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Behaviour of polymer dispersed cholesteric droplets with negative dielectric anisotropy in electric fields

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The behaviour of chiral, polymer dispersed cholesteric liquid crystals with negative dielectric anisotropy in electric fields has been studied for a system with large cholesteric pitch (several μm) using polarizing microscopy. A uniformly oriented region appears in the centre of the droplets for voltages above a threshold voltage. We find that the radius of this region increases exponentially with increasing field strength, while the threshold voltage decreases with increasing drop diameter and with increasing pitch. Investigation of the dynamics reveals a single step mechanism with a time constant of a few seconds when a field is suddenly switched on. The switch-off process is more complex and much slower.

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1. Introduction

Polymer dispersed nematic liquid crystal droplets have been extensively studied during the last decade owing to their suitability for electro-optic display applications [1]. Recently, however, it has been shown that chiral polymer dispersed droplets also have promising applications. Such chiral droplets with small pitch and negative dielectric anisotropy show electro-optic colour effects [2, 3] and can be used to produce switchable colours. These effects are due to the cholesteric material in the droplet being transformed from a non-selectively reflecting to a selectively reflecting helicoidal texture [4] by applying an electric field.

Emulsions of cholesteric droplets having a large cholesteric pitch (several μm) have been extensively studied for many years [5–10]. These systems do not reflect visible light selectively, but exhibit characteristic fingerprint textures when viewed between crossed polars. The spacing between the fingerprint lines corresponds to half the pitch [8]. Earlier studies have been devoted to an analysis of the director configuration for different boundary conditions at the droplet surface [5–8] and to the behaviour of cholesteric droplets under the influence of magnetic fields [7, 9]. Recently, Yang and Crooker [10] have investigated the influence of electric fields on droplets with a large diameter (50–70 μm) and with a pitch of several μm. These large droplets show many of the characteristics of smaller ones and so form a suitable model system for the investigation of the physical principles of the chiral polymer dispersed liquid crystal display.

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The aim of the present paper is to study the behaviour of large cholesteric droplets in electric fields in more detail. Results concerning the influence of droplet size, cholesteric pitch, and applied voltage on the director field are presented. Some qualitative results on the dynamics of the reorientation are also given.

2. Experimental

Samples consisted of a mixture of 47·3 per cent (by weight) of the negative dielectric anisotropy nematic mixture ZLI 2806 (E. Merck, Darmstadt) [11], 2·7 per cent chiral CE2 (Merck Ltd, Poole), and 50·0 per cent poly-(vinyl-butyral) (PVB). The components were mixed together with chloroform, then placed on an electrically conducting slide where the chloroform was allowed to evaporate partially at room temperature. The sample thickness was established with 31·2 μm diameter glass spheres or 72 μm thick Mylar spacers. After complete evaporation of the chloroform at 130°C, the sample was covered by a second conducting slide. In order to obtain large cholesteric droplets, the samples were cooled from 130°C to 80°C at 0·02°C min^{-1}. Phase separation between the monomer and the polymer started at about 115°C.

In order to study the influence of the cholesteric pitch, a sample with a chirality gradient was constructed. For this purpose a contact preparation was made in which two nematic mixtures (50 per cent ZLI-2806, 50 per cent PVB) were prepared, one of which was chiralized by the addition of 0·34 per cent of the highly chiral additive (*S*,*S*)-1,2-Di-phenyl-1,2-bis-[4′-{4″-(4‴-heptylcyclohexyl)-benzoyloxy}-benzoyloxy]-ethane (DL47) [12]. These mixtures were placed next to each other on a slide and allowed to mix partially before the chloroform had completely evaporated. The resulting sample had a pitch gradient which varied from 3 μm on one side of the sample to infinity at the other.

The sample temperatures were controlled to within 0·01°C by a computer controlled PID thermostat (Instec). The samples were observed in transmission between crossed polarizers using a Zeiss Universal microscope. All of the applied voltages were 1 kHz; the reported voltages are rms values.

