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Chiral twisting of a smectic-*A* liquid crystal

M. S. Spector,[1] S. K. Prasad,[1,2] B. T. Weslowski,[1,3] R. D. Kamien,[4] J. V. Selinger,[1] B. R. Ratna,[1] and R. Shashidhar[1]
[1]*Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Code 6950, Washington, D.C. 20375-5348*
[2]*Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India*
[3]*George Mason University, Fairfax, Virginia 22030*
[4]*Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

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Chiral twisting of the molecular orientation within the layer of a smectic-*A* liquid crystal has been investigated using circular dichroism spectroscopy. The results indicate that a rotation of the layers away from the alignment direction is induced by the surface electroclinic effect. This leads to an interfacial region where the molecular director twists from the alignment direction until it reaches the layer normal direction. A theory is presented to explain the observed field and temperature dependence of the circular dichroism.

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I. INTRODUCTION

The addition of chirality to the molecular structure of smectic liquid crystals leads to unique materials properties that have allowed for the development of fast, high-resolution display devices [1]. Molecular chirality results in ferroelectricity in the tilted smectic-C^* liquid crystalline phase [2]. In the nontilted smectic-*A* phase, rotational symmetry about the molecular long axis rules out any spontaneous polarization in the bulk. However, application of an electric field parallel to the smectic layers breaks this symmetry due to the coupling of the field to the transverse dipole moment and leads to an induced tilt relative to the layer normal, the electroclinic effect [3,4]. A similar symmetry-breaking effect can also arise due to surface interactions. Unidirectional rubbing of a cell surface is commonly used to align liquid crystals so that their long axes are along the rubbing direction. In the smectic-*A* phase, the layer normal is also typically parallel to the rubbing direction resulting in the planar or bookshelf geometry. However, Nakagawa *et al.* observed that for a smectic-*A* composed of chiral molecules, the optic axis is rotated with respect to the rubbing direction [5]. This result was attributed to a polar interaction between the liquid crystal molecules and the surface that gives rise to a surface electroclinic effect [5,6]. Subsequent studies on another material found that the rotation angle of the optic axis can be as large as 18° [7].

Detailed studies by Chen and coworkers, using optical second-harmonic generation, found 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 [8]. Taking the optic axis to be parallel to the layer normal in the bulk, this suggests that direction of the layer normal is determined by surface interactions and remains constant as one moves from the surface to the bulk. Thus, unlike the field-induced electroclinic effect that results in a uniform tilt of the director over the entire thickness of the cell, the surface electroclinic effect is a localized effect that is restricted to a boundary layer near the cell surface. This layer is much thinner than the wavelength of visible light, since a uniform optic axis and good extinction are observed when a thick cell is viewed between crossed polarizers [7]. In the interfacial region, the molecular director twists by Ψ from the rubbing axis until it reaches the layer normal direction as one moves away from the surface to the interior of the cell as illustrated in Fig. 1. The thickness of the boundary layer ξ is determined by the correlation length of tilt fluctuations in the smectic-*A* phase. Using ellipsometry, Chen *et al.* found the expected divergence of ξ with decreasing temperature near the smectic-*A* to smectic-C^* transition [8].

In this paper, we use circular dichroism (CD) spectroscopy to directly probe the chiral twist between the surface and bulk states. Circular dichroism is a sensitive measure of the twisted orientation of molecules with an appropriate chromophore in the chemical structure of the molecule. Past studies have found large CD peaks in the ferroelectric smectic-C^* phase and pretransitional effects in the smectic-*A* phase when approaching the smectic-C^* phase [9]. This chiral order arises from helical variation of the azimuthal tilt direction from layer to layer and is observed for light propagating perpendicular, but not parallel, to the smectic layers. The present work represents the first observation of CD due to the chiral order induced by the surface electroclinic effect and is only observed when the light is propagating parallel to

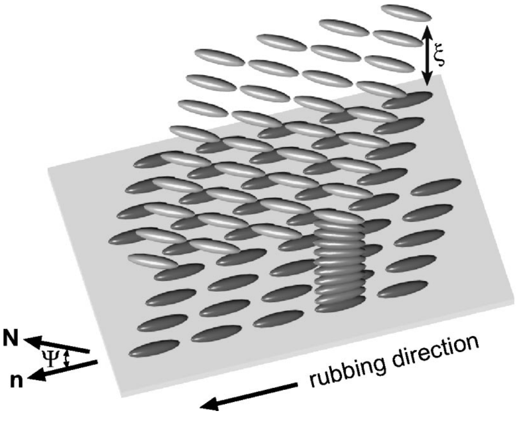

FIG. 1. Schematic representation of the surface electroclinic effect. At the surface, the molecular director **n** lies along the rubbing direction, while the layer normal **N** deviates by an angle Ψ. In the boundary layer of thickness ξ, the director twists from the rubbing axis until it reaches the layer normal direction, while **N** remains constant.

