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Dynamics of polymer-dispersed cholesteric liquid crystals

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Abstract. — We have studied the electrooptic properties of droplets of cholesteric liquid crystal dispersed in a polymer. Application of AC electric fields to the droplets leads to a conversion of the droplet from a nonreflecting to a selectively reflecting appearance. When the field is suddenly switched on, the switching times are found to decrease strongly with increasing field strength, with increasing temperature and with decreasing drop size. For the switching off process, both switching times and microscopic textures indicate that two different relaxation processes can occur, depending on the applied voltage and on the drop size.

1. Introduction.

Polymer-dispersed nematic liquid crystals (PDLC), which have proved to be suitable for electrooptic display applications, have been extensively investigated during the last decade [1]. This idea has been extended by Crooker and Yang [2], who have recently invented a display using polymer-dispersed cholesteric liquid crystals (PDCLC). This new device provides switching between two states of different reflectivity. However, unlike nematic PDLC displays, there is also a color effect.

In the PDCLC display, chiral nematic (i.e., cholesteric) materials with negative dielectric anisotropy and high chirality are used. If the pitch $p$ is sufficiently small, these substances are known to exhibit a strong selective reflection in the visible wavelength range [3] according to the equation

$$
\lambda = np
$$

(1)

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(\(n\) is a mean refractive index), provided that the helix structure is uniformly oriented and that the sample is observed along the helix axis. If cholesteric materials are dispersed as small droplets in a polymer matrix, anchoring causes a planar director orientation everywhere at the droplet surface. This surface orientation leads, in turn, to a complicated configuration of the director field. Thus, in the absence of a field, such droplets do not show selective reflection. However, for materials with negative dielectric anisotropy, application of an electric field causes a reorientation of the cholesteric structure to a uniform orientation of the helix axis along the field direction. Consequently, the display shows a bright selective reflection if sufficiently high voltages are applied.

The director configurations occurring in cholesteric droplets have been studied earlier by microscopic investigations of dispersed chiral liquid crystals exhibiting large pitch [4-10]. The observation of characteristic fingerprint textures indicates a configuration known as the Frank-Pryce model [4, 5]. Application of both magnetic [7, 8] and electric fields [9, 10] has revealed a reorientation of the director field inside the droplets under the influence of the field.

This paper focuses on experimental determination of the dynamic behaviour of the electrooptical switching in PDLC samples. Using the same material as reported in reference [2], we investigate the dependence of the switching times on applied voltage, temperature and droplet size. In sections 3.1-3, we describe measurements of the intensity of reflected light \(\text{versus}\) time if step voltages are applied to the sample. Section 3.4 contains some complementary microscopic observations.

### 2. Experiment.

The material under investigation consists of 50.0 % (by weight) poly-(vinylbutyral) (PVB; Aldrich, U.S.A.), 22.0 % chiral monomer CE2 (British Drug House, Great Britain) and 28.0 % of the wide temperature range nematic mixture ZLI 2806 (Merck, Germany) exhibiting negative dielectric anisotropy.

Samples were prepared by first mixing the components together with chloroform. Glass spheres with a diameter of either 9.7 \(\mu m\) or 31.2 \(\mu m\) were added to define the sample thickness. A glass slide coated with an electrically conducting ITO layer was covered by the mixture and the chloroform was allowed to evaporate for several hours. Then, the sample was heated to 130 °C in order to complete the evaporation of the solvent and the sample was covered by the second ITO-coated glass slide. In order to obtain drops of uniform size, the sample was cooled down from 130 °C to 90 °C with a cooling rate ranging from \(-3 °C/\text{mn}\) to \(-0.01 °C/\text{mn}\). The appearance of cholesteric droplets was observed at about 105 °C. Depending on the cooling rate, drop diameters between about 4 \(\mu m\) (for fast cooling) and about 32 \(\mu m\) (for slow cooling) were obtained.

The temperature of the sample was regulated using a pulsewidth controlled PID thermostat (Instec/Apple IIe) with an accuracy better than ±0.01 K. The sample was observed in reflection using a Zeiss Universal microscope with crossed polarizers. A Jarrel Ash monochromator and photomultiplier were connected to the microscope tube in order to measure the reflected intensity spectrum or the intensity at constant wavelength \(\text{versus}\) either field strength or time. 1 kHz alternating voltages were used throughout; reported voltages are rms values.

### 3. Results.

Under the influence of ac electric fields, our samples selectively reflect at the wavelength given by equation (1). Typically, we observed a spectral halfwidth between 40 and 50 nm for
the reflection peak. The spectra have been previously published [2, 11]. The dependence of the reflectivity on the field strength shows a threshold behaviour. Above the threshold \( E_0 \), the reflectivity increases continuously until reaching saturation at \( E \approx 2 \times 3 \times E_0 \). The threshold voltage \( E_0 \) was found to decrease with increasing temperature — from 28 V/9.7 \( \mu \)m at 67.3 °C to 20 V/9.7 \( \mu \)m at 95.0 °C for \( c_{\text{chiral}} = 22.0 \% \) CE2. The cholesteric pitch of our material — and thus the selective reflection wavelength — also decreases with increasing temperature. Reported intensities were measured at the respective wavelength of maximum reflectivity.