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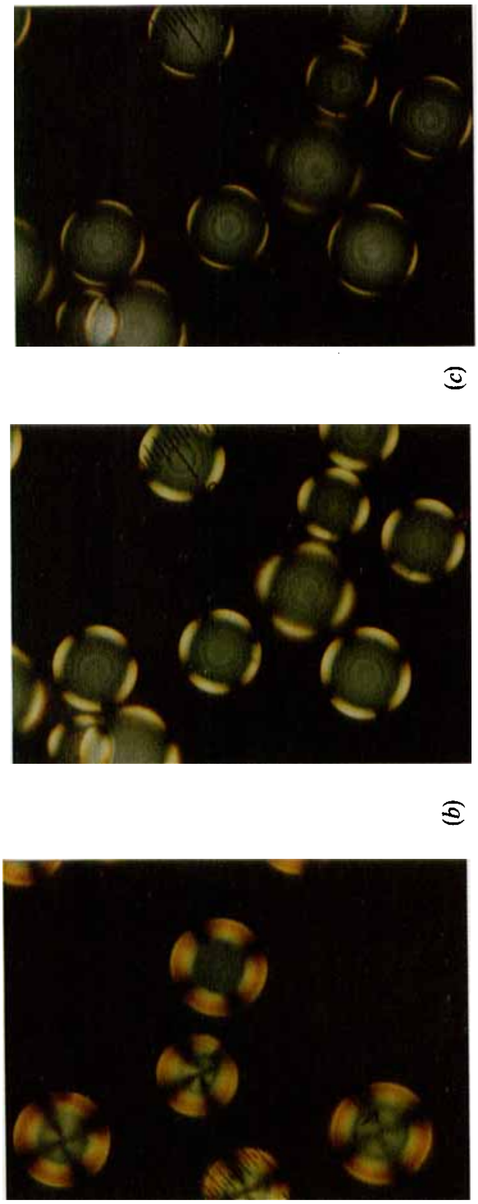
3. Results

3.1. *Statics*

When the electric field was absent, droplets displayed characteristic spherulitic fingerprint patterns (see figure 1 (*a*)). In agreement with earlier results [10], the fingerprint lines either formed spirals without any disclination line, or concentric circles with a disclination line extending along a single radius perpendicular to the direction of observation. These patterns indicate that the director configuration of the droplets in the field-off state corresponds to the Frank–Pryce model [5, 6]. In this model, the pitch axes are everywhere radial and topological conflicts are resolved by a single $s=2$ disclination line extending radially from the centre to the surface. The spiral pattern is a result of looking along the disclination line; the concentric pattern occurs when looking perpendicular to it [8].

Figure 1. Cholesteric droplets for different voltages in a sample containing 2·7 per cent CE2, 47·3 per cent ZLI 2806, and 50·0 per cent PVB (80·0°C, sample thickness 31·2 μm). (*a*) $U=0$: the drops show fingerprint lines with half-pitch spacing; (*b*) $U=30$ V: Uniform region of the radius *r* appears at the droplet centre. (*c*) $U=50$ V: *r* increases with increasing voltage.

Figure 5. The appearance of the drops after about 15 s after a voltage of 50 V is suddenly switched off (the sample shown in figure 1.)



(a) (b) (c)

Figure 1.

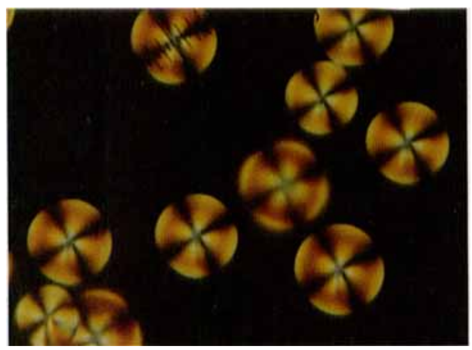


Figure 5.

