

## Helix unwinding of doped cholesteric liquid crystals

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By introducing benzoyl–benzene into a cholesteric liquid crystal, the helix unwinding voltage was reduced. This reduction was roughly proportional to the concentration of the dopant and was present for driving frequencies across the audio spectrum. It is believed that this voltage reduction is primarily due to a perturbation of the intermolecular coupling in the liquid crystal mixture. It was found that so long as the long-range order was not destroyed, the helix unwinding voltage could be reduced by as much as 24% at 60 Hz. © 2001 American Institute of Physics.  
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Bistable cholesteric liquid crystal displays (LCDs) are characterized by high driving voltages. This makes the application of cholesteric LCDs to high information displays difficult. In this study we examine the possibility of reducing the unwinding voltage by partial destruction of the order parameter, which was accomplished by the use of additives to the liquid crystal. In addition, we also examined the physics of adding such dopants by fitting the data to empirical theories.

Helix unwinding of cholesteric liquid crystals was first studied theoretically by de Gennes and Prost<sup>1</sup> and by Meyer.<sup>2</sup> Experiments on long-pitch cholesteric liquid crystals subsequently confirmed the predictions that the pitch diverged logarithmically at the critical field and the cholesteric–nematic phase transition was observed. The influence of the anchoring energy and the cell thickness on the helix unwinding process was also revealed in the cano-Grandjean disclination experiment.<sup>3</sup> The minimization of free energy favors the nematic phase if the thickness is less than the unperturbed pitch.<sup>4</sup> For the parallel-plates configuration, the unwinding actually occurs below the critical  $d/p$  ratio. Above this ratio, the cholesteric will develop a periodic pattern or isolated fingers.<sup>5,6</sup> At an ac electric field, the problem becomes complicated since ion segregation cannot be neglected, especially for liquid crystals of negative dielectric anisotropy.<sup>7,8</sup> The critical voltage exhibits a dispersive characteristic in the frequency domain and it is lower than the unwinding and Frederick transition voltages. It is known as the Carr–Helfrich effect, which prevails in nematic and cholesteric liquid crystals.<sup>9,10</sup>

At the cholesteric–nematic phase transition, Baessler *et al.* concluded that, based on Debye's theory, the phase transition was caused by the interaction between the electric field and the permanent molecular dipoles. The frequency dependence is given by<sup>11,12</sup>

$$E_U^2(\omega) = E_U^2(0) \left( 1 + \frac{\omega^2}{\omega_r^2} \right), \quad (1)$$

where  $E_U(0)$  is the root mean square (rms) unwinding field at zero frequency and  $\omega_r$  is the dipole relaxation frequency.

In this letter, we show that, contrary to Baessler *et al.*'s results, the helix unwinding voltage saturates at high frequency, with a smooth maximum at several hundred Hz. This characteristic cannot be simply extended by Hurault's treatment.<sup>10</sup> The spectral reflectivity and the frequency dependence of the unwinding field were studied as a function of nonmesogenic dopant concentration. We shall use de Gennes and Prost's result adapted for the electric counterpart,<sup>1</sup> and the corresponding dc unwinding field is given by

$$E_U(0) = \frac{\pi^2}{p_0} \sqrt{\frac{4\pi k_{22}}{\Delta\epsilon}}, \quad (2)$$

where  $p_0$  is the unperturbed pitch,  $k_{22}$  is the twist elastic constant, and  $\Delta\epsilon$  is the dielectric anisotropy. Since the space charge effects are central to the electrohydrodynamic instabilities and the helix unwinding, the following empirical relation that has the Lorentzian term is suggested to fit the experimental data:<sup>13</sup>

$$V_U(\omega) = \frac{V_U(0)}{\zeta} \left( \frac{\zeta + \omega^2\tau^2}{1 + \omega^2\tau^2} + \frac{\omega\kappa}{\sqrt{1 + \omega^2\kappa^2}} \sqrt{\frac{\zeta + \omega^2\tau^2}{1 + \omega^2\tau^2}} \right), \quad (3)$$

where  $\zeta$  is a dimensionless quantity and it depends on the material properties of the liquid crystal mixture whereas  $\tau$  and  $\kappa$  are empirical time constants associated with the unwinding. These are consistent with the hydrodynamic relaxation of the helix unwinding at which at least two time constants are necessary for the experimental fitting. Since the pitch is independent of the order parameter, the elastic constant and dielectric anisotropy expressed in order parameter  $S$  are<sup>3</sup>

$$k_{22} = L_1 S^2, \quad (4)$$

$$\Delta\epsilon = \Delta\epsilon_{\max} S,$$

where  $L_1$  is a constant determined by the Landau–de Gennes equation and  $\Delta\epsilon_{\max}$  is the anisotropy at the perfect alignment stemming from the polarizability of molecules. They do not depend on the driving ac frequency. By combining Eqs. (2) and (4), the dc unwinding field becomes

