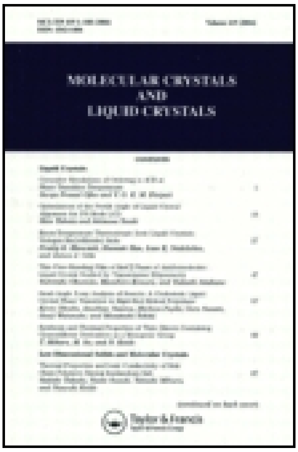

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X-Ray Study of Liquid Crystal Alignment: Evidence for an Alternate Mesophase at the Free Surface?

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X-Ray Study of Liquid Crystal Alignment: Evidence for an Alternate Mesophase at the Free Surface?

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We studied the alignment of the free surface of a liquid crystal film as a function of depth using grazing incidence x-ray diffraction. We have produced well defined gratings on soda lime glass using conventional photolithography. After treatment with MAP, the substrates induced homogeneous alignment with a preferred orientation along the direction of the grooves in the bulk of an 8CB film in the SmA phase at room temperature. At the air/liquid crystal interface, these molecules align homeotropically.

Using conventional Bragg diffraction, we observed a layer spacing of 31.5 Å for the perpendicularly aligned molecules near the surface (2q = 2.8°). However, using a collimated beam in the grazing incidence geometry at a nominal incident angle of 0.00°, a diffraction peak with a large angular spread at 2q = 2.2° showed a layer spacing of 40.1 Å at the surface. With a slight increase in angle, a small peak at 2q = 4.4° (d-spacing of 20 Å) emerged. As the incident angle was further increased, a peak at 2q = 2.8° appeared and the peak at 2.2° moved towards 2.8°. It is possible that the topmost layers are in the antiferroelectric SmA_2 phase, in which the molecules lie head to head with a double layer spacing of approximately twice the molecular length, and that the 4.4° peak is a second harmonic from the SmA_2 double layer. Note, too, that this spacing is consistent with the monolayer SmA_1 phase. The angular spread in the 2.2° peak could be caused by fluctuations toward a smectic Ã phase. Because the SmA_2 phase is not stable in the bulk, it is either a surface or a grating induced effect. With increasing depth, the bulk bilayer spacing is reestablished.

Keywords: thin films, x-ray diffraction, mesophases

INTRODUCTION

The long-range orientation of the liquid crystalline molecules is the product of a delicate balance of intermolecular forces.[1] Thus even a weak external perturbation causes significant changes in the macroscopic properties of the liquid crystals. This property, coupled to the abundance of liquid crystalline materials in diverse temperature and pressure ranges, as well as optical properties, has led to the use of liquid crystals in display, memory and sensing devices.[2,3] Any progress in the field of applications is closely related to the increased understanding of the behavior of liquid crystals and the nature of their interactions.

Liquid crystal devices consist of a film of liquid crystalline material encased between two slabs of (metalized) glass which have been prepared in order to induce a particular arrangement of the molecules.[4,5] The molecules must interact with this substrate strongly enough that the arrangement subsists for reasonable depths and over a reasonable surface area. Here, "reasonable" depends on the needs of the particular application. On the other hand, this interaction must be weak enough that the molecules can be rotated by the application of an electric, magnetic or optical (laser) field. This arrangement is achieved using the so-called weak-interaction substrate preparation method.[4] In this method, the surface of the substrate is coated with a polymerizable material and rubbed to produce a grooved structure which forces the molecules to align parallel or almost parallel to the plane of the substrate, along the direction of the grooves. The liquid crystal molecule anchoring depends on the substrate preparation. It is important to understand the interactions taking place at the LC-substrate interface and these affect the behavior of the molecules within the bulk of the film in order to tailor the LC anchoring according to need. From a more basic point of view, despite the considerable number of theoretical and experimental works dealing with this azimuthal anchoring of LC molecules by grooved surfaces, the LC-solid interface is still not well understood.

