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Express Letter

Liquid Crystal Biaxiality at the Polymer Alignment Surface Studied Using Infrared Dichroism

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Using infrared dichroism technique and wedge cell, we have investigated the surface order of nematic liquid crystal at the polymer alignment surface. The results show that the order parameter at surface is much lower than that of bulk, and a light biaxiality exists at the interface between a liquid crystal and the alignment layer. The distribution of both order parameter and biaxiality parameter over the liquid crystal layer follows an exponent function. [DOI: 10.1143/JJAP.43.L312]

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Liquid crystal (LC) alignment at a solid interface has attracted much attention in recent decades, both because it is an interesting fundamental problem in the statistical mechanics of nonuniform, ordered fluids and because of its importance in liquid crystal devices. However, it is still a poorly understood phenomenon. The surface order parameter of a liquid crystal at a solid interface has been investigated both theoretically[1–4] and experimentally[5–7] as an important parameter that describes the characteristics of the interface. A nematic liquid crystal is generally considered optically uniaxial in bulk form, while at an alignment surface it may show biaxiality close to the wall. Some theoretical treatments have involved local biaxiality,[3] while there are few experimental studies of the biaxiality of nematic liquid crystals near an interface.[8] This study examined the biaxiality of nematic liquid crystals at a rubbed polyimide surface.

By restricting the second rank tensors, the nematic order parameter can generally be described using an ordering matrix, traceless tensor Q_{ij}

$$Q_{ij} = \langle (3\xi_i\xi_j - \delta_{ij})/2 \rangle \tag{1}$$

where ξ is a unit vector along the long molecular axis, δ_{ij} is a unit matrix, and $i, j = x, y, z$ denote the axes of the laboratory coordinate system. The brackets $\langle\ \rangle$ represent the statistical average taken over all molecules. By choosing z parallel to the director of the nematic liquid crystal, the tensor can be diagonalized. For the uniaxial case, only one element is left, namely $Q_{zz} = -2Q_{xx} = -2Q_{yy}$. By contrast, for the biaxial case, there are two independent elements, Q_{zz} and $D = Q_{xx} - Q_{yy}$. As usual, Q_{zz} characterizes the deviation of the long molecular principal axis from the director. The order parameter D represents the azimuthal angle dependency of the distribution of the molecular principal axis. Using the Euler angles θ and ϕ to specify the orientation of a particular molecule in the (x, y, z) coordinate system, the two independent order parameters $S = Q_{zz}$ and D are given by:

$$Q_{zz} = \langle 1/2(3\cos^2\theta - 1) \rangle \tag{2}$$
$$D = Q_{xx} - Q_{yy} = \langle 3/2 \sin^2\theta \cos 2\phi \rangle$$

When the transition moment parallels the principal axis of a molecule, considering a gradient from surface to bulk, the order parameter can be determined by the infrared absorption:

$$\overline{S} = \frac{1}{d}\int S(x)\mathrm{d}x = \frac{1}{2}\frac{2A_z - (A_x + A_y)}{A_z + A_x + A_y} \tag{3}$$

$$\overline{D} = \frac{1}{d}\int D(x)\mathrm{d}x = \frac{3}{2}\frac{A_x - A_y}{A_z + A_x + A_y} \tag{4}$$

where A_i (i=1, 2, 3) is the absorption coefficient of the liquid crystal along x, y, and z axes, respectively. For the uniaxial case, $A_x = A_y$. For a homogeneously aligned nematic cell, A_y and A_z are easily obtained using a polarizer, while A_x, the absorption along the axis perpendicular to the substrate, is difficult to measure. Since for a given liquid crystal layer, $A_x + A_y + A_z$ should be constant despite a change in order, we estimated A_x from the difference in the total absorption between the nematic state and isotropic phase.

$$(A_x)_{\mathrm{nematic}} = 3(A'_z)_{\mathrm{iso}} - (A_z + A_y)_{\mathrm{nematic}} \tag{5}$$

A wedge cell was prepared using 1-mm-thick ($15 \times 30\,\mathrm{mm}^2$) CaF_2 coated with polyimide (AL1051, JSR Corporation, Japan). To achieve a homogeneous alignment, the polyimide was antiparallel rubbed with nylon (YO-15-N, Yoshikawa Kasei Co. Ltd., Japan). Since we confirmed that the bulk pretilt angle was $\langle 1.1^\circ$ by the rotating crystal method, we neglected the pretilt angle in the following treatment. The cells were spaced using 4-μm-thick Mylar strips on one side, and variation in thickness across each cell was controlled by carefully adjusting the pressure to produce uniform interference fringes. The cells were filled by capillary action and the quality of the alignment was confirmed by microscopic observations. 4-n-Pentyl-4′-cyanobiphenyl (5CB, N-I 34.5°C, provided by Chisso Co., Japan) was used due to its suitable nematic range and because its transition moment of –C≡N stretching vibration parallels the principal long axis.