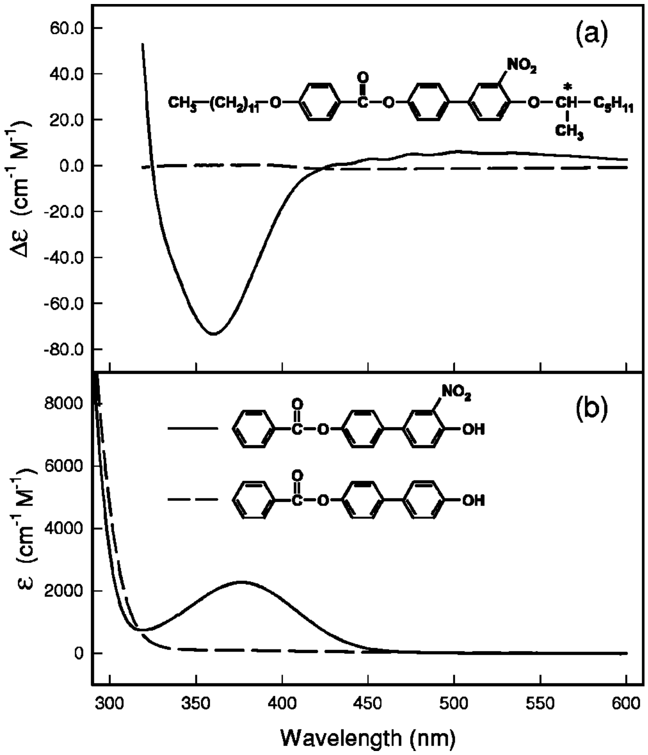

FIG. 2. (a) Circular dichroism of KN125 in planar geometry (solid line) and homeotropic geometry (dashed line). Both spectra were recorded at 25 °C on the (R)-enantiomer with no applied field. The chemical structure of KN125 is shown with the chiral center indicated by $*$. (b) Absorption spectra of precursor compounds HNBB (solid line) and HBB (dashed line) in solution. Also shown are the chemical structure of HNBB, the core of KN125 without the acyl chains, and HBB, the same molecule without the laterally substituted nitro group.

the smectic layers. Our results show the existence of a strong twist over a wide temperature range in the smectic-*A* phase. We have also studied the effect of an applied electric field that shows a complex behavior depending upon the temperature.

II. EXPERIMENTAL PROCEDURE

The liquid crystal used in our studies, KN125, was synthesized using established procedures [10]. The chemical structure of this molecule is shown in Fig. 2. This material exhibits a large electroclinic effect over a wide temperature range [11]. The phase sequence for KN125 upon heating is Crystal – 29 °C – Smectic-*A* – 80 °C – Isotropic. The smectic-*A* phase can be supercooled below 25 °C for several days without crystallizing. CD studies were performed on a Jasco J-720 spectropolarimeter. All data are given in units of molar circular dichroism $\Delta\varepsilon \equiv \varepsilon_L - \varepsilon_R$, where $\varepsilon_{L(R)}$ is the molar decadic absorption coefficient for left- (right-) circularly polarized light (e.g., the ratio of transmitted to incident intensity is $I_t/I_i = 10^{-\varepsilon c d}$, where c is the molar concentration and d is the pathlength in cm).

Studies in the planar geometry were performed using commercial liquid crystal cells (E.H.C. Co., Tokyo) with a nominal cell gap of 2.5 μm. These cells had a rubbed polyimide surface layer and were mounted in an Instec MK1 hot stage. The cells were oriented so that the sample optic axis was rotated by 45° from the optic axis of the polarization modulator in the spectrometer to eliminate artifacts from the inherent birefringence of the sample (see discussion below). A 100 Hz bipolar square wave of variable amplitude was applied to 1 cm^2 ITO electrodes. All fields are given in RMS voltage. For probing the CD along the layer normal direction, a cell having a 12 μm gap and treated with octadecyltrichlorosilane to promote homeotropic alignment (molecules perpendicular to the surface) was used.

