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Putting liquid crystal droplets to work: a short history of polymer dispersed liquid crystals

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A Commentary on the paper “Reorientation dynamics of polymer dispersed nematic liquid crystal films”, by P. Drzaic. First published in *Liquid Crystals*, 3, 1543-1559 (1988).

I am pleased and honoured that the editors of *Liquid Crystals* have chosen my paper *Reorientation dynamics of polymer dispersed liquid crystal films* [1] as one of the notable papers for the first twenty years of the Journal. Polymer dispersed liquid crystal (PDLC) systems captured the imagination of a large part of the display and liquid crystal communities for an extended period of time, as evidenced by the fact that well over 1000 papers and 1000 patents have been generated on liquid crystal dispersions since work began in the field over 20 years ago. With the opportunity to offer a commentary on the work, I will provide a short synopsis of the evolution of the field of polymer dispersed liquid crystals, and the role that my paper played in that development.

The first polymer dispersed liquid crystal devices were demonstrated by James Ferguson. He has had a long history in the development of liquid crystal devices and, along with Schadt and Helfrich, is recognized as an inventor of the twisted nematic liquid crystal display. In the course of experimentation in microencapsulating liquid crystals, Ferguson noted that blending a nematic liquid crystal with a water-based solution of polyvinylalcohol enabled him to cast a turbid, flexible film. This electro-optical “paint” could be coated onto a plastic sheet itself coated with indium-tin oxide (ITO). Once dried, another sheet of ITO-based film could be laminated on the other side. Applying an AC voltage across the turbid film enabled it to clear, providing a means to a flexible, large area optical shutter. He also determined that a dichroic dye dissolved in the nematic liquid crystal enabled a device that was both scattering and had high absorbance in zero field, but become transparent and weakly absorbing at high fields. Ferguson filed his first U.S. patent in this area in 1981, which was granted in 1984 [2].

Rather than try to commercialize the technology on his own, Ferguson traveled the country looking for licensees for the technology to undertake its development. He eventually settled on an agreement with Silicon Valley-based Raychem Corporation which received an exclusive license from Ferguson for his patents in this field. Raychem decided that it would try to commercialize the technology by forming a small start-up company to develop switchable windows and flexible displays. This company, Taliq Corporation, was formed in 1983, and coined the term ‘NCAP’ for this electro-optical material.

My involvement in liquid crystals began at this time. After receiving a Ph.D. in chemistry from Stanford University with a thesis on gas phase ion photochemistry, I had joined Raychem Corporation and began my transition to materials chemistry with work in developing conductive polymers. I soon became involved in the liquid crystal project, though, due to the fact that my extensive background in optics proved useful in evaluating these early PDLC prototypes. I was invited to join Taliq as their instrumentation specialist, and over time became their primary liquid crystal scientist as we worked to improve these systems.

It quickly became apparent that while the first Ferguson patents accurately described the means to construct these devices and their macroscopic properties, much of the description of the microscopic structure, the textures of the liquid crystal, and some explanations of the electro-optical effects were either incomplete or incorrect. My first scientific publication in liquid crystals described my work on elucidating a refined understanding of the basic structure and operation principles of these devices [3], a paper that has subsequently been cited nearly 300 times as a basic reference to these systems [4].

Independently and in about the same time period, another form of polymer dispersed liquid crystals was

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being developed at the Liquid Crystal Institute at Kent State University by J. William Doane and his students [5]. Doane noted an electric-field modulated scattering effect in mixtures of an epoxy resin cured in contact with a liquid crystal. This observation led to the determination that phase separation of the liquid crystal during the formation of a polymer film from a liquid precursor provided a general path to a liquid crystal/polymer composite [6]. This group coined 'Polymer Dispersed Liquid Crystals' and 'PDLC' for these materials – terms that today are most generally applied to all of the different variations of liquid crystal/polymer composites.

These and other reports led to a great deal of excitement in the commercial display industry and in the scientific community as well. On the scientific side, there was considerable interest in understanding the fundamental behavior of liquid crystals in these systems with large surface-to-volume ratios and curved boundary conditions. Additionally, there was intense work on extending PDLC systems into new sets of materials and fabrication processes. The interplay between the polymer precursors, the liquid crystal, and the fabrication processes was delightfully complex, and there was tremendous variety in the film structure reported by workers in the field. Morphologies ranged from clearly-defined droplet structures to those showing an open-shell structure with interpenetrating polymer and liquid crystal domains. Interestingly, the macroscopic electro-optical properties of many of these systems were quite similar, so that these systems could all compete for the same applications.

