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X-ray study of substrate-induced alignment of a smectic A liquid crystal

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We have performed a structural study of the liquid crystal (LC) octylcyanobiphenyl (8CB), deposited on gratings and flat surfaces, using high resolution X-ray scattering as a function of film thickness. 8CB is a room temperature smectic A_2, with a layer spacing of 31·6 Å. Glass was used as substrate and treated with either one of the organic surfactants MAP or DMOAP. Surface tension forces cause the liquid crystal molecules to align perpendicularly with respect to the plane of the substrate at the air interface. Competing with the LC–air interface, which is a strong aligner, a grating at the LC–substrate interface produces distortions in the smectic layering with an excess of elastic energy, which favours alignment parallel to the substrate and the grooves. Our purpose was to detect the onset and evolution of parallel alignment as a function of film thickness. The studies used 9 keV (1·403 Å) X-rays focused to a spot size of 2 mm^2 at the sample position. In-plane scans, which detect the smectic layers perpendicular to the plane of the substrate, were done at angles $\phi = 0°$ and 90° with respect to the gratings to ascertain the molecular orientation, at a nominal X-ray incidence angle of $\alpha = 0°$. In order to observe regions of varying smectic layer orientation within the film, we performed a series of scans where the out-of-plane tilt angle χ changed from 0°, corresponding to scattering in the plane of the film, to 90°, which corresponds to scattering normal to the surface of the film. The results from these scans were fitted to a multilayer model where the orientation of the smectic layers varies as a function of film depth. The analysis confirmed our earlier observations that surface tension at the air interface plays a dominant role in the alignment of the LC molecules.

1. Introduction

The molecular arrangement in a liquid crystal film differs in the bulk compared to that at surfaces and interfaces. The ordering in liquid crystal (LC) films is in general stronger than in bulk samples, and in freely suspended films a quasi-smectic phase appears [1]. An LC film deposited on to a grooved substrate experiences a competition between the aligning forces at the LC–air interface, which force the molecules to align normal to the surface, and the aligning forces at the LC–substrate interface, which forces the molecules to align parallel to the plane of the substrate.

Short range molecular forces and long range elastic forces influence LC alignment, and compete when they are not acting in parallel [2]. For a smectic LC, splay is the only deformation allowed by the requirement that the separation between smectic layers remain constant [3]. We found previously [4] that for 8CB in the smectic A phase deposited on gratings with periods of 9, 15 and 24 μm, surface tension was the dominant aligning force, followed by surface topology. Surface anchoring, the dominant aligning force for nematic LCs [5], does not play a significant role in the alignment of smectic LC molecules. The presence of a grating produces an excess in the Frank elastic energy because the periodic small amplitude distortion causes the smectic layers to compress and bend [3]. For a 9 μm grating and a 30 Å smectic layer spacing, a distorted region

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approximately 1 mm thick appears. This results in a very long range force favouring the alignment of the molecules in a smectic LC parallel to the gratings. However, we found that the presence of an LC–air interface reduces the influence of the solid substrate on the film, since the free surface of the LC is a stronger aligner [5]. Our earlier observations suggest that the influence of the free surface penetrates approximately 30 μm into the film, which results in the absence of alignment along the gratings in films thinner than 30 μm. Thicker films show the presence of regions of molecular alignment parallel to the gratings.

We have shown the usefulness of X-ray scattering in the study of small aligned regions in films of 8CB in the smectic phase, and to examine the effect of substrate topology on the alignment of this phase. In this paper, we present the results of a structural X-ray study on smectic 8CB films, where the thickness of the films was changed systematically from 6 μm to 42 μm. The films were deposited on gratings of 9 μm repeat distance and on flat glass substrates [4, 6]. The purpose of our measurements was to investigate the onset and evolution of parallel alignment as a function of film thickness. We fitted our results to a multilayer model where the orientation of the smectic layers varies as a function of film depth.

2. Experimental methods

As in previous studies, we used octylcyanobiphenyl (8CB) purchased from EM Industries and used with no further purification. The 9 μm period grating was produced on soda lime glass microscope slides using conventional photolithography in a class 1000 clean room. Details of the preparation appear in [4] and [7]. After fabrication, the gratings were treated with the chemical surfactants MAP (*N*-methylaminopropyltrimethoxysilane) or DMOAP (*n*-octadecyldimethyl[3-(trimethoxysilyl)-propyl]NH_3Cl), obtained from Petrarch Systems, following the procedure described by Kahn *et al.* [8].