III. RESULTS

The CD spectra of KN125 measured in two geometries are shown in Fig. 2(a). These spectra were both taken at 25 °C with no applied field. It was ascertained using optical microscopy that the sample had a uniform optic axis and was in the smectic-*A* phase, with no signs of crystallization. The spectra in Fig. 2(a) reveal a large peak around 362 nm when the molecules are aligned in the planar geometry (solid line), while such a peak is not seen for homeotropic alignment (dashed line). The small wiggles at longer wavelengths are interference effects due to the finite thickness of the sample. Two precursor compounds were also studied to establish the origin of the peak in the CD spectra. The first precursor, denoted HNBB, consisted of the core of KN125 without the acyl chains, and the second, HBB, consisted of KN125 without either the chains or the nitro substitution. Absorption spectra of these compounds in solution, along with their chemical structures, are shown in Fig. 2(b). A broad peak centered near 360 nm appears in the HNBB spectra (solid line) and is absent in the HBB spectra (dashed line). This shows that the peak in the CD spectra at 362 nm reflects an electronic transition related to the laterally substituted nitro group. The wavelength indicates that the $n_a \rightarrow \pi^*$ transition is slightly red-shifted due to coupling of the nitro electronic orbitals to those in the biphenyl group [12]. It should be pointed out that the CD peak shown in Fig. 2 is more than 2000 times larger than the intrinsic CD of KN125 in solution ($\Delta\varepsilon_{355} = -0.035$ cm^{-1} M^{-1} in acetonitrile). Comparison of the CD and UV spectra gives a dissymmetry factor $g \equiv \Delta\varepsilon/\varepsilon = -0.36$.

An important test of chiral phenomena is to study the CD spectra from opposite enantiomers, since any effect that arises purely from the handedness of the molecule, should change sign, but not magnitude, when the chirality of the molecule is reversed. In Fig. 3, we show the CD spectra from both enantiomers of KN125 at 25 °C in planar cells. We clearly see that reversing the molecular chirality leads to a concurrent change in the sign of the CD peak, but no change in its magnitude.

Although this large CD signal implies a twist of the chiral molecules, we have to carefully eliminate all possible experimental artifacts that could be contributing to the CD signal. One obvious problem can be caused by a misalignment of the rubbing directions at the two surfaces leading to a small twist through the cell. We have performed experiments using numerous cells, both commercially obtained and fabricated in house, taking care in each case to see that the rubbing directions at the two surfaces are accurately antiparallel (within 1°). We find the peak magnitude varies by less than

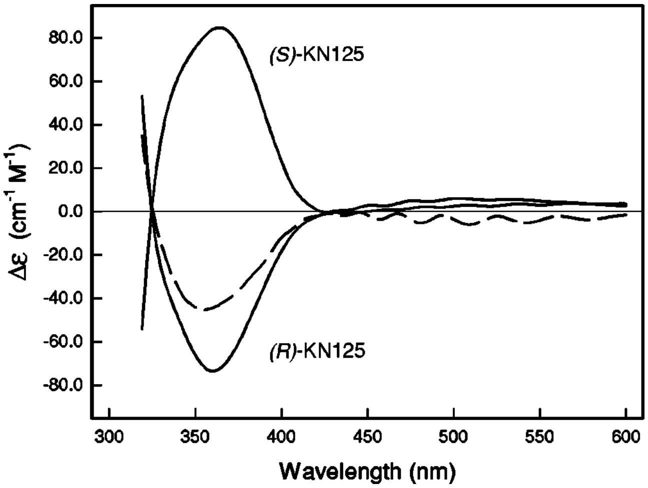

FIG. 3. Circular dichroism from opposite enanatiomers of KN125 in at 25 °C. The solid lines show the spectra from KN125 in cells with an alignment layer on both sides, while the dashed line shows (R)-KN125 in a single-sided alignment layer cell.