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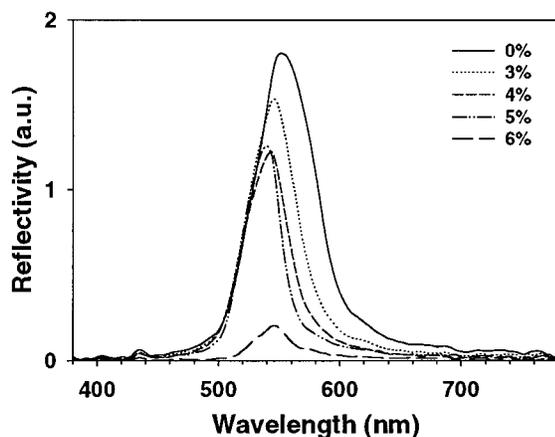


FIG. 1. Spectral reflectivity of 4  $\mu\text{m}$  planar cholesteric doped at different concentrations of benzophenone.

$$E_U(0) = \frac{\pi^2}{p_0} \sqrt{\frac{4\pi L_1}{\Delta\epsilon_{\text{max}}}} \sqrt{S}. \quad (5)$$

Equations (3) and (5) are the main results that we want to confirm experimentally. In addition to being physically interesting, Eq. (5) provides a means of reducing  $E_U$ . One can reduce the helix unwinding voltage simply by reducing the order parameter. However, the order parameter should not be reduced so much that the liquid crystal property is also destroyed. So there should be an optimal value of  $S$ .

The effect of varying order parameter on the helix unwinding voltage was studied experimentally using standard sample cells. The LC cell was made with unrubbed polyimide, which was spin coated on ITO glass with a pretilt of about  $2^\circ$ . The cell gap was approximately 4  $\mu\text{m}$ . The undoped cholesteric mixture was made by dissolving 24.8 wt% of left-handed S811 chiral molecules to nematic mixtures ZLI-6204 (positive dielectric anisotropy) from Merck. Benzoyl-benzene (benzophenone) of 99% purity was mixed with the cholesteric as the dopant.

First, the effect of the dopant on the reflectance spectrum was measured. For this measurement, the doped cholesteric cell was aligned at an oblique angle to the incident rays. A commercial xenon lamp system with good collimation and a PR650 spectrophotometer were used. The spectral data were collected at a small angle offset from the principal reflection direction. This was important in order to minimize the effect of Fresnel reflections at air-glass interfaces. The incident angle was about  $10^\circ$ . A high voltage pulse at 1 kHz was used to reset the samples to the planar state first. A long delay time was allowed to make sure that there was no slow long time constant relaxation before the measurement was taken.

The results are plotted in Fig. 1. It can be seen that the reflection peak for the undoped case is at about 550 nm. This peak shifts to shorter wavelengths as the doping concentration increases. The reflectivity and full width at half maximum (FWHM) spectral width are also reduced. However, at about 5% doping concentration, the reflectivity ceases to change before it drops abruptly at higher concentration. The peak in the latter case shows only a slight variation. The percentage change in the peak reflectance wavelength is given by<sup>1,3</sup>

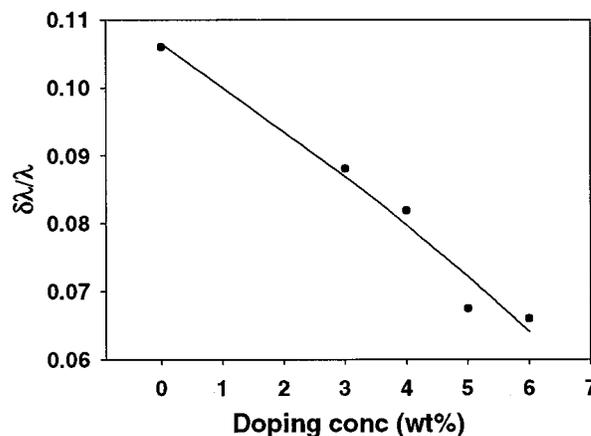


FIG. 2. Ratio of the FWHM to the reflection peak vs the doping concentration of benzophenone.

$$\frac{\delta\lambda}{\lambda} = \frac{\Delta n}{\langle n \rangle}, \quad (6)$$

where  $\lambda$  and  $\langle n \rangle$  are the reflection peak and average refractive index, respectively. This relation does not depend on the apparent pitch.

Figure 2 shows the relative spectral shift as a function of doping concentrations. A systematic trend can be observed. On the other hand, since the variations of reflectivity and reflection peak follow a similar pattern from 0% to 5%, it can be deduced that the apparent pitch actually changes with the doping concentration. This implies that the average refractive index plays a minor role in comparison with the apparent pitch. Therefore, it is direct confirmation that the birefringence is influenced by the dopant.