Presently, most information obtained on the alignment of liquid crystals by different substrates has been obtained using light in the visible or near-visible range.[6–8] Some experiments have measured the phase retardation (related to the birefringence) of the liquid crystal using monochromatic light from a He-Ne laser (λ = 627 nm). Typical cell sizes lie in the range 1 μm to 75 μm in thickness. The onset of order in these films is observed by measuring the extinction of light going through the sample under crossed polarizers. The uniform extinction obtained in many of these experiments suggest that sample alignment occurs over a surface area equal to the illuminated area (in the order 0.5 mm^2 or less in a laser experiment) and for depths comparable to the wavelength of the incoming beam. Other techniques, such as second harmonic generation, are surface specific, and give information about the first molecular layer at the surface or interface of a film.[4] Glancing angle ellipsometry provides information on the coherence and orientation of the ordered interfacial molecular layers.[8] A technique that provides structural information is needed to further complete the picture of the LC-solid interfacial region.

We present the results of a grazing incidence x-ray diffraction experiment on films of octylcyanobiphenyl (8CB) deposited on 15 μm repeat period grating which was etched photolithographically on soda lime glass. The top of the film was left open to air, in order to avoid the problem of absorption of x-rays by the glass substrate. At the free end of the film, the liquid crystal molecules tend to align perpendicularly with respect to the plane of the substrate, corresponding to having the smectic planes parallel to the plane of the substrate. The molecules close to the substrate should tend to align along the plane of the substrate, corresponding to smectic planes perpendicular to the plane of the substrate. There is a competition between the LC-air interface and the LC-substrate interface which may reduce the effect of the substrate on the film. The purpose of our experiment is two-fold: a) to investigate how the LC structural conformation and molecular orientation with respect to the substrate vary as a function of increasing distance form the air-LC interface to the LC-substrate interface; and b) to study how the systematic change in the parameters of the aligning grating, such as the repeat period, the depth and the groove thickness, affects the LC molecular alignment.

EXPERIMENTAL

Octylcyanobiphenyl (8CB) is a room temperature smectic which is very stable in air over time. The compound is a rod-like molecule length 22.1 Å, which exhibits two LC mesophases in the bulk: a bilayer smA_2 phase, with a layer spacing of 31.6 Å and a nematic phase. In order to control better the topography and cleanliness of our substrates, we used conventional photolithography, using a chemical etch of buffered HF, to prepare gratings on soda lime glass of uniform period and depth. The gratings have periods of 6, 9, 12, 15, 18, 21 and 24 μm, a maximum depth of 5 μm and a surface area of 1 cm^2. These gratings were treated with a 1% solution of methylaminopropyltrimethoxysilane (MAP), a compound which is known to induce parallel, azimuthally random alignment of the LC molecules. We applied 8CB to the gratings thus prepared in the smectic phase, then heated it cyclically until the desired alignment was achieved. This alignment was verified optically. The films were loaded into a sample holder which was placed in turn in a four-circle diffractometer for the x-ray measurements.

X-ray reflection and glancing angle techniques[9] have been used to study thin liquid crystal standing films[9–14] and to successfully observe the evolution of smectic-like layering at the surface of nematic films.[15] The glancing incidence x-ray scattering technique combines the principles of Bragg diffraction and total external reflection. X-rays are incident on the sample at an angle close to the critical angle for total reflection, χ_c. This enables specular relfection and surface specificity. χ_c is equal to 0.151° for 8CB. By varying the x-ray incident angles close to the critical angle for the particular material studied, different depths at the surfaces and interfaces of the films can be examined. In addition, by rocking the sample around the surface normal, diffracted beams are observed emanating from the surface at very shallow angles. The corresponding diffraction vectors lie parallel to the surface of the film.

We used Cu Kα_1 provied by an Elliott GX-13 rotating anode generator with a fine focus source diameter of 100 μm, operating at 2.7 kW, to perform the x-ray diffraction measurements. Two configurations were used. The first consisted of a vertical focusing LiF(200) monochromator and a flat LiF(200) analyzing crystal which yielded an in-plane longitudinal resolution of 0.005 Å^{-1} full width at half maximum (FWHM) with a corresponding transverse resolution of 0.0007 Å^{-1} FWHM. The vertical resolution was determined by slits after the monochromator and before the detector. These were left wide open. The sample was placed at the focal point of the monochromator crystal in the center of a Huber 4-circle goniometer. A focusing mirror placed between the monochromator and the detector resulted in a beam convergence between 3 and 6 mrad perpendicular to the plane of the sample in the second configuration. The sample was adjusted so that the center of the beam was parallel to it. In this position, the angle of incidence χ was 0.00°. The angle of incidence was varied between 0.00° and 0.25° in steps of 0.05°. A twodimensional detector of 512 × 512 square pixels of size 0.192 mm and placed 394.5 mm behind the sample recorded the data from these runs.