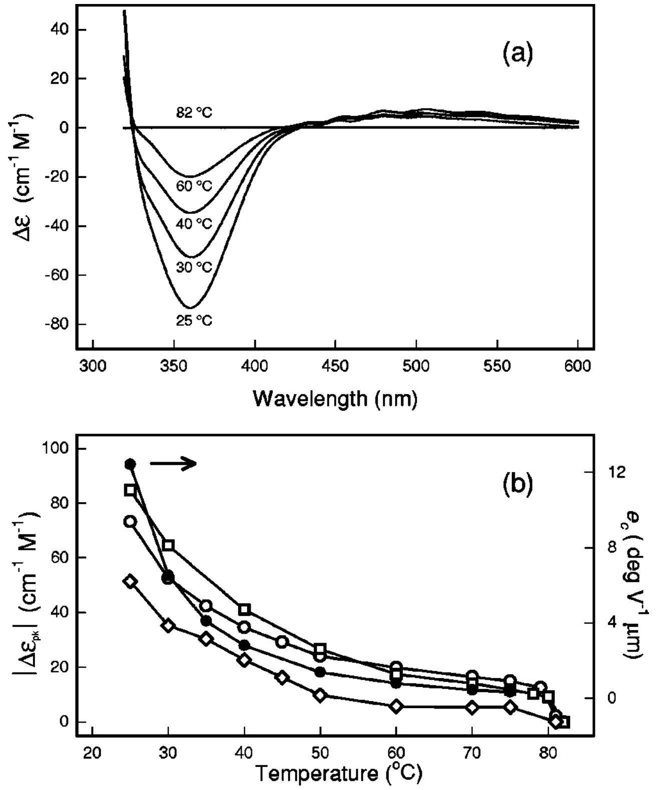

FIG. 4. Temperature dependence of the circular dichroism of KN125. (a) The CD spectrum of the (R)-KN125 at different temperatures in the absence of an applied field. As the temperature increases, the magnitude of the peak decreases and becomes unobservable above the melting temperature. The position of the peak does not change with temperature. (b) The magnitude of the CD peak versus temperature for (R)-KN125 (○) and (S)-KN125 (□) in cells with double-sided alignment and for (R)-KN125 in a single-sided alignment cell (◇). Also shown is the temperature dependence of the electroclinic coefficient (●).

10% between cells under similar conditions (temperature, field, alignment layer). More importantly, we always observe a negative CD peak from the (R)-enantiomer of KN125, while the (S)-enantiomer always gives a positive peak.

Another important factor to consider is the effect of linear dichroism. A number of authors have discussed the difficulties in deconvoluting the linear and circular contributions to signals obtained using polarization-modulation spectroscopy [13–15]. In particular, Shindo and co-workers [15] have elegantly addressed this problem using the Stokes-Mueller formalism [16]. They find that the CD signal measured in a polarization-modulation spectrometer is given by

$$\Delta\varepsilon_{\mathrm{meas}}=\Delta\varepsilon_{\mathrm{true}}+\frac{1}{2}[(\mathrm{LD}')(\mathrm{LB})-(\mathrm{LD})(\mathrm{LB}')]+(\mathrm{LD}'\sin 2\theta-\mathrm{LD}\cos 2\theta)\sin\alpha \qquad (1)$$

where LD (LB) is the linear dichroism (birefringence) with respect to the optic axis of the material, LD′ (LB′) is the linear dichroism (birefringence) with respect to an axis rotated 45° from the optic axis around the direction of light propagation, θ is the angle between the optic axis of the sample and that of the spectrometer, as defined by its optical modulator, and α is an angle representing any imperfections in the optical modulator due to misalignment or residual birefringence. Note that in these units $\mathrm{LD}=\varepsilon_{\parallel}-\varepsilon_{\perp}$ and $\mathrm{LB}=4\pi(n_{\parallel}-n_{\perp})/(c\lambda_0 \ln 10)$, where c is the molar concentration, λ_0 is the vacuum wavelength of the incident light, and $n_{\parallel(\perp)}$ is the index of refraction parallel (perpendicular) to the optic axis. Similar relations hold for LD′ and LB′. The first component of the measured signal is the true CD signal which is independent of θ. The second term is a combination of the linear dichroism and linear birefringence as measured both along the optic axis of the sample and at 45° to it. It is also rotationally independent and is only nonzero for a biaxial sample where $\mathrm{LD}', \mathrm{LB}' \neq 0$. Since we find the linear dichroism at 45° to be at least 10^3 times smaller than that measured along the optic axis, $[(\mathrm{LD}')/(\mathrm{LD}) \lesssim 10^{-3}]$, our sample is approximately uniaxial and we ignore the second term. The final term in Eq. (1) is a rotationally dependent term due to the interaction between a nonideal optical modulator and a sample with linear dichroism. Indeed, we find that the measured CD signal has a small rotationally dependent component which does not change sign when the chirality of the molecule is switched [17]. The angular dependence of this component is consistent with a small misalignment of the photoelastic modulator ($\alpha = 1.1°$).

Shindo *et al.* also consider additional artifacts due to a partially polarizing detector and imperfect harmonic response of a lock-in amplifier [15]. A quartz depolarizer inserted before the detector produces no change in the measured CD ruling out the former. The latter is very difficult to quantify. However, no evidence of such artifacts is seen when an achiral, linearly anisotropic sample is studied. When the sample is aligned so that the optic axis of the liquid crystal is 45° with respect to the modulator, the contribution to the CD due to linear effects is expected to vanish in a uniaxial sample. All measurements discussed in this paper were made in such a geometry.