On the commercial side, PDLC films promised a way to develop large area, flexible displays. Since polarizers were not required to observe the optical effect, it seemed possible to develop new displays that would be significantly brighter than traditional twisted nematic displays. A particular area of interest was in large-area switchable windows for buildings. PDLCs enable futuristic windows that could be "opened" and "closed" electronically thus controlling privacy. Liquid crystal material manufacturers were particularly interested in these large area applications, as it could lead to the consumption of liquid crystal materials hundreds of times greater than possible for displays.

A number of companies and university research groups became quite active in the PDLC area, and significant advances were made in the types and performance of PDLC systems. Aside from Taliq and Kent State, some notable early participants included groups at Asahi Glass, Hughes Research Labs, General Motors, Dai Nippon Ink, the University of Ljubljana, Case Western Reserve and the Wright-Patterson Air

Force Base. Due to the difficulty in working with the emulsion-type PDLC system introduced by Ferguson, these other groups worked nearly exclusively on developing variations on the phase separation-type PDLC systems introduced by Doane.

One problem of intense practical interest was control of the dynamics of the optical switching for PDLC films. To achieve video-capable performance in displays, PDLC systems needed to switch relatively quickly (on the order of 10 ms), with minimal hysteresis effects, and maintaining control over grayscale. Switching times for PDLC systems were widely variable across systems, ranging from submillisecond switching times up to hundreds of milliseconds. Some materials had similar rise time and fall time characteristics, but more often the rise time was much faster than the fall time for PDLC displays. While it was obvious that aligning the liquid crystal droplets with the electric field controlled the dynamics, the fact that the macroscopic light scattering was a collective effect of many droplets obscured the exact details at the microscopic level. Some intriguing details were reported: for example, a two-stage response had been noted by Doane in the decay response in his devices [6], with the slow response attributed to the reorientation of the optic axis of the droplets. Few additional details were available, though, and in many systems it was unresolved whether the distribution in droplet sizes and shapes could cause the distribution in response times.

Another critical area of development was the reduction in the operating voltage for these devices. On the device level, high switching voltages meant expensive electronic drivers and reduced operating lifetimes for the displays, so there was immense practical interest in getting the switching voltage of these devices down to 10 V or lower. Reports for the operating voltage of PDLCs were all over the map, ranging from 6 V by Hirai *et al.* at Asahi Glass [7], to operating voltages of well-over 100V for window prototypes. Some of this difference arose from the fact that a wide range of film thicknesses were employed for different PDLC systems, with films ranging from less than 10 microns to 25 microns or more. Since these are field-effect devices, thicker films require higher voltages. There was also a recognition that smaller droplets require higher reorientation fields than larger droplets, due to the increased curvature of the nematic within small cavities [3, 6]. Small-droplet films with higher reorientation voltages often switched faster than lower-voltage films and the explanation commonly offered at the time was that the enhanced surface area in small drops provided the stronger restoring force necessary to return the droplets to their zero-field rest state. Nevertheless, film thickness

and droplet size did not provide an explanation for all of the variations seen.

It is in the context of these two problems (high switching voltages and a wide variation in switching times) that the 1988 *Liquid Crystals* paper 'Reorientation Dynamics' was developed. The paper made a contribution in establishing firm mechanistic explanations for both the dynamic response and magnitude of the field response. There are several aspects of the paper worth mentioning:

- The use of both dichroic dye absorbance effects as well as scattering effects provided a solid connection between the macroscopic electro-optical response and the microscopic orientation of the nematic. The connection between dichroic dye absorbance and nematic alignment was much more straightforward, and in some ways sensitive, than simply relying on interpreting complex scattering behaviour alone.
- A two-stage risetime was observed for the first time and related to the two-stage decay time noted in this and in other work.
- I was able to reject the hypothesis that the distribution in droplet sizes was responsible for the distribution in response times, enabled by a high degree of characterization of film structure.
- The two-stage reorientation properties of the film were related to the microscopic bipolar structure of the nematic droplets, and the presence of disclinations within the droplet.
- The use of variable-length addressing pulses, for the first time, showed that hysteresis effects could be suppressed with sufficiently short pulse lengths, consistent with limiting the ability of the surface to reorient itself.
- The paper firmly established the hypothesis that the anisotropic droplet shapes led to an increase in the elastic free energy of the droplets as they underwent alignment by the electric field. This droplet-shape anisotropy is sufficient to account for the relaxation of the droplets, with no need to invoke surface forces as the restoring mechanism, other than requiring that strong uniform planar alignment be present.