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When an AC field is applied, a uniform grey region appears in the centre of each droplet (see figures 1 (*b*) and (*c*)). By analogy with small-pitch cholesteric droplets, which show selective reflection in the central region, we conclude that the structure is helicoidal (planar), with the director always perpendicular to the field and the helix axis aligned along the field direction. This is the most stable orientation for materials with negative dielectric anisotropy in electric fields.

The radius r of the central region increases with increasing voltage in a step-like fashion (see figure 2). Starting from zero voltage, no change is noticed until the voltage exceeds a threshold U_{step}. Above this threshold, r increases by steps, with step size equal to half a pitch. Each step corresponds to the disappearance of one fingerprint line and a rotation of the director pattern at the periphery of the central region by 180°. Figure 2 shows the variation of r with the voltage for four different drops of total radius R. By varying the cooling rate, it was possible to grow droplets with R between 26 μm and 55 μm. As determined from the distance between fingerprint lines, the pitch for these drops was 2·9 μm. Although there is as yet no theory for the behaviour of r with U, reasonable fits to the function

$$r(U)=R[1-\exp(-(U-U_0)/U')] \tag{1}$$

were obtained, as seen by the solid lines in figure 2. Both the threshold voltage U_{step} and the fitting parameters U_0 and U' decrease with increasing drop size. The results for U_{step} and U' are shown in figures 3 (*a*) and (*b*). Note that there is some hysteresis between the curves for increasing field (on) and decreasing field (off).

For droplets oriented with their radial disclination lines perpendicular to the field direction, a change in the radius of the central region was accompanied by a tangential movement of the disclination line. The direction of motion could be either clockwise or counter-clockwise in different droplets, but the motion for a particular droplet was opposite for the field-on and field-off processes. Also, for the same droplet the direction of disclination motion was reproducible as the field was cycled on and off. This memory

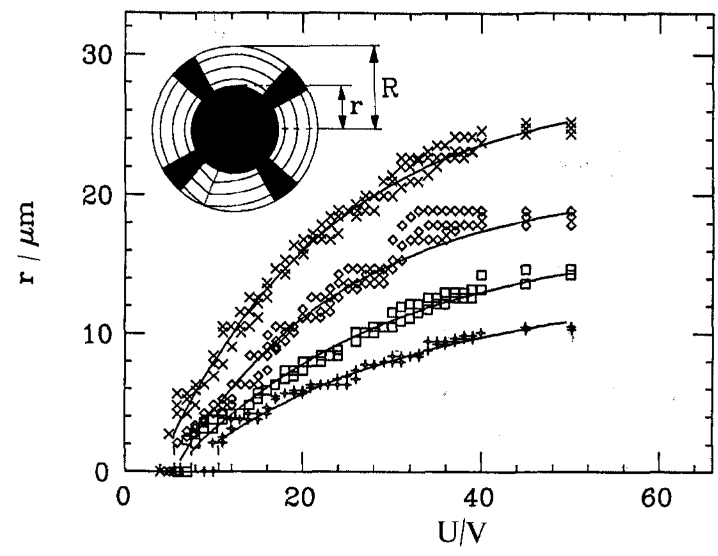

Figure 2. The radius r of the field-induced central region versus voltage U for different drop radii R. The solid lines are fits to equation (1) R: (×) 28 μm, (◇) 21 μm, (□) 17 μm, (♦) 13 μm.

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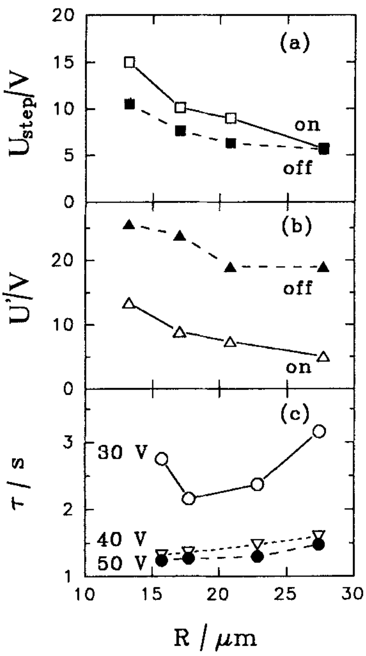

Figure 3. The dependence of various drop parameters on the droplet radius R. (*a*) U_{step}. On (off) refer to increasing (decreasing) voltages. (*b*) U' (see equation (1)). (*c*) Switch-on time (see equation (2)).