Having thus eliminated experimental artifacts, we shall now discuss the effect of temperature and applied electric field on the CD spectra. Figure 4 shows the temperature variation of the CD peak in the absence of an applied electric

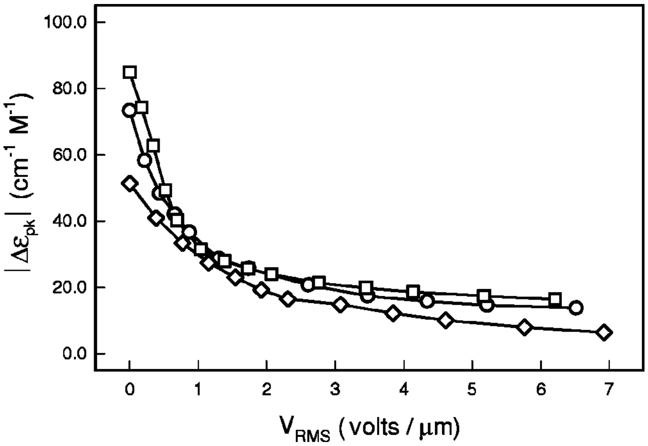

FIG. 5. Field dependence of the circular dichroism of KN125 at 25 °C. The magnitude of the CD peak versus applied electric field is shown for (R)-KN125 (○) and (S)-KN125 (□) in cells with double-sided alignment and for (R)-KN125 in a single-sided alignment cell (◇).

field. CD spectra at five different temperatures are shown in Fig. 4(a) for (R)-KN125. As the temperature increases, the magnitude of the CD peak continually decreases, but its position remains unchanged. This confirms that the observed effect is due to preferential absorption of right-circularly polarized light, as opposed to a preferential scattering effect, where the wavelength of the CD peak is expected to shift with temperature. Figure 4(b) shows the temperature dependence of the CD peak magnitude, $\Delta\varepsilon_{pk}$, for both enantiomers of KN125 at 25 °C with no applied field. We see that both enantiomers show a similar decrease in $\Delta\varepsilon_{pk}$ with increasing temperature. However, the CD peak does not continually vanish as the isotropic transition is approached. Rather, there remains a small remnant value over a wide temperature range in the smectic-*A* phase right up to the melting point.

When an AC electric field is applied across the sample at 25 °C, we also find a change in the magnitude of the CD peak, but not in its position. As the field is increased, the CD peak magnitude continually decreases, as shown in Fig. 5. Both enantiomers show a similar field dependence of the peak CD. However, the CD peak does not completely disappear at high fields. Instead, we find a small residual CD signal at high field ($\Delta\varepsilon_{pk} = -14.7$ at 25 °C, 5.2 V/μm) which is similar to that seen in Fig. 4(b) at higher temperatures and no field ($\Delta\varepsilon_{pk} = -14.9$ at 75 °C, 0 V/μm). This remnant CD indicates the existence of a small twist which cannot be unwound by electric field or thermal effects.

As the temperature is increased in the smectic-*A* phase, the situation becomes more complex. The field dependence of the peak magnitude is shown for both enantiomers at 40 and 60 °C in Fig. 6(a). Near 40 °C, the peak magnitude is relatively field independent (open symbols). At higher temperatures, $\Delta\varepsilon_{pk}$ begins to increase with field, as seen in the data at 60 °C (filled symbols). The temperature dependence of the peak circular dichroism of (R)-KN125 is shown for three different fields in Fig. 6(b). We find significant differences in the temperature dependence of the CD peak at different fields. At zero field, the peak decreases monotonically as the temperature is increased as also shown in Fig. 4(b). At an intermediate field of 2.6 V/μm, the peak CD is relatively temperature independent, while at large field, 5.2 V/μm, the peak initially increases with temperature to a maximum value around 60 °C and then begins to decrease. At all fields the peak goes to zero at the isotropic phase transition. Similar behavior is also seen in the (S)-enantiomer. This complex dependence of the CD on both temperature and field provides further evidence that the observed results are not artifacts due to linear effects, since measurements of the linear dichroism along the optic axis reveal that it is weakly dependent on both temperature and an applied AC field [17].