Since its publication, this paper has been often cited as providing a baseline for the operational principles of PDLC devices. Many of these referring papers also studied the dynamics of the liquid crystal reorientation in new types of PDLC devices, although new structures and materials for devices have led to several variations on this theme. For example, recent work by Fernandez-Nieves *et al.* has used the diffraction from a uniform array of liquid crystal droplets as a probe of liquid crystal response and has seen evidence of separate bulk and surface reorientation [8]. In another example,

Sharma *et al.* observed even more complex switching behaviour in gamma-irradiated PDLC devices which they attributed to the effects of charge distribution within the device, in addition to the nematic reorientation [9]. Simulation work by Chan has added some refinement to our understanding of the detailed microscopic reorientation within the droplets [10].

Significant refinement has also occurred in our understanding of the factors that affect the reorientation voltages for PDLC films. The 1988 *Liquid Crystals* paper helped establish the importance of droplet shape anisotropy; subsequent theoretical work provided guidance as to the reorientation fields expected for different droplet shapes [11, 12]. Based on both the range of available liquid crystal properties and the droplet size and shape anisotropy commonly seen in films at that time, reorientation fields of 2–5 V/ μm for a 1 micron droplet are expected in the strong anchoring regime, consistent with experimental measurements on several systems.

Nevertheless, over time, experimental evidence became plentiful that it was possible to produce PDLC films that operated at much lower fields, closer to 1 V/ μm in several polyacrylate-based photocured PDLC devices [7, 13, 14]. It is now known that one way a particular polymer interface could enable these low fields was through the mechanism of reducing the anchoring free energy for the surface, so that the nematic weakly prefers a uniform planar orientation. In this way, the surface accommodates the liquid crystal droplet shape by not requiring strong curvature within the droplet, as strong anchoring conditions would. The droplet shape anisotropy still drove the relaxation process, but because of weak anchoring conditions the elastic free energy within the droplet was reduced significantly, so that weaker fields are now sufficient to reorient the nematic droplet. These effects have been noted in several places [15–18].

Later work also led to the refinement of the light scattering models for PDLC devices, helping explain how so many films with disparate structures can show similar light scattering behaviour. The common thinking early on was that the light scattering came primarily from a mismatch in the extraordinary refractive index of the liquid crystal to the polymer matrix in randomly oriented droplets. When an electric field aligned the nematic director in a common direction, the relative match of the ordinary index of the liquid crystal to the polymer matrix produced a clear state. We were able to show that, in fact, the intense light scattering in the zero-field state arises predominantly from the mismatch in refractive index from neighbouring domains of liquid crystal, each domain possessing a randomized director

orientation in zero field [19, 20]. These randomized orientations lead to localized variations in the phase of light traversing the cell, which then scatter through interference in the far field. The basic mechanism for micron-sized domains appears well-described by the anomalous diffraction approximation for light scattering, with Žumer doing pioneering work in developing the basic theoretical framework on isolated droplets [21].

After years of development, the performance of PDLC films was improved tremendously, with several groups showing devices with good optical switching at low voltages, with reasonable response times, and in films with few or no defects. Commercial products and prototypes were introduced for large area windows, flexible, direct view displays, active matrix displays, and as the engine within liquid crystal projectors. Nevertheless, commercial interest in PDLC devices has waned and with only a few niche applications remaining today in switchable windows and in direct-drive flexible displays. What happened? In each application area, the reasons were somewhat different.

- For large area windows, high prices have worked against large scale adoption of these windows; prices currently appear to run around US\$1000/m² installed. Nevertheless, switchable windows are still commercially available today. Nippon Sheet Glass sells PDLC windows under the brand name 'UMU', and Saint-Gobain sells PDLC-based 'Privalite' windows. These products do attract considerable attention when installed, so are typically seen in high-profile locations where a high price can be justified [22, 23]. Unfortunately, since the turbid state of the film is strongly forward scattering, PDLC films do not provide much of an energy control function which removes energy efficiency as a rationale for installing the films.
- For direct view flexible displays, there are several issues that limit the ability of the displays to compete against established displays. Since PDLC displays cannot reliably be multiplexed, it has not proved possible to achieve high resolution without using a costly active matrix backplane. For direct drive devices, only a limited pixel count (usually segmented alphanumeric) can be supported, which limits the types of applications. The one well-established display uses dichroic-mode PDLC (NCAP) devices. Large area and flexible displays often integrated underneath touch-sensitive panels continue to be offered for sale by Xymox Corporation [24]. It should be noted that it is difficult to use scattering-mode PDLC to make a high-contrast display, as a consequence very few examples of direct-view scattering mode displays exist.

