

Alignment of nematic butoxybenzilidene octylaniline by surface-relief gratings

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The effect of surface-relief gratings on alignment of the nematic phase of butoxybenzilidene octylaniline has been studied for gratings of 1- μm and 300-nm period with grating depth from 22 to 410 nm. A planar-to-homeotropic alignment change was observed on flat surfaces and interpreted quantitatively by a model invoking the entropy change due to smectic short-range order imposed by the surface in the homeotropic state. The alignment change was suppressed by gratings of sufficient depth or short enough period.

I. INTRODUCTION

Much work has been devoted in recent years to the problem of nematic-liquid-crystal alignment on solid surfaces. This alignment depends both on the topography of the surface¹⁻⁵ as well as on its chemistry.⁵⁻¹¹ The former is essentially a geometric effect whose influence on the Frank elastic energy can be calculated provided that the surface topography is sufficiently well known. This provision has been met to a great extent by the recent progress in planar-fabrication technology.¹² The role of the chemical nature of the surface has been much more controversial^{5,8,11} and is still not fully understood. Even the predominance of weak anchoring on "clean" glass surfaces¹³ seems still to be disputed.¹⁴ We report here an example which shows clearly the existence of weak anchoring on glass and quartz surfaces. The liquid crystal considered was butoxybenzilidene octylaniline (40.8); the transition temperatures between the different phases of this material are $T_{IN} = 78.2^\circ\text{C}$, $T_{NA} = 63.77^\circ\text{C}$, $T_{AB} = 49.76^\circ\text{C}$, and $T_{KB} = 38.0^\circ\text{C}$. (The subscripts *IN* stand for the isotropic-nematic transition, *NA* for the nematic-smectic-*A* transition, *AB* for the smectic-*A*-smectic-*B* transition, and *KB* for the solid-smectic-*B* transition.) The 40.8 director was found to exhibit a "transition" in the nematic phase in which it suddenly flipped from a high-temperature parallel (homogeneous) configuration to a low-temperature perpendicular

(homeotropic) orientation to the substrate. (The opposite flip near the isotropic phase has often been observed^{8,15,16} and will not be considered here.) In this paper we investigate the influence of square-wave gratings of various periods and depths on this observed change of the molecular orientation in order to elucidate the interaction between surface-relief structure and the wall anchoring energy.

II. FABRICATION OF SQUARE-WAVE GRATINGS

The substrates used consisted either of polished fused quartz or float glass (Corning product No. 7059). Both types of substrates gave essentially identical results unless otherwise stated. We constructed gratings of 3000 Å and 1- μm period with depths ranging from 220 to 4100 Å.

Gratings of the 3000 Å period were fabricated using the following steps (see Fig. 1). A 100-Å-thick layer of chromium was put onto the substrate by electron-beam evaporation; this was followed by the spinning of a 500-Å-thick layer of Shipley AZ1350J resist diluted 1:7 with thinner. The gratings were exposed holographically using the 3250-Å line of a helium-cadmium laser. After development of the resist, the chromium was etched chemically to produce a mask for reactive ion etching of the substrate in CHF_3 gas^{17,18} at a pressure of 1.3 Pa and a substrate self-bias of -550 V. The glass

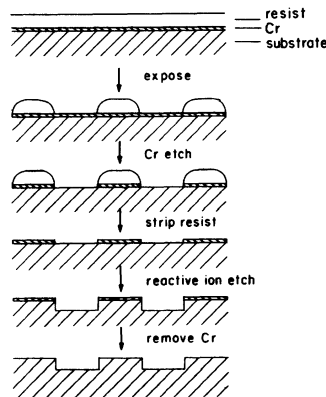


FIG. 1. Schematic representation of the steps involved in fabricating a square-wave grating.

had a very low etch rate (45 Å/min) compared to the quartz (380 Å/min). Consequently, in order to reduce possible contamination by metal atoms from the glass, the glass substrates were cleaned in a dilute nitric acid solution (after removal of the Cr) prior to the usual cleaning steps described below. The depth of 3000-Å gratings varied from 220 to 1400 Å.