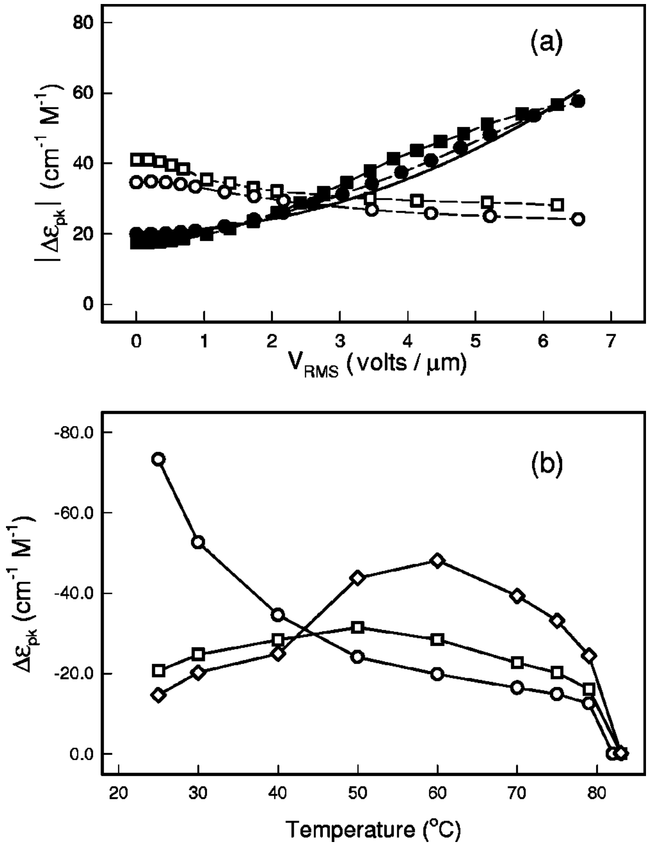

FIG. 6. Field dependence of the circular dichroism of KN125 fields at higher temperatures. (a) The magnitude of the CD peak versus electric field for for (R)-KN125 (○) and (S)-KN125 (□). The open symbols represent data at 40 °C, while the filled symbols are at 60 °C. The dashed lines are guides to the eye, while the solid line represents a fit of the (R)-KN125 data at 60 °C to the quadratic behavior of Eq. (12). (b) Temperature dependence of the magnitude of the CD peak of (R)-KN125 (○) at applied fields of 0.0 V/μm (○), 2.6 V/μm (□), and 5.2 V/μm (◇).

IV. DISCUSSION

A number of possible explanations may describe the origin of the large CD peak observed in the planar, but not homeotropic, geometry. The possibility of experimental artifacts was discussed in detail above. Another possible explanation is in-plane chiral fluctuations of the type proposed by Lubensky, Kamien, and Stark [18]. While the smectic-*A* phase has no macroscopic chiral order, it is possible for the molecular chirality to bias the thermal fluctuations of the molecules giving the system local, or short-range, chiral order. However, since a smectic-*A* cannot support long-range twist deformations [19], these fluctuations can only extend over a few molecules and are unlikely to be responsible for the large enhancement we see in the CD spectra.

Instead, we believe the large chiral effect is due to a twisting of the director induced by the surface electroclinic effect discussed earlier. Here, the polar interactions at the cell wall-liquid crystal interface act like an applied field, causing the molecules to be tilted with respect to the layer normal by an angle Ψ. Since the molecules are strongly anchored by the rubbing, the layer normal is then tilted by Ψ from the rubbing direction as depicted in Fig. 1. The direction of the layer normal established by the surface propagates unchanged into the bulk. The layer normals induced by opposing cell interfaces are rotated in opposite directions since the interfaces are mirror images of each other. This implies that the molecules in the two interfacial regions twist in the same direction so that the net twist induced by the two cell walls is twice that from a single interface. However, this also implies that the layer normal rotates by 2Ψ between the two surfaces. Since uniform twisting of the layer normal is energetically disfavored in the smectic-*A* phase [19], this rotation presumably occurs over a very small distance in a twist grain boundary inside the cell [20]. Patel, Lee, and Goodby observed such defects in thin cells, but not in thicker cells where only one domain was seen [7]. In the thick cells, the observation of a single domain with optic axis not parallel to the rubbing direction was attributed to preferential growth of one of the two possible layer normal directions into the bulk [7]. We observe good optical extinction when the cell is viewed between crossed polarizers with one polarizer aligned along the optic axis and find the optic axis of the sample is rotated by about 10° from the rubbing direction. Interestingly, this 10° offset is similar to the zero field mosaicity measured in x-ray diffraction experiments on the same material [21]. We find that the offset angle changes by less than a degree over the entire smectic-*A* phase.

Further support for the surface electroclinic effect model is obtained by studying a cell with single-sided alignment. Recent work has shown that KN125 can be well aligned in a cell where only one side has rubbed polyimide on it, the other surface being plain conducting (ITO) glass [22]. The thickness of the cell was approximately the same as the double-sided alignment layer cell described earlier. Figure 3 shows the CD spectra from such a single-sided alignment layer cell containing (*R*)-KN125. We find that the CD peak is decreased compared to the double-sided cell, but still quite large. In fact the peak magnitude is slightly larger than half that from the double-sided cell, possibly indicating a reduction in twist at the grain boundary. This observation rules out chiral fluctuations in the bulk as a major contributor to the observed CD, since such fluctuations should only depend on the thickness of the cell and not on whether one or both sides have an alignment layer. We also find the temperature and field dependence of the CD peak in the singled-sided alignment layer cell follows that of the double-sided cell, as shown in Figs. 4(b) and 5, respectively (diamonds).