- PDLC devices initially looked attractive as a polarizer-free modulator for liquid-crystal-on-silicon (LCOS) projection engines, with the promise of improved throughput compared to twisted nematic modulators. Both Raychem-Hitachi [25] and Asahi Glass [26] were able to demonstrate working projectors based on PDLC light engines. The development of high-quality devices took many years, though, and concurrent improvements in efficiency in conventional projection technologies were sufficient to prevent the market introduction of PDLC devices.

Nevertheless, the great body of work in PDLC devices remains and it is always possible that interest could be renewed in this field if the large area and/or flexible characteristics of the display become desirable. A relatively complete summary of work in PDLCs up until 1995 can be found in my monograph *Liquid Crystal Dispersions* [27] and in *Liquid Crystals in Complex Geometries* edited by Crawford and Žumer [28]. Much significant work has occurred in the subsequent decade as well, though space does not allow review of that work here.

I shall close by congratulating the founding Editors of *Liquid Crystals*, Edward Samulski and Geoffrey Luckhurst, on the establishment of *Liquid Crystals*. In particular, the care and effort that they and their Editorial Board put into submissions to this Journal has done much to drive its success. I was the happy beneficiary of this care – the first referee to look at the 'Reorientation Dynamics' manuscript recommended rejection, commenting that 'the manuscript fails to provide sufficient new material to justify its publication'. Professor Samulski took a personal interest in obtaining additional reviewers, and the further review provided both an affirmation of the novelty of the work and useful guidance that resulted in the final published form for the manuscript. I appreciate the extra time that Professor Samulski took in overseeing the review process and history indicates that this was time well spent.

References

- [1] P.S. Drzaic. *Liq. Cryst.*, **11**, 1543 (1988).
- [2] J.L. Ferguson. U.S. Patent 4,435,047 (1984).
- [3] P.S. Drzaic. *J. Appl. Phys.*, **60**, 2142 (1986).
- [4] Data obtained from ISI Web of Science, Thomson Scientific.
- [5] Ironically, this work was done only a few miles away from Ferguson's initial work at his private company in northeast Ohio.
- [6] J.W. Doane, N.A. Vaz, B.-G. Wu, S. Zumer. *Appl. Phys. Lett.*, **48**, 269 (1986).
- [7] Y. Hirai, S. Niiyama, H. Kumai, T. Gunjima. *Proc. SPIE*, **1257**, 2 (1990).
- [8] A. Fernandez-Nieves, D.R. Link, D. Rudhardt, D.A. Weitz. *Phys. Rev. Lett.*, **92**, 105503 (2004).

- [9] S.C. Sharma, L. Zhang, A.J. Tapiawala, P.C. Jain. *Phys. Rev. Lett.*, **87**, 105501 (2001).
- [10] P.K. Chan. *Liq. Cryst.*, **28**, 207 (2001).
- [11] B.-G. Wu, J.H. Erdmann, J.W. Doane. *Liq. Cryst.*, **5**, 1453 (1989).
- [12] P.S. Drzaic, A. Muller. *Liq. Cryst.*, **5**, 1467 (1989).
- [13] T. Fujisawa, H. Ogawa, K. Maruyama. *Proc. Japan Display* (Kyoto; Soc. Info. Display), **2989**, 690 (1989).
- [14] D. Coates, S. Greenfield, M. Goulding, E. Brown, P. Nolan. *Proc. SPIE*, **1911**, 2 (1993).
- [15] K.R. Amundson, M. Srinivasarao. *Phys. Rev. E*, **58**, R1211 (1998).
- [16] T. Yamaguchi, Y. Kawata, Y. Mori. *Appl. Phys. Lett.*, **72**, 1170 (1998).
- [17] Y.H. Cho, B.K. Kim. *J. Poly. Sci. Part B*, **36**, 1393 (1998).
- [18] P.S. Drzaic. *Polym. Preprints* (American Chem. Soc.), **213**, 253-POLY Part 2 APR 13 (1997).
- [19] P.S. Drzaic, A.M. Gonzales. *Appl. Phys. Lett.*, **62**, 1332 (1993).
- [20] P.S. Drzaic. *Mol. Cryst. Liq. Cryst.*, **261**, 383 (1995).
- [21] S. Žumer. *Phys. Rev. A*, **37**, 4006 (1998).
- [22] <http://inhabitat.com/blog/2006/02/19/super-smart-privacy-glass/>.
- [23] http://www.sumitomo.gr.jp/english/discoveries/special/102_03.html.
- [24] <http://www.ncapdisplays.com/>.
- [25] Y. Nagae, K. Ando, A. Asano, I. Takemoto, J. Havens, P. Jones, D. Reddy, A. Tomita. *SID Tech. Digest*, 223 (1995).
- [26] Y. Ooi, Y. Hirai, M. Kunigata, S. Niiyama, H. Kumai, T. Wakabayashi, T. Gunjima. *SID Tech. Digest*, 227 (1995).
- [27] P.S. Drzaic. *Liquid Crystal Dispersions*. World Scientific, Singapore (1995).
- [28] G.P. Crawford, S. Žumer (Eds), *Liquid Crystals in Complex Geometries*. Taylor & Francis, London (1996).