3.1 EFFECT OF FIELD STRENGTH. — In order to investigate the dynamic behaviour, we have measured the reflected intensity \( I \) at the selective reflection wavelength versus time \( t \) after a constant ac voltage is suddenly applied to the sample (Fig. 1, inset). We find that \( I(t) \) is well fit by a sum of two exponentials:

\[
I(t) = I_0 + \Delta I [x e^{-\tau_1 t} + (1 - x) e^{-\tau_2 t}] .
\] (2)

The two switching times \( \tau_1 \) and \( \tau_2 \) are plotted versus the rms value of the applied voltage in figure 1. Both time constants decrease exponentially with increasing voltage. For field strengths between 20 V/9.7 \( \mu \)m and 60 V/9.7 \( \mu \)m, this dependence is approximately described by the relation

\[
\log \tau \propto -E ,
\] (3)

as shown by the straight line in figure 1. The appearance of two relaxation times has also been observed in nematic droplets [12] where they are due to reorientation of the director field in the bulk of the droplet and movement of disclinations at the drop surface, respectively. Chiral droplets undergo a texture change, however, and we have not yet identified two unique processes.

![Graph showing switch-on time versus field strength](image)

**Fig. 1.** — Switch-on time versus field strength for \( T = 95 \) °C, \( \lambda = 452 \) nm. \( I(t) \) is fit by a sum of two exponential functions (inset, solid lines), so that the behaviour of the sample is described by two time constants for each voltage. Solid lines are straight line fits to equation (4).
The results for the switching off process are shown in figure 2. The inset shows the intensity versus time for initial turn-off voltages of $E = 25 \text{ V/9.7 } \mu\text{m}$, $35 \text{ V/9.7 } \mu\text{m}$, and $50 \text{ V/9.7 } \mu\text{m}$. We note, however, that only the lower voltage range is reasonably fit by exponentials (solid lines in inset). For $E > 50 \text{ V/9.7 } \mu\text{m}$, $I(t)$ was found to exhibit negative curvature at the switch-off time. In order to compare the switching times for different voltages, the switch-off times in figure 2 are therefore the times for the reflectivity to return to 10% of its original value, irrespective of curve shape.

![Figure 2](image)

**Fig. 2.** — Switch-off times $\tau_{off}$ (where the intensity returns to 10% of its initial value) versus field strength for $T = 95 ^\circ\text{C}$, $\lambda = 452 \text{ nm}$. In contrast to the switch-on process (Fig. 1), $I(t)$ is fit by exponentials only for $E < 50 \text{ V/9.7 } \mu\text{m}$ (inset). For $E > 50 \text{ V/9.7 } \mu\text{m}$, $I(t)$ has negative curvature at the switch-off time.

3.2 **TEMPERATURE EFFECTS.** — Temperature increases the switching times (measured at $E = 50 \text{ V/9.7 } \mu\text{m}$) by about two orders of magnitude as the temperature is reduced within the cholesteric temperature range (Fig. 3). The temperature dependence of the switch-on time constants $\tau_{1,\text{on}}$ and $\tau_{2,\text{on}}$ (Eq. (2)) is well described by an Arrhenius equation according to the relation

$$\ln (\tau_{i,\text{on}}) \propto \frac{\varepsilon_i}{k} T,$$

where the activation energy $\varepsilon_i$ depends on the applied electric field strength. From figure 3a, we obtain the activation energies $\varepsilon_{1}/k = 27.8 \text{ K}$ and $\varepsilon_{2}/k = 25.9 \text{ K}$ from the slopes of $\ln \tau_{1,\text{on}}$ and $\ln \tau_{2,\text{on}}$, respectively.

When the field is switched off, we find different curve shapes for $I(t)$, depending on the temperature. For lower temperatures, $I(t)$ is fit by a single exponential, with a time constant $\tau_{off}$. $\tau_{off}$ exhibits an Arrhenius temperature dependence (Fig. 3b, solid line) with a slope similar to that obtained for $\tau_{1,\text{on}}$ and $\tau_{2,\text{on}}$. For higher temperatures ($T > 95 ^\circ\text{C} \rightleftharpoons T^{-1} \approx 2.72 10^{-3} \text{ K}^{-1}$), $I(t)$ is not exponential and the relaxation times can be very slow. From
these experiments and from the results reported in section 3.1, we conclude that two different relaxation mechanisms exist. The occurrence of the slow mechanism at high temperatures may not be an intrinsically thermal effect, but rather due to the dependence of other parameters, such as the threshold field $E_0$, on temperature.