The IR absorbance at different polarizations was measured with an FT-IR spectrometer (FTS-60A/896, Bio-Rad Laboratories Inc., U.S.A.). The temperature was controlled using a homemade controller with better than 0.1°C stability. The temperature was set at 30.5 and 38.0°C for the nematic and isotropic phases, respectively. A wire-grid polarizer with an extinction coefficient of 98% at $2230\,\mathrm{cm}^{-1}$ was used. The optical axis of the sample was oriented at 45° or −45° to the slit direction of the measuring instrument to remove the instrument polarization. By aligning the polarizer parallel to the rubbing direction, the absorbance A_z was obtained. After rotating the polarizer by 90°, A_y was recorded. Instead of the area absorption values, we determined the height absorption values A_z and A_y at the peak absorbance wavelength.

The cell gap profile of one typical sample is shown in Fig. 1. The linear relationship between the total height

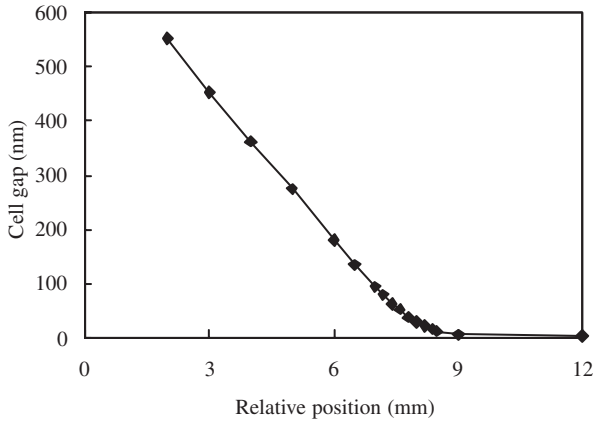

Fig. 1. The cell gap profile of a wedge sample.

absorbance and the thickness of the LC layer was confirmed by comparing the total IR absorbance ($A_z + 2 \times A_y$) with the retardation obtained at the thicker part of a wedge cell using an ellipsometer (The cell gap was 1∼2 μm, so the effect of the interface layer can be neglected) and the total absorption coefficient 2.43×10^{-4}/nm for 5CB was used to determine the thickness of the LC layer. The cell is a nearly perfect wedge with an extremely small wedge angle of 7.5×10^{-5} radians, while the change in thickness at the thin area is much slower. This made it possible to analyze the infrared dichroism of an ultrathin LC layer down to 10 nm.

The thickness dependence of order parameters S and D for one typical sample in the wedge is shown in Fig. 2. The solid lines were obtained by assuming an exponential distribution of order S and D over the LC layer (see eq. 6) according to the Landau-de Gennes theory.[9)]

$$S(x) = (S_b - S_s)\exp(-x/2\xi_s) \quad D(x) = D_s \exp(x/2\xi_d) \quad (6)$$

Where, S_b and S_s are the order parameters in the bulk and at the interface, respectively, D_s is the biaxiality parameter of the liquid crystal at the interface, and ξ_s and ξ_d are the coherence lengths for S and D, respectively.

Since the absorbance was measured over the layer, we used eqs. (3) and (4) to fit the data, as indicated in Fig. 2.

Since the surface order and biaxiality are imposed by the interface and are correlated with the bulk via the same mechanism, we expect that $\xi_s = \xi_d$ for the same sample. Indeed, the results showed that $\xi_s = \xi_d$, in contrast to the results presented by Araki *et al.*,[8)] where $\xi_d \gg \xi_s$.

The order S at surface (S_b=0.22) is much lower than that of the bulk (S_b=0.475), which is consistent with the results Barmentlo obtained using the second-harmonic generation method,[7)] and with the fully leaky guided modes of Hallam.[10)] Unlike the dichroic ultraviolet absorption method presented by West *et al.*,[6)] we did not observe any decrease in order as thickness increased, while they observed a minimum order near 35 nm for a thin layer of liquid crystal on a rubbed polyimide-coated substrate. This suggests that the sharp drop of order near 35 nm is related to the interface between the liquid crystal and air. As for D, D_s=0.08 shows light biaxiality at the interface, while D tends to zero in the bulk, as expected.

