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Small-angle x-ray scattering study of flow alignment of a thermotropic liquid crystal in the nematic and smectic phases

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The capillary flow alignment of the thermotropic liquid crystal 4-*n*-octyl-4′-cyanobiphenyl in the nematic and smectic phases is investigated using time-resolved synchrotron small-angle x-ray scattering. Samples were cooled from the isotropic phase to erase prior orientation. Upon cooling through the nematic phase under Poiseuille flow in a circular capillary, a transition from the alignment of mesogens along the flow direction to the alignment of layers along the flow direction (mesogens perpendicular to flow) appears to occur continuously at the cooling rate applied. The transition is centered on a temperature at which the Leslie viscosity coefficient α_3 changes sign. The configuration with layers aligned along the flow direction is also observed in the smectic phase. The transition in the nematic phase on cooling has previously been ascribed to an aligning-nonaligning or tumbling transition. At high flow rates there is evidence for tumbling around an average alignment of layers along the flow direction. At lower flow rates this orientation is more clearly defined. The layer alignment is ascribed to surface-induced ordering propagating into the bulk of the capillary, an observation supported by the parallel alignment of layers observed for a static sample at low temperatures in the nematic phase.

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Soft matter is, by its nature, susceptible to flow under appropriate conditions. Understanding the flow behavior of soft matter is important not only to gain fundamental insights into rheology and its relationship to nanostructure, but also because these materials are often subject to flow during processing. Thermotropic liquid crystals are attractive systems to study flow alignment as they are single component materials, and a wide variety of liquid crystal phases can be accessed depending on the material and conditions. The flow behavior of these phases is of great interest due to the complex dependence on different anisotropic (Leslie) viscosity coefficients, which can lead to distinct macroscopic states of alignment depending on flow geometry, shear rate, the presence of defects, etc.

The cyanobiphenyl liquid crystals (nCBs) are important for applications in liquid crystal displays. In this paper we study the alignment under capillary flow of 4-*n*-octyl-4′-cyanobiphenyl (8CB), the phase behavior and physical properties of which have been very widely studied, making it an ideal model material. It undergoes the following sequence of transitions on heating from the smectic-*A* (S_A) phase to the nematic phase (N) to the isotropic phase (I) [1,2]:

$$K \leftarrow 21.5\ ^\circ\mathrm{C} \rightarrow S_A \leftarrow 33.6\ ^\circ\mathrm{C} \rightarrow N \leftarrow 40.5\ ^\circ\mathrm{C} \rightarrow I.$$

The alignment of 8CB under shear flow was first investigated by Safinya *et al.* [2] via small-angle x-ray scattering (SAXS) using a Couette geometry, probing the orientation in the $(\mathbf{v},\mathbf{e})$ and $(\nabla\mathbf{v},\mathbf{e})$ planes. Here $\mathbf{v}$ is the flow direction, $\nabla\mathbf{v}$ denotes the shear gradient direction, and $\mathbf{e}$ is the neutral direction. With reference to Fig. 1, they observed the *b* state in the nematic phase at high temperature close to the isotropic state, a region of coexisting *a* and *b* orientations at intermediate temperature, and the *a* orientation at lower temperature, approaching the nematic-smectic *A* transition temperature T_{NA}. Subtle differences in the *a* state were distinguished based on the orientation of diffuse scattering features. Later, Panizza *et al.* correlated the viscosity of 8CB in the smectic phase under Couette shear with changes in the orientation state as probed by SAXS [3] but did not examine the nematic phase. Several rheology studies have indicated that in the nematic phase, 8CB is flow aligning at high temperature, but so-called director tumbling occurs as T_{NA} is approached [4–6]. This phenomenon had first been observed for other low molar mass nematogens based on birefringence measurements [7,8]. Director tumbling corresponds to the escape of the director from the flow plane. This has also been analyzed using the Ericksen-Leslie equations for the dynamics of a nematic phase [9–13]. The balance of torques from the hydrodynamic motion of the nematic fluid and the additional torque on the pretransitional smectic fluctuations leads to the prediction that regimes of flow alignment and tumbling depend on a parameter defined as follows:

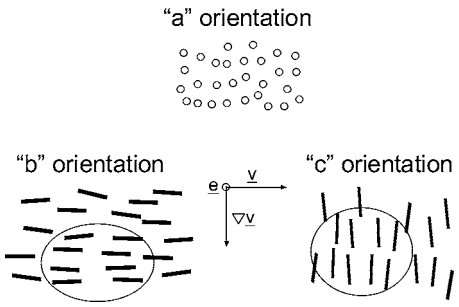

FIG. 1. Schematic of the three orientations of the nematic phase under flow. Regions of smectic fluctuations are highlighted.