Gratings of the 1- μm period were fabricated using conformable photomasks; these were 600-Å chromium on 0.2-mm Corning 0211 glass, patterned with 1- μm -period gratings by holographic lithography and chemical etching. The glass and quartz substrates were coated with 500 Å of Cr followed by 4000 Å of AZ1350B photoresist. The gratings were then replicated by conformable photomask lithography¹⁹ using the same etching procedure described above. The main reason for chemically etching a pattern in chromium applied directly on the substrate itself is that it is simple. The method has, however, one serious drawback: occasional islands of chromium may remain in the grooves after chemical etching. At least in the case of quartz, with its high etch rate, this can lead to rough groove bottoms and the profile then deviates from the ideal square-wave form. However, the fact that gratings fabricated by different techniques behaved similarly in our experiments indicates that small deviations from the ideal square-wave profile do not play a critical role. For example, we made a pair of 1- μm -period gratings using chromium lift off¹⁹ in place of chemical etching. In this technique the Cr is evaporated after the photolithography step and deposited on the substrate only in the areas where the resist has been exposed and developed. Subsequently the Cr is "li-

fted off" by dissolving the resist and little or no residue remains in the area between the Cr stripes deposited on the substrate. After reactive ion etching, these gratings had flat-bottomed grooves but behaved the same as gratings produced by the more simple process. Another pair of shallow (depth $\sim 200\text{Å}$) 1- μm -period gratings had been fabricated earlier²⁰ using 4000 Å of AZ1350B resist spun on the glass directly; the resist was exposed by conformable mask photolithography and used as a mask for Ar ion etching. Since the etch depth was shallow, redeposition²¹ was a minor problem and the side walls were close to vertical. Gratings fabricated by this third method also showed alignment properties similar to a pair of reactive ion etched gratings of the same period and depth obtained from Shaver.¹³ We therefore feel that subtle differences in grating fabrication technique and properties have little effect on their behavior in aligning liquid crystals.

Before use with liquid-crystal materials, all gratings and substrates were cleaned by immersion in hot (80°C), 15% H₂O₂ for typically 1 h followed by immersion in filtered deionized water for 30 min. Finally, they were subjected to 30 min of uv ozone cleaning, after which they were always evenly wetted by water vapor, and Newton fringes could be seen in receding water films. This indicated they were free from organic contaminants. Gratings could be reused by repeating the above procedure after first removing the liquid crystal by solvents such as trichloroethylene, acetone, and isopropyl alcohol.

III. ALIGNMENT EXPERIMENTS WITHOUT GRATINGS

A sandwich consisting of two smooth float glass plates separated by a 25- μm Mylar spacer was filled with 40.8 in the isotropic phase with no applied magnetic field. In order to determine the molecular alignment at high temperatures the sample was slowly cooled through the isotropic to nematic transition in a magnetic field of 5 kOe.

A sharp Fredericksz transition in the K_1 geometry^{22,23} (magnetic field applied perpendicular to the substrate of a planar oriented sample) clearly showed that the director was oriented parallel to the substrate (Fig. 2). Figure 2 plots the changes of the phase difference $\delta\Psi = (2\pi/\lambda)\delta(d\Delta n)$ between ordinary and extraordinary rays as a function of the magnetic field. The birefringence and with it $\Psi = (2\pi/\lambda)d\Delta n$ are constant up to the Fredericksz

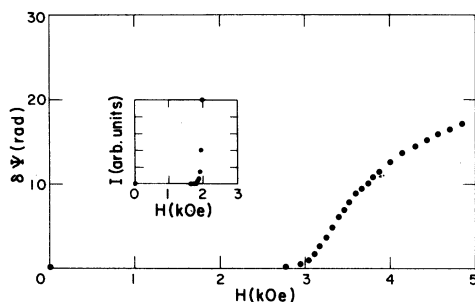


FIG. 2. Main figure: Fredericksz transition for a 25- μm -thick sample between smooth glass plates in the K_1 configuration (H field perpendicular to the substrate). The figure shows the change in phase shift between ordinary and extraordinary rays. Inset: Similar transition in the K_3 geometry for a homeotropic sample; the transmitted intensity between crossed polarizers is shown. For both experiments $\lambda = 6328 \text{ \AA}$.

transition field $H_c' \sim 3.2 \text{ kOe}$ after which Δn rapidly starts to decrease, corresponding to the increase in $|\delta\Psi|$. The slight rounding of the transition apparent in Fig. 2 is probably due to some misalignment of the substrate plane with respect to the magnetic field and places an upper bound of 1 deg on the angle between the director and the substrate.