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-spherical 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

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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 do 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 ($S > 0.70$) 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 1.0μ (0.5 – 2μ diameter range), and a 'large'

droplet emulsion with a mean volume diameter of $3.3\ \mu$ ($1\text{--}7\ \mu$ 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 $10.5 \pm 0.5\ \mu$ thick. Absorbance vs. voltage curves show that the large droplet film is saturated at $100\ \text{V}$, 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 $3.2\ \mu$, coated to a dry thickness of $25\ \mu$. 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 ($25\ \mu$ thick, $25\ \mu$ 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 $20\ \text{W}$ 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 $29\ \mu$ (some of the solution leaked under the spacer to give 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 $2\ \text{C}$ for the PVA films, and $4\ \text{C}$ 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, $30\ \mu\text{s}$ 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 $0.5\ \text{Hz}$ 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 $21 \pm 1^\circ\text{C}$.

Percent haze vs. voltage for the scattering samples was measured using a Hunterlabs Calorimeter (Model D25P-9). The drive waveform was a $60\ \text{Hz}$ 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

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

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 regimes 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 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

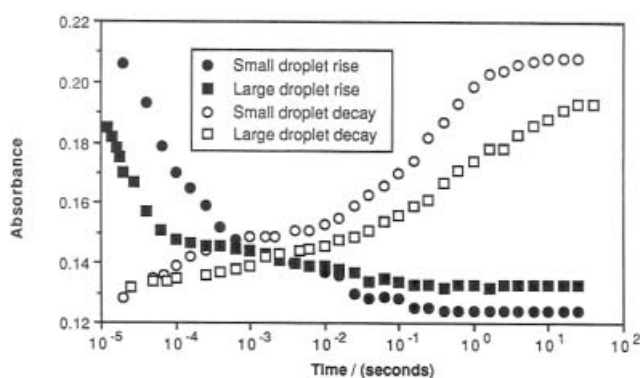


Figure 1. Rise and decay times of the absorbance of two polymer dispersed nematic liquid crystal films. The mean volume diameter of the nematic droplets in the 'large' droplet film is $3.3\ \mu\text{m}$, and $1.0\ \mu\text{m}$ in the 'small' droplet film.

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

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

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 electrooptic 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 $5\text{--}7\times$ 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 ($\gamma_1=0.24 \text{ kg m}^{-1} \text{ s}^{-1}$, K (average) $=1.4 \times 10^{-11} \text{ N}$), 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 films 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 micro-seconds) 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 (2a). 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 (2b), 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 (2a) to (2b) shows a large optical effect.

However, the director field in (2b) 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 minimize its elastic energy by rotating the point defects within the droplet so that they are aligned with the electric field (2c). 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 (2c) is now in its

