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Reorientation dynamics of polymer dispersed nematic liquid crystal films

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The electro-optical dynamics, hysteresis effects, and microscopic structure of polymer-dispersed films of nematic liquid crystal are probed in order to gain insight into the operation of this new class of liquid crystal light valves. In tracking the rise and decay response times of these devices, it appears that there are both 'fast' (0·1–1·0 ms) and 'slow' (10–1000 ms) processes that occur in the film. A model is proposed which explains these results, in which the reorientation of the nematic droplets takes place in two stages: a fast reorientation by the nematic within the bulk of the droplet, followed by a slower rotation of the nematic nearer the droplet surface (including the point disclinations). This model agrees with a similar proposal made by Doane *et al.* in a previous study of related films. This model is also used to explain both the behaviour of the films in response to short voltage pulses and hysteresis effects present in the film. The response time of these films can be tailored by adjusting the droplet size within the film, as well as the choice of the drive waveform and voltage. The non-spherical shape of the nematic droplets in the film is proposed to be the most important factor controlling the electro-optic properties of these devices. Data is presented which shows that the more distorted the nematic cavity, the more quickly the film decays, and the higher the field required for reorientation. It is proposed that the minimization of deformation energy of the nematic in a non-sperical cavity is the primary driving force for relaxation in these films, rather than previously postulated 'surface interactions'.

1. Introduction and background

Dispersions of micron-sized droplets of nematic liquid crystal in a polymer matrix form the basis of an important new class of electro-optical devices [1, 2, 3]. In these devices, the unpowered nematic/polymer film scatters light very efficiently, and is milky (translucent) in appearance. When an electric field is applied across the film, the film clears to achieve a high degree of transparency. A pleochroic dye may be incorporated into the nematic to give an electrically controllable absorption in addition to the controllable scattering. In many ways, these films possess the durability and processing advantages of polymers coupled with the electro-optical responsiveness of liquid crystals. Since the polymer surrounds and contains the nematic, it is easy to make curved and/or large devices. Single piece light valves greater than three square meters in area have been constructed from these types of films.

The operation of these light valves can be understood on the basis of an electric field-controllable reorientation of the nematic director field within each droplet. For the films used in this study, the nematic director field within the droplets possesses a bipolar orientation [2, 4, 5, 6]. In this configuration, the nematic is aligned parallel to the droplet wall, the director field possesses cylindrical symmetry within a droplet, and there are two point disclinations at opposite sides of the droplet. In the unpowered film, the symmetry axes of all the droplets are randomly oriented. The scattering observed in the unpowered film arises from the mismatch in the refractive index of the polymer and the extraordinary refractive index of the nematic. Light crossing the polymer/nematic interface is refracted due to this mismatch, and repetitive refractions across multiple droplets results in a highly scattering state. When the film is powered, the director fields within the droplets align with the applied electric field. If the ordinary refractive index of the nematic is near that of the polymer, light entering the film normal to the film surface (parallel to the applied field) sees little change in refractive index in crossing the polymer/nematic interface. The light is transmitted without refraction, and a transparent film results.

If a high order parameter positive pleochroic dye is present in the nematic, the same scattering mechanism is still operative, but a controllable absorption also exists in the film. In the unpowered state, the random distribution of the droplet's symmetry axes means light of all incoming polarizations will be absorbed, and a highly absorbing film results. When the film is powered, the dye is oriented along with the nematic so that the transition dipoles of the dye molecules are perpendicular to the polarization vectors of the incoming light, and the macroscopic absorption of the film is reduced.

Presently there are two distinct processes for making films of polymer dispersed nematic droplets. The first involves the emulsification of the nematic in an aqueous solution of a film-forming polymer [1, 2]. The polymer may be either truly water soluble (e.g. polyvinyl alcohol), or exist as a colloidal dispersion of polymer particles in water (e.g. a latex). This emulsion is then coated onto a conductive substrate and allowed to dry, during which time the polymer coalesces around the nematic droplets. Laminating a second conductive substrate to the dried film completes the device. The second method involves mixing the nematic with a low to medium molecular weight prepolymer to form an isotropic solution [3]. The polymerization process is initiated with heat or light, and as the polymer chains grow the solubility of the nematic in the polymer drops. At some point nematic droplets nucleate *in situ* from the polymer, and the polymer forms a shell around the droplets as the polymerization is completed. The physics behind the operation of both type of films appear to be very similar, as will be discussed later.

In this paper we shed some light on two questions regarding the electro-optical response of these films: 'How do they turn on?' and 'Why to they turn off?'. To answer the first question, we probe the electro-optical dynamics of polymer dispersed liquid crystal films. In both the optical rise and decay of these films we see effects that occur in two distinct time regimes. These films also show hysteresis effects, which will be described. We will propose a model for the droplet reorientation that explains the dynamical and hysteresis effects observed. The key assumption made in this model is that while the nematic within the centre of a droplet is free to respond quickly to an applied field, the nematic near the polymer wall is constrained to reorient much more slowly. This results in two time regimes in the orientation process of the droplets.

The model confirms and expands on observations made [3] by Doane *et al.*, where two time regimes were noted for the decay of the scattering response of polymer/nematic droplet films made by the nucleation method. The two regimes were ascribed to a fast relaxation of the director within the droplet, followed by a reorientation of the optic axis of the droplet. In this paper we put that hypothesis on much firmer ground by studying the reorientation process in greater detail. First, the use of pleochroic dye absorbance rather than film scattering allows us to have greater confidence in tying a microscopic picture of nematic reorientation to the film's macroscopic response. Secondly, the difference in the two time regimes observed here spans 3–4 orders of magnitude, much greater than in the previous study. This difference allows us to rule out dispersion in the nematic droplet size as the cause of a dispersion of response time. Thirdly, we report here the first observation of two time regimes in the risetime of the cell response, and tie this to the droplet reorientation model. Finally, we relate the droplet reorientation model to film hysteresis effects and the response of the film to short voltage pulses, lending additional weight to the validity of the model.

To answer the second question (why do the films turn off?) we will propose that the non-spherical shape of the droplets in a polymer matrix is the critical factor in the operation of these devices. While droplet shape has been recognized as important in the past [3], the restoring force in these films has invariably been ascribed to unspecified 'surface interactions' [3, 7] (i.e. the surface of the polymer wall imparts a preferred orientation on the droplet alignment direction). In this study we will offer evidence that surface interaction are secondary in importance to droplet shape, which is the primary determinant of the electro-optical properties of these films. In this model for nematic in a nonspherical droplet, the total elastic deformation energy of the nematic will depend on the orientation of the nematic within the droplet. The film 'turns off' once the electric field is removed because the droplets reorient to minimize this elastic deformation energy. The degree of distortion of the droplet will determine both the field required to turn the film on, as well as the decay time of the oriented film.