As the sample was cooled, homeotropically aligned regions could be seen (by orthoscopic observation) to form around 65°C . These grew rapidly at the expense of the planar (homogeneous) regions. The flip to homeotropic alignment became complete between 0.5 and 1°C above the nematic–smectic- A transition; occurrence of the flip was extremely sensitive to sample purity and cleanliness of the surfaces. That the new alignment was indeed homeotropic was checked by conoscopic observation in the microscope. In addition, a Fredericksz transition experiment was performed in the K_3 geometry²² for a sample of $50\text{-}\mu\text{m}$ thickness. The magnetic field was applied parallel to the plates and the increase of the transmitted intensity through crossed polarizers was measured with a photo cell. The onset of the transition was equally sharp as in the previous geometry (see the inset of Fig. 2), indicating the director was within 1 deg of being perpendicular to the substrate.

There was a large temperature hysteresis in the alignment change: on warming the sample, the homeotropic alignment was preserved up to approximately 68°C after which the flip back into the planar alignment occurred. Surprisingly enough the system “remembered” the previous direction of planar alignment and flipped back into exactly this

same direction. A similar memory effect has also been observed by Shaver¹³ and Cheng and Boyd.²⁴ The samples were not hermetically sealed and so a decrease in T_{NA} of $\sim 100 \text{ mK/d}$ was observed, presumably due to hydrolysis from moisture in the air. This did not, however, affect the results of the alignment experiments.

IV. THE EFFECT OF SQUARE-WAVE GRATINGS ON DIRECTOR ALIGNMENT

Our results appeared to be independent of whether the substrate was quartz or glass, and so we shall discuss them together. As was pointed out in the introduction, even shallow submicron square-wave gratings^{13,25} have excellent aligning properties for nematic-liquid crystals. Well above the smectic- A phase we found well-defined planar alignment along the grooves of $250\text{-}\text{\AA}$ (quartz) and $340\text{-}\text{\AA}$ (glass) deep gratings of the $1\text{-}\mu\text{m}$ period. The flip of the director to the homeotropic orientation occurred at only a slightly lower temperature in the region of the grating than in the smooth region of the substrate. On warming, hysteresis was observed and uniform planar alignment was restored around 70°C . With $1\text{-}\mu\text{m}$ -period gratings of $850\text{-}\text{\AA}$ (glass) and $4100\text{-}\text{\AA}$ (quartz) depth, however, the flip to homeotropic orientation did not occur even on cooling into the smectic- A phase, although it occurred as usual over the smooth regions of the substrate.

The behavior of $3000\text{-}\text{\AA}$ -period gratings was quite different. For gratings of depth 440 \AA (both quartz and glass) as well as one 1400 \AA deep (quartz) and even a poor quality one 220 \AA deep in glass, the grating served to prevent completely the homeotropic flip that occurred on the smooth portion of the substrates. We illustrate this in Fig. 3 with two photographs of the boundary region of a $3000\text{-}\text{\AA}$ -period $440\text{-}\text{\AA}$ deep grating in glass. The sample is viewed between crossed polarizers and is rotated 45° between Figs. 3(a) and 3(b). Evidently, the regions outside the grating remain dark at both positions of the sample, indicating homeotropic alignment. These photographs are actually of the supercooled B phase at room temperature, but observations showed no change in alignment as the sample was cooled through the A and B phases.

Since it is not possible to distinguish between a perfectly parallel and a tilted parallel orientation of the director to the surface by mere orthoscopic observation, a number of experiments were performed