RESULTS AND DISCUSSION

A "conventional" θ-2θ x-ray scan on the film showed a resolution limited peak corresponding to the interdigitated bilayer A_d phase ($2\theta = 2.8°$), with the smectic layers parallel to the plane of the substrate. A θ scan at fixed $2\theta = 2.8°$ shows a sharp peak at $\theta = 1/2(2\theta)$ over a very broad angular background. We show this in Figure 1. Increasing depths within the film can be probed by increasing the angle of incidence about the critical angle for 8CB (0.151°) using the second configuration. We can examine the structure of those layers further within the film by comparing the results of scans obtained from two successive incident angles. Figure 2 illustrates the results of two such subtractions, between $\chi = 0.00°$ and $0.05°$ (Figure 2a) and between $\chi = 0.05°$ and $0.10°$ (Figure 2b). We summarize the results of these subtractions as follows. At low angles of incidence, our measurements show a strong peak centered at $2\theta = 2.2°$, which corresponds to a layer spacing of 40.1 Å. This peak is surrounded by a diffuse scattering halo which increases in angular spread with increasing incident angle. A second peak at 2.31° appears at $\chi = 0.10°$ (see Figure 2b). The value for 2θ corresponding to this peak increases monotonically with increasing angle of incidence, reaching a value of 2.56° at $\chi = 0.25°$. The

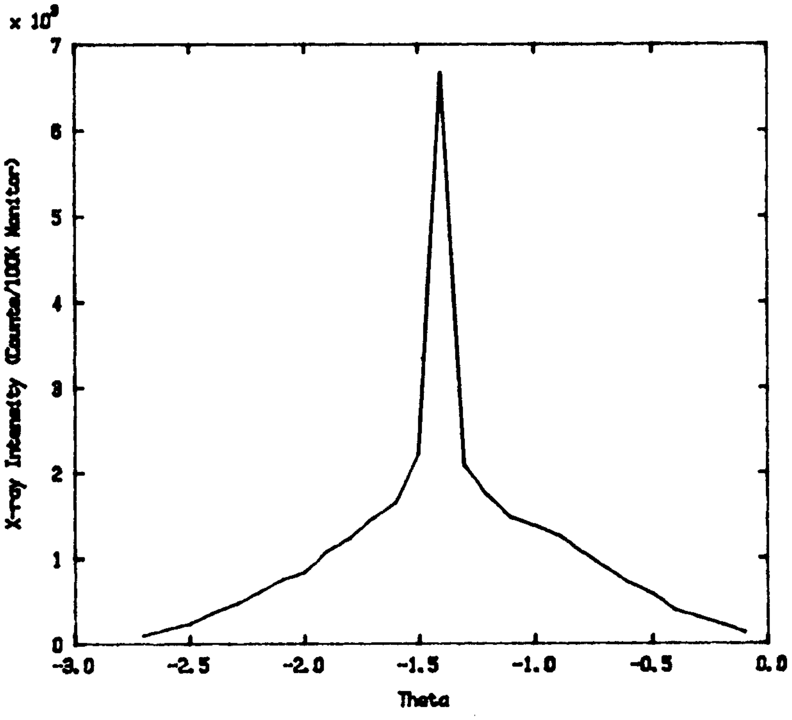

FIGURE 1 θ scan at $2\theta = 2.8°$, showing the peak at 1.4° sitting on a broad angular background.