In order to explain the complex field dependence of the CD spectra with increasing temperature, we consider two temperature regions. At low temperature (~25–35 °C), the CD peak decreases rapidly with applied field, while at high temperature (~50–80 °C), the CD increases with field. In the low-temperature region, the material responds as though it were near the smectic-*A* to smectic-*C** transition. This is also seen in the optical response of KN125, where the electroclinic coefficient e_c is found to increase sharply with decreasing temperature as shown in Fig. 4(b) (solid circles). The divergence of e_c indicates an apparent transition to a tilted smectic phase at ~20 °C, whose occurrence is preempted by crystallization.

Similar pretransitional behavior is also expected to affect the surface properties of the liquid crystal. Near the apparent bulk transition, the surface region should freeze into an ordered phase — either a tilted, chiral smectic phase, with a twist of the molecular director from layer to layer, or the chiral-stripe phase discussed in Ref. [23], with a twist of the molecular director in the smectic layer plane. In either case, the chiral environment of the director should enhance the CD signal compared with the uniform smectic-*A* phase. As the temperature decreases, the penetration depth of the ordered phase into the interior should increase, and hence the CD signal should increase. Indeed, Chen *et al.* confirmed that the size of the interfacial region diverges as the smectic-*C** transition temperature is approached [8]. This is consistent with the result shown in Fig. 4(b) that $|\Delta\varepsilon_{pk}|$ increases sharply as the temperature decreases near the apparent transition. Furthermore, when a voltage is applied across the cell, the twist of the director in the ordered phase should be at least partially suppressed, leading to a decrease in the CD signal [24]. This agrees with the observation in Fig. 5 that $|\Delta\varepsilon_{pk}|$ decreases as the electric field increases in this temperature range. However, the twist in the interfacial region cannot be unwound by the field, leaving a remnant CD at high field.

At high temperature, the behavior should be quite different. In this temperature regime, surface freezing becomes unimportant, and the liquid crystal is purely in the smectic-A phase. For that reason, the chiral twisting of the director should be dominated by the surface electroclinic effect. To find the profile of the electroclinic tilt angle near a surface, we must minimize the free energy subject to the appropriate boundary conditions. The free energy can be written as

$$F=\int d^3x[\tfrac{1}{2}K_2|\nabla\theta|^2-\tfrac{1}{2}a(\mathbf{n}\cdot\mathbf{N})^2-s(\mathbf{E}\cdot\mathbf{n}\times\mathbf{N})(\mathbf{n}\cdot\mathbf{N})]$$

$$=\int d^3x[\tfrac{1}{2}K_2|\nabla\theta|^2-\tfrac{1}{2}a\cos^2\theta-sE\sin\theta\cos\theta], \tag{2}$$

where $\mathbf{n}$ is the molecular director, $\mathbf{N}$ is the layer normal, θ is the tilt angle between $\mathbf{n}$ and $\mathbf{N}$, and K_2 is the twist elastic constant. Note that this free energy is invariant under the symmetries $\mathbf{n}\rightarrow-\mathbf{n}$ and $\mathbf{N}\rightarrow-\mathbf{N}$. The final term represents the bulk electroclinic coupling of the tilt angle to the field, with s known as the structure coefficient [25]. In the limit of small θ, this free energy reduces to the more familiar expression $F=\int d^3x[\tfrac{1}{2}K_2|\nabla\theta|^2+\tfrac{1}{2}a\theta^2-sE\theta]$, plus a constant.

To minimize the free energy, we rewrite it in the form

$$F=\int d^3x[\tfrac{1}{2}K_2|\nabla\theta|^2-\tfrac{1}{4}a'\cos 2(\theta-\theta_0)], \tag{3}$$

plus an irrelevant constant, where

$$a'=[a^2+(2sE)^2]^{1/2}, \tag{4a}$$

$$\theta_0=\frac{1}{2}\arctan\frac{2sE}{a}. \tag{4b}$$

In the bulk, the minimum of the free energy is $\theta=\theta_0$; i.e., θ_0 is the bulk electroclinic tilt. Near a surface defined by $y=0$, the minimum of the free energy is given by the Euler-Lagrange equation

$$-K_2\frac{d^2\theta}{dy^2}+\frac{1}{2}a'\sin 2(\theta-\theta_0)=0. \tag{5}$$

This differential equation is a standard sine-Gordon soliton equation. Because of the surface electroclinic effect, we impose the boundary condition $\theta=\Psi$ at $y=0$, where Ψ is the surface tilt. In the bulk, the boundary condition is $d\theta/dy\rightarrow 0$ as $y\rightarrow\infty$. Solving the Euler-Lagrange equation with these boundary conditions gives the tilt profile

$$\theta(y)=\theta_0+2\arctan\left[\left(\tan\frac{\Psi-\theta_0}{2}\right)e^{-y/\xi}\right], \tag{6}$$

where $\xi=(K_2/a')^{1/2}$ is the tilt correlation length.