The thickness of the films was varied systematically with the use of a high precision 0·5 μl resolution pipette set to dispense 5 μl of material at a time. This latter dispensing process was tested for reproducibility in-house before the experiments. Glass samples were weighed before and after the addition of liquid crystal, using a 0·1 mg resolution analytical balance; 1 μl is equal to 1 mg of material. The addition of 5 μl of material results in an increase of approximately 5 μm in the thickness of the films. The sample is carefully distributed over the grating area (1 cm^2) using a warm wire or a piece of Teflon tubing. The 8CB is heated into the isotropic phase after each addition with the use of a hot air blower. We used this process to change the thickness of the films *in situ* at the National Synchrotron Light Source. At the experimental site, the sample was mounted on an aluminium post, which caused a very rapid cooling cycle once the blower was removed. The final slide was weighed at the end of the experiment, and the thicknesses of the films on the 9 μm grating presented here were determined to be 6, 11, 17, 22, 26, 31, 36 and 42 μm respectively. Similarly, films of 8CB were deposited on a flat glass slide treated with MAP. Their final thicknesses were 7, 14, 21, 28 and 44 μm.

The X-ray scattering experiments were performed at the National Synchrotron Light Source, beamline X22B, using 9 keV (1·403 Å) X-rays, focused on a spot of 2 mm^2 at the sample position. The detector slits were kept at a 10 (vertical) × 4 (horizontal) mm^2 opening. The samples were mounted on a four circle Huber goniometer. In order to study the orientation of the smectic layers in the films, we performed both out-of-plane (001) as well as in-plane ((*h*00) and (0*k*0)) Bragg scans. The former give information on the smectic layers aligned parallel to the plane of the

substrate, whereas the latter give information on the smectic layers aligned perpendicular to the plane of the substrate (molecules parallel to the substrate). The grating direction was chosen to coincide with the k direction on the plane. In addition, we performed a series of χ scans on the films to observe the evolution of the inplane peaks in the film. One can study the regions of varying smectic layer orientation by changing the value of the angle χ: this scan is equivalent to changing the value of the out of plane component of l in reciprocal space. We performed these scans at angles corresponding to the directions along the gratings ([01l] direction) as well as directions perpendicular to the gratings ([10l] direction). The diffraction angles θ, 2θ were held constant at the Bragg value for 8CB. At $\chi = 90°$, the observed scattering corresponds to smectic layers parallel to the surface of the gratings (molecules perpendicular to the plane of the substrate). Conversely at $\chi = 0°$, the signal observed corresponds to smectic layers aligned perpendicular to the plane of the substrate (molecules parallel to the plane of the substrate). The nominal angle of incidence α in these runs was 0° for 9 keV X-rays. Finally, we performed azimuthal ϕ-scans at $\chi = 0°$ and $\chi = 10°$ in order to observe the degree of in-plane disorder. For these scans, $\phi = 0°$ corresponds to the [01l] direction.

3. Experimental results and discussion

The results obtained from the χ scans described above for the 11, 22, 31 and 42 μm films on a grating appear in figure 1 (*a*). The corresponding Bragg scans along the direction of the gratings (0k0) are shown in figure 1 (*b*). We find that films less than 22 μm thick show no in-plane signal at either azimuthal orientation. The in-plane signal increases with increasing thickness above this value. Note that the in-plane regions are not sharp at $\chi = 0°$. Instead, there is a distribution of orientations about $\chi = 10°$. Near $\chi = 0°$, shadowing by the sample and the small X-ray incidence angle cut off part of the signal.