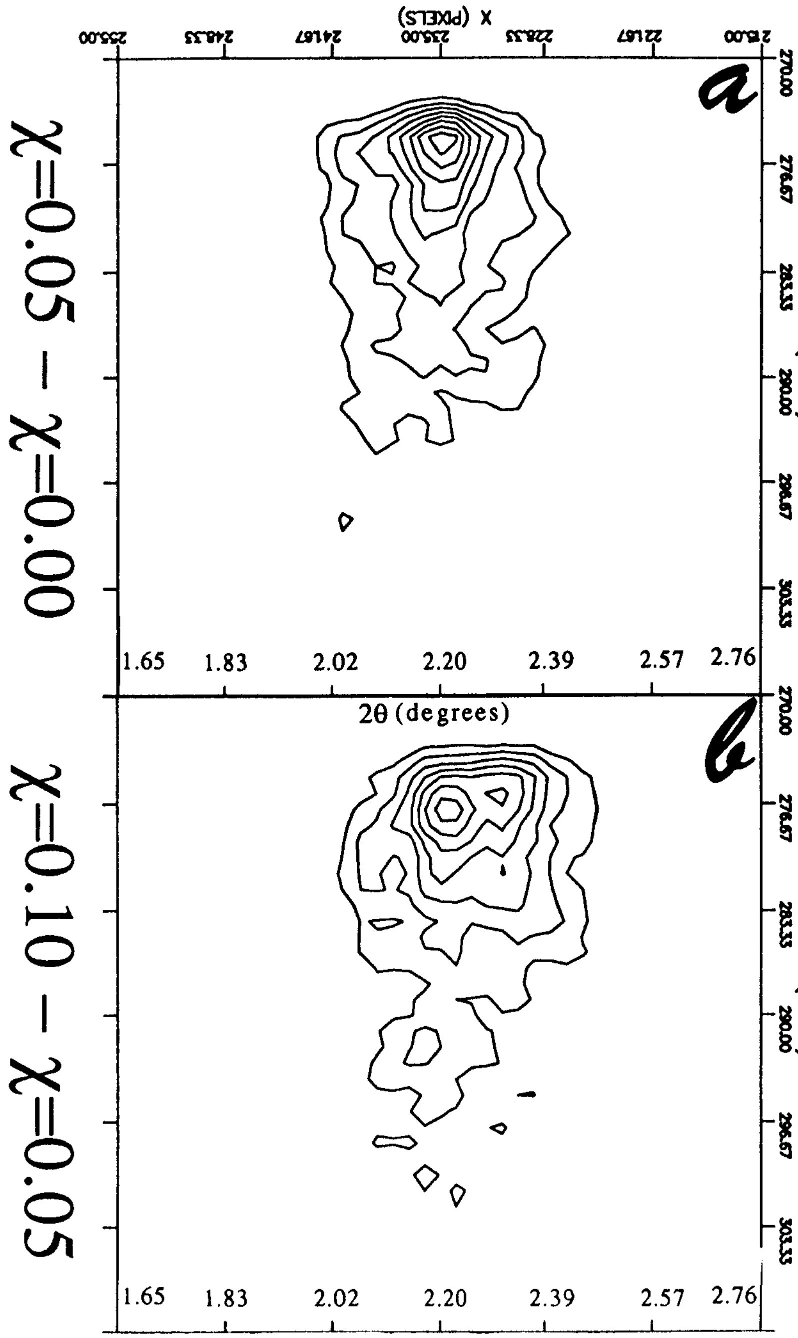

FIGURE 2 Contour subtractions comparing the results of scans taken at two successive angles of incidence. a) 0.05° − 0.00°; b) 0.10 − 0.05. See text for an explanation.

