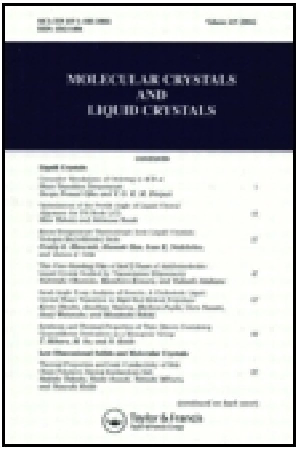

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Surface Electroclinic Effect in a Smectic-A Liquid Crystal

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Version of record first published: 18 Oct 2010

To cite this article: Mark Spector, Brian Weslowski & R. Shashidhar (2004): Surface Electroclinic Effect in a Smectic-A Liquid Crystal, Molecular Crystals and Liquid Crystals, 412:1, 435-442

To link to this article: http://dx.doi.org/10.1080/15421400490431958

Mol. Cryst. Liq. Cryst., Vol. 412, pp. 435/[2045]–442/[2052], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490431958

SURFACE ELECTROCLINIC EFFECT IN A SMECTIC-*A* LIQUID CRYSTAL

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Polar interactions between liquid crystal molecules and cell surfaces give rise to the surface electroclinic effect. This results in rotation of the layer normal away from the alignment direction near the surface and an interfacial region where the molecular director twists from the alignment direction until it reaches the layer normal direction. We have investigated the molecular orientation within the smectic layer using linear and circular dichroism spectroscopy. Contrary to theoretical predictions, the magnitude of the surface electroclinic tilt is relatively temperature independent, while the bulk electroclinic coefficient strongly depends on temperature.

Keywords: eletroclinic; smectic-A; linear dichroism

INTRODUCTION

Rubbing of a polymer film applied to the cell surface is commonly used to align liquid crystals so that the long axes of the molecules near the interface lie along the rubbing direction. In the non-tilted smectic-*A* phase of non-chiral molecules, the alignment direction typically propagates into the bulk, so that the layer normal is parallel to the rubbing direction, resulting in the planar or bookshelf geometry. For chiral molecules in the smectic-*A* phase, application of an electric field parallel to the smectic layers breaks the rotational symmetry about the molecular long axis due to the coupling of the field to the transverse dipole moment and leads to an induced tilt, the electroclinic effect [1]. Nakagawa *et al.* observed a similar symmetry breaking due to surface interactions in a chiral smectic-*A* compound [2]. In this case,

We thank Jawad Naciri for synthesis of the samples used in our studies and S. K. Prasad, J. V. Selinger, and B. R. Ratna for helpful discussions. This work was supported by the Office of Naval Research and the Naval Research Laboratory.

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the surface electroclinic effect resulting from a polar interaction between the liquid crystal molecules and the surface causes rotation of the optic axis with respect to the rubbing direction [2,3]. Subsequent studies on other materials found large rotation angles of 18° [4] and 24° [5].

Detailed experiments using optical second-harmonic generation, confirmed that the molecules anchored at the cell surface are oriented along the rubbing direction, while the optic axis of the bulk is rotated with respect to the rubbing direction by an angle Ψ [6]. The surface electroclinic effect is a localized effect which is restricted to a boundary layer near the cell surface much thinner than the wavelength of visible light [4]. In the interfacial region, the molecular director twists by Ψ from the rubbing axis to the layer normal direction as one moves away from the surface to the interior of the cell as illustrated in Figure 1. Using ellipsometry, Chen *et al.* found that the thickness of the boundary layer, ξ, diverges with decreasing temperature near the smectic-A to smectic-C^* transition [6].