The frequency dependence of the transmittance in the cross polarization geometry was also measured. A laser beam at 543.5 nm was used to monitor the transmittance every second as the ac voltage was gradually increased. The null point in transmittance was determined as the unwinding voltage and was confirmed under an optical microscope. The behavior of the cholesteric-nematic phase transition observed under the microscope at different frequencies was quite interesting. At low frequency, the distorted helical structures are observed as vibrating energetically as the field approaches the critical value. The helical axes lie effectively in plane. Helix unwinding begins at the spacers and the nematic phase grows from there. At several hundred Hz, the motion of domain boundaries becomes nonuniform. In this case, the helix unwinding undergoes two stages. The initial stage is similar to that at low frequency but the nematic phase is not homogeneous. Distorted helical structures that resemble an isolated fingerprint texture coexist and are unwound from the finger-like tips.

At high frequency, the helical structure vibration and the motion of domain boundaries are not noticeable. Stable topological textures such as closed-loop and isolated fingerprint-like textures coexist and are readily unwound as the field increases. Saturation in unwinding voltage was obvious at high frequency. The actual cause of this saturation and the smooth bump were not clear although we believed that it should be due to the ion segregation and the non-Newtonian viscous flow gradient in the deformed elastic me-

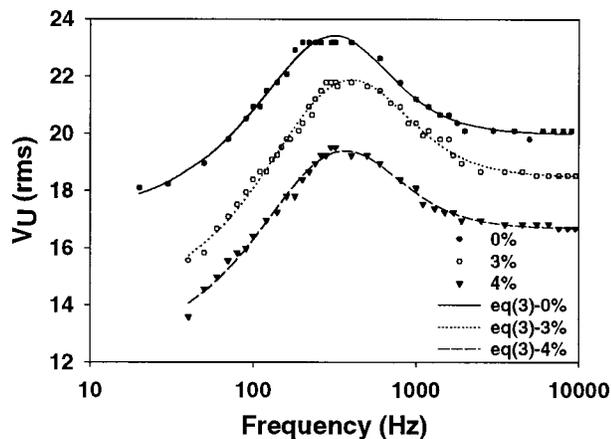


FIG. 3. Frequency dependence of the rms helix unwinding voltage at different benzophenone concentrations in wt %.

dium. Usually, they are significant at low and intermediate frequencies. At the unwinding voltage, the deformation and flow gradient are so large that the perturbation approaches breakdown and the interplay of these effects will make the frequency dependence intricate.

In Fig. 3, the rms unwinding voltage was plotted as a function of the ac field frequency with different concentrations of benzophenone. The lines (solid, dotted, and dashed) were theoretical fits using Eq. (3). It can be seen that the agreement with data and theory is good. The values of the parameters used in the fitting procedure are listed in Table I. The shapes of the curves in Fig. 3 are very similar. Physically, the reduction in the unwinding voltage can be explained as follows. The nonmesogenic dopant, such as benzophenone, which does not exhibit the nematic phase but has a rod-like structure, effectively screens the intermolecular coupling between liquid crystal molecules and thus reduces the long-range order. This effectiveness depends on the steric and the dipole-dipole interactions, which essentially determine the quasinematic order of the cholesteric phase.<sup>3</sup> These interactions can be easily upset by doping with the nonmesogenic compounds. Voltage reduction, low frequency rolloff, and high frequency saturation have also been ob-

TABLE I. Fitting parameters for the frequency dependence of helix unwinding voltage.

	$V_U(0)$ (V)	$\zeta$	$2\pi\tau$ (ms)	$2\pi\kappa$ (ms)
0%	17.033	2.706	2.299	3.389
3%	13.954	2.510	1.524	4.034
4%	12.300	2.475	1.737	4.479

served in 4-benzyl-biphenyl, diphenyl-2-pyridymethane, and triphenyl-triazine. In addition, the cholesteric phase is destroyed in all the doped cases when the dopant concentration is greater than about a few percentage. Therefore, we conclude that this phenomenon is attributed to a reduction of the order parameter.

Figures 1 and 3 are important in determining the appropriate amount of dopants to reduce the helix unwinding voltage. From Fig. 1, it is concluded that the doping concentration should not be higher than 5%, at which point the reflectivity of the cholesteric liquid crystal display has decreased by almost 25%. From Fig. 3, it can be seen that at 4% doping concentration, the unwinding voltage is reduced by 15% at typical operation frequencies and more than 24% at lower frequencies. This is a significant reduction for bistable cholesteric displays where  $6 \text{ V}/\mu\text{m}$  is typical for the helix unwinding voltage. For a  $6 \mu\text{m}$  cell, the unwinding voltage becomes 24 instead of 36 V.

In summary, we have derived a formula that relates the order parameter and the helix unwinding voltage in a cholesteric liquid crystal. The frequency dependence is also obtained. These formulas agree quite well with experimental observation. The reduction in unwinding voltage of doped cholesteric was attributed to a perturbation in the order parameter. Its extent depended on the structural and chemical properties of the doping chemicals. For benzophenone, it was shown that a small concentration of 4% could produce a sizeable change in the unwinding voltage.

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