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effect may be due to the fact that at the highest field ($E = 60\,V/31{\cdot}2\,\mu m$) a small non-oriented layer persisted at the droplet surface. If this layer retained its orientation direction on the droplet surface, that direction could determine the orientation in the volume of the drop when the field is reduced.

Tangential motion of the disclination line was also observed in the sample containing CE2 as well as for large chiral concentrations ($p \leqslant 3\,\mu m$) in the contact preparation containing DL47. For small chiral concentrations in the contact preparation, however, a different behaviour was observed. When the spacing between the fingerprint lines was large (greater than about one fifth of the droplet radius), an increase of the radius of the central region caused the spacing between the unconverted fingerprint lines in the remainder of the droplet to decrease. This pitch compression was not accompanied by any transverse motion of the disclination line and appears to be driven by the strength of the boundary conditions between the central and outer regions of the drop. The effect of pitch on the behaviour of r with U is shown for two pitches in figure 4. A complete study of the dependence of $r(U)$ on the pitch has not yet been made, but from figure 4, a doubling of the pitch has caused U_{step} and U_0 to decrease by about 50 per cent and U' to decrease by about 40 per cent.

3.2. *Dynamics*

In order to investigate the dynamics of switching, step voltages with different amplitudes were applied to or removed from the sample. The switch-on process is characterized by a continuous growth of the reoriented region in the centre of the droplets, as we have described. The switch-off process, however, is found to exhibit a more complex three-step mechanism. In the first step, the uniform central region

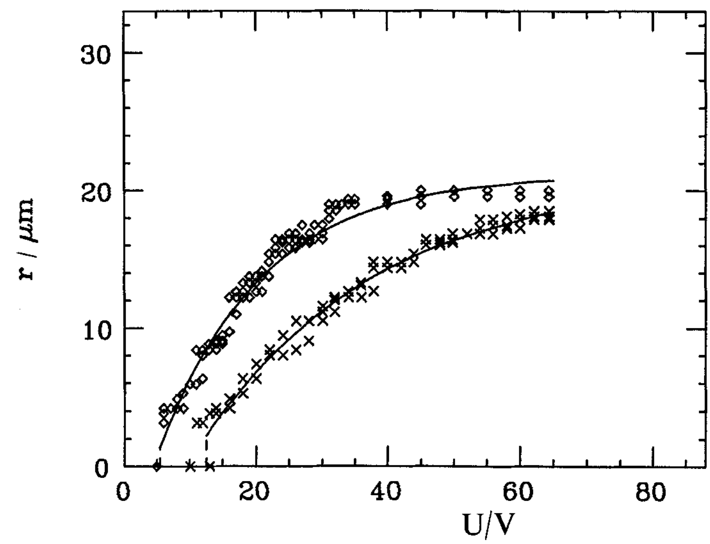

Figure 4. Radius r of the field-induced central region versus U for droplets with different values of pitch. Solid lines are fits to equation (1) P: (◇) 6·3 μm, (×) 3·4 μm.

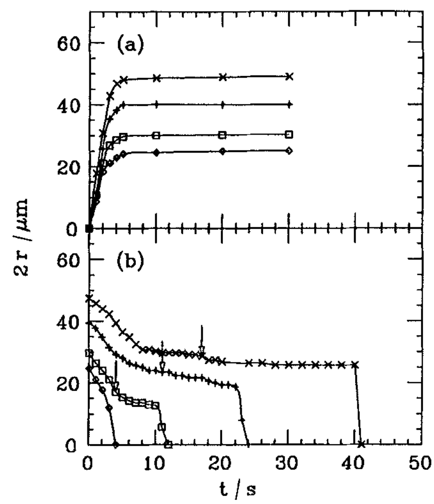

Figure 6. The diameter of the field-induced oriented region versus time for a step voltage of 40 V for the sample described in figure 1. (a) U_{on}, (b) U_{off}.

