

Recent progress in dichroic polymer-dispersed liquid crystal materials

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Abstract

Polymer dispersed liquid crystal films incorporating dichroic dyes can be used to produce high-performance reflective displays using either glass or plastic substrates. The absorbance of PDLC films is predictable, based on a simple alignment model. The photostability properties of the dichroic dyes is an important device criterion. The photostability of dyes can depend on the choice of substrate. With plastic substrates dye fading occurs under aerobic conditions, while in glass substrates any photoreactions are anaerobic in nature; these differences can lead to significant lifetime differences in displays.

Introduction

Liquid crystal displays have made portable computer and video devices possible. Compared to other display technologies, liquid crystal devices offer a flat profile and relatively low power consumption. Highly-multiplexed supertwist and active matrix-driven twisted nematic devices dominate the current generation of portable liquid crystal devices. These displays offer good contrast, but the presence of polarizers in these devices requires the use of backlighting to give a bright, easily readable display. However, polarizer-based LC displays are presently ill-equipped to give good brightness and contrast without backlighting. Dichroic-based nematic dispersions, when coupled with active matrix electronic drivers, offer a means of achieving displays with good brightness and contrast characteristics without backlighting.

Polymer dispersed liquid crystal (PDLC) films consist of micron-sized nematic droplets dispersed in a polymer matrix.¹ These films can be constructed using an aqueous-based emulsion method, or by one of several phase separation techniques. PDLC materials without dyes typically possess a scattering zero-field (unpowered) state and a transparent high-field (powered) state. If the liquid crystal contains a dichroic dye, the unpowered state can be strongly absorbing as well as scattering, while the powered state will be weakly absorbing and transparent.

This paper describes the generalized construction and operation of dichroic PDLC films, along with the factors which control the dichroic absorbance within these films. Some aspects of the photostability of dichroic dyes in PDLC films are discussed. Finally, some present and future applications of PDLC materials are listed.

PDLC basics

Good reviews on the basic aspects of PDLC films exist.^{1, 2} Several methods have been developed to create liquid crystal dispersions. Here, we concentrate on *emulsification* methods, which uses mechanical shear to disperse the liquid crystal (an organic oil) into an aqueous solution of a film-forming polymer. The aqueous phase can either contain a water-soluble polymer (like polyvinyl alcohol) or can be a colloidal suspension of water-insoluble polymer particles (*i.e.*, a latex paint). This emulsion is coated onto a conductive substrate and allowed to dry, which forms a polymer film with embedded microdroplets. A second conductive substrate is laminated to the cell to form the PDLC device. Typical droplets sizes are on the order of a few microns, while film thicknesses can range from 5 μm to over 20 μm .

PDLC dichroic absorbance

Dichroic PDLC displays can possess contrast ratios similar to the best optics obtainable by phase-change (White-Taylor) displays.³ An approximate model for the dichroic response of dichroic PDLC displays has appeared.⁴ Here, these ideas are put on a firmer quantitative basis. The assumptions behind

this model are:

- The liquid crystal within each droplet adopts a bipolar orientation, where the nematic director is oriented primarily along a single symmetry axis of the droplet.⁵
- At zero fields the symmetry axis of each droplet is oriented within the film plane, a result of the anisotropic shrinkage of the polymer film during drying. However, the orientation is randomized within the plane.
- At high fields the symmetry axis of each droplet rotates to become aligned along the field direction.

This model of alignment (in-plane at low fields, perpendicular to the film at high fields) is supported by capacitance measurements of emulsion-based PDLC films at low and high fields.⁶

Since PDLC films possess strong scattering properties, it is necessary to correct for film scattering when estimating the dichroic response of the films. This can be done by using an integrating sphere as the detector: all light passing through the film, scattered or not, will be collected by the integrating sphere. Additionally, a film "blank" (a PDLC film matched for droplet size and thickness, but containing no dye) is used to correct for reflection losses (both specular and scattering). Two parameters are measured: A_{off} , the dye absorbance at zero field, and A_{on} , the dye absorbance at high fields.

It is possible that the absorbance properties of the PDLC films may be complicated by the scattering properties of these films. Film scattering may increase the path length of light passing through the film, and lead to an increased absorbance in the powered state. Additionally, the curved surfaces found within PDLC films may cause significant deviations from the simple in-plane and out-of-plane alignment proposed for unpowered and powered films. We show here, however, that the measured absorbance values for the dichroic response of PDLC films do not appear to depend strongly on film scattering.

For the simple alignment described here, we expect that the dichroic absorbance of these PDLC films at zero field (A_{off}) and high field (A_{on}) should follow the Beer-Lambert law, given by

$$A_{off} = -\epsilon_{off}bc \quad (1)$$

$$A_{on} = -\epsilon_{on}bc \quad (2)$$

where ϵ_{off} and ϵ_{on} are the effective extinction coefficients of the dye at zero field and high fields, respectively, b is the film thickness, and c is the dye concentration within the film. If scattering effects strongly affect dye absorbance, then the extinction coefficient for the dye absorbance should vary strongly with the film scattering. Film scattering can be enhanced by using a high-birefringence liquid crystal, small droplet sizes, or by employing thick films. Thus, if film scattering is important then significant deviations from the Beer-Lambert law should be seen.

