Abstract

A nematic twist cell, in which the two polymer-coated substrates are rubbed and then rotated by an angle $\theta_0$, results in a strong chiral environment at the surfaces. In the presence of an applied electric field, a combination of the chiral environment and the rub-induced breaking of the $C_\infty$ rotation axis at the surfaces results in a rotation of the molecular director in the substrate plane, viz., a surface electroclinic effect. Using this twist cell geometry, we separate out and quantify the strength of the rub-induced two-fold rotational symmetry from that of the chiral symmetry. Our primary result is that the strength of the mechanically-induced $C_2$ rotational symmetry, which is proportional to the electroclinic response, scales linearly with the rub-induced topographical rms roughness and increases with increasing rubbing strength of the polymer. Our results also suggest that the azimuthal anchoring strength coefficient is relatively insensitive to the strength of the rubbing.
Symmetry plays a central role in many physical phenomena. When two or more symmetries are altered simultaneously, it becomes difficult to quantify the “strengths” of each symmetry individually. Such a case may occur, for example, when a chiral pattern is scribed into a spatially isotropic substrate [1]. The scribing process not only breaks mirror symmetry at the surface, but also breaks the $C_\infty$ rotational symmetry perpendicular to the surface. When the chiral surface is covered with an achiral nematic liquid crystal, an electroclinic effect (ECE) localized at the surface obtains [2,3], whereby the nematic director rotates by an angle $\Delta \theta$ in a plane perpendicular, and proportional, to an applied electric field $E$. But until now it’s been very difficult to separate out the consequences of the rubbing-induced rotationally broken symmetry from the rubbing-induced chiral symmetry, both of which are required for the observation of this phenomenon. In this work we report on an experimental technique that creates the chiral environment using a different approach (a nematic twist cell [4]), which allows us to separate the effects of rotational symmetry breaking from chiral symmetry breaking. In particular, we have quantified the strength of the surface’s two-fold rotational symmetry, which is proportional to the magnitude of the surface electroclinic effect, and find that it scales linearly with the rms surface roughness when the surface is mechanically rubbed (in order to break the $C_\infty$ symmetry). The results demonstrate how one may sort out the individual effects of multiple symmetries acting on a system simultaneously.

Recently we established that a macroscopic mechanical torsional strain can induce molecular-level chirality — actually conformational deracemization — in a configurationally achiral nematic phase [4], thereby giving rise to an electroclinic effect. In that work we fabricated a LC cell in which the rub-induced easy axes were arranged to induce a near 20° twist of the nematic director from one substrate to the other. The resulting director twist couples to
the conformational deracemization of the LC molecules, breaking the symmetry between right- and left-handed molecular conformations and providing a chiral environment throughout — albeit strongest at the surfaces. Our model [4] suggested that the enantiomer excesses $\varepsilon$ in the bulk and $\varepsilon_s$ at the two surfaces are proportional to the imposed inverse helical pitch $P^{-1}$. Using a special optical geometry to account for the director’s helical twist, we measured the surface electroclinic effect in the nematic phase. The susceptibility $d\Delta\theta/dE$, which also is known as the electroclinic coefficient $e_c$, was found to be proportional to the imposed torsional strain, and therefore to the induced chiral strength at the surfaces. But unlike previous methods, this technique [4] allows us to control separately the chiral strength (by changing the imposed twist angle $\theta_0$) and the strength of the two-fold rotation axis (by changing the strength of the polymer rubbing). We therefore adapt this method [4] to control and measure the strength of the rotational symmetry breaking by examining the electroclinic coefficient $e_c$ as a function of rubbing strength for a fixed imposed helical pitch, and thus for a fixed chiral strength.