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shrinks, i.e. the radius r becomes smaller. In the second step, before r becomes zero, a reorientation of the central region to a metastable state takes place (see figure 5). In this state, the outer shell, which shows the usual characteristic fingerprint lines and radial disclination line, is clearly separated by a wall from the inner central region. The central region appears bright, shows no fingerprint lines and no disclination, but has a maltese cross at its centre. This intermediate state of the droplet may persist for several seconds or even up to several minutes. Finally, in the last step, the central region reorients suddenly, the wall collapses and the fingerprint lines return, and the disclination line eventually becomes extended completely to the centre of the droplet.

The variation of the radius of the central region with time is shown in figure 6 (*a*) for the switch-on process and in figure 6 (*b*) for the switch-off process. Note that both processes are made faster by an increase of the switched voltage, and that the switch-on process is always much faster than the switch-off process. For the switch-on process, the temporal dependence of the central region radius was well-fitted by a single exponential of the form

$$r(t) = R[1 - \exp(-t/\tau)]. \tag{2}$$

Here τ is a function of both R and the switch-on voltage U and is displayed in figure 3 (*c*). In general, τ decreases with increasing voltage, especially below 40 V. Above 40 V, τ also increases slightly with increasing drop size. For the switch-off process, the presence of intermediate metastable states led to a non-exponential $r(t)$. In general, however, the switch-off time decreases with decreasing droplet size. The vertical arrows in figure 6 (*b*) indicate the time when the sudden reorientation of the droplet centre occurred.

4. Conclusions

We have investigated the behaviour of polymer dispersed cholesteric droplets in electric fields as a function of several parameters. In agreement with earlier results [10], we observe that the director configuration in the field-off state is described by the Frank-Pryce model [5, 6]. When an electric field is applied, a reoriented central region of radius r appears. Above an initial threshold field, r increases in half-pitch steps with increasing field and, for slowly decreasing fields, the process is reversed. We find that the dependence of r on the electric field is exponential, and that the threshold field decreases with increasing drop diameter and increasing pitch, respectively.

Results for the dynamic behaviour of r show that r increases exponentially with time for switch-on, but for switch-off, metastable intermediate structures appear which lengthen the switch-off times. For display applications, it can be concluded , therefore, that small drop sizes and high electric fields are desirable for the fastest response to changes in the field. Recent investigations on small pitch systems [3], however, show that for fields sufficiently strong to align the outermost surface layer of a droplet a completely different relaxation mechanism can occur. This mechanism is characterized by a reorientation to the field-off state starting from the centre of the droplet. This behaviour was not observed in the mixtures reported here.

To summarize, we have confirmed the known director configuration in cholesteric droplets for both zero and non-zero electric fields. In addition, we present data showing the dependence of the radius of the reoriented central region on the electric field, chirality, drop size, and, for suddenly switched fields, on time. A remaining question concerns the shape of the reoriented region. This shape cannot be determined in all directions from our experiments since we have only observed the projection of the drops along the field direction. To clarify this question, observations of droplets perpendicular to the field are being carried out.

A theoretical description of our results is still lacking. Zumer *et al.* [13] have calculated the elastic free energy for different cholesteric director configurations in the equal elastic constant approximation. In the field-off state, they expect a configuration containing a diametrical $s = 1$ disclination line to be most stable instead of the structure with a radial $s = 2$ disclination line as observed here. With respect to electric fields, they predict a complete transition to helicoidal alignment at a threshold voltage, while we observe a continuous increase of the reoriented region within the drop. Thus significant differences remain between experiment and theory. In this respect, we expect our data to provide guidance to further theoretical work.

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