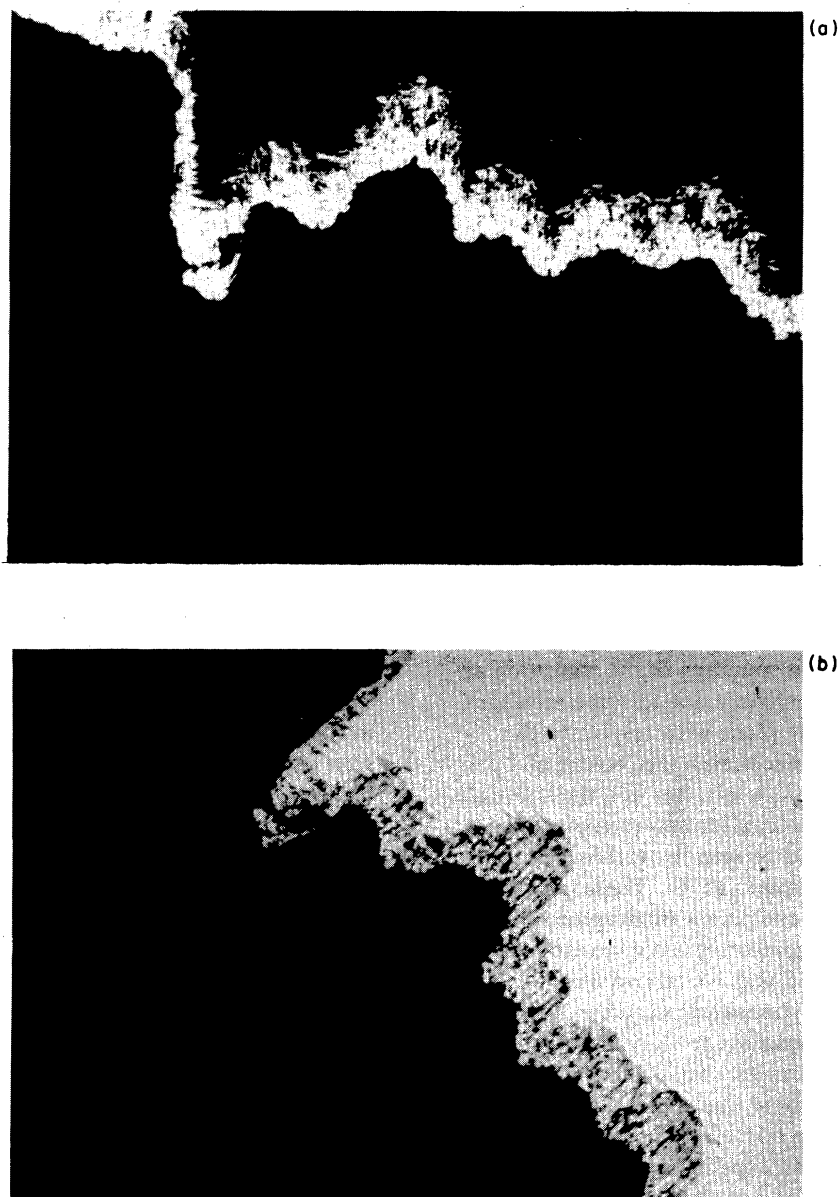


FIG. 3. Orthoscopic observation of a 50- μm -thick sample between crossed polarizers. The lower part of the figure shows the sample region aligned by a 3000- \AA -period grating; the upper part is between smooth glass plates. (a) The grating grooves are parallel to one polarizer axis. (b) The grooves are at 45° to each polarizer axis.

in order to rule out a finite tilt angle. Conoscopic observation corresponded to that expected for the average optic axis in the plane of the substrates. From the Fredericksz transition in the K_1 geometry of Fig. 4 (experiment performed on quartz gratings only), we concluded that the tilt angle was zero within the accuracy of our experiment (~ 1 deg). Hence the director lay quite accurately in the

plane of the substrates. That it was also parallel to the grooves could be seen from the Fredericksz transition in the K_2 geometry,²² where the magnetic field was applied perpendicular to the grooves in the substrate plane. An equally sharp transition was observed as in the other cases (inset Fig. 4). The quantity measured in this case was the angle of rotation δ of the conoscopic interference figure²²

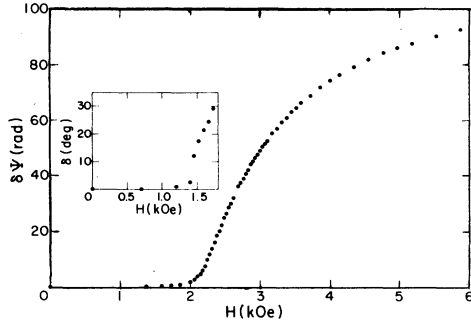


FIG. 4. A Fredericksz transition at 63.70°C in K_1 geometry of a sample aligned between two parallel 3000-Å-period gratings of 360 Å depth is shown in the main figure; this is the analog of the main part of Fig. 2. The insert shows a Fredericksz transition in the K_2 geometry (planar sample, H perpendicular to director in the sample plane) with a 50- μm -thick sample aligned by a 3000-Å-period 440-Å-deep grating pair (same sample as Fig. 3) at 69.75°C.

as a function of the magnetic field. A confirmation that the director was parallel to the grooves was also obtained from the characteristic light scattering from the layer undulation mode in the smectic- A phase.²²

We conclude this section by remarking that this is the first observation, to our knowledge, that square-wave gratings of sufficiently small period or sufficient depth can induce planar alignment of a nematic-liquid crystal even when weak surface anchoring forces favor homeotropic orientation. We intend to address the theoretical explanation of this observation in a subsequent article.