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$$\lambda = -\frac{\gamma_2}{\gamma_1} = -\frac{\alpha_3 + \alpha_2}{\alpha_3 - \alpha_2}. \quad (1)$$

Here α_2 and α_3 are Leslie viscosity coefficients, γ_1 is the rotational viscosity, and γ_2 is the irrotational torque coefficient. If $\lambda > 1$, flow alignment occurs and the director aligns at a so-called Leslie angle defined by

$$\theta_L = \frac{1}{2}\cos^{-1}\left(\frac{1}{\lambda}\right). \quad (2)$$

If $\lambda < 1$, nonaligning behavior (tumbling) is observed. The transition from $\lambda < 1$ to $\lambda > 1$ is calculated (using measured Leslie viscosity coefficients) to take place for 8CB at $T = 38.36\ ^\circ\mathrm{C}$ [12]. Other techniques including dielectric permittivity measurements [14] and light scattering [15] have also been used to investigate the onset of nonaligning flow in 8CB.

Despite this prior work, we are not aware of prior x-ray scattering studies of thermotropic liquid crystals under capillary flow. In contrast to the Couette geometry previously employed by Safinya *et al.* [3] capillary flow has the obvious disadvantage that it is not possible to access the $(\nabla \mathbf{v}, \mathbf{e})$ plane, i.e., the *a* orientation. Furthermore, the shear rate is not uniform, because there is a gradient from the capillary wall. However, the study of soft materials under flow in capillaries is of intrinsic interest since this geometry is often encountered during the delivery of material. In addition, it is possible to study higher flow rates and surface effects more easily than using a Couette geometry. Under capillary flow, we observe a fascinating interplay between bulk flow alignment and surface-induced alignment in 8CB and an unexpected orientation in the nematic phase under flow.

The sample of 4-*n*-octyl-4′-cyanobiphenyl was purchased from Kingston Chemicals (Hull, UK) and used without further purification. SAXS experiments were performed on station 16.1 at the Synchrotron Radiation Source, Daresbury Lab, UK. The x-ray wavelength was $\lambda = 1.4$ Å. SAXS patterns were collected with a two-dimensional (2D) multiwire gas-filled detector. The wave number scale ($q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle) was calibrated using a sample of wet collagen (rat-tail tendon).

Further details on the beamline can be found elsewhere [16]. The x-ray beam profile was reduced using a lead aperture to reduce parasitic scattering from the capillary walls. The beam profile was a horizontal slot about 0.5 mm high and 8 mm long, parallel to the horizontal capillary.

We have developed a capillary flow device for use in time-resolved scattering studies of flow-induced alignment of soft materials [17]. A central part of the capillary flow device is a computer-controlled peristaltic pump that allows controlled volume and time dispensing. The flow rate is recorded and the unit is interfaced to a PC for acquisition of flow-rate data. We used borosilicate glass capillaries with a diameter $D = 2$ mm. The accessible flow rates were in the range $Q = 0.1$ to 6 ml min^{-1}. These correspond to Newtonian shear rates at the wall of $\dot{\gamma} = 4Q/\pi R^3 = 2.1\ \mathrm{s}^{-1}$ to $127\ \mathrm{s}^{-1}$. The actual flow rate will differ for non-Newtonian fluids, and for this reason we quote flow rates Q. Temperature control was achieved by placing the capillary in a brass heating block connected to a water bath. A large part of the tubing was also enclosed in Perspex vessels connected in series to the same water bath. The capillary is perpendicular to the x-ray beam. Considering the narrow beam profile, the x rays can be considered to be essentially incident along a flow gradient direction, although this is cylindrically degenerate in flow through a circular capillary.