A twist cell was prepared using indium-tin-oxide (ITO) coated glass substrates that were spin-coated with the planar-alignment agent RN-1175 polyamic acid (Nissan Chemical Industries). The coated substrates were baked for 60 min at 250 °C. The polyimide surfaces then were rubbed with a cotton pile cloth (YA-20-R, Yoshikawa Chemical Co., Ltd.) attached to the cylindrical roller of an Optron rubbing machine, with roller radius $r = 4$ cm. The average length of the cotton fiber was 1.85 mm, the fiber diameter 6.8 µm, and fiber density $\sigma_f = 1411$ threads cm$^{-2}$. The substrate was translated at a speed $s = 0.29$ cm s$^{-1}$ one time ($N = 1$) beneath the rubbing cylinder, which was rotated at $n = 12$ revolutions s$^{-1}$. In order to achieve a continuous variation of the rubbing strength, the slides were tilted under the rubbing cylinder, such that one end of the slides (at $x = 2.8$ cm) was elevated by an angle of $1.2^\circ$ on the bed of the rubbing
machine. The bed then was raised until the tips of the cotton fibers osculated the slides (with no deformation $\delta$ of the fiber pile, i.e., $\delta = 0$) at position $x = 0.25$ cm (near the lower end of the slide); thus from $x = 0$ to 0.25 cm the rubbing strength $n_f = 0$. Here $n_f$ is defined as the number of fibers passing a position of unit width, and is given by $n_f \approx (2r\delta)^{1/2}2\pi Nn r \sigma_f / s$ [Ref. 5]. The fiber pile at the elevated end of the slide was deformed by $\delta = 0.058$ cm, such that $\delta$ varied approximately linearly with position along the substrate. Thus, using this gradient rubbing technique, $n_f$ was made to vary monotonically with $x$.

Two gradiently-rubbed substrates were placed together to form a cell of thickness $d = 5.2 \mu m$, such that their rubbing directions, i.e., their “easy axes”, were rotated in the cell's plane by an angle $\theta_0 = (30 \pm 1)^o$ with a right-handed twist. The cell was filled with a negative dielectric anisotropy phenyl benzoate liquid crystal 9O04, which has a phase sequence on cooling Iso – 86$^o$ – N – 70$^o$ – Sm-A – 62$^o$ – Sm-C – 50$^o$ – Sm-B – 35$^o$ – Cryst and a structure given in Ref. 4.

The optical setup for the ECE experiments, which is based on a modification of the classical electroclinic geometry [6] that accounts for the imposed director twist in the cell, is described in detail elsewhere [4]. An ac electric field was applied across the cell, and the detector output was fed into both a dc voltmeter and a lock-in amplifier that was referenced to the driving frequency $f$. The ac intensity $I_{ac}$, its phase relative to $E$, and the dc intensity $I_{dc}$ were computer recorded as $|E|$ was ramped upward with time over 500 s. Figure 1 shows $I_{ac}/4I_{dc}$ — this corresponds to the field-induced director rotation $\Delta \theta$ at the substrates [4] — at $f = 1000$ Hz for different values of $n_f$. The electroclinic coefficients $e_c$ (at $f = 1000$ Hz) vs. $n_f$ correspond to the slopes of the data in Fig. 1.

The topography of the gradient-rubbed slides was characterized in two ways: i) by measuring the optical retardation (the “form retardation”) of the rub-induced scratches and ii) by
measuring the surface topography using an atomic force microscopy (AFM). Dealing first with
method i, we separated the form retardation $\alpha_{\text{scratch}}$ associated with the scratches from the
molecular component $\alpha_{\text{PI}}$ associated with the alignment of polyimide. To accomplish this,
optical retardation measurements of the substrate in air (which facilitate a measurement of
$\alpha_{\text{scratch}} + \alpha_{\text{PI}}$) and the substrate immersed in the near index matching fluid methyl benzoate
(Fisher Scientific; which measures $\alpha_{\text{PI}}$ only) were performed using a modulated Pockels cell;
details are described elsewhere [7,8]. Figure 2 shows $\alpha_{\text{scratch}} + \alpha_{\text{PI}}$, as well as $\alpha_{\text{PI}}$, as a function of
rubbing strength. Note that the difference between the two quantities at a given $n_f$ corresponds to
the form retardation $\alpha_{\text{scratch}}$. Figure 3a shows the dependence of $e_c$ and $\alpha_{\text{scratch}}$ on $n_f$. We note
that a minimum rubbing strength is required before the onset of grooves; this effectively is a
yield stress [9,10,11].