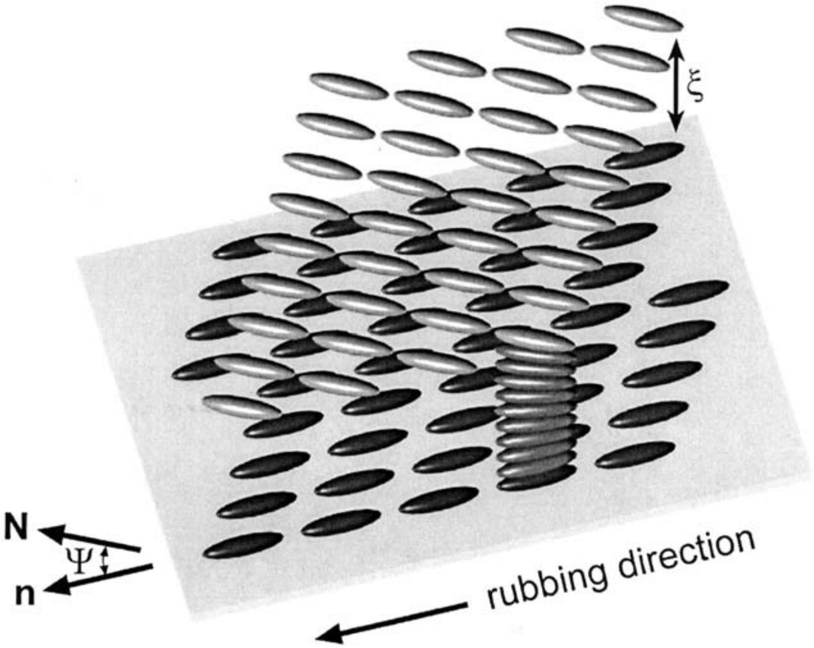

FIGURE 1 Schematic representation of the surface electroclinic effect. At the surface, the molecular director **n** lies along the rubbing direction, while the layer normal **N** deviates by an angle Ψ. In the boundary layer of thickness ξ, the director twists from the rubbing axis until it reaches the layer normal direction, while **N** remains constant. Reprinted from Ref. [7] with permission of the author. Copyright 2000 by the American Physical Society.

We recently reported that twisting in the interfacial region of a chiral smectic-*A* leads to a large peak in the circular dichroism (CD) spectrum of the compound KN125 [7]. These results indicated a significant twist over a wide temperature range in the smectic-*A* phase and had an unusual field dependence of the CD peak magnitude. A decrease in the CD peak magnitude with increasing temperature approximately paralleled the temperature dependence of the bulk electroclinic coefficient. In this paper, we report on detailed studies of the temperature dependence of the surface electroclinic tilt using linear dichroism spectroscopy. Our results indicate that the surface tilt is very weakly temperature dependent in contradiction to theoretical predictions based upon a polar interaction between the surface and the liquid crystals.

EXPERIMENTAL SETUP

The liquid crystal KN125 has the chemical structure shown in Figure 2 and the phase sequence Crystal −29°C–Smectic-*A* −81°C–Isotropic upon heating. The smectic-*A* phase can be supercooled below 25°C for several

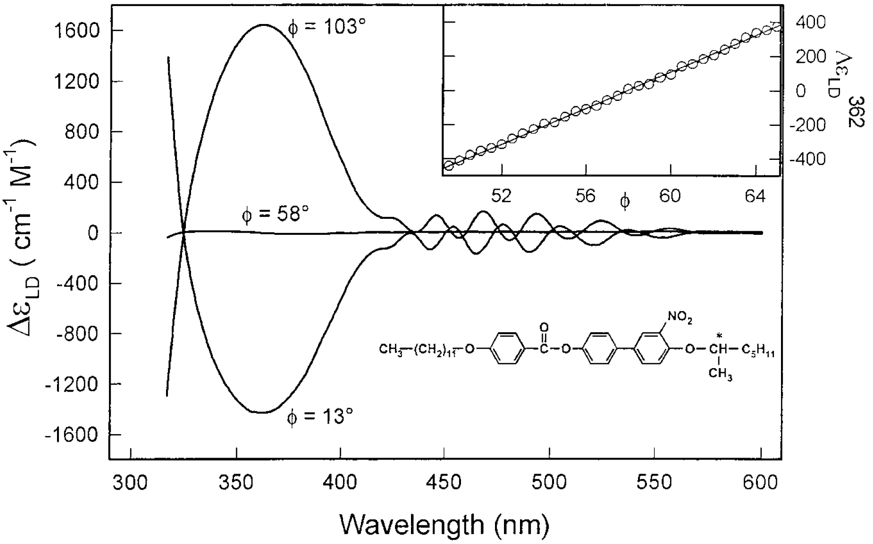

FIGURE 2 Linear dichroism spectra of KN125 as a function of angle of rotation ϕ between the rubbing direction and the optic of the spectrometer. The inset shows the magnitude of the peak at 362 nm as a function of ϕ in the vicinity of the zero crossing. The line is a fit to Eq. (1). The chemical structure of KN125 is also shown with the chiral center indicated by *.

days without crystallization. This molecule exhibits a large electroclinic effect over a wide temperature range [8]. Studies were performed in 2 μm glass cells where only one side has rubed polyimide on it, the other surface being plain conducting (ITO) glass [9]. Cells were positioned in an Instec MK1 hot stage mounted on a motorized rotation stage so that the rubbing direction corresponds to the zero position of the stage.