2. Experimental

The materials used to construct guest-host polymer dispersed nematic droplet films were a high order parameter ($S > 0{\cdot}70$) black azo dye mixture (M-778, Mitsui Toatsu), a nematic host with positive dielectric anisotropy (ZLI 1840, EM Industries), and polyvinyl alcohol (PVA) (Vinol 205, Air Products). The PVA was purified by Soxhlet extraction with methanol prior to use. 5·0 g of a 1 per cent M778/ZLI 1840 mixture was added to 15 g of a 20 per cent aqueous solution of the PVA, and emulsified with a laboratory stirrer. Droplet sizes were measured using a Multisizer particle size analyzer (Coulter Industries). Two emulsions were made; a 'small' droplet emulsion with mean volume diameter of 1·0 μ (0·5–2 μ diameter range), and a 'large' droplet emulsion with a mean volume diameter of 3·3 μ (1–7 μ diameter range). After degassing the emulsion, a knife blade was used to coat thin layers of the emulsions onto indium–tin oxide (ITO) coated polyester film (Andus Corporation). After allowing the films to dry for an hour, another piece of ITO/polyester was laminated on top of the dried emulsions to make cells. The cells were allowed to further dry in an 85°C oven for a day or more prior to measurement. The thickness of the two cells used in these experiments were measured using an interference technique, and are nominally $10{\cdot}5 \pm 0{\cdot}5\,\mu$ thick. Absorbance vs. voltage curves show that the large droplet film is saturated at 100 V, while the small droplet film achieves 90% of saturation at that voltage.

For the scattering films, E7 (BDH) was used as the nematic. The aqueous-based PVA film was made as described above, with a droplet mean volume diameter of 3·2 μ, coated to a dry thickness of 25 μ. The film made by the nucleation method was constructed by mixing a 1·6 : 1 mixture (by weight) of E7 and NOA 65 UV curable adhesive (Norland Products). A drop of this solution was placed in the centre of a teflon ring spacer (25 μ thick, 25 μ diameter) set on a piece of ITO/polyester. A second piece of polyester/ITO was laminated to form a cell, and the cell clamped between glass plates. The polymer was cured using a 20 W longwave U.V. lamp (UVP, Model UVL-21), with the cell placed one-half inch from the lamp. Visually the film appeared quite uniform, with a thickness (by interferometry) of 29 μ (some of the solution leaked under the spacer to given a cured cell thickness slightly larger than the spacer thickness). These films are similar to a previous report of nucleation-type films using UV-curable polymers [7 (*b*)].

The clearing point of the nematic in each of these films differed from the neat nematic by no more than 2 C for the PVA films, and 4 C for the NOA 65 film. Thus we are confident that the dielectric and elastic properties of the nematic in these films are not significantly altered from those values of the neat nematic.

For response time measurements the cells were mounted to a 10 in. integrating sphere (Labsphere) equipped with a radiometric detector (United Detector Technology 61AC, 30 μs risetime). The response of the detector was recorded using a digital oscilloscope (Nicolet 3091). The light source for these experiments was an Oriel stabilized xenon-mercury lamp light source equipped with a water filter. Using the lamp condensing lens and an external aperture, the slowly diverging light beam was aligned so that it passed through the entrance and exit ports of the integrating sphere without being detected. For the guest-host films, absorbance was measured by mounting the cell on the entrance port and placing a diffuse reflector at the exit port. It was determined using non-dyed nematic droplet films that this measurement arrangement is sensitive only to changes in the absorbance of the film; changes in the films' scattering are small effects compared to the absorbance changes, and can be neglected. For the scattering (non guest-host) films, the sample was mounted at the entrance port, but the exit port was left open. In this way, the detector in the integrating sphere is sensitive to scattered light, similar to the 'haze' measurement we have used previously to characterize the scattering of these films [2, 8].

Electrical signals were generated using a function generator (Wavetek 187) coupled to a d.c.-coupled broadband amplifier (Krohn–Hite 7500). For the risetime and decay time experiments, a 0·5 Hz square waveform was used (decay times were measured after powering the cell for *c* 10 seconds before shorting the sample). For the decay experiments, the electric field was removed by shorting the cell plates together. All experiments were performed at 21 ± 1°C.

Percent haze vs. voltage for the scattering samples was measured using a Hunterlabs Calorimeter (Model D25P-9). The drive waveform was a 60 Hz square wave.

For the scanning electron micrograph, the PVA/nematic droplet film was frozen in liquid nitrogen, sectioned, and then had a thin layer of gold sputtered on top of it prior to the microscopy. The relatively hard PVA films gave good electron micrographs, with sharp demarcation of the droplet cavity and film. Micrographs made from the softer NOA-65 did not section as cleanly, but the essential features of cavity size and shape remain clear and reproducible.

3. Film response dynamics

In this study, the reorientation of the nematic droplets is mapped by following the change in absorbance of a pleochroic dye-doped nematic droplet/polymer film. From Beer's law (1), the absorbance of the film can be approximated by the relative absorbance of randomly aligned and electric field-aligned dye molecules. In (1), A represents the film absorbance, b the cell thickness, c_0 the total dye concentration, a^*c the product of the extinction coefficient and molar fraction, respectively, of the dye in either the rest or powered state, and A_{misc} other miscellaneous losses such as reflection and scattering. Since the dye molecules are distributed uniformly throughout the nematic, the relative absorption of the film will

$$A = A_{\mathrm{misc}} + bc_0 * [(a * c)_{\mathrm{rest}} + (a * c)_{\mathrm{powered}}] \quad (1)$$

reflect the degree of orientation of the total volume of nematic within the film. In analysing dye absorption rather than scattering, we avoid the necessity of a complete understanding of the relationship between the microscopic nematic director configuration within a droplet and the film's macroscopic scattering profile in order to map the nematic reorientation. This allows us to have much greater confidence in tying microscopic reorientation processes of the nematic within the film to the macroscopic response of the film.