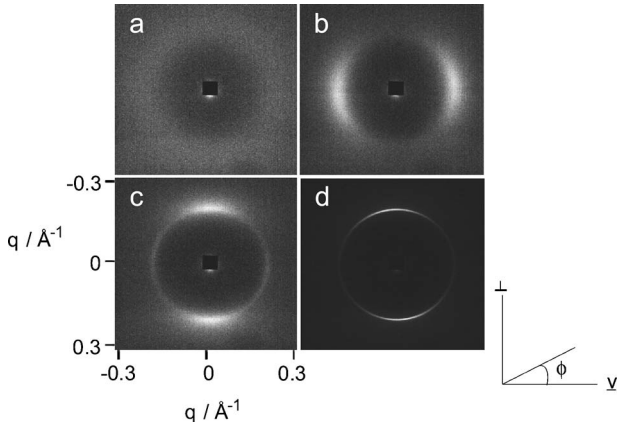

FIG. 2. SAXS patterns obtained during cooling from $T = 50\ ^\circ\mathrm{C}$ to $T = 30\ ^\circ\mathrm{C}$ under flow at $Q = 0.1$ ml/min. The axis system is also shown. (a) $T = 43.8\ ^\circ\mathrm{C}$, (b) $T = 40.0\ ^\circ\mathrm{C}$, (c) $T = 33.8\ ^\circ\mathrm{C}$, (d) $T = 31.3\ ^\circ\mathrm{C}$.

To investigate the influence of flow on alignment, starting from an initially unoriented state, for each experiment the sample was first heated into the isotropic phase ($T = 50\ ^\circ\mathrm{C}$). The sample was then slow cooled ($0.5\ ^\circ\mathrm{C}$/min) in the absence of flow or during flow at $Q = 0.1$ ml/min or $Q = 6.0$ ml/min. Figure 2 shows representative frames (15 s each) of SAXS data obtained during a cooling ramp in the presence of flow at $Q = 0.1$ ml/min. Figure 2(a) was obtained at $T = 43.8\ ^\circ\mathrm{C}$ in the isotropic phase. A broad diffuse ring of scattering is observed. Figure 2(b) shows a SAXS pattern at $T = 40.0\ ^\circ\mathrm{C}$ in the nematic phase, while Figure 2(c) shows SAXS data at a lower temperature $T = 33.8\ ^\circ\mathrm{C}$, still in the nematic phase. Diffuse scattering, somewhat sharper than in the isotropic phase and resulting from smectic fluctuations, can be observed. There is a clear transition in orientation, to be discussed shortly. Finally Fig. 2(d) shows SAXS data in the smectic *A* phase. The sharp pseudo-Bragg peak is centered on $q^* = (0.199 \pm 0.001)\ \text{Å}^{-1}$, corresponding to a smectic domain spacing $d = (31.5 \pm 0.2)$ Å, in good agreement with previously reported values [18,19].

The transition in orientation in the nematic phase on cooling is from a state with flow aligned mesogens [Fig. 2(b)] to one in which the pretransitional smectic fluctuation layers lie along the flow direction, i.e., the mesogens are normal to the flow direction. This corresponds to the orientations *b* and *c*, respectively, in Fig. 1, using the notation adopted for smectic phases [2]. The transition appears to occur continuously, although to confirm this, slower cooling rates would also need to be applied. The apparently continuous nature of the transition can be seen by analyzing the angular variation of scattered intensity in a band centered on q^*. For each frame in a time series the intensity profile $I(\phi)$ was calculated (ϕ is defined in Fig. 2). A contour plot showing the series of 160