V. THE HOMEOTROPIC TO PLANAR TRANSITION

In this section we propose an explanation for the planar to homeotropic alignment change that occurred on smooth substrates as the nematic phase of 40.8 was cooled towards the smectic- A phase. The director will choose a surface orientation which minimizes the free energy of interaction with the glass or quartz substrate. We suppose this free energy to be the result of two contributions. The first of these comes from an orientation-dependent interfacial tension between the liquid-crystal molecules and the glass; we may approximate this by $W_0 - W_s \cos^2 \beta$, where β is the angle between the liquid-crystal molecules and the normal to the surface. A positive value of W_s favors homeotropic alignment. The second contri-

bution arises from a loss of translational entropy along the direction of the nematic director if molecules are oriented perpendicular to the surface; in other words, a locally smooth substrate will impose smectic- A short-range order²² in a boundary layer near the surface if the director is oriented with a significant component along the normal to the surface. We may treat this quantitatively using a slightly modified form of the smectic contribution to the free energy.²⁶ The smectic order consists of a one-dimensional density wave whose wave vector we take to be q_0 along the z direction. The order parameter ψ is defined by writing the density as

$$\rho = \rho_0 [1 + \text{Re}(\psi e^{iq_0 z})]. \quad (1)$$

Then the free energy per unit volume may be written

$$\Phi = \Phi_N + \frac{1}{2} \alpha [|\psi|^2 + \xi_{\parallel}^2 |\nabla_z \psi|^2 + \xi_{\perp}^2 |(\nabla_{\perp} + iq_0 n_{\perp}) \psi|^2], \quad (2)$$

where Φ_N is the free energy of the nematic phase with $\psi=0$, ξ_{\parallel} and ξ_{\perp} are the correlation lengths for ψ along and transverse to z , and ∇_{\perp} and n_{\perp} are components of the gradient operator and nematic director transverse to z . The form of the ∇_{\perp} term in (2) requires the director and the wave vector of the smectic-order parameter to be parallel for minimum free energy. In the nematic phase, $\alpha = \alpha_0 (T/T_c - 1)^{\gamma}$ where $\gamma \simeq 1.31$ and T_c is the temperature of the nematic-smectic transition; the correlation lengths diverge as $(T - T_c)^{-\nu}$ with $\nu \simeq 0.67$. If the angle β is close to $\pi/2$, the surface will not impose smectic order. However, with $\beta \sim 0$, there will be a boundary layer of thickness $\sim \xi_{\parallel}$ where ψ is not zero. If for small β we assume a flat substrate so that $\nabla_{\perp} \psi = 0$, Eq. (2) becomes

$$\Phi = \Phi_N + \frac{1}{2} \alpha (|\psi|^2 + \xi_{\parallel}^2 |\nabla_z \psi|^2 + \beta^2 q_0^2 \xi_{\perp}^2 |\psi|^2). \quad (3)$$

The ξ_{\perp}^2 term in (3) means that if $\psi \neq 0$ is imposed by the surface, the free energy will be lowest with molecules perpendicular to the surface ($\beta=0$). Thus we understand why we observe either $\beta \simeq 0$ (when the minimum free energy occurs with $\psi \neq 0$) or $\beta \simeq \pi/2$ (when the minimum free energy occurs with $\psi=0$). To estimate which situation obtains, we ignore the director elastic energy and assume β is independent of position. The volume integral of (3) must be minimized, which leads to an Euler

equation whose solution is $\psi(z) = \psi_0 \exp(-z/\xi_{||})$, where ψ_0 is the value of the order parameter at the surface of the substrate. Substituting this result into (3) and including the interfacial tension, the total free energy (per unit area) of interaction of the liquid crystal with the surface of the substrate becomes either

$$W = W_0 - W_s + \frac{1}{2} \alpha \xi_{||} \psi_0^2 \quad (4a)$$

or

$$W = W_0 \quad (4b)$$

depending on the molecules being perpendicular (4a) or parallel (4b) to the substrate.

As a test of our hypothesis, we examine the quantitative predictions of Eq. (4). We know quite accurately²⁷ that $\xi_{||} = 4.68(T/T_c - 1)^{-0.69}$ Å. The value of α is more difficult to estimate. As a very rough guess we would expect $\alpha_0/2$ to be about kT_c per molecule; this leads to $\alpha_0 \simeq 1.5 \times 10^8$ erg/cm³. For a more refined guess we may combine specific heat measurements²⁸ with a parametric form²⁹ for the equation of state in the critical region. The result is similar, that α_0 is $(4 \pm 2) \times 10^8$ erg/cm³. If the flip from planar to homeotropic occurs at $T_c + 1$ °C, then our model requires $W_s \simeq 0.25$ erg/cm², which is not an unreasonable value for weak anchoring at the glass or quartz surface.