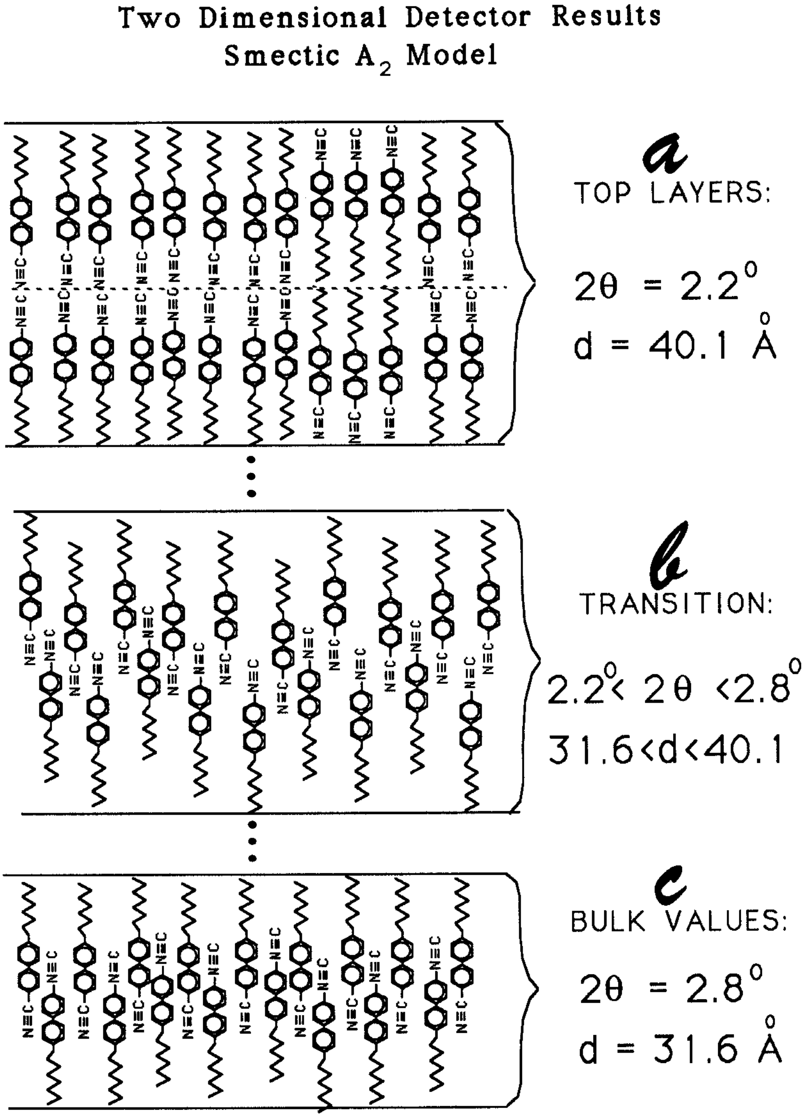

FIGURE 3 Possible model that explains the observed diffraction peaks: a) The first few layers at the free surface of the film are in the smectic A_2 phase, with fluctuations toward the smectic $\tilde{A}$ phase, which are responsible for the broad background observed in the θ scan shown in Figure 1; b) There is a region where the molecules begin to interdigitate, as manifested by the shift to higher angles of the 2.2° and 4.4° peaks; c) The bulk smectic A_2, is present below these surface layers.

contribution from the 2.2° peak vanishes at higher angles. We note that the peak shift is not due to the increase in incident angle, which would effectively reduce the value of 2θ. In addition to the peak at 2.2°, we observed a peak at 2.8° at all angles, which corresponds to the bulk layer spacing for 8CB of 31.6 Å. This peak increases in intensity with increasing angle of incidence. Finally, we also observe the presence of a very weak peak at 4.4°, which corresponds to a layer spacing of 20.07 Å, and which also increases with increasing incident angle.

We interpret our data as follows. The peak centered at 2.2° is consistent with having the LC molecules arranged in the antiferroelectric smectic A_2 bilayer phase,[16] which is characterized by a layer spacing equal to twice the length of the molecules, with the polar-CN heads facing each other. The diffuse halo surrounding this peak may correspond to fluctuations within the layers into the smectic $\tilde{A}$ phase, in which the molecular dipole is modulated in the plane of the smectic layers. These two phases are confined to the first few layers in the film. As the incident angle and penetration depth increases, the film structure becomes that of the bulk bilayer smectic A_2' phase. Finally, the peak at 4.4° corresponds to the second harmonic of the 2.2° peak, but is also consistent with the smectic A_1 monolayer phase, in which the layer spacing equals the molecular length and the molecular dipole is oriented randomly within the smectic layers. There is an indication in our data that the layers that as the penetration increases, the molecules start separating again, with the reappearance of peaks at 2.15° and 4.38° respectively at $\chi = 0.25°$. This may indicate the appearance of a transition region; however, at this point our observations are hindered by the attenuation of the x-ray beam. We summarize the model just described in Figure 3.