Figure 1 shows the 100 volt risetime and decay time of the 'large' and 'small' nematic droplet films. In both films, the absorbance vs. log time curve drops rapidly upon application of a field, but then shows an abrupt change in slope in the 10^{-3} to 10^{-4} s time range. Since the absorbance of the films directly reflects the total fraction of oriented nematic, these data indicate that in powering the film, the majority of the nematic is oriented in a submillisecond time frame, with a smaller fraction of the nematic responding over a much longer period of time. The difference in the temporal range of these 'fast' and 'slow' responses spans approximately three to four orders of magnitude. Additionally, the large droplet film responds more quickly than the small droplet film.

Similarly, there are two time reqimes present in the decay response of the film absorbance, with a fast (c 1–10 ms) response followed by a larger, slower (tens to hundreds of milliseconds) response. These measurements indicate that in each film a small fraction of the nematic relaxes in a short, millisecond time frame, while the bulk

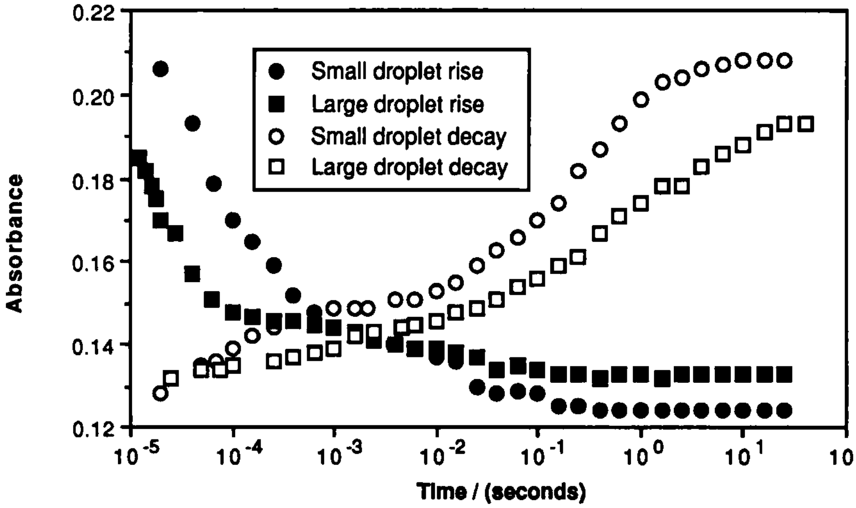


Figure 1. Rise and decay times of the absorbance of two polymer dispersed nematic liquid crystal films. The mean volume diameter of the nematic droplets in the 'large' droplet film is 3·3 μ, and 1·0 μ in the 'small' droplet film.

of the nematic requires hundreds of milliseconds to fully relax. The smaller droplet film now decays more quickly than the large particle film.

A straight line in a plot of absorbance vs. log time can be taken to mean that the molecular reorientation process can be approximated by some exponential function, with an associated time constant. A significant change in slope in this curve means that some fraction of the nematic in the film is responding with a second, longer time constant. Both the rise and decay responses of the films in figure 1 show both a fast and a slow response. This either means that different subsets of the droplet population are responding with markedly different time constants, or that each droplet shows both a fast and a slow response during its reorientation. We will examine both possibilities, and argue that each droplet possesses both a fast and a slow orientation response.

One possibility that might explain the wide temporal response range is the size dispersion of the nematic droplets. One can think of each cavity within the film as a miniature cell containing the nematic, with the dispersion of these cell sizes leading to a dispersion of the response times. Order of magnitude estimates for the dispersion of the decay response times can be made by borrowing from models used to describe the dynamics of a simple Frederiks transition in planar cells [9, 10]. The decay time of such a simple cell (ignoring fluid flow effects and assuming a simple twist geometry) is

$$t_{\text{decay}} = \frac{\gamma_1 d^2}{\pi^2 K}, \tag{2}$$

given by (2). In (2), t_{decay} is the exponential time constant for decay, γ_1 is the nematic rotational viscosity, d is the cell thickness, and K is an elastic constant. Equations similar to (2) have been used to model the temporal response of twisted nematic, cholesteric/nematic phase change, and dynamic scattering cells [8, 11]. In all of these cells the decay time varies as d^2, showing the generality of this equation for simple nematic relaxation.

While the present films contain the nematic in spheroidal cavities rather than planar cells, they are similar to the previously mentioned devices in that the electro-optic effect is due to director realignment. Thus, we can expect the decay response of the present system, if it consists solely of a simple director relaxation mechanism, to depend on the nematic droplet size in a way similar to the d^2 dependence observed in planar cells. Noting that there is a dispersion of 5–7 × in droplet diameters in these films (*vide supra*), we predict a factor of 25 to 50 in the dispersion in response times based on droplet diameters. However, the results in figure 1 show approximately a 10^3 to 10^4 dispersion in the decay times of these films. From these data we can infer that a process other than simple director realignment is responsible for the dispersion in response time in these films.

In fact, we find that applying equation (2) to these polymer/nematic droplet films predicts decay times similar to the fast decay response shown in figure 1. Using measured [2] values for ZLI 1840 ($\gamma_1 = 0{\cdot}24\,\text{kg}\,\text{m}^{-1}\,\text{s}^{-1}$, $K(\text{average}) = 1{\cdot}4 \times 10^{-11}\,\text{N}$), the calculated decay time for $d = 1$ micron is 1·7 ms, and for $d = 3\,\mu$, 15 ms. This temporal range is of the same order of magnitude of the 'fast' time response seen in the decay response of both films. As also predicted by the equation, films with small droplets will decay faster than filsm with large droplets.

The application of risetime equations for planar cells to the nematic droplet system is much more problematical than the decay equation. Rise-time equations for planar cells are typically valid only for fields near the threshold field [7], which is itself a poorly defined value for these nematic droplet films. Still, the 'fast' temporal response observed in these films is on the same order of magnitude (tens of microseconds) of the experimental risetimes of cholesteric/nematic phase change and twisted nematic cells operated at fields in the 10^7 V/m range [8] (the field used in these present experiments).

From the above discussion, it can be postulated that the fast temporal decay of these films can be ascribed to a simple realignment of the director field within a droplet. The fast risetime response is also likely to be due to simple director realignment. However, there also exists longer response processes for both the rise and decay which needs to be accounted for. Figure 2 shows a schematic for a simple model which explains these results. In the unpowered film, nematic droplets possess the bipolar configuration, with the nematic aligned tangentially at the droplet wall (2*a*). The symmetry axis of each droplet is aligned randomly within the plane of the film (the nonspherical shape of the cavity does constrain the droplet symmetry axis to lie within the plane of the film; *vide infra.*) Upon application of the field, the nematic within the centre of each droplet aligns quickly with the field. This process leads to the droplet in (2*b*), where the bulk of the nematic is aligned with the applied field, but the bipolar defects are still placed near where they were in the unpowered film. Since most of the nematic is aligned with the field in this step, the process (2*a*) to (2*b*) shows a large optical effect.