Images of the rubbed surfaces were made with an Agilent 5500 atomic force microscope.
A Veeco model RTESPPW AFM cantilever/stylus was used in contact mode, where we first
made several images to verify that the stylus made no observable change to the surface
topography. To obtain quantitative roughness data for the scratches at different $n_f$, we
performed scans with a resolution of 1024 pixels and a scanning speed of 0.5 lines s$^{-1}$ over an
area of 90 $\mu$m x 90 $\mu$m. The rms roughness, as well as $e_c$, are plotted vs. $n_f$ in Fig. 3b.

The frequency-dependent surface electroclinic coefficient $e_c$ for the twist-induced
deracemization cell is given by [4]

$$
d\Delta \theta / dE = e_c(\omega) = C e^{-i\omega t} \left[ W_2^o + i\omega \eta K_{22} \tanh \left( 2 \sqrt{i\omega \eta / K_{22}} \right) \right] 
$$

where $C \propto C_{\text{int}} \varepsilon_s$, $C_{\text{int}}$ is a coefficient that reflects both the chiral interactions between the liquid
crystal and alignment layer and the strength of the two-fold rotation axis, $K_{22}$ is the twist elastic
constant, $\eta$ is the twist viscosity, and $\omega = 2\pi f$. At $f = 1000$ Hz the second term in the
denominator of Eq. 1 dominates and \( e_c \propto C \propto C_{\text{int}} \varepsilon_s \) for a given cell thickness and frequency. But as noted in Ref. 4, \( \varepsilon_s \) is proportional to the deviation \( \theta \) of the equilibrium director orientation from the easy axis due to a non-infinite anchoring strength coefficient \( W_2^\phi \), where \( W_2^\phi \) is the coefficient of the surface free energy term quadratic in the deviation of the director’s azimuthal orientation from the easy axis direction [12]. Since \( \theta = -K_{22} \theta_0 / 2 \left( K_{22} + W_2^\phi d / 2 \right) \) [Ref. 4], we find that the electroclinic coefficient \( e_c \propto C_{\text{int}} / \left( K_{22} + W_2^\phi d / 2 \right) \). Taking \( K_{22} = 2.5 \times 10^{-12} \text{ N} \) [Ref. 13] and a typical value of \( W_2^\phi = 5 \times 10^{-6} \text{ J m}^{-2} \) [Ref. 14], we see that the anchoring term dominates the denominator in the expression for \( e_c \), i.e., \( e_c \propto C_{\text{int}} / W_2^\phi \).

Our experimental results demonstrate that the electroclinic coefficient increases with rubbing strength \( n_f \), as shown in Fig. 1. Figures 3a and 3b show that \( e_c \), which is approximately proportional to \( C_{\text{int}} / W_2^\phi \), is proportional to the component of optical retardation \( \alpha_{\text{scratch}} \) due to the rub-induced striated surface, as well as to the rms topography itself. Turning to the factors \( W_2^\phi \) and \( C_{\text{int}} \) separately, there is ample evidence from the literature that \( W_2^\phi \) is not strongly sensitive to rubbing strength. Oka, et. al.15 observed a sharp increase in \( W_2^\phi \) for very weak rubbing (corresponding to \( n_f \) approximately one-tenth of the smallest nonzero value used in our experiment), above which \( W_2^\phi \) is almost constant with increasing rubbing strength. Likewise, using an atomic force microscope to scribe a polymer alignment layer, Rastegar et al. showed that \( W_2^\phi \) is nearly independent of the vertical scribing force for fixed line separation [16]. The low \( n_f \) saturation of \( W_2^\phi \) [Ref. 15] suggests that the polymer’s orientational order parameter at the surface saturates for weak rubbing. But Fig. 2 shows that the optical retardation \( \alpha_{\text{pol}} \) due to only the alignment of the polymer backbone (but not the surface corrugations) rises slowly with
increasing rubbing strength, apparently saturating at large $n_f$. The continued increase of $\alpha_{PI}$ with $n_f$ in Fig. 2 suggests that the interior of the polyimide layer is being heated toward the glass transition temperature [17], and therefore becomes ordered more deeply into the layer with increasing rubbing strength. This results in an increasing integrated birefringence $\alpha_{PI}$ with increasing $n_f$, although not an increase in $W_2^\phi$.

