Surface-Induced Static Undulations in Multilayer Films of Liquid-Crystalline Polymers

by

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**Performing Organization**: Department of Chemistry, University of Florida, Gainesville, FL 32611-7200

**Sponsoring Agency**: Office of the Chief of Naval Research, 800 North Quincy Street, Arlington, VA 22217-5000

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imperfections associated with the smectic layer order. Rocking scans through this diffuse scattering are shown in Fig. 2 for the first three Bragg peaks of Fig. 1. These scans consist of broad diffuse scattering accompanied by a resolution limited peak due to specular reflection. It may be recalled that Davidson and Levelut have reported similar diffuse bands perpendicular to the 00L axis for bulk samples of polysiloxane liquid-crystal polymers. These bands were attributed to undulations of longitudinally correlated rows of mesogens. The widths and amplitudes of the diffuse peaks of our LB multilayer shown in Fig. 1 are not consistent with such longitudinal undulations. We shall show that the diffuse scattering for the liquid-crystalline polymer is in fact due to static undulations of the smectic layers induced by the roughness of the substrate surface.

Quantitative analysis of the diffuse scattering of Fig. 2 is similar to that used by Sinha et al. for solid surfaces. For a single rough surface, the scattered intensity is given by

$$S(\vec{q}) = \frac{1}{q_z^2} \int \int dX dY e^{i q_z (X X' + Y Y')} C(X, Y) e^{-i(q_x X + q_y Y)}.$$ 

$X$ and $Y$ are the Cartesian separations of two points on the surface $S_o$ with an average layer normal in the $Z$ direction. $C(X, Y)$ is the surface height-height correlation function. This is related to the average roughness across the sample $g(X, Y) = \langle [z(X, Y) - z(0)]^2 \rangle$. For many isotropic solid surfaces $g(R = (X^2 + Y^2)^{1/2}) = AR^{2h}$ describing so-called self-affine roughness. $h = D_H - 3$, where $D_H$ is the fractal dimension of the surface. For systems of finite size (and measurement techniques with limited spatial resolution) $g(R) \rightarrow 2\sigma^2$ for large $R$, where $\sigma$ is the rms roughness of the surface. A functional form satisfying these limits is

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Figure 3, which plots the central portion of the 002 rocking curve with fits for three different values of $h$, demonstrates this sensitivity.

Thermally induced layer undulations also contribute to the diffuse scattering from the multilayer. To estimate this contribution, the layer displacement correlation function was calculated following Holyst. Using the above values of $B$ and $K$ used to estimate $L$, and air/film and film/substrate interfacial tensions of 30 dyn/cm and 10 dyn/cm, respectively, the layer displacement correlation function, $\langle u_{ih}(R)u_{ih}(0) \rangle$ for the center of a 30-layer film is plotted in Fig. 5. Such thermal induced fluctuations are not conformal i.e. $C_{ij}(R)$ decays quickly for $i\neq j$. Hence this estimate represents an upper limit. For comparison, the layer undulation correlation function determined by the fits to the data in Fig. 2 is also plotted.

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film. As stated above, the large value of the compression modulus in these
liquid-crystal polymer films induces a large smectic penetration depth $L$. It
is energetically less costly to propagate layer undulations parallel to the layer
normal at the expense of in-plane director splay. Hence substrate roughness
plays a major role in the smectic layer structure. The specular reflectivity of
x-rays from the silicon substrate was measured to characterize its surface
roughness. The substrate consists of a monolayer of octadecyltrichlorosilane
(OTS) chemisorbed to the native oxide of a polished (100) silicon wafer.
This data is shown in Fig. 4, along with the corresponding electron density
profile. The data and fit agree very well with previous results on OTS
coated silicon obtained by Tidswell et al.\textsuperscript{3} The modeling technique has been
thoroughly discussed in Ref. [3]. The analysis yields an alkyl chain region
with a density $\rho/\rho_s=0.38 \pm 0.03$ and a thickness of $21 \pm 0.5 \text{ Å}$, indicative of a
well-formed monolayer with a maximum chain tilt of 22°. As is the case
with homeotropic alignment of bulk liquid-crystal samples by alkylsilanes,
Figure captions:

Figure 1. Specular and off-specular scans for a 29-layer liquid-crystal polymer film. The latter has been offset by a factor of five for clarity. Four Bragg reflections (layer spacing \(c=45.7\) Å) are evident in the specular data revealing a well ordered layer structure. The mosaic of the layer normal is limited to \(0.07^\circ\). The \(q_z\) dependence of the amplitude of the subsidiary maxima is discussed in Ref. 11. The off-specular scan was taken at a trajectory \(q_x=0.006q_z\). Diffuse scattering, sharply peaked at \(q_z\) of the Bragg reflections, is evident. The width of these peaks are similar to the primary maxima of the specular scan, implying that the associated layer undulations are replicated layer to layer. Inset shows chemical structure of the copolymer.

Figure 2. Rocking scans across the (a) 001, (b) 002 and (c) 003 Bragg reflections of Fig. 1. The incident beam in (a) was attenuated to avoid detector saturation near the peak. Open circles denote experimental data. Solid lines represent best fits to the model described in the text.

Figure 3. Enlargement of data and best fits to the 002 rocking curve for different values of \(h\). Solid line: \(h=0.25\), short dashed line: \(h=1\), dashed-dot-dot line: \(h=2\). All fits have been convolved with instrumental resolution. Inset: interfacial undulation correlation functions determined from fits to the rocking curve data (circles) and calculated from the model of Holyst for thermal undulations (triangles). The latter, calculated at the midpoint of a 29-layer film with \(K=1\times10^{-6}\) dyn, \(B=2.5\times10^9\) dyn/cm\(^2\), \(\gamma_{air/film}=30\) dyn/cm and \(\gamma_{film/substrate}=10\) dyn/cm. The compressibility of the interdigitated layer consisting of the side-chain mesogens and alkyl chains of the silanes, \(B_0=2.5\times10^7\) dyn/cm\(^2\).

Figure 4. Specular reflectivity normalized to Fresnel reflectivity (open circles) and fit to the model of Ref. [3] (solid line). The corresponding electron density profile is shown in the inset.
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