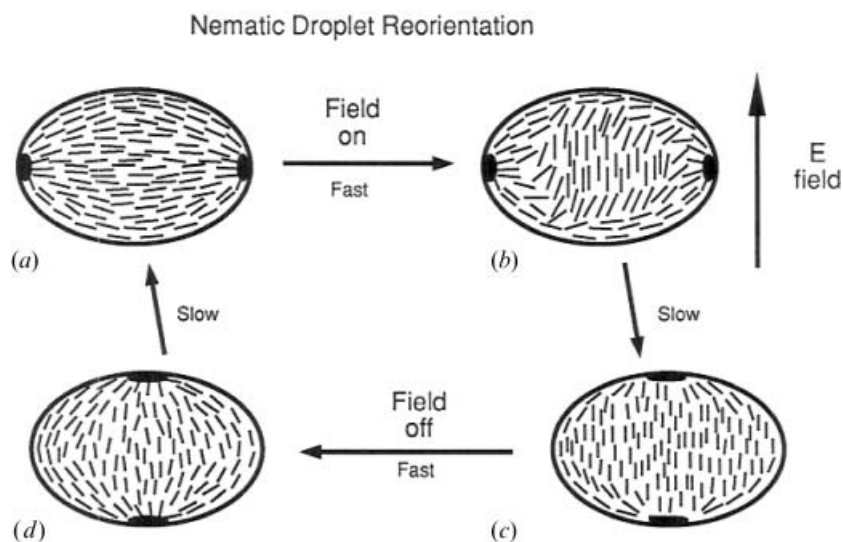


Figure 2. Model for the two stage risetime and decay time response of polymer dispersed nematic liquid crystal films. Upon application of an electric field, the nematic near the centre of the droplet in the rest configuration (a) quickly orients with the field, leading to (b). This is a fast, large optical 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.

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 μ s pulse, the film shows a large optical

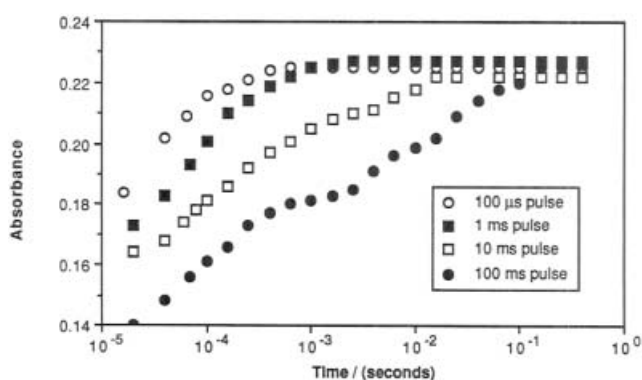


Figure 3. Decay times of a polymer dispersed nematic liquid crystal film, responding to 100 V DC pulses of various durations.

response, but also decays quite rapidly (1 ms). As the length 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

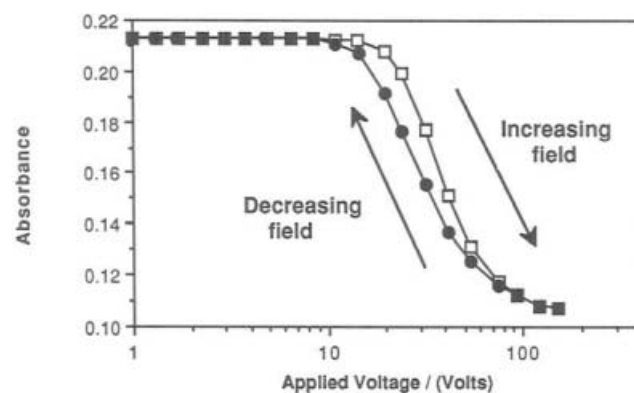


Figure 4. Absorption vs. voltage curve for the 'small' particle size film. Note the hysteresis effect, leading to higher absorbance while raising the applied voltage, compared to reducing the voltage.

with the field (droplet 2c). As the field is reduced, the droplets will relax to state (2d) 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 (2b) or (2d), 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 (2d) is better aligned with the applied field than the droplet (2b) since the symmetry axis of the droplet in (2d) still lies along the applied field direction. A droplet in state (2d) will possess a lower absorbance than a droplet in (2b) due to this greater alignment. If droplets exist preferentially in state (2b) while increasing the applied field, and in (2d) 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 $5-7 \times$ 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 (2d) refracts light less than the droplet (2b) 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 (2a) and (2b). In (2b), 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 (2a) 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 (2b) to (2c) 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 (2b) is better aligned with the electric field than (2a), so that (2b) should always show less absorption than in 2a (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. Secondly, 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