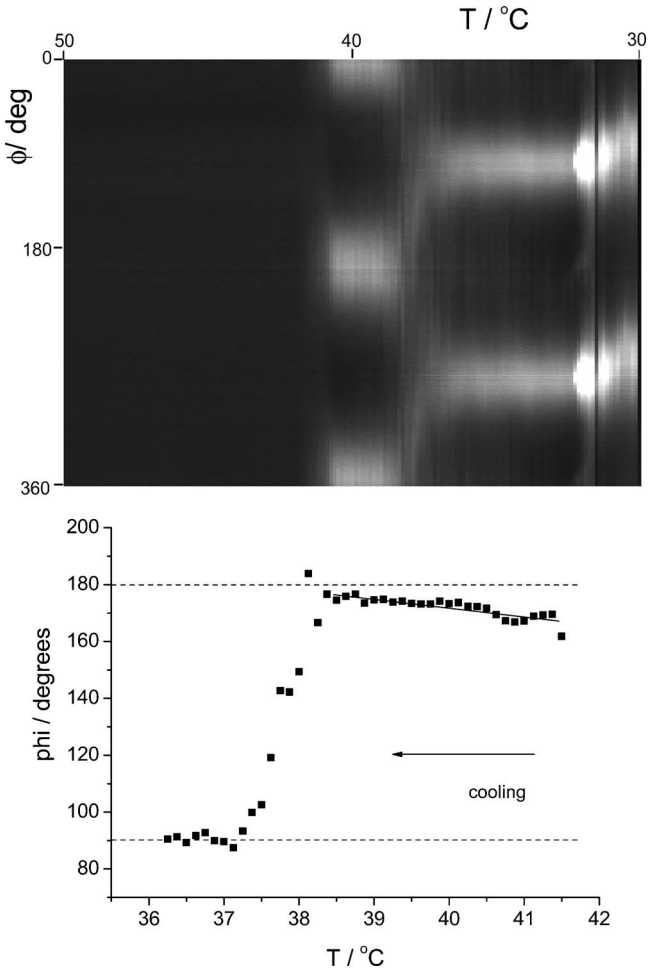

FIG. 3. (a) Contour plot of azimuthal intensity profiles for a sample under flow at $Q=0.1$ ml/min. (b) Variation of the angle at which $I(\phi)$ is maximum for the central peak moving to the 90° peak from Gaussian peak fitting of azimuthal intensity profiles. The solid line is a guide to the eye showing the decrease in the tilt angle of the left-hand scattering arc [cf. Fig. 2(b)] with respect to the equator ($\phi=180°$).

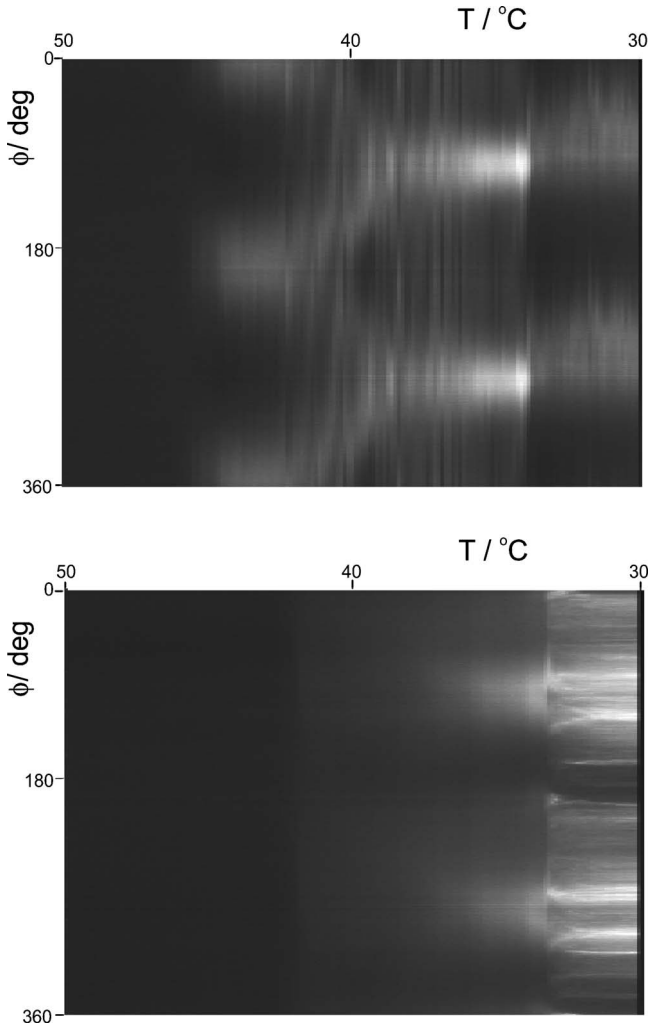

FIG. 4. (a) Contour plot of azimuthal intensity profiles for a sample under flow at $Q=6.0$ ml/min. (b) Contour plot of azimuthal intensity profiles for a sample at rest.

