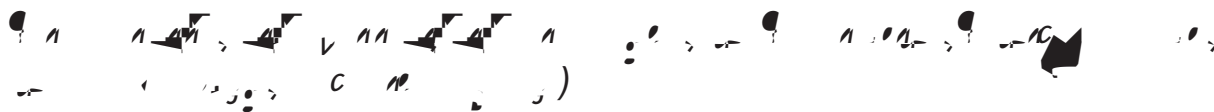


Orientation of a Helical Nanofilament (B4) Liquid-Crystal Phase: Topographic Control of Confinement, Shear Flow, and Temperature Gradients



The liquid-crystal (LC) phases of bent-core molecules have been of great interest because of their unusual polar and chiral properties, as well as their exotic collective behavior, including the formation of macroscopic chiral structures from achiral molecules.^[1–9] The bent-core molecules strongly nanosegregate, leading to the formation of polar and chiral arrangements of the bent cores into planar or modulated layers. Subtle interactions between layers can be manipulated to produce a variety of ferro- or anti-ferroelectric phases.

Among the most mysterious and interesting of these new phases is the B4, a locally layered phase with hexatic or semi-crystalline ordering of the layers, showing large optical rotation and light scattering which suggests a strongly chiral local structure. Recently, it has been shown that the B4 is a phase of spontaneously self-assembling helical nanofilaments (HNFs), the morphology of which is driven by a tendency for local saddle splay deformation of the semicrystalline layers.^[7] These nanofilaments, shown in Figure 1b for the bent-core material NOBOW (benzoic acid, 4-[(E)-[4-(nonyloxy)phenyl]imino)methyl]-1,1'-(1,3-phenylene)ester) (Figure 1a) grow from the higher temperature isotropic or fluid bent-core phases with a well-defined pitch of the helical twist and lateral structure and dimensions. The bulk B4 is a close packing of HNFs in which the filament axes are parallel to one another and their layer twist becomes macroscopically coherent. In the filament growth process a nucleation event establishes the handedness of a filament and this handedness is transferred to subsequently growing filaments to form large ($\approx 100\text{-}\mu\text{m}$ dimension) homochiral domains with either right-handed and left-handed characteristics. Atomic force microscopy (AFM) imaging of the air/LC surface of the B4 reveals this bulk structure,

showing clearly the collective ordering of the HNF helices (Figure 1c).^[7]

Dr. D. K. Yoon, Dr. Y. Yi, Y. Shen, Prof. I. I. Smalyukh, Prof. N. A. Clark
Department of Physics and Liquid Crystal Materials Research Center
University of Colorado
Boulder, CO 80309-0390, USA
E-mail: noel.clark@colorado.edu

Dr. E. D. Korblova, Prof. D. M. Walba
Department of Chemistry and Liquid Crystal Materials Research Center
University of Colorado
Boulder, CO 80309-0215, USA

Prof. I. I. Smalyukh
Renewable and Sustainable Energy Institute
University of Colorado
Boulder, CO 80309, USA

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Upon cooling from the isotropic phase NOBOW forms the B2, a fluid smectic phase with spontaneously polar ordering of the bent cores in the layers and tilt of the molecular planes from the layer normal.^[1,4] The B2 layers preferentially orient normal to the Si wafer/LC and glass/LC interfaces and parallel to the LC/air interface (Supporting Information, Figures S1–S3). These orientations are evidenced by the appearance of toroidal focal conic defects in thin films on flat glass or Si and in the 10- μm -width channel (Supporting Information, Figure S4).^[18] Upon the transition to the B3 phase some degree of in-plane hexatic ordering appears, but the layer textures do not change. The transition to the B4 phase is strongly first order, with the development of more crystal-like in-plane ordering and a substantial decrease in the layer spacing, the new phase appearing in the form of helical nanofilaments.^[7] Basically, a single HNF in the B4 phase looks like a rope of width $w \approx 35 \text{ nm}$ and half pitch $p \approx 130 \text{ nm}$ in which \approx

temperature, and Δ_x is the distance over which this temperature drop is achieved. With no air flow, taking $\Delta_x \approx 1$ cm, one obtains $\approx 400 \text{ W m}^{-2}$ and a temperature gradient in the LC at its surface of $\nabla T \approx 0.002 \text{ }^\circ\text{C } \mu\text{m}^{-1}$. With air flow one estimates a boundary layer thickness $\Delta_x \approx 2 \text{ } \mu\text{m}$ and $\nabla T \approx 10 \text{ }^\circ\text{C } \mu\text{m}^{-1}$, and a LC surface temperature $\approx 50 \text{ }^\circ\text{C}$ cooler than the Si, with contours shown in Figure 3. The 2D simulation of the temperature distribution in the channel (Figure 3a) shows the lowest LC temperature along the LC centerline at the air/LC interface.

The factors relevant to the observed ordering of the HNFs are as follows:

- (i) **Confining effect of the silicon channel:** The confining effect of the silicon channel makes the mesogenic units (bent-core molecules) align parallel with side wall and perpendicular to the bottom as shown in Figure 2. Near the LC/air interface the HNFs prefer to orient parallel to the surface^[7] and the molecular anchoring parallel to the channel side wall induces, in absence of air flow, some HNF alignment in the LC/air interface plane upon cooling, with the HNFs generally normal to the side wall, as shown in Figure 2a and Figure S6, Supporting Information. As now discussed, the principal benefit of the channels is to provide a well-defined thermal gradient and LC flow orientation in the presence of air flow.
- (ii) **Thermal gradient:** Without air flow the LC temperature in the channels is only a few 0.001

topographic modulation of the HNF half pitch. Since the thermal distribution of the LC in the channels is largely the same for air flow parallel and normal to the channel, this observation points to the mechanical response of the

The structure of the B4 phase in the channels either with or without air flow was also studied optically. DRLM images of NOBOW cooled in the channels without air flow show very dark grey and bluish optical morphology that are characteristics of B4 phase, with brightness that is increased when the crossed polarizer and analyzer are rotated to 45° relative to the channel direction (Figure 4a–c and Figure S9, Supporting Information), a result of weak birefringence due to the wall induced alignment (Figure 3a). Optical anisotropy is also found in B4 phase of NOBOW aligned by air fl

