

# Dichroic ultraviolet absorption of thin liquid crystal films

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Cyanobiphenyl liquid crystals absorb strongly in the ultraviolet. These absorption bands are highly dichroic. The dichroic ratio changes as a function of order parameter and orientation of the liquid crystals. Plots of the dichroic ratio as a function of film thickness demonstrate that the polymer alignment layer not only imposes an orientation on the liquid crystal director but also lowers the order parameter of the liquid crystal near the polymer surface. A sharp decrease in dichroic ratio occurs at film thicknesses near 35 nm, suggesting a phase transition which may be caused by the appearance of a biaxial phase or smectic layering at the air interface. © 1995 American Institute of Physics.

Liquid crystal alignment at a solid interface is a poorly understood phenomenon; however, surface anchoring and alignment of liquid crystals are crucial to all liquid crystal electro-optic applications. The surface order parameter of a liquid crystal at a solid interface has been investigated both theoretically<sup>1-4</sup> and experimentally.<sup>5-7</sup> Surface order parameter has been predicted to be either larger or smaller than the bulk order parameter, depending on models used and boundary conditions. Generally, direct measurements of the surface order parameter have used birefringence measurements near the nematic to isotropic phase transition, and have typically found the surface order parameter to be larger than the bulk.

In this letter we report dichroic ratios for films of E7 of varying thickness on rubbed polyimide-coated quartz plates. The plates were prepared by spin coating a polyimide solution (Du Pont 2555). The plates were then soft baked at 100 °C for 90 s, followed by a hard bake at 200–250 °C for 60 min. Reproducible results were achieved by hand rubbing the plates ten times with a velvet cloth, eliminating the need to machine rub. Liquid crystal films were prepared by spin coating solutions of E7 in hexane on the plates. Thickness was controlled by varying the concentration of the E7 solution (0.05%–4.0%, by weight), as well as the spin speed (2000–4000 rpm).

Absorbances were measured using a Perkin-Elmer λ4B spectrophotometer. Incident light was polarized using an Oriel ultraviolet (UV) linear dichroic polarizer. For each cell, a background correction was performed using the bare, rubbed polyimide-coated quartz substrate, with rub and polarization directions parallel. UV absorbance measurements of the substrate prior to coating with E7 indicated that the rubbed polyimide exhibited a small UV dichroism. After spin coating with E7, absorbance of each cell was measured with the rub direction parallel and perpendicular to polarization. Orientation was varied by rotating the sample, while maintaining horizontal polarization. Figure 1 shows the absorption spectra for parallel and perpendicular orientations of a thin E7 film. Peak absorbances for both orientations were near 290 nm.

Dichroic ratios were calculated using absorbances at 290 nm, corrected for differences in base line absorbance (mea-

sured at 360 nm), as well as for orientational differences in absorbance of the rubbed polyimide. The corrected absorbance at 290 nm ( $A_{290}$ ) is given by:

$$A_{290} = (A_{290 \text{ LC}} - A_{360 \text{ LC}}) - (A_{290 \text{ PI}} - A_{360 \text{ PI}}), \quad (1)$$

where “LC” subscripts refer to the absorbances after coating with liquid crystal, while “PI” subscripts refer to absorbances of bare polyimide-coated quartz. Corrected  $A_{290}$  values were calculated for both parallel and perpendicular orientations for each cell. Dichroic ratios were calculated from the corrected  $A_{290}$  absorbances:

$$R_{290} = A_{290 \parallel} / A_{290 \perp}. \quad (2)$$

Film thickness (or path length)  $L$  was estimated from the isotropic extinction coefficient of E7 ( $\epsilon_i$ ) and the isotropic absorbance ( $A_i$ ) using Beer's law:

$$A_i = \epsilon_i c L, \quad (3)$$

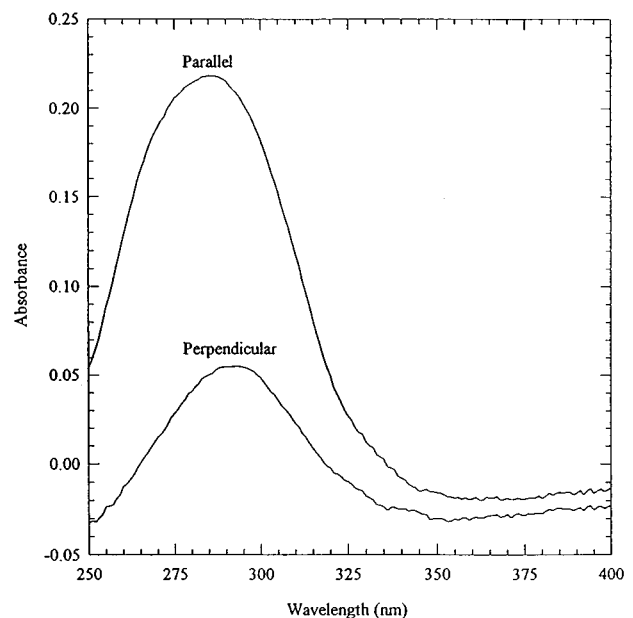


FIG. 1. Parallel and perpendicular absorbance spectra of a thin E7 film.

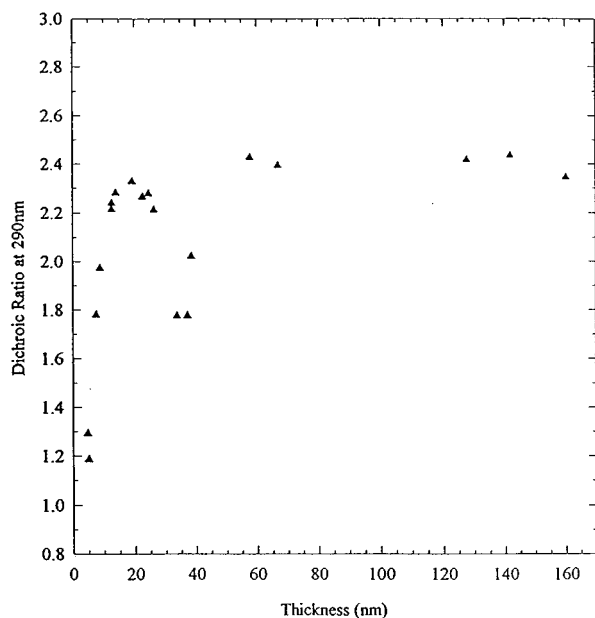


FIG. 2. Dichroic ratio as a function of film thickness for thin E7 films on rubbed polyimide.

where  $c$  is the concentration of E7 expressed in weight fraction units. The isotropic extinction coefficient was determined by measuring UV absorbance of a solution of 0.001% E7 in hexane using a 1 cm quartz cuvette. The measured peak absorbance was 0.645. Since the concentration of E7 in the solution ( $10^{-5}$  in weight fraction units) and the path length (1 cm) are known, the extinction coefficient can be calculated. This gives a value of  $6.45 \times 10^4 \text{ cm}^{-1}$  or  $6.45 \times 10^{-3} \text{ nm}^{-1}$ . Isotropic absorbances of the thin films of E7 on rubbed polyimide were calculated from parallel and perpendicular values:

$$A_{290i} = (A_{290\parallel} + 2A_{290\perp})/3. \quad (4)$$

Since the concentration of E7 layer in weight fraction units is equal to 1, the thickness of the E7 layer can be calculated:

$$L = A_{290i} / (6.45 \times 10^{-3} \text{ nm}^{-1}). \quad (5)$$

Figure 2 shows a plot of the dichroic ratio as a function of film thickness. Since the thinnest films have the lowest absorbance and, hence, lowest signal-to-noise ratio, the uncertainty is highest for thin films. For the thinnest films measured, uncertainty in the dichroic ratio is approximately  $\pm 0.3$ , with an uncertainty of thickness of  $\pm 0.6$  nm. From Fig. 2, we conclude that the dichroic ratio decreases significantly with decreasing thickness below 15 nm. The actual value of the dichroic ratio becomes difficult to estimate below approximately 7 nm. For thicknesses above 10 nm, the uncertainty is small enough to have little effect on the shape of the curve.