We note that *neither the smA$_2$, the smA$_1$, nor the sm$\tilde{A}$ phases exist for bulk 8CB.* Furthermore, these phases have not been observed previously, either in free-standing films of 8CB or in films prepared such that the alignment at the LC-substrate interface is homeotropic.[17] Our results suggest that substrate preparation may influence the presence of these new phases near the film surface. Behavior similar to this has been observed before in free standing films of a different LC compound: the phase diagram of the freely suspended film was so strongly film-thickness dependent that for one very thin film, two phases were present which were not stable in the bulk.[18] In another study, an antiferroelectric SmA_2 phase was seen at the surface of a liquid crystal film which has only SmC and SmA_1 phases in the bulk.[14]

The model described above constitutes *one* possible interpretation of our data. Another viable interpretation follows. The presence of the diffuse nematic-like scattering at very low incidence angles may be caused by oscillations of the LC director at the free surface of the crystal. The oscillations describe a cone of diffuse scattering. The angle subtended by this cone increases with increasing depth within the film, suggesting the presence of increased disordering due to the competition between the LC-air and LC-glass interfaces.

This is a novel area of interest in the study of LC films, which requires further study. Our measurements also suggest that the LC structure continues to change at depths not attainable in our present setup because of attenuation problems.

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References

1. F. J. Kahn, *Physics Today*, **35**, 66 (1982).
2. I. C. Khoo and Y. R. Shen, *Optical Engineering*, **24**, 579 (1985).
3. See, for example, N. A. Clark, *Phys. Rev. Lett.*, **55**, 292 (1985).
4. F. J. Kahn, *Appl. Phys. Lett.*, **22**, 386 (1973).
5. For a review of work prior to 1979, see J. Cognard, *Molec. Cryst. Liq. Cryst.*, Supplement 1, (1982).
6. S. T. Wu and U. Efron, *Appl. Phys. Lett.*, **48**, 624 (1986). H. Ben Ouada, H. Hommel and A. P. Legrand, *J. de Physique*, **47**, 909 (1986).
7. See, for example, H. Birceki, in *Liquid Crystals and Ordered Fluids*, p. 853 (1984; J. A. Castellano, *Liquid Crystals and Ordered Fluids*, p. 763 (1984); D. W. Berreman, *Mol. Cryst. Liq. Cryst.*, **21**, 215 (1973).
8. W. Chen, L. J. Martinez-Miranda, H. Hsiung and Y. R. Shen. *Phys. Rev. Lett.*, **62**, 1860 (1989); *Mol. Cryst. Liq. Cryst.*, **179**, 419 (1990).
9. W. C. Marra, P. Eisenberger and A. Y. Cho, *J. Appl. Phys.*, **50**, 6927 (1979).
10. B. M. Ocko, A. Braslau, P.S. Pershan, J. Als-Nielsen and M. Deutsch, *Phys. Rev. Lett.*, **57**, 94 (1986).
11. B. D. Swanson, H. Stragier, D. J. Tweet and L. B. Sorensen, *Phys. Rev. Lett.*, **62**, 909 (1989).
12. P. S. Pershan, A. Braslau, A. H. Weiss and J. Als-Nielsen, *Phys. Rev. A*, **35**, 4800 (1987).
13. P. S. Pershan, *Colloque de Physique*, **50**, Suppl. 10, C7-1 (1989).
14. E. F. Gramsbergen, W. H. de Jeu and J. Als-Nielsen, *J. Physique*, **47**, 711 (1986).
15. B. Ocko, pre-print (1990).
16. See, for example, C. R. Safinya, W. A. Varady, L. Y. Chiang and P. Dimon, *Phys. Rev. Lett.*, **57**, 432 (1986), and references therein.
17. J. Collett, P. S. Pershan, E. B. Sirota and L. B. Sorensen, *Phys. Rev. Lett.*, **52**, 356 (1984).