VI. SUMMARY

We have found that square-wave gratings can produce parallel alignment of the nematic-liquid crystal 40.8 even though the interfacial tension at the surface favors perpendicular alignment. The shorter the grating period and the greater the grating depth, the more effective is the grating in producing the alignment. A simple model explains the flip from planar to homeotropic alignment on smooth substrates as the sample is cooled to just above the smectic-*A* phase, and suggests that smectic short-range order imposed by the surface plays an important role in the free energy of interaction of the liquid crystal with the substrate under weak anchoring situations. A research program to provide a more detailed and quantitative test of these ideas is underway.

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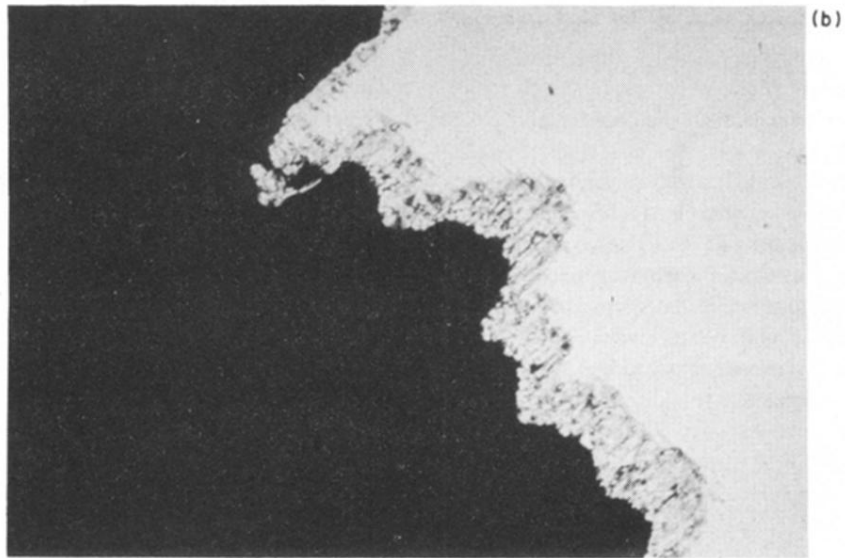
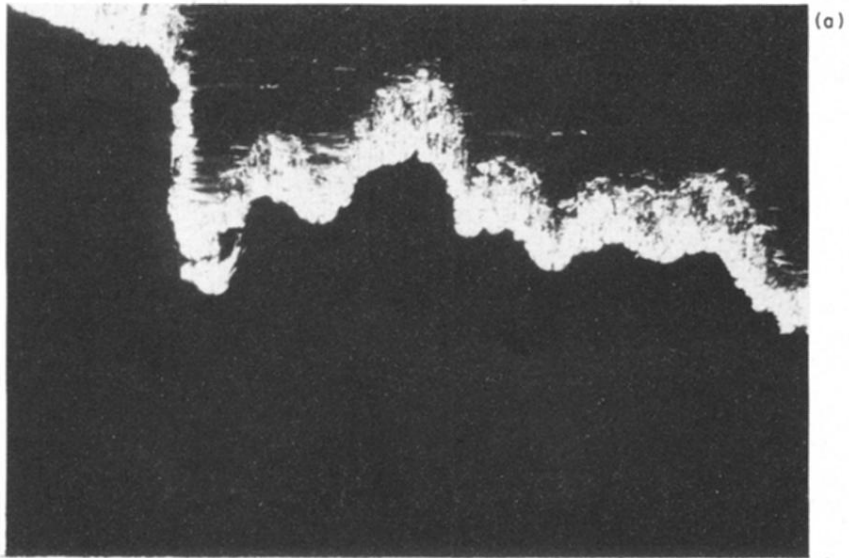


FIG. 3. Orthoscopic observation of a $50\text{-}\mu\text{m}$ -thick sample between crossed polarizers. The lower part of the figure shows the sample region aligned by a $3000\text{-}\text{\AA}$ -period grating; the upper part is between smooth glass plates. (a) The grating grooves are parallel to one polarizer axis. (b) The grooves are at 45° to each polarizer axis.