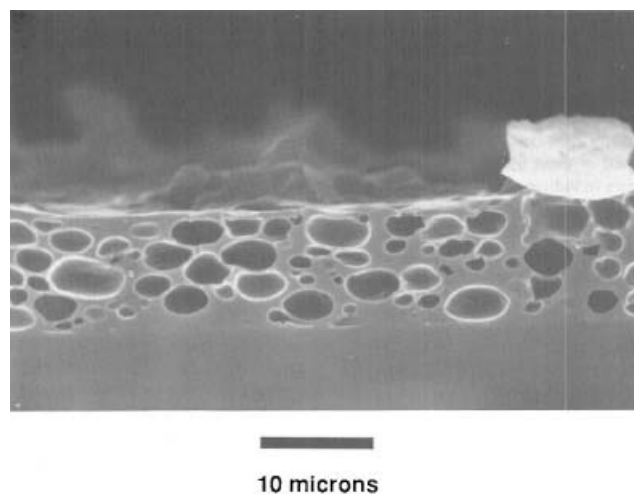


Figure 5. Scanning electron micrograph of a polymer/nematic liquid crystal film (nematic removed). This is the 'large droplet' film used in the response time measurements in figure 1.

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

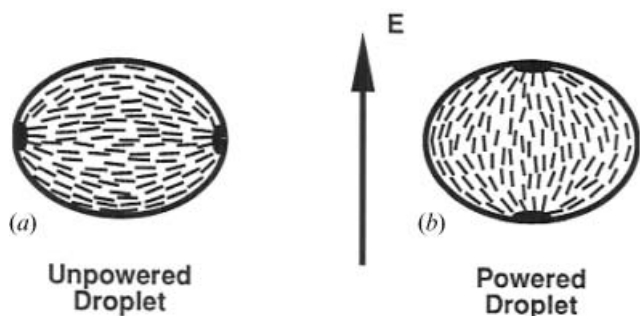


Figure 6. Bipolar droplets with different orientations in oblate droplets. It is qualitatively apparent that the director field in (b) is more highly curved than in (a), and thus at higher energy.

the nematic is rotated within the non-spherical cavity. In the oblate cavity structure shown in figure 5, the minor axis of the ellipsoid 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

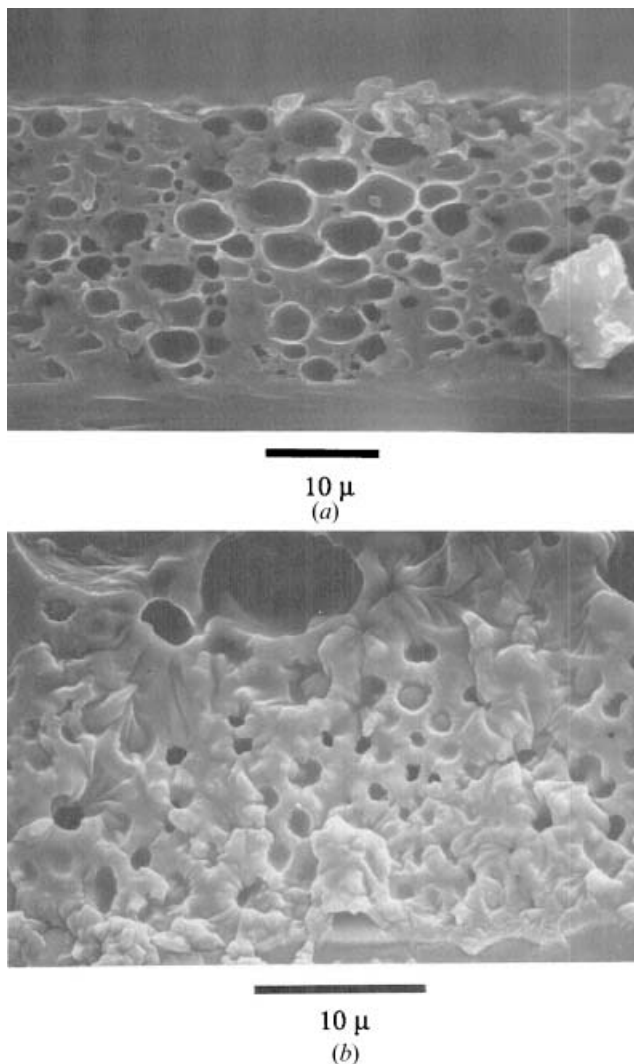


Figure 7. Scanning electron micrographs of E7/PVA (a) and E7/NOA 65 (b) polymer/nematic liquid crystal films. The droplets in the NOA 65 film are somewhat smaller and more spherical than the cavities in the PVA film.