The magnitude of the dichroic ratio reflects both the order parameter and orientation of the liquid crystal films. Thick films will homogeneously align at the polyimide layer, and the director will rotate continuously to a perpendicular alignment at the air interface,<sup>8,9</sup> as shown in Fig. 3. For very thin films the elastic energy of the liquid crystal precludes

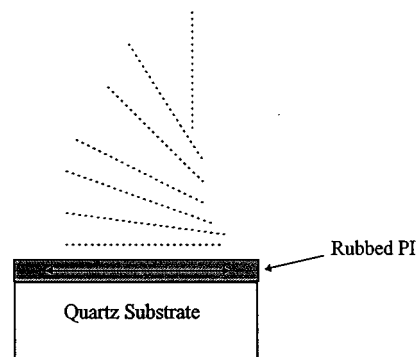


FIG. 3. Schematic of liquid crystal directors in a thin film with homogeneous alignment at polymer interface and homeotropic alignment at air interface.

the nearly  $90^\circ$  rotation of the director required to maintain preferred alignment at both interfaces. If the alignment energy is greater at the air interface, very thin films will adopt a homeotropic alignment. In this case, the dichroic ratio for very thin films would approach 1, in agreement with our experimental results; however, the dichroic ratio should increase steadily with film thickness and asymptotically approach half the value of that for completely homogeneously aligned E7. The minimum value observed near 35 nm cannot be explained using this model.

If the alignment energy at the rubbed polyimide interface is greater than at the air interface, the dichroic ratio would approach a maximum value as the film thickness is decreased, the inverse of what is observed. A decrease in the dichroic ratio for very thin films, however, could result from a decrease in the order parameter near the polyimide interface.

The low dichroic ratio of thin films, as well as the minimum in the dichroic ratio observed for film thicknesses around 35 nm, can be explained by assuming that thin films are homogeneously aligned and have low order parameter. As film thickness increases, the order parameter and, hence, dichroic ratio increase. The low dichroic ratio observed for thin films could also result from a large tilt angle at the surface. A large tilt angle, however, would not explain the observed increase in dichroic ratio with thickness; the tilt angle would remain constant or increase with increasing film thickness. Using the crystal rotation method, we measured a tilt angle of  $2.4^\circ$  for E7 in an antiparallel rubbed Du Pont 2555 polyimide cell. We conclude, therefore, that the thinnest films are homogeneously aligned, with low tilt angle and low order parameter. These results do not allow us to determine whether the low order parameter is maintained at the polyimide interface in thicker films.

A transition at approximately 20 nm allows homeotropic alignment at the air interface. The sharp drop in dichroic ratio near 35 nm indicates that the transition to homeotropic alignment is not analogous to a Fredericksz transition; rather, the steepness of this change suggests some type of phase transition. Recent work on hybrid geometries indicates that it is possible for a nematic liquid crystal to undergo a transition from a uniaxial to a biaxial phase as the thickness of the film is decreased below a critical thickness.<sup>10</sup> The

thickness was estimated to be on the order of 100 Å for typical elastic constants. This prediction is in reasonable agreement with our experimental results, in which the biaxial phase presumably disappears for film thicknesses greater than about 35 nm. Above this thickness, the elastic constants of the liquid crystal could sustain a continuous director transition from homogeneous to homeotropic alignment, as shown in Fig. 3. With increasing thickness, the dichroic ratio would asymptotically approach half the value expected for a film completely homogeneously aligned.

Another possible origin for the sharp drop in dichroic ratio near 35 nm is the formation of surface smectic order at the air interface. Such smectic layering has been observed experimentally in cyanobiphenyl compounds.<sup>11</sup> Assuming that homogeneous alignment is favored for the thinnest films, such a layer would preclude a uniform change from homogeneous to hybrid structure with increasing film thickness. Instead, there would be an abrupt appearance of the homeotropic surface layer, accompanied by an equally abrupt drop in the dichroic ratio. As the thickness of the film increases further, the dichroic ratio would increase, due to increasing thickness of the homogeneous layer. Our results are also consistent with this explanation.

Future work in this area will examine the dichroic ratio versus thickness curve for thin liquid crystal layers on various polymer surfaces to determine whether the trends observed here are common to many surfaces or are peculiar to the particular polyimide surface used in this study. We also intend to study variations in dichroic ratio as functions of surface-induced tilt angle and of rub strength.

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