Figure 2 shows azimuthal ϕ scans of the in-plane signal. There is considerable azimuthal disorder in the thick films. Further, the reproducibility of the azimuthal peaks is poor, varying with every temperature cycling. This degree of disorder was not

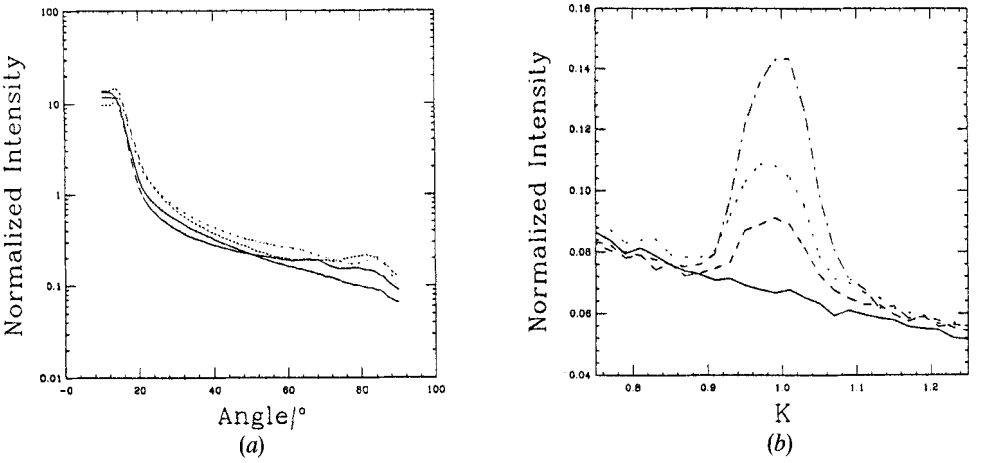

Figure 1. (*a*) χ scans for the 11 (——), 22(- - -), 31 (— — —) and 42 (- — - — - — -) μm 8CB films on a 9 μm repeat distance grating on glass. Angle = 90 − χ. (*b*) Corresponding in-plane k-scans for the samples above.

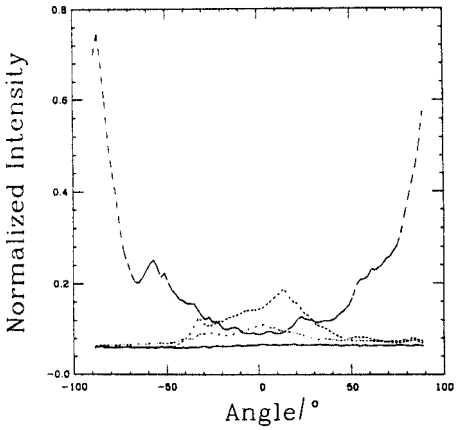

Figure 2. Azimuthal ϕ scans for the series of films presented in figure 1.

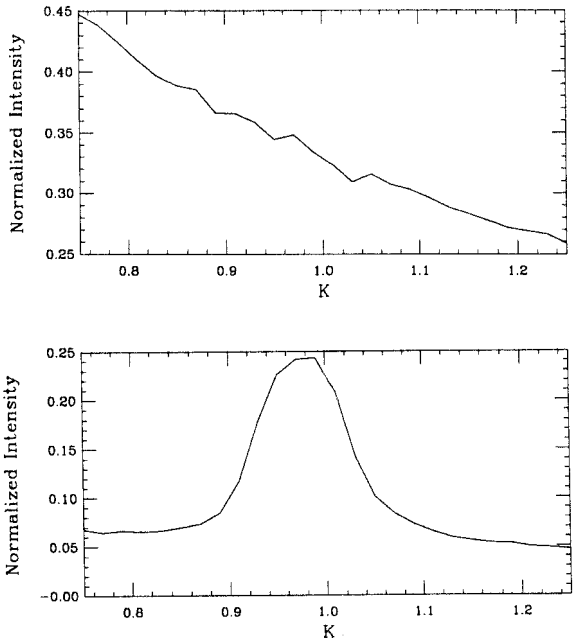

Figure 3. In-plane scan on a 27 μm thick film deposited on a 15 μm repeat distance grating on glass at an incidence angle of 0° (nominal). Upper panel: 8 keV X-rays, $\lambda = 1{\cdot}625$ Å; lower panel: 9 keV X-rays, $\lambda = 1{\cdot}409$ Å.

observed in previous runs. This effect seems to be related to the fast cooling rate experienced by the films when prepared *in situ*. A comparison between these results and those obtained from films grown using a slower cooling cycle will be discussed in a future communication [9].

We show an in-plane Bragg scan along the grating directions for a 27 μm film, obtained using 8 keV (1·651 Å) X-rays in the upper panel of figure 3. The angle of incidence is $\alpha = 0°$. The lower panel shows the same scan on the same film, taken with 9 keV (1·403 Å) X-rays at the same angle of incidence. This scan shows the presence of

the in-plane peak, even at nominal grazing incidence. We note that the peak can be observed for 8 keV if the sample is tilted such that $\alpha = 0{\cdot}4°$. Since 9 keV X-rays penetrate deeper inside the film, this result seems to suggest that in-plane scattering originates mostly in regions buried in the film, close to the substrate surface.