The stage was set inside a Jasco J-720 spectropolarimeter so that the zero position was parallel to the optic axis of the photoelastic modulator and the rubbed surface faces the incident beam. In this geometry, the measured linear dichroism (LD) is the difference in absorption parallel and perpendicular to the rubbing direction $\Delta\varepsilon_{\mathrm{LD}} \equiv \varepsilon_{\|} - \varepsilon_{\perp}$. If we then rotate the cell by ϕ, the linear dichroism will vary as

$$\Delta\varepsilon_{\mathrm{LD}}(\phi) = \Delta\varepsilon_{\mathrm{LD}}(\Psi)\cos 2(\phi - \Psi) \tag{1}$$

exhibiting a maximum when $\phi = \Psi$, that is where the optic axis of the material is parallel to the optic axis of the spectrometer, and passing through zero at $(\phi - \Psi) = \pm 45^\circ$. Here we have adopted the convention of Shao *et al.* [5], wherein the sign of Ψ is that of $(\hat{z} \times \hat{n}) \cdot \hat{s}$, where $\hat{z}$ is parallel to the optic axis, $\hat{n}$ is along the rubbing direction, and $\hat{s}$ is the surface normal. By this definition, the clockwise twisting of the molecules as one moves away from the surface, as depicted in Figure 1, gives a positive Ψ.

Since the spectropolarimeter relies on an AC modulation of the polarization and subsequent lock-in amplification of the detected signal (at 2ω for LD measurements), it is quite sensitive to small values $\Delta\varepsilon_{\mathrm{LD}}$. Thus, by measuring the angular dependence of $\Delta\varepsilon_{\mathrm{LD}}$ near $\pm 45^\circ$ and fitting it to Eq. (1), we are able to measure relative changes in the optic axis to an accuracy of better than 0.05°. However, the limitations imposed by mounting the cell in the rubbing machine and, subsequently, in the hot stage, resulted in absolute accuracy of ±2°.

RESULTS AND DISCUSSION

The angular dependence of the linear dichroism spectra of KN125 is shown in Figure 2. These spectra were taken on the *R*-enantiomer at 25°C with no applied field. The spectra in Figure 2 reveal a large peak at 362 nm, corresponding to the $n_a \rightarrow \pi^*$ transition of the laterally substituted nitro group [7]. The spectra have the greatest positive amplitude of $1530\,\mathrm{cm}^{-1}\ \mathrm{M}^{-1}$ at $\phi = 103^\circ$ and greatest negative amplitude at 13°. Since the transition dipole is transverse to the long axis of the molecule, a negative peak is expected when the optic axis of the liquid crystal is parallel to the optic axis of the spectrometer, that is $\phi = \Psi$. At an orientation 45° off of the optic axis, $\phi = 58^\circ$, $\Delta\varepsilon_{\mathrm{LD}}$ is nearly zero. The inset of Figure 2 shows the angular dependence of $\Delta\varepsilon_{LD}$ at 362 nm near $\phi = 58°$. The line is a fit of the data to Eq. (1) which gives $\Psi = 13.05°$. Spectra for the *S*-enantiomer show a similar trend, with $\Delta\varepsilon_{LD}$ passing thru zero at $\phi = 33.4°$, giving $\Psi = -11.60°$.

Using this procedure, we are able to obtain the temperature dependence of the surface electroclinic tilt as shown in Figure 3. Here we plot the data for the *R*- and *S*-enantiomer as solid circles and squares, respectively, with the magnitude of the negative tilts of the *S*-enantiomer shown for comparison. Both sets of data show a small, but measurable, decrease in $|\Psi|$ with increasing temperature. While the temperature dependence of the two enantiomers approximately parallels each other, they differ in magnitude by about 1.3°. This is likely due to the uncertainty in mounting the cells as discussed above. The temperature dependence of Ψ, changing by 1.5° between 25 and 75°C, is much weaker than that of the bulk electroclinic tilt at 5 V/μm of the two enantiomers, also shown in Figure 3 as open circles and squares for the *R*- and *S*-enantiomer, respectively.

The surface electroclinic tilt has been calculated by Xue and Clark using an extention of the Landau free energy for the electroclinic effect with the

