimum column length, h_{\min} , if it does not fold. Assuming that the polymer chain, **3**, is sufficiently flexible that a single polymer molecule can form a column, then its minimum length, in the hexagonal phase, is well-defined:

$$h_{\min} = V_c / (2\sqrt{3}r^2) = 110 \text{ Å}$$

where r is the column radius ($=22 \text{ Å}$) and $V_c = M/(\rho N_A)$ is the volume of a single polymer chain. M , ρ , and N_A are molecular weight, density, and Avogadro's number, respectively. For a film thickness less than h_{\min} , homeotropic orientation would require column folding. Apparently, to avoid this, the planar orientation is selected instead (Figure 4b,c), and a terraced morphology develops. Planar films up to 13 layers (approximately 500 Å thick) have been observed. It is not clear what factors determine the transition thickness, between homeotropic and planar orientation. We would expect polydispersity to promote planar orientation for somewhat thicker films, if the columns are not folded, because it would lead to surface roughness and poor organization at the surface. The polydispersity of **3** has

been measured to be 1.1, which may be significant in this context.¹⁸ In contrast, there is no evidence of planar alignment in ultrathin films of the nonpolymeric amphiphiles **1** and **2**, for which h_{\min} is much less, approximately 5.7 Å.

Therefore, the polymeric backbone along the column has profound effects on the alignment of ultrathin films, i.e., those with a thickness of the order of a few column diameters. Although ultrathin small-molecule films can be prepared in a homeotropic orientation, as with thicker films, polymeric films behave differently: relatively thick films are aligned homeotropically, while ultrathin films are planar. The film thicknesses of these planar films are quantized, because they must contain an integral number of layers of cylinders, and the resulting morphology is therefore terraced. The planar orientation forms apparently so that the polymeric columns do not have to fold.

Conclusion

The structure and thin-film morphology of thermotropic hexagonal columnar liquid crystal films were investigated. The orientation of the columns was controlled by surface anchoring. Homeotropic orientation occurs most readily on an evaporated carbon substrate, and planar alignment of the amphiphilic molecules is favored on a water surface. TEM experimental results confirm the phase identification of the supramolecules, in which ordered cylindrical moieties are packed on a hexagonal lattice. Planar alignment of asymmetric compounds is favored on a water surface. However, planar alignment of a symmetric dendrimer was not possible. These observations suggest a monolayer formation at the water interface.

Film thickness has a significant influence on the morphology, especially of the polymeric material. Ultrathin small-molecule films, i.e., those having a thickness on the order of a few column diameters, were prepared in the homeotropic orientation, as with thicker films. Polymeric films, however, behaved extremely differently: relatively thick films were aligned in the homeotropic orientation, while ultrathin films were planar. The film thickness of these planar films is quantized, because they must contain an integral number of layers of cylinders, and the resulting morphology is terraced. The planar orientation forms apparently so that the polymeric columns do not fold.

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