The above results are fitted to a multilayer model, consisting of a series of layers which may have different thicknesses, orientations and mosaic (angular) spreads. The scattering is proportional to

$$I \propto \exp[-2x\mu/(\sin\alpha\cos\chi)], \tag{1}$$

where α is the angle of incidence of the X-ray beam, μ is the average length for 9 keV X-rays [7], and $2x$ is the pathlength of the X-rays inside the sample. The model uses a lorentzian distribution, which describes better the fluctuations of the smectic layers [3, 10].

We summarize the results of our analysis. Films 6, 11 and 17 μm thick on a grating require only a single homeotropic layer, with the LC molecules aligned perpendicular to the substrate surface. The 22 μm thick film is described better by considering a second 7 μm thick homogeneous layer, with the LC molecules aligned parallel to the surface of the substrate. The 26 μm film requires a 6 μm thick homogeneous layer. However, the 31 μm film is described better by a single homeotropic layer, which seems to indicate that the region of thickness 22–31 μm is unstable. The 36 μm film consists of a 10 μm thick homeotropic layer and a 26 μm thick homogeneous layer. Finally, the 42 μm film consists of a 37 μm disordered homogeneous layer. The table summarizes these calculations. Figure 4 (*a*)–(*d*) shows the results of the fitting for the 11, 22, 31 and 42 μm films on a grating.

In contrast to the above fits, analysis of the scans taken on similar thickness films deposited on a flat glass substrate always required a thin homogeneous layer, oriented approximately 75° from the normal to the surface. This can be seen in figure figure 4 (*e*)–(*f*), which shows results for the 14 and 21 μm films. Deviations in the fit for $\chi = 70°$–$80°$ are caused by the saturation of the X-ray signal at these angles.

The above calculations indicate that the homeotropic layer extends 15 μm or more into all but the thicker ($\geqslant 36$ μm) films. This is consistent with previous observations, and gives a quantitative estimate of the extent of the surface tension forces on the molecular alignment. In the thicker samples, the surface layer is considerably thinner. This can be attributed again to the heating cycle used. The hot air blower used to heat the samples after adding LC pushed on the LC, forcing the molecules to flow. Surface

Summary of results from fitting the χ scans for films deposited on a 9 μm repeat distance grating to the multilayer model.

Film thickness/μm	Homeotropic layer thicknesss/μm/mosaic	Homogeneous layer thickness/μm	Goodness of fit†
6	6·0/10°	—	0·02
11	11·0/10°	—	0·02
17	17·0/10°	—	0·04
22	15·0/10°	7·0	0·04
26	20·0/10°	6·0	0·06
31	31·0/10°	—	0·06
36	10·0/10°	26·0	0·05
42	5·0/10°	37·0	0·03

† Goodness of fit taken between 20° and 80°.