However, the director field in (2*b*) does not possess the lowest elastic deformation energy possible for the droplet (in the presence of an electric field). There is substantial curvature in the director field near the walls of the droplet, and the droplet can

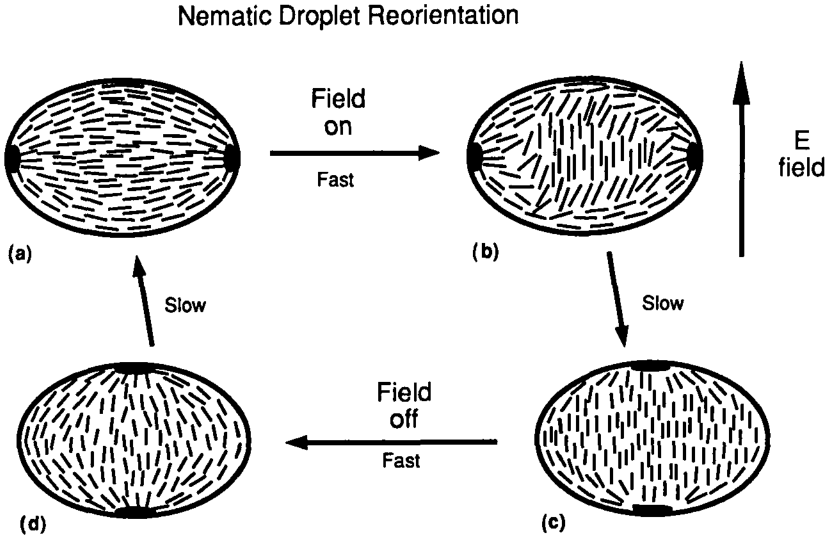


Figure 2. Model for the two stage risetime and decay time response of polymer dispersed nematic liquid crystal films. Upon application of an electric field, the nematic near the centre of the droplet in the rest configuration (*a*) quickly orients with the field, leading to (*b*). This is a fast, large optical response. The surface layer (and defects) of the droplet then rotate to achieve state (*c*), giving a slower, smaller optical response. Upon removal of the field, the nematic near the centre of the droplet relaxes, leading to (*d*). This is a fast but results in a small optical effect. Finally, the surface layer of the nematic slowly reorients to return the droplet to state (*a*). This is a large optical effect.

minimize its elastic energy by rotating the point defects within the droplet so that they are aligned with the electric field (2 *c*). Such a rotation of the point defects has been observed in nematic droplets using polarized microscopy [2, 13]. This is a slow response, reflecting the difficulty in the coordinated movement of the point defects within the droplet, as well as increased resistance to viscous flow near the droplet wall. The droplet (2 *c*) is now in its lowest energy state possible for the droplet. The actual volume of nematic reoriented in moving from (2 *b*) to (2 *c*) is small, resulting in a small optical effect. The reorientation mechanism illustrated in figure 2 is consistent with the magnitude and speed of the risetime data shown in figure 1.

When the electric field is removed, the bulk of the nematic within the droplet is able to respond in a quick decay process. However, the major relaxation process within an aligned droplet is a slight splaying of the director field towards the sides of the droplet in order to relax the rigid alignment induced by the electric field (2 *d*). The symmetry axis of the droplet is still aligned with the electric field direction, so the optical effect will be small. Finally, the droplet returns to the configuration it possessed prior to application of the field. This process requires both the movement of the surface layer of the nematic and a rotation of the nematic within the bulk of the droplet. Again, such a process is slow, leading to the long (tens to hundreds of milliseconds) times observed in the film decay. However, this slow process involves the reorientation of most of the nematic within the droplet, and gives a large optical effect. These two processes are consistent with the data shown for the decay responses in figure 1. This type of mixed 'fast' and 'slow' response for both the rise and decay of nematic droplet/polymer films have been observed for a large number of films, with different liquid crystal compositions. As mentioned in the introduction, these observations are consistent with the observations of Doane *et al.* in studying scattering films made by the nucleation method.

Figure 3 shows another set of data which can also be explained with the above model. These data show the decay times of the small particle film following a 100 V d.c. pulse, varying the length of the pulse. It is seen that for a 100 μs pulse, the film shows a large optical response, but also decays quite rapidly (1 ms). As the length

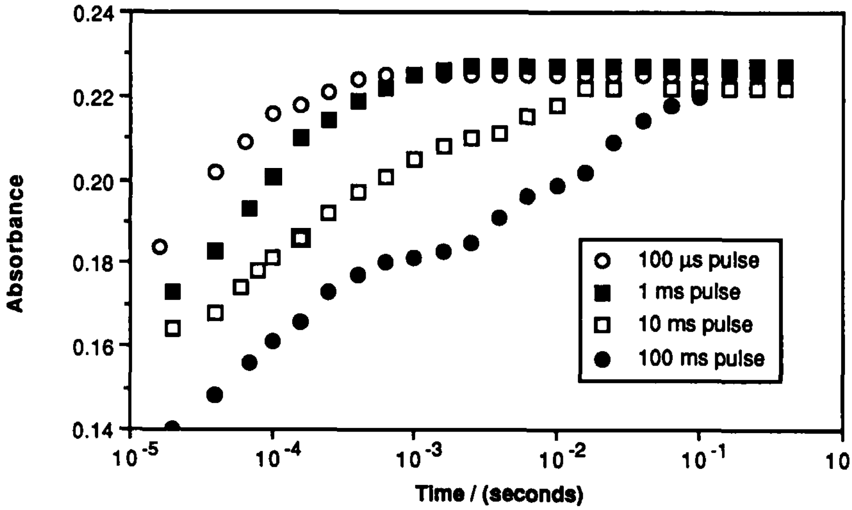


Figure 3. Decay times of a polymer dispersed nematic liquid crystal film, responding to 100 V DC pulses of various durations.

of the pulse grows, the length of the decay response also increases, becoming hundreds of milliseconds for a 100 ms pulse. These data are readily explained by referring to figure 2. The result of a short pulse is to take the droplet from state (2 *a*) to state (2 *b*), where the bulk of the nematic has reoriented, but the point defects have moved only slightly. If the field is now removed before the droplet can rotate into state (2 *c*), the decay response is expected to be rapid, since the decay reorientation does not involve the point defects of the droplet. As longer and longer pulses are applied, the droplet point defects will be move, placing the droplet in state (2 *c*) as this occurs, the decay response will increase, since the movement of the point defects within the droplet is slow. As the droplets rotate, however, a better alignment of the total volume of nematic will be achieved, and a larger optical response will be observed. These effects illustrate that variations in the drive waveform offer the opportunity of controlling the decay response of these films.