3.3 DROP SIZE EFFECTS. — Different drop sizes were obtained for the same sample cell by cooling the sample from $130 \, ^\circ C$ to $90 \, ^\circ C$ with different cooling rates. Time constants (measured for field $150 \, V/31.2 \, \mu m$) tend to increase with increasing drop diameter $D$ for both the switch-on and the switch-off processes (Fig. 4). These dependencies do not follow any obvious mathematical rule, such as $\tau_{i, on} \propto D^2$, as might be expected from a purely diffusive process. For the switch-off process, $I(t)$ again shows two time dependences, with the very slow mechanism occurring for $32 \, \mu m$ droplets.

3.4 MICROSCOPIC OBSERVATIONS. — Microscopic observations reveal that the selective reflection originates from a uniformly oriented region in the center of the droplet with its helix axis oriented along the field direction (Fig. 5a). The diameter of these regions grows with
increasing field strength. This observation is in agreement with microscopic investigations on large cholesteric droplets with a pitch of several μm [9, 10].

For small droplets, the dynamics of the reflectivity change corresponds to a reversible growth and shrinkage of the oriented region in the drop center. The material at the periphery of the drop is not, however, oriented by the field. For large droplets, we observed that high field strengths can orient the entire drop, including the surface region. For these droplets the selectively reflecting appearance is quite stable from a few seconds up to several minutes (depending on the drop size and the field strength) after the voltage is switched off. After this time, a non-reflecting region appears in the center of the drop while it is still selectively reflecting at the periphery (Fig. 5b). This droplet configuration seems metastable: after some randomly determined time, the droplet texture undergoes a complete reorganization and returns to the spheralitic texture. This slow relaxation process corresponds to those cases where \( I(t) \) has negative curvature just after the switch-off time.

4. **Summary and conclusions.**

Our results demonstrate the influence of the parameters field strength, temperature and droplet size on the dynamic behavior of the electric field effect in cholesteric droplets confined in small spherical cavities in a polymer matrix. Previous investigations [9] on the static behaviour of such droplets have shown that the director configuration within larger droplets with large cholesteric pitch is described by the spherulite model [4] which is characterized by planar anchoring at the droplet surface. In these previous studies, the same materials (but different compositions) were used as in the system reported here and the ratio between the drop diameter \( D \) and the pitch \( p \) was similar \( (D/p \sim 50 \, \text{μm}/5 \, \text{μm}) \) to that of our samples \( (D/p \approx 5 \, \text{μm}/300 \, \text{nm}) \). Therefore, the director configuration in our droplets is most likely described by the same model. In agreement with previous investigations [9], the selective reflection occurring in our samples under the influence of electric fields is due to the appearance, in the center of each droplet, of a helicoidal structure with the helix axis parallel to the field. On increasing voltage, the diameter of this reoriented region grows continuously with increasing field strength.

Fig. 4. — Influence of the drop diameter \( D \) on the switching times \( \tau_{1, \text{on}}, \tau_{2, \text{on}} \) and \( \tau_{\text{off}} \) for \( E = 150 \, \text{V}/31.2 \, \text{μm} \).
Fig. 5. — (a) Textures of relatively small droplets at moderate field strength: the central regions exhibit a uniform planar texture which become continuously smaller when the voltage is switched off. (b) Texture of large drops about 10 min after switching off a high voltage ($E = 100 \, V/31.2 \, \mu m$). Some of the larger drops show an inverse relaxation process: a non-planar oriented region appears in the center, while at the outside of the drop the helix axis remains oriented parallel to the former field direction.

We have shown that the switch-on times for polymer-dispersed chiral droplets is reduced by high voltages, high temperature, and small droplet diameters. The intensity versus time curve can be well described by a double exponential function, and the temperature dependence of the time constants is described by an Arrhenius relation. However, for the switch-off process,
both intensity measurements and microscopic investigations indicate that two different relaxation mechanisms can occur. For small droplets and small voltages the reorientation to the spherulitic texture proceeds inward from the surface of the droplet. For large droplets, high voltages can induce a director configuration which is metastable when the external field is removed. In this case the reorientation starts from the center of the droplet. We conclude that in the first case a persisting boundary layer at the polymer/liquid-crystal interface is not affected by the field and can initiate the relaxation, while in the second case high field strengths cause change of the director field in the entire volume of the drop. This leads to an extremely slow relaxation for high electric field strengths.

With respect to display applications, our results indicate that small droplet sizes and high temperatures favour fast switching. Concerning the applied field strength, compromises have to be found: high voltages hasten the switching on process, but too high voltages can cause very long switch-off times. On the other hand, PDLC displays may be interesting as storage devices due to their very slow relaxation at low temperatures.

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