frames obtained during a cooling run from 50 °C to 30 °C is shown in Fig. 3(a). The transition in orientation occurs over 1.1 °C starting at 38.4 °C. The transition to a smectic phase is signaled by the steep increase in peak intensity and sharpening of the peak at 32.1 °C (this is lower than the nematic–smectic-*A* transition temperature T_{NA} in the absence of flow). Further analysis was undertaken to investigate the reorientation. The azimuthal intensity profiles $I(\phi)$ were fitted to sums of Gaussian functions in order to determine the angular maximum. Figure 3(b) shows the variation in the angle at which $I(\phi)$ is a maximum, considering the evolution of the initially central peak [$\phi \simeq 180°$, Fig. 3(a)] into the peak at $\phi \simeq 90°$. The transition appears to be continuous. These data also quantify the observed decrease in tilt of the smectic fluctuations as the temperature is reduced in the nematic phase. The two arcs in Fig. 2(b) are clearly tilted from the equator. The tilt angle decreased to near zero ($\delta=180-\phi=3°$) as temperature decreased.

We also performed a similar experiment, cooling from 50 °C to 30 °C under flow at a higher flow rate ($Q=6.0$ ml/min). A similar transition in orientation from *b* to *c* states was observed, although the transition temperature was lower and the transition extended over a wider temperature interval. Figure 4(a) shows a contour plot of a series of azimuthal intensity profiles, to compare to Fig. 3(a). The onset of the *b* orientation occurred at higher temperature. The nematic-smectic transition also occurred at a temperature closer to that in the absence of flow. Further work is in progress to investigate more fully the influence of flow on T_{NA}. There seem to be enhanced fluctuations in orientation around the preferred *c* state at lower temperature, as compared to the data in Fig. 3(a). This may suggest greater tumbling of the director under flow at a higher flow rate. In addition, there is a significant increase in intensity of the main azimuthal peaks in the nematic phase prior to the transition to the smectic *A* phase. The origin of this is at present unclear.

As a reference for comparison to the azimuthal intensity profiles obtained under flow, Fig. 4(b) shows data obtained in the absence of flow. The initial heating to 50 °C drives the

sample into the isotropic phase, and should erase all prior memory of flow orientation (the sample had previously been subjected to flow at $Q=6.0$ ml/min). Indeed, no orientation was observed initially. However, as temperature was reduced, the *c* orientation was observed in the nematic phase as T_{NA} was approached, and to a certain extent in the smectic phase, although some splitting of the pseudo-Bragg peaks was observed. These data suggest that surface-induced alignment is important in driving the *c* orientation, since this is observed in the absence of flow in the nematic phase as T_{NA} is approached.

In the high temperature range of the nematic phase we observe a tilt of the director, the tilt angle decreasing as temperature reduces. This is consistent with Eq. (2) since $\lambda > 1$ is a decreasing function of temperature. The condition $\lambda=1$ corresponds to the onset of director tumbling. This is expected to occur at $T=38.4\,^{\circ}$C [12,20,21]. This corresponds closely to the onset of the orientation transition we observe. The data in Figs. 3 and 4 indicate that there is preferential alignment of the director perpendicular to the flow below this temperature. Particularly at high flow rates the fluctuations in the SAXS intensity (on a 15 s time scale) indicate that there is director tumbling. This time scale is in good agreement with calculations on the reorientation of the director in tumbling flow for 8CB near T_{NA} [13]. We believe that the preferential orientation of layers along the capillary axis results from the propagation of surface-induced alignment into the bulk.

In summary, we have observed via SAXS a transition in alignment in the nematic phase of 8CB under capillary flow upon reducing temperature. At high temperature mesogens align along the flow direction. At low temperature there is evidence for tumbling, especially at high flow rates, although there is a preferred direction for mesogen alignment perpendicular to the flow direction (i.e., pretransitional smectic layers along the flow direction). The selection of this latter orientation is ascribed to surface-induced ordering, an interpretation supported by the observation of this configuration for a sample in the absence of flow.

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