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-cured polymer. It is noted in those studies that the

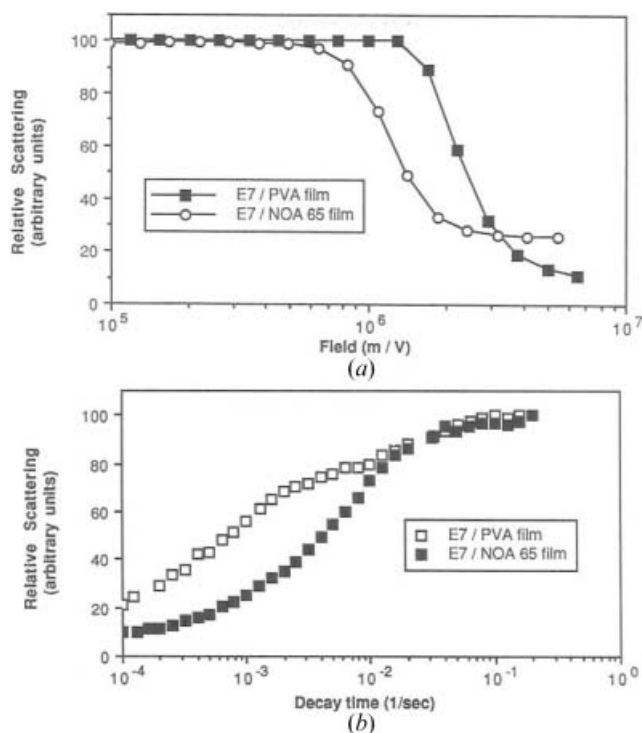


Figure 8. (a) Percentage haze vs. field curves for the E7/PVA and E7/NOA 65 polymer/nematic liquid crystal films. (b) Decay response for the two films.

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 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 is 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 its 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.

Acknowledgements

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References

- [1] J.L. Ferguson. *SID Dig. Tech. Papers*, **16**, 68 (1985).
- [2] P.S. Drzaic. *J. appl. Phys.*, **60**, 2142 (1986).
- [3] J.W. Doane, N.A. Vaz, B.-G. Wu, S. Zumer. *Appl. Phys. Lett.*, **48**, 269 (1986).
- [4] R.B. Meyer. *Phys. Rev. Lett.*, **22**, 918 (1969).
- [5] E. Dubois-Violette, O. Parodi. *J. Phys., Paris*, **C4**, 57 (1969).
- [6] P. Candau, S. Le Roy, F. Debeauvais. *Molec. Crystals liq. Crystals*, **23**, 283 (1973).
- [7] (a) A. Vaz, Nuno, W. Smith, George, GPaul, Jr. *Molec. Crystals liq. Crystals*, **146**, 1 (1987); (b) A. Vaz, Nuno, W. Smith, George, G. Paul Montgomery, Jr., *Molec. Crystals liq. Crystals*, **146**, 17 (1987).
- [8] ASTM standard D-1003, American Society for Testing and Materials.
- [9] L.M. Blinov. *Electro-optical and Magneto-optical Properties of Liquid Crystals*, 116–118 (1983).
- [10] E. Jakeman, E.P. Raynes. *Physics Lett. A*, **39**, 69 (1972).
- [11] G.H. Heilmeier, L.A. Zanoni, L.A. Barton. *I.E.E.E. Trans. Electron. Dev.*, **17**, 22 (1970).
- [12] Data sheets from E. Merck, Darmstadt.
- [13] These observations require the construction of a thin film, dilute in nematic droplets, sandwiched between ITO coated glass plates. See references [2] and [17] for the technique used in constructing these cells.
- [14] P.S. Drzaic, (unpublished results).
- [15] J.W. Doane, G. Chidishimo, N.A.P. Vaz, US Patent 4,688,900.
- [16] N.A. Clark. *Phys. Rev. Lett.*, **55**, 292 (1985).
- [17] For droplets of similar shape, one observes an inverse dependence of the saturation field for a droplet and that droplet's diameter; see [2].
- [18] Occam's razor, or the Law of Parsimony, states that 'plurality should not be assumed without necessity'.
- [19] J.L. West, J.W. Doane, S. Zumer, U.S. Patent 4,685,771.
- [20] P.S. Drzaic, A. Muller, *Liq. Crystals* (submitted).
- [21] M.J. Press, A.S. Arrott. *Phys. Rev. Lett.*, **33**, 403 (1974).
- [22] P.S. Drzaic. *Molec. Crystals liq. Crystals*, **154**, 289 (1988).