4. Hysteresis and low field scattering effects

Figure 4 shows a hysteresis effect present in polymer/nematic droplet films. At low fields, the absorbance of the film is higher if the field was achieved by increasing the applied field from zero, compared to lowering the applied field from a saturating voltage. This effect is well explained by considering the proposed model for droplet reorientation. It is reasonable to expect that at low fields only the bulk nematic reorients, and the nematic near the surface reorients only very slowly, if at all. This would lead to droplets in the film existing preferentially in the state shown in (2 *b*). As the film is powered to high fields, all the droplets reorient to align with the field (droplet 2 *c*). As the field is reduced, the droplets will relax to state (2 *d*) and eventually return to their rest positions.

From this argument we can see that at voltages intermediate between zero and saturation, most the droplets within a film will exist in states close in form to either (2 *b*) or (2 *d*), depending, respectively, on whether the applied voltage is increasing or decreasing. From figure 2, it is qualitatively apparent that more of the nematic in droplet (2 *d*) is better aligned with the applied field than the droplet (2 *b*) since the

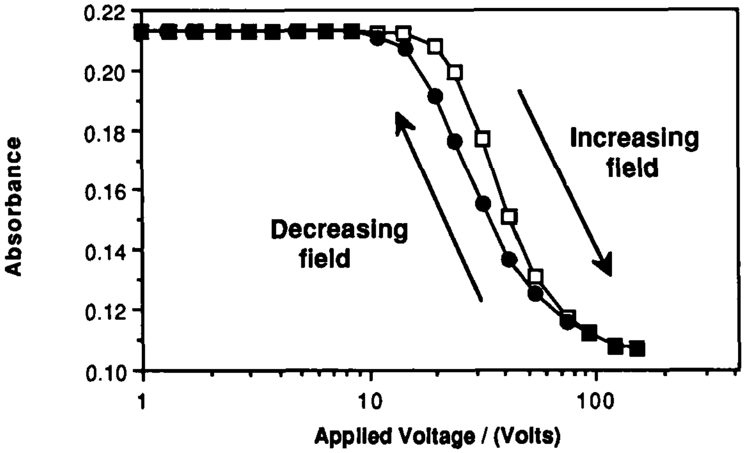


Figure 4. Absorption vs. voltage curve for the 'small' particle size film. Note the hysteresis effect, leading to higher absorbance while raising the applied voltage, compared to reducing the voltage.

symmetry axis of the droplet in (2*d*) still lies along the applied field direction. A droplet in state (2*d*) will possess a lower absorbance than a droplet in (2*b*) due to this greater alignment. If droplets exist preferentially in state (2*b*) while increasing the applied field, and in (2*d*) while decreasing the applied field, a hysteresis effect will occur.

This hysteresis effect is seen only at relatively low applied fields in these devices, and is relatively small. The likely cause of this small effect is the dispersion in the droplet size of the nematic within the polymer (well over a factor of 5–7 × in droplet diameter in the present films). It has been shown that the field required to reorient bipolar nematic droplets in PVA films scales inversely with the droplet diameter [2]. At low voltages, only the largest droplets within the film are responding to the field, and a hysteresis effect may be seen. At higher voltages, many differently sized droplets are in various stages of reorientation, masking the hysteresis effect present in any one droplet size range.

Similar hysteresis effects are seen in the scattering response of these films, in that the scattering at a low voltage is higher while increasing the field compared to decreasing the field. This is again readily explained if the droplet (2*d*) refracts light less than the droplet (2*b*) due to its better alignment with the field (recall the mechanism for light scattering described in the introduction). Scattering hysteresis effects have also been seen (but previously unexplained) in films made by the nucleation technique [7]. It is likely that the cause of those hysteresis effects are the same as postulated here.

Another property of nematic droplet/polymer films is also well explained by the model shown in figure 2. If one maps the light scattering properties of these films it is seen that at low fields the scattering *increases* slightly, followed by its normal decrease at higher fields. This effect can be explained by comparing the director fields within droplets (2*a*) and (2*b*). In (2*b*), there is a significant spatial change in the director orientation in moving from the wall of the droplet to the droplet centre; light is refracted as it passes through the polymer/nematic interface, and then will be refracted again as it passes through the centre of the droplet. In (2*a*) the director field is more or less uniform throughout the droplet, so light is only refracted at the interfaces. This change in director orientation will increase the refraction of light as it travels through the droplet, and thus lead to a macroscopic increase in the scattering of the film. As the droplet changes from (2*b*) to (2*c*) the expected decrease in film scattering will occur.

Although the scattering of a film increases at low voltages, the absorbance of dye in the film does not. Macroscopically one observes only a smooth decrease in the absorbance of films containing pleochroic dyes. As shown in figure 2, the director field (and thus the dye molecules) within (2*b*) is better aligned with the electric field than (2*a*), so that (2*b*) should always show less absorption than in 2*a* (as reflected by experiment).

5. The importance of being oblate

To this point we have glossed over a very important aspect of the operation of these films: why do they turn off? From a thermodynamic sense, the electric field supplies the energy to reorient the droplets; elastic deformation forces oppose this reorientation, and provides the impetus for the droplets to return to their rest condition. In this section we will briefly discuss the nature of this elastic deformation, and make a novel proposal for the major relaxation mechanism in these films.

Nematic droplets can be suspended in a fluid (e.g. glycerin) and an electric field used to rotate the droplets' symmetry axes. In these cells, once the electric field is removed the droplets do not reorient (at least on the order of tens of seconds) [14]. In a glycerin matrix, there is no restoring force inducing the droplets to return to a preferred orientation. Thermal motions will slowly cause the droplet's symmetry axes to rotate, but this process is orders of magnitude slower than the reorientation observed in the polymer films. Thus, there is some unique polymer/nematic interaction which causes the droplets to relax quickly once the applied field is removed.

It has been observed [2] that in polymer/nematic droplet films, each droplet possesses a preferred, unique alignment direction. If this alignment is disturbed either by aligning the nematic with an electric field or by heating it into the isotropic state, the preferred alignment direction is recovered when the field is removed or the film cooled. Under favourable conditions, it is possible to use a polarizing microscope to actually watch the point defects of a bipolar droplet move under the influence of an electric field to align with the field, and return to their previous positions as the field is removed [2, 13]. Thus there is good evidence that the restoration of the film once the field is removed is due to some reduction of elastic energy, and is not simply due to thermal fluctuations of the alignment direction of the nematic droplets.