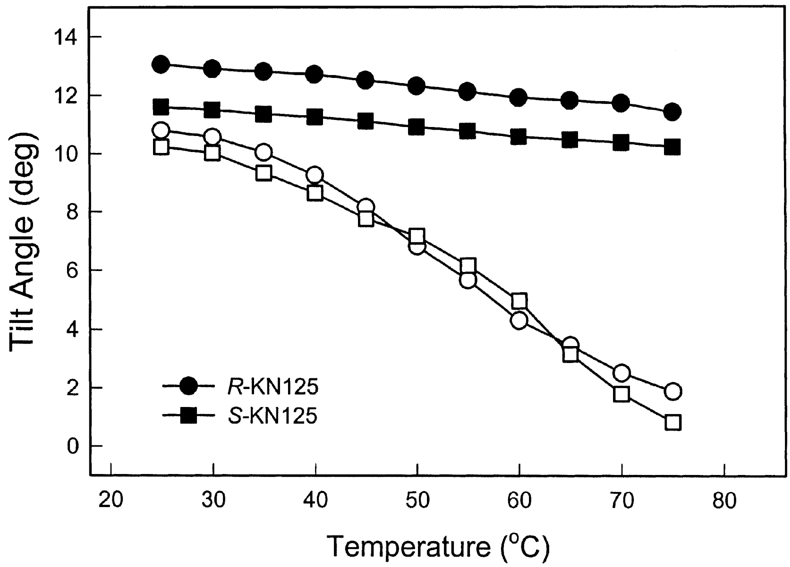

FIGURE 3 Temperature dependence of the surface electroclinic tilt angle (filled symbols) and bulk electroclinic tilt angle at 5 V/μm (open symbols) for *R*-KN125 (circles) and *S*-KN125 (squares). For *S*-KN125, $-\Psi$ is plotted for ease of comparison.

TABLE 1 Comparison of Experimental Measurements of Surface Electroclinic Tilts in Chiral Smectic-*A* Liquid Crystals

	Nakagawa *et al.* [2]	Xue and Clark [3]	Patel, Lee, & Goodby [4]	Chen *et al.* [6]	This work	Shao *et al.* [5]
Liquid Crystal	unspecified	BDH 764E	C121M7	10 S Cl Isoleucine	KN125	W415
Alignment	Rubbed Polyvinyl alcohol	Shearing	Rubbed Polybutylene-terphthalate	Rubbed Polyimide and Nylon	Rubbed Polyimide	Rubbed Nylon
Surface Tilt	4°	$<2°$	18°	7° (Pl) 10° (Nyl)	13°	24°
Thermal Behavior	None	$\boldsymbol{\Psi}$ increases with decreasing T	None	None	None	None

addition of a polar interaction between the surface and the liquid crystals [3]. The bulk electroclinic effect can be described by the free energy [1]

$$F_{\text{bulk}} = \int d^3x \left[\tfrac{1}{2}a\theta^2 + \tfrac{1}{4}b\theta^4 - sE\theta + \tfrac{1}{2}K_2|\nabla\theta|^2\right] \tag{2}$$

where θ is the field-induced tilt angle, K_2 is the twist elastic constant, s is the structure coefficient describing the coupling of the tilt angle to the field [10], and we have already minimized the free energy for the polarization to obtain $P = \chi(E + s\theta)$. This expansion in small θ has been generalized for larger angles [7], but those details are not necessary for this discussion. Minimizing Eq. (2) in the limit of small θ, gives a bulk value of $\theta_B = e_c E$, where the electroclinic coefficient, given by $e_c \equiv s/a \sim (T - T_{AC})^{-1}$, is expected to diverge at the smectic-*A* to smectic-*C** transition. Addition of a polar interaction at the surface, $F_{\text{surf}} = -\lambda P$, to the free energy results in an exponential decay of the tilt away from the surface at $y = 0$,

$$\theta(y) = \theta_B + (\Psi - \theta_B)e^{-y/\xi}, \tag{3}$$

where $\Psi = \lambda/a\xi \sim (T - T_{AC})^{-\frac{1}{2}}$ and $\xi = \left(K_2 \Big/ \sqrt{a^2 + (2sE)^2}\right)^{\frac{1}{2}} \sim (T - T_{AC})^{-\frac{1}{2}}$. Thus, the surface electroclinic tilt is predicted to show a strong temperature dependence, diverging as $\sqrt{e_c}$ near the smectic-*A* to smectic-*C** transition.

In fact, most experiments on the surface electroclinic effect do not show strong temperature dependence, as summarized in Table 1. In addition to the results reported here, experiments on compounds showing even larger surface electroclinic tilts also found nearly constant Ψ over a wide temperature range [4,5]. However, these experiments relied on direct microscopic observations which are not sensitive to small changes in Ψ. It is interesting to note that the only experiment that did report a temperature dependent Ψ used shearing of uncoated cells to align the liquid crystal, rather than a rubbed polymer film, and reported small values of Ψ [3]. Chen *et al.* reported a polymer dependence of the surface tilt with nylon giving larger Ψ than polyimide [6]. Shao *et al.* have speculated that the orientation of the surface layers is locked in when the layers are formed at the isotropic to smectic-*A* transition and is difficult to change as the temperature is lowered further [5]. However, in both their and our experiments the magnitude of the surface electroclinic tilt is close to the maximum saturation value of the bulk electroclinic effect at low temperature. Thus, although the effect is likely due to polar interactions between the polymer film and the liquid crystals, it remains a theoretical challenge to reconcile this with the observed temperature independence of Ψ.

In conclusion, we have measured the temperature dependence of the surface electroclinic tilt using linear dichroism spectroscopy. This technique enables us to accurately determine small changes in Ψ. We find only a weak temperature dependence of the surface tilt, which contradict a simple model of surface polar interactions.

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