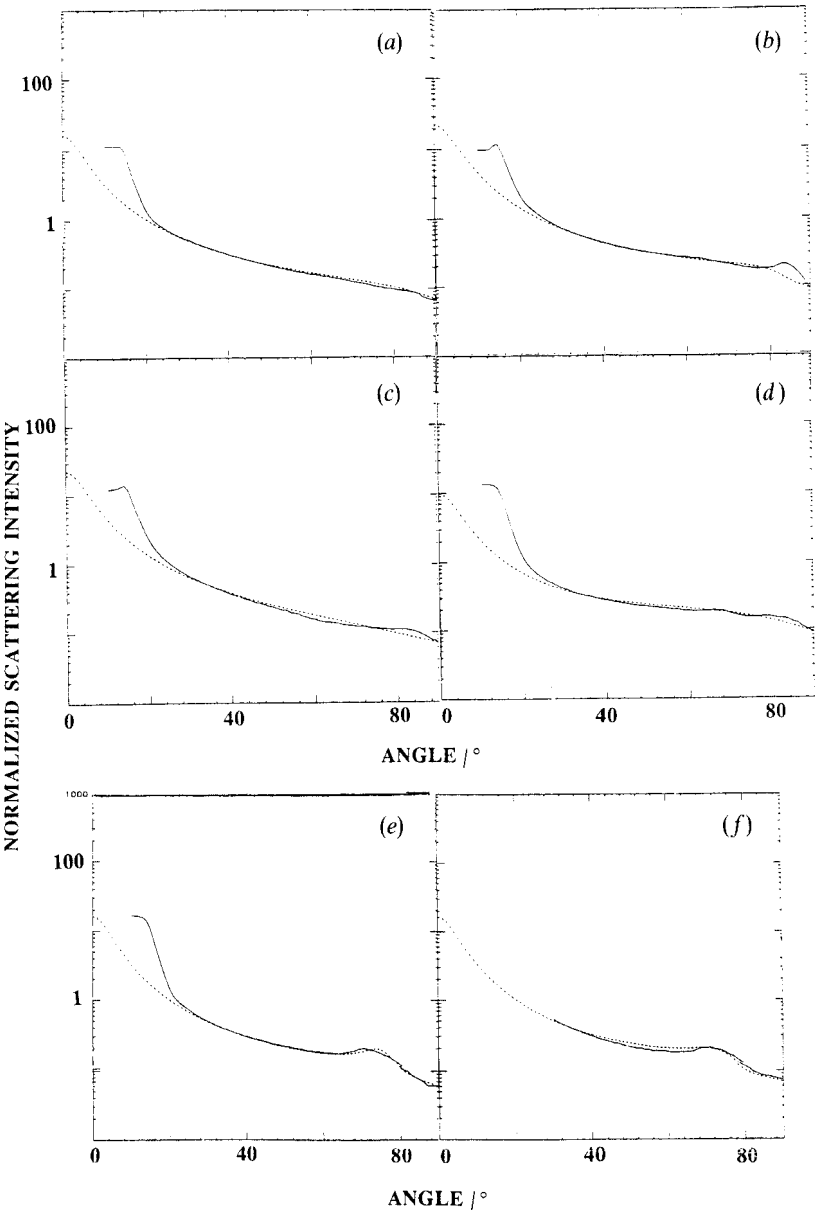

Figure 4. χ scans (solid lines) and fits to the multilayer model described in the text (dotted lines): (*a*) 11 μm film on a 9 μm grating; (*b*) 22 μm film on a 9 μm grating; (*c*) 31 μm film on a 9 μm grating; (*d*) 42 μm film on a 9 μm grating; (*e*) 14 μm film on flat glass; (*f*) 21 μm film on flat glass. Angle $= 90 - \chi°$.

tension kept the thinner films in place; however, the flow, and the resulting surface distortion was more pronounced in the thicker films, where the surface to volume ratio is smaller. This process induced a higher degree of disorder, which was frozen into the film by the rapid cooling once the heat was removed. A slower cooling rate with less surface distortion should allow the film to reach equilibrium and a higher degree of order: we do not expect it to affect the presence of the in-plane signal, seen previously in more slowly cooled samples [4]. The competition of aligning forces is evident once again in this process.

4. Conclusions

We performed a series of X-ray measurements on smectic A 8CB films deposited on grated substrates and on flat glass. The thickness of the films was varied systematically *in situ* to obtain information on the onset and extent of the homogeneously aligned smectic layers. The films had two competing interfaces, the air–LC and the LC–substrate. For the grated substrate, the air–LC interface dominates the aligning forces, and all films smaller than 30 μm exhibit homeotropic alignment of the LC molecules. The aligning influence of the air–LC interface extends for approximately 15 μm or 5000 smectic layers into the substrate. In thicker films, the gratings induce a degree of uniform homogeneous alignment in the direction of the grating grooves. These regions are apparently concentrated near the surface of the substrate. The thickness region 22–31 μm appears to be an unstable region. Very thick films may have as much as a 36 μm disordered homogeneous layer. The cooling rate and the cooling procedure, which allow the molecules to respond to the influence of both the air and the substrate surfaces, play an important role in the alignment of the LC molecules, and may influence the degree of disorder of the homogeneous layers. This study confirmed our earlier observations stating that the surface tension is the most important aligning force in this system, followed by surface topology.

Work in progress involves the comparison between these results and results obtained using a slower and gentler cooling process, as well as a comparison of the effect on alignment by gratings of different repeat distances.

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