One potential mechanism for a preferred alignment direction is to postulate a preferred alignment direction at the polymer/nematic interface. In this model, the nematic director near the surface of the droplet does not change its orientation significantly while the interior of the droplet aligns with the electric field. The anchoring of the nematic at the wall determines the rest configuration of the droplet, and provides the impetus for relaxation once the electric field is removed. Such 'surface interactions' have been mentioned in the past as the cause of the droplets' relaxation [3, 7, 15].

To make this hypothesis viable it is necessary that some sort of preferred alignment in the polymer due to polymer–nematic interactions arise during the film-forming process (if the preferred alignment direction varies randomly across the cavity surface, the interactions would average to zero and there would be no preferred direction). However, there is some evidence that such aligning forces may not be easily achieved in these films. A study by Clark [16] examined the ability of nematics and smectics to induce alignment in various polymers by placing the mesophase in contact with the polymer surface. In that study, there were no cases where a nematic was able to induce a preferred alignment in a polymer film, although smectic A and G phases were able to induce alignment in some hydrophobic polymers. Secondarily, hydrophilic films (including PVA) were particularly resistant to induced alignment; in that study neither a smectic A, a smectic G, nor a nematic phase could induce alignment in a PVA film.

In a film that induces strong, directional surface alignment, it is unlikely that the nematic director configuration could rotate to align with the field; instead, the nematic near the surface would remain near its initial configuration (strong anchoring) and the nematic in the interior of the droplet would orient with the field (state (*a*) to (*b*) in figure 2). As shown in the previous section, however, visual, response time, and hysteresis effects are consistent with an actual rotation of the droplets' symmetry axes once a field is applied. These observations argue against surface interactions as being the source of droplet decay in the films studied here.

A more reasonable origin for the elastic deformation within a droplet can be inferred from the scanning electron micrograph of figure 5. This is a micrograph of a nematic/PVA film, with the nematic removed by solvent extraction. It is seen that none of the droplets in the film is spherical; most are flattened in the plane of the substrate, as well as possessing other deviations from sphericity. Examination of droplets from both the top and the side indicate that most droplets in these dispersion tend to form distorted, oblate-like structures. Electron micrographs of films made by the nucleation method are also often highly non-spherical [3] although not necessarily oblate (*vide infra*).

In this second model, the nematic director at the surface of the droplet is free to rotate within the droplet plane, as long as it remains tangential to the wall. However, the total elastic deformation energy within the droplet will depend on the orientation of the symmetry axis of the director field. In the unpowered state, the symmetry axis is aligned along a direction which minimizes the elastic deformation energy. The application of an electric field reorients the nematic so that the elastic deformation energy is increased. Removal of the field allows the nematic to relax to its initial, lowest energy state. While droplet shaping effects have been described in the past as a means of *altering* film properties, the present hypothesis goes far beyond that statement in proposing that in most cases the film electro-optics are completely determined by the droplet shape.

As shown qualitatively in figure 6, the director field of a bipolar, ellipsoidal nematic droplet is more highly curved if the droplet's symmetry axis does not lie along the major axis of the ellipse, and thus is at higher energy. In order to reorient the nematic within a droplet, the electric field must overcome the increase in elastic energy that occurs when the symmetry axis of the nematic is rotated within the non-spherical cavity. In the oblate cavity structure shown in figure 5, the minor axis of the ellipsoid

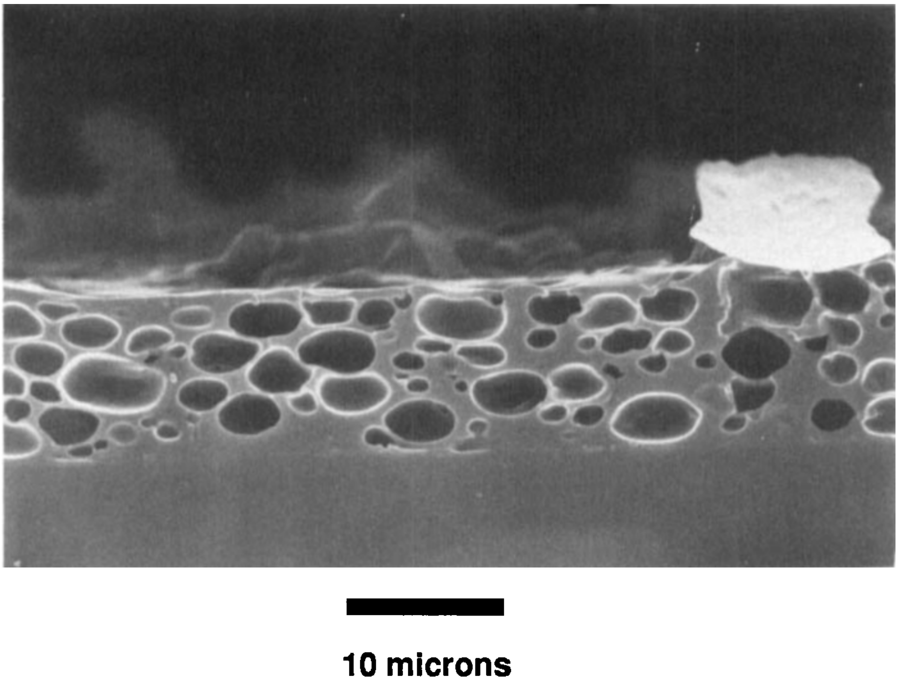


Figure 5. Scanning electron micrograph of a polymer/nematic liquid crystal film (nematic removed). This is the 'large droplet' film used in the response time measurements in figure 1.

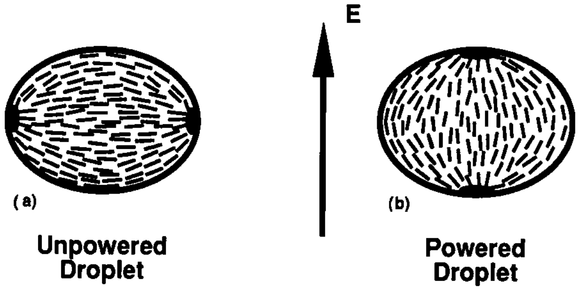


Figure 6. Bipolar droplets with different orientations in oblate droplets. It is qualitatively apparent that the director field in (*b*) is more highly curved than in (*a*), and thus at higher energy.

lies along the electric field direction, so that the application of the electric field rotates the nematic into a state with high deformation energy. Once the field is removed, there is a strong impetus for the droplet's symmetry axis to rotate back to its initial position.