To observe the profile of the order parameter S and the biaxiality parameter D over the LC layer, we redrew them

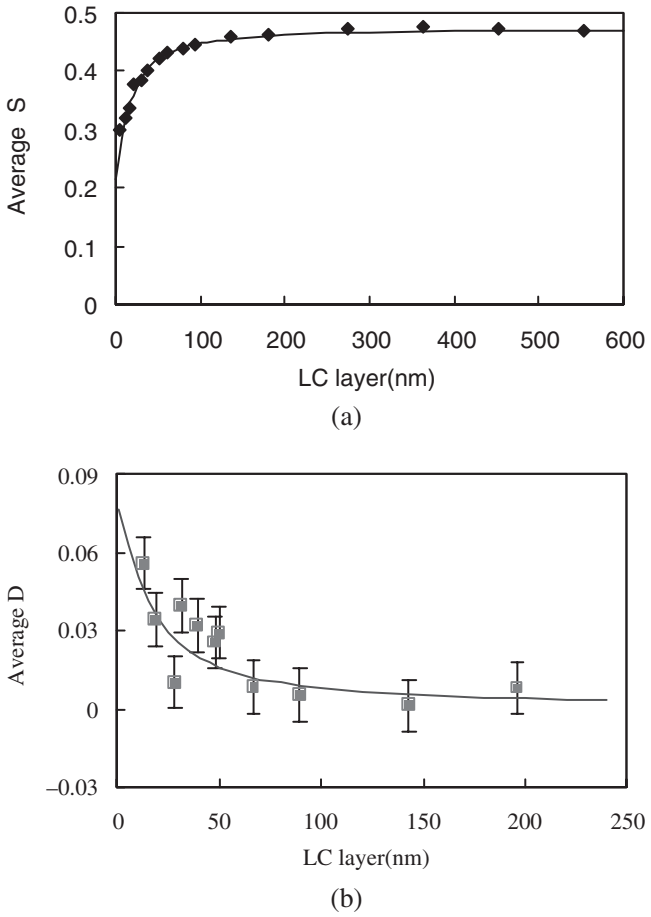

Fig. 2. The thickness dependence of average order parameter S and average biaxial parameter D in a wedge cell. The solid lines are best-fit results.
(a) $\bar{S}(d) = S_b - \frac{2\xi_s}{d}(S_b - S_s)\left(1 - e^{-\frac{d}{2\xi_s}}\right)$ With S_s=0.22, S_b=0.475, ξ_s=5nm
(b) $\bar{D}(d) = \frac{2D_s\xi_d}{d}\left(1 - e^{-\frac{d}{2\xi_d}}\right)$ With D_s=0.08, ξ_d=5nm

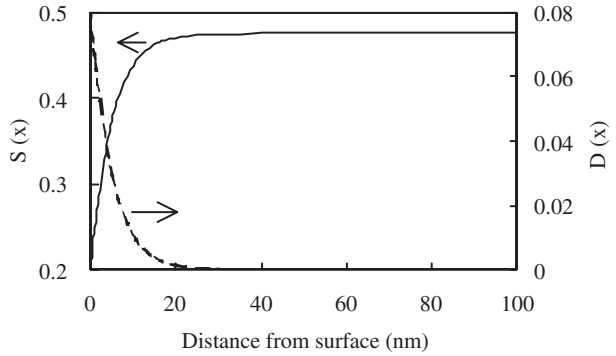

Fig. 3. The profile of order parameter S and biaxiality parameter D over LC layer. The solid line represents S and dash line shows D.

according to eq. (6) in Fig. 3, which shows that S increases quickly from a lower surface order to bulk order, while D decreases from 0.08 for the surface to 0 for the bulk when moving away from the interface. Taking $4\xi_{(d\text{ or }S)}$ as its thickness, the interface layer is estimated to be about 20 nm.

In conclusion, we clarified that light biaxiality exists at the interface between a liquid crystal and the alignment layer. The distribution of biaxiality parameter D over the liquid crystal layer follows an exponent function. The fact that S

and D had the same coherence lengths confirmed the reliability of the experimental results. The results also indicated that the interface layer is about 20 nm thick. However, we only used one polyimide in our experiment. To check whether interface-induced biaxiality of nematic liquid crystals exists in general, and to understand the characteristics of the interface in more depth, more experimental results are necessary.

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