Thus, assuming that $W_2^\phi$ in our experiment is approximately constant, we can conclude that $e_c$ is proportional to $C_{int}$. We note that the two-fold rotation axis $C_2$ about the normal to the interface becomes a $C_\infty$ in the absence of an easy axis at the substrate. In consequence, in the absence of rubbing, and therefore in the absence of the $C_2$ axis, the symmetry is too high to support an electroclinic effect, and $C_{int}$ and $e_c$ vanish (Fig. 3b). The appearance of an easy axis when the alignment layer is rubbed breaks the $C_\infty$ rotation, allowing for a nonzero electroclinic coefficient. The apparent scaling of $e_c$ with both the form retardation $\alpha_{scratch}$, which is proportional to the depth of the scratches, as well as to the rms roughness — these represent the same physical phenomenon (grooves) — suggests that strength of the $C_2$ symmetry breaking is proportional to the groove depth. In principle such a result could have been obtained by varying the rubbing strength on an inherently chiral alignment layer, although no such report exists in the literature. Another possible approach would involve using an inherently chiral liquid crystal at a variably-rubbed achiral alignment layer. But in this case any surface signal would be overwhelmed by the large bulk electroclinic effect. The only extant result that examines the surface ECE vs. rubbing strength comes from our group, where we scribed a chiral pattern into a polyimide alignment layer using an atomic force microscope [1]; this chiral pattern simultaneously served as the easy axis for orientation. There we found that the surface ECE increases with increasing scribing force, although the technique could not distinguish between
the effects of scribing on the chiral strength and on the strength of the two-fold symmetry axis (i.e., the easy axis) contribution. The present method, on the other hand, facilitates this distinction. Here the chiral strength at the surface depends principally on the director deviation $\theta$ from the easy axis, which by polarizing microscope observations was found to vary little with rubbing strength due to the near constant $W_2^\rho$. Thus the $n_f$ dependence of our surface ECE derives primarily from the strength of the rubbing-induced two-fold symmetry axis, where $C_{\text{int}}$ is approximately proportional to the rms surface roughness induced by rubbing.

In summary, we have examined the surface nematic electroclinic effect as a function of rubbing strength. We found that above a minimum rubbing strength — this is effectively a yield stress — grooves are created. These striations break the $C_\infty$ rotational symmetry at the surface, which in conjunction with the chiral symmetry induced by the imposed director twist creates a sufficiently reduced symmetry to facilitate a surface electroclinic effect. The strength of the ECE was found to be proportional to the roughness of the topography associated with easy axis grooves. A consequence of this proportionality is that the azimuthal anchoring strength coefficient $W_2^\rho$ is nearly constant with rubbing strength, consistent with reports in the literature.

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Figure Captions

Fig. 1. The intensity ratio $I_{ac} / 4I_{dc}$ vs. applied electric field for five different values of the rubbing strength $n_f$ listed in the legend. The lines represent linear fittings.

Fig. 2 Retardation in air $\alpha_{\text{scratch}} + \alpha_{\text{PI}}$ and in liquid $\alpha_{\text{PI}}$ (red solid circles) vs. rubbing strength $n_f$, after subtracting the background retardation at $n_f = 0$

Fig. 3 (a) Left axis: The electroclinic coefficient $e_c$ (blue solid squares) vs. rubbing strength $n_f$. Right axis: The groove retardation $\alpha_{\text{scratch}}$ (red solid circles) vs. $n_f$. (b) Left axis: $e_c$ (blue solid squares) vs. $n_f$. Right axis: The rms roughness (red solid circles) vs. $n_f$. Error bars for $e_c$ and the rms roughness are shown.