There is a great deal of evidence that shows that in elliptical cavities the symmetry axis of bipolar droplets will adopt a preferential direction. For example, stretching a polymer/nematic droplet film causes the droplet cavities within the film to form ellipsoids, and the symmetry axis of the nematic droplets' director fields to align along the major ellipsoidal axis (stretch direction) [3, 14]. This alignment can be observed microscopically by noting the alignment direction within the droplets using a polarizing microscope. Macroscopically, a stretched film will show a polarized scattering effect [14, 15] (and polarized absorption, if a pleochroic dye is present [14]).

Figures 7 and 8 offer evidence that droplet shape strongly affects the macroscopic properties of these films. Figure 7 (*a*) is an electron micrograph of an E7/PVA film; it looks quite similar to the micrograph of figure 5 in that the cavities are highly oblate. Figure 7 (*b*) shows a micrograph of an E7/NOA 65 film. The average cavity shape in this film is somewhat smaller but much more spherical than in the PVA based film. From the previous arguments, then, we would expect a much higher deformation energy for the nematic in the powered PVA film than in the NOA 65 film.

Figures 8 (*a*) and (*b*) provide evidence that this is indeed the case. Figure 8 (*a*) shows haze vs. field curves for the two films. It is obvious that the highly oblate droplets in the PVA film require a higher field to orient than the rounder NOA 65 film, despite the fact that the PVA-film droplets are on average somewhat larger than the NOA 65-film droplets [17]. Figure 8 (*b*) shows the decay response of the same two films. The PVA film decays much more quickly than the NOA 65 film, showing that the restoring force in the PVA film is much stronger than in the NOA 65 film. Both of these observations are consistent with the hypothesis that the cavity shape is controlling the electro-optic response of the nematic in these films. It is not clear that a surface anchoring mechanism would discriminate between the two films in the same manner.

Additional evidence supporting this postulate exist in the literature. Studies by Vaz *et al.* compare nucleation-type films made from a thermally-cured epoxy and a UV-curved polymer. It is noted in those studies that the thermally-cured films the droplets appear nearly spherical, while the U.V.-cured film droplets show a much more irregular appearance. Electro-optical curves of scattering response vs. voltage for films of similar thickness show that the U.V.-cured film requires 2–3 × the voltage of the epoxy samples. The droplet shape hypothesis provides a simple explanation

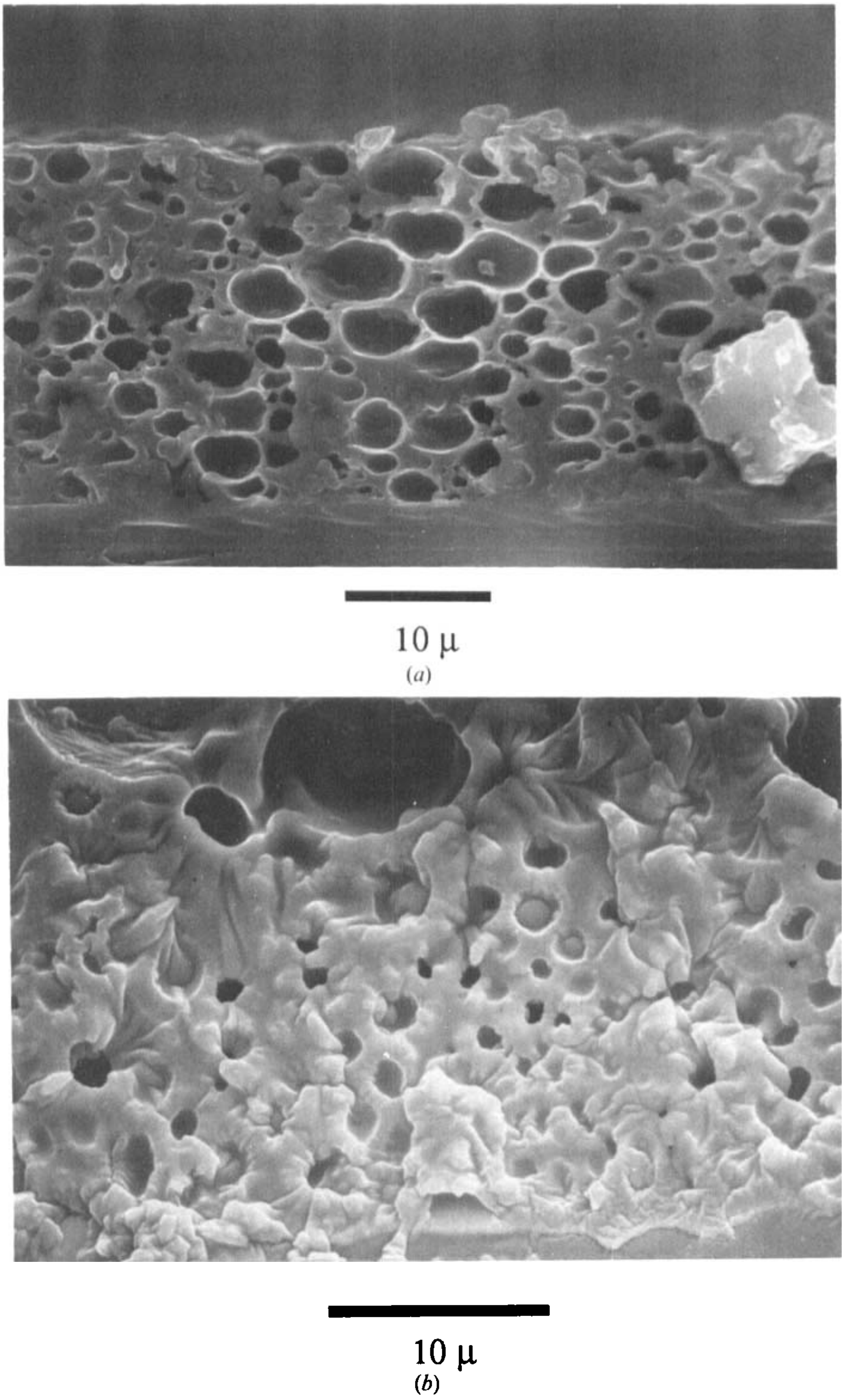
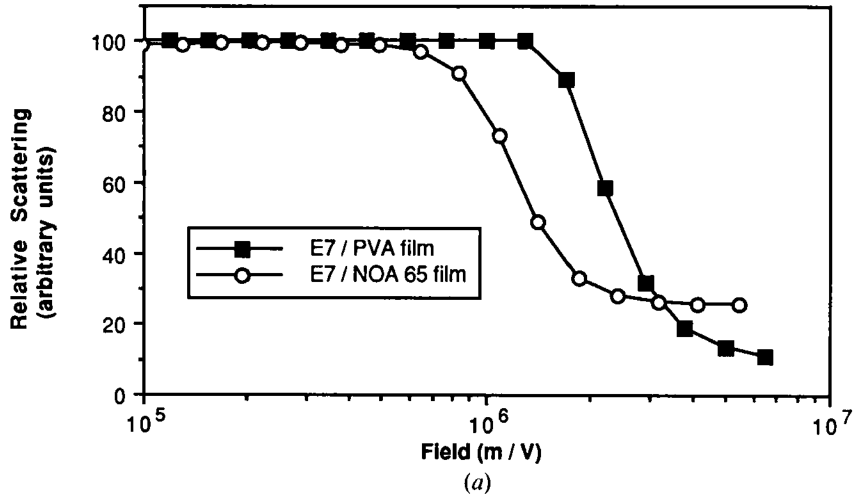