In principle, one might want to calculate the CD signal from the tilt profile $\theta(y)$. In practice, however, the CD signal is a complex molecular property that depends on the detailed interactions of the liquid crystal with light. Even without a theory for the optical properties of the molecules, we can say that the CD signal is a chiral optical property that depends on the chiral parameters of the system. From the tilt profile, we can determine how typical chiral parameters depend on the applied electric field. The simplest chiral parameter that one might calculate is the integrated twist

$$Q_1(E)=\int_0^\infty dy\frac{d\theta}{dy}. \tag{7}$$

This integrated twist is fixed by the boundary conditions to be $Q_1(E)=\theta_0-\Psi$. Because the experiment averages over the front and back surfaces of the cell, and over the full period of an AC electric field, it is appropriate to calculate the average chiral parameter

$$\overline{Q_1}(E)=\frac{Q_1(E)+Q_1(-E)}{2}=-\Psi. \tag{8}$$

Note that this chiral parameter is independent of E. However, there are many measures of chirality which can correlate with the CD signal [26]. One possibility, allowed by symmetry, is

$$Q_3(E)=\int_0^\infty dy\left(\frac{d\theta}{dy}\right)^3, \tag{9}$$

which is not fixed by the boundary conditions. From Eq. (6) we find the field-averaged result

$$\overline{Q_3}(E)=\frac{Q_3(E)+Q_3(-E)}{2}=\frac{1}{4\xi^2}[-2\Psi+\sin 2\Psi\cos 2\theta_0]. \tag{10}$$

This result shows that the average chiral parameter $\overline{Q_3}(E)$ is nonzero only when the system has a nonzero surface electroclinic tilt Ψ. This average chiral parameter is nonzero at $E=0$ and grows larger in magnitude as E increases. For that reason, in the high-temperature regime, we expect that an applied field should also give an increase in the CD signal. This is consistent with the experimental results of Fig. 6. Furthermore, we can estimate how much the applied field should increase the CD signal. The result above implies that

$$\frac{\overline{Q_3}(E)-\overline{Q_3}(0)}{\overline{Q_3}(0)}=\frac{\dfrac{1}{\cos 2\theta_0}-1}{1-\dfrac{\sin 2\Psi}{2\Psi}}\approx\alpha E^2, \tag{11}$$

with $\alpha=3e_c^2/\Psi^2$, where $e_c\equiv d\theta_0/dE|_{E\rightarrow 0}=s/a$ is the bulk electroclinic coefficient, and the approximation holds for small θ_0 and Ψ. We have $\Psi\approx 10°$ at all temperatures and $e_c=0.78$ deg $(\mathrm{V}/\mu\mathrm{m})^{-1}$ at 60 °C, and hence we expect $\alpha\approx 0.018$ $(\mathrm{V}/\mu\mathrm{m})^{-2}$. By comparison, the solid line in Fig. 6(a) shows a fit of the 60 °C data to the parabolic form

$$\Delta\varepsilon_{pk}(E)=\Delta\varepsilon_{pk}(0)(1+\alpha E^2), \tag{12}$$

which gives the coefficient $\alpha=0.046$ $(\mathrm{V}/\mu\mathrm{m})^{-2}$. Thus, our simple model gives at least the right order of magnitude for the sensitivity of the CD signal to applied electric field.

Of course, $\overline{Q_3}(E)$ is not the only pseudoscalar measure of chirality. While $\overline{Q_1}(E)$ was independent of E, we could consider

$$Q_1(E;Y)=\int_0^Y dy\frac{d\theta}{dy}. \tag{13}$$

where Y would be the lengthscale over which surface effects modify the smectic order leading to an enhanced CD signal. Because of the nonlinear dependence of $\theta(y)$ on E in Eq. (6), the chiral parameter $\overline{Q_1}(E;Y)$ will depend quadratically on E. Moreover, if $Y\sim\xi$, the coefficient of the quadratic term will have the same order of magnitude as α calculated above. This will be a generic feature of any chiral parameter constructed from $\theta(y)$ – the quadratic coefficient will always be of order e_c^2/Ψ^2, in agreement with the experimental result.

In conclusion, molecular twisting within the layer of a chiral smectic-*A* has been studied using circular dichroism spectroscopy. The results have been discussed in terms of a model based on the surface electroclinic effect. At high temperatures, where the bulk is purely smectic-*A*, an applied field leads to an increase in the chiral parameter Q_3 which can account for the observed field dependence of the CD spectra. At lower temperatures, surface effects enhance the chiral, pretransitional behavior.

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