Figure 7. Scanning electron micrographs of E7/PVA (*a*) and E7/NOA 65 (*b*) polymer/nematic liquid crystal films. The droplets in the NOA 65 film are somewhat smaller and more spherical than the cavities in the PVA film.



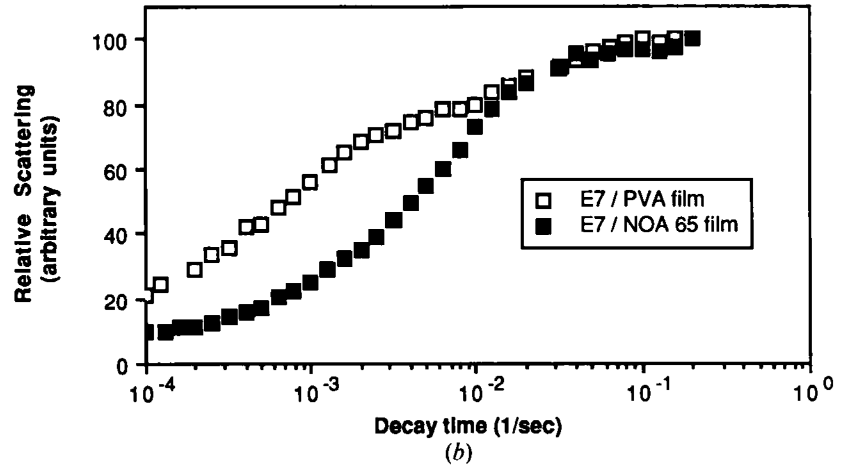


Figure 8. (*a*) Percentage haze vs. field curves for the E7/PVA and E7/NOA 65 polymer/nematic liquid crystal films. (*b*) Decay response for the two films.

for these results. Again, the energy required to reorient the nematic in a droplet will increase with increased distortion of the droplet. The change in deformation energy in reorienting the highly spherical epoxy-based droplets is less than the more distorted U.V.-cured sample, and thus requires a smaller field for saturation.

A second example from the literature shows that stretching a nematic droplet/polymer film decreases the decay response time significantly [3]. As in the previous example, the powered droplet is in a higher energy state in a distorted, rather than a round, droplet, and so the restoring force for the film decay in increased.

These arguments show that deviations from sphericity of the nematic droplets in these films are sufficient to explain a wide variety of data involving the voltage required to orient these films, as well as decay time effects. Using Occam's razor [18], it is unnecessary to invoke the presence of strong surface anchoring as a mechanism to cause relaxation of the nematic droplets, since the data presented so far are well explained solely through known droplet shape effects.

These arguments do not preclude the possibility of nematic-polymer alignment interactions being present in the film, but merely infer that they are usually secondary in importance to the shape anisotropy of the droplet. Indeed, there is evidence in the patent literature that in specialized cases surface alignment forces may be induced in these films if the droplet shape anisotropy is small. In one of these cases, the polymer in a nematic droplet/polymer film is softened by heat, and a strong field applied. If the film is cooled in the presence of the field and the field then removed, the nematic shows a temporary (days or longer) memory effect [19]. This is almost certainly due to the nematic influencing the orientation of the polymer backbone during cooling, and then the frozen polymer influencing the nematic orientation once the field is removed. However, it is expected that the droplets will be highly spherical in these films, since the droplets are forming in a slowly cooling, slowly hardening polymer. In a spherical cavity there will be little energy difference between different orientations of the nematic, and surface alignment forces may become dominant. Examples also exist [15] where an epoxy polymer is slowly cured in the presence of a magnetic or electric field to produce a film which shows similar polarization effects, although in these cases neither the shapes of the droplets nor the magnitude of the effect has been precisely characterized. Again, some evidence suggests that these droplets will be highly spherical [7 (*a*)] and as such droplet shape effects will be minimized.

It is expected that future work will more clearly delineate effects in these films caused by droplet shape compared to surface orientation effects. At present, however, a large body of evidence is consistent with the hypothesis that droplet shape anisotropy is the primary determinant in determining the field required to orient these films, as well as their decay response.

6. Conclusions

The reorientational dynamics of films of polymer dispersed nematic liquid crystal have been used to gain some insight to the microscopic processes that occur within the films. Both the dynamical response and hysteresis effects are well explained by a two-step model for droplet reorientation, where the bulk of the nematic within a droplet is able to respond more quickly to the presence (or absence) of a field that nematic near the surface. These results show that the response time of these devices can be engineered both through control of the droplet size and film thickness, and also by the electronic drive scheme used to power the film.

There are many indications that a non-spherical droplet shape is the critical factor causing the film to relax to it's initial state, once the electric field is removed. Reduction of stored elastic energy is the driving force causing each droplet to return to its preferred rest state. Additional work exploring the effects of droplet shape on film properties is underway, and a more extensive and quantitative analysis of the electro-optical effects responsible for the thermodynamics of nematic droplets in a polymer film will appear elsewhere [20].

Finally, it should be noted that these results may be unique to these films containing nematic droplets with the bipolar configuration. Nematic droplets in either the axial [21] and radial [22] nematic droplet configurations may show dramatically different results, due to the different defect structures within the droplets.

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