We test this idea by plotting the absorbance of films at high and low field vs. thickness (Figure 1). All films possessed the same mean droplet size and dye concentration, but varied in choice of liquid crystal birefringence and film thickness, which affect film scattering. The linearity found in Figure 1 indicates that the dichroic response of these films is not strongly affected by scattering within the film.

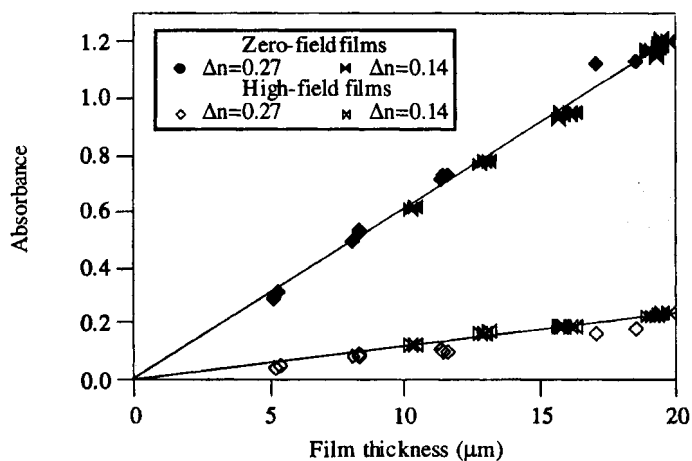


Fig. 1 Absorbance vs. thickness for PDLC films at zero fields and high fields. The linear relationship between absorbance and thickness suggests that film scattering does not strongly affect the absorbance properties of dyes within the PDLC film.

To test the simple alignment model stated earlier, the absolute absorbance of the dye at zero fields and high fields can be measured and related to the dichroic order parameter S for the system. S is typically measured in a glass cell with the liquid crystal homogeneously aligned (alignment parallel to the glass plate), and is given by

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \quad (3)$$

where A_{\parallel} and A_{\perp} represent the dye absorbance measured using a polarizer aligned parallel to and perpendicular to the director orientation, respectively. For the simple alignment model described above,

$$A_{off} = \frac{1}{2}(A_{\parallel} + A_{\perp})\psi_{off} \quad (4)$$

$$A_{on} = A_{\perp}\psi_{on} \quad (5)$$

A_{off} will simply be an average of A_{\parallel} and A_{\perp} , as one-half the light incident on any droplet will possess a polarization aligned along A_{\parallel} and the other half along A_{\perp} . In comparison, in the field-aligned state A_{on} will equal the absorbance of the light polarized perpendicular to the long axis of the director. The terms ψ_{off} and ψ_{on} are correction factors, designed to account for deviations from this simple alignment model ($\psi_{off} = \psi_{on} = 1$ for perfect agreement).

We also define the absorbance A_{iso} , the absorbance of the dye in the isotropic state, as

$$A_{iso} = \frac{1}{3}(A_{\parallel} + 2A_{\perp}) \quad (6)$$

A_{iso} provides a means of determining the absolute dye concentration within the film, as there are no alignment effects in the isotropic phase. A_{iso} can be measured for a PDLC film by heating the film above the clearing temperature of the nematic.

Combining the previous equations leads to

$$A_{off,calc} = \frac{1}{2}(S + 2)A_{iso}\psi_{off} \quad (7)$$

$$A_{on,calc} = (1 - S)A_{iso}\psi_{on} \quad (8)$$

which allows for the calculation of A_{off} and A_{on} based on the experimental measurement of A_{iso} and S . Additionally, A_{off} and A_{on} can be measured experimentally for the same films. Thus, the experimental correction factors ψ_{off} and ψ_{on} can be determined from

$$\psi_{off} = \frac{A_{off,measured}}{A_{off,calculated}} = \frac{A_{off,measured}}{\frac{1}{2}(S + 2)A_{iso}\psi_{off}} \quad (9)$$

and

$$\psi_{on} = \frac{A_{on,measured}}{A_{on,calculated}} = \frac{A_{on,measured}}{(1 - S)A_{iso}\psi_{on}} \quad (10)$$

Choosing the field to measure A_{on} is somewhat arbitrary, as there is no well-defined "saturation voltage" for most samples. For these measurements, we chose an arbitrary field of 10 V/ μm to assure saturation for all the samples tested.

Table 1 shows the results of these measurements. ψ_{off} shows some variation, ranging between 0.94 to 1.05. There is not a strong correlation between ψ_{off} and the nematic birefringence, indicating again that film scattering does not impact ψ_{off} significantly. The only notable effect appears in the last two rows, where the average size of the nematic droplets is varied. Here, a smaller droplet size does lead to a modest increase in ψ_{off} . In any case, the observation that ψ_{off} is near 1.0 for most films indicates that that any curvature of the director field near the polymer walls does not significantly reduce the in-plane alignment of the nematic within films at zero field.

Table 1. Comparison of predicted vs. measured dichroic absorbance for PDLC films

Nematic	Δn	Droplet MVD [#] (μm)	Order parameter ^{&}	Ψ_{off}	Ψ_{on}
E49	0.27	3.2	0.81	0.96	1.04
ZLI 3219	0.21	3.2	0.80	0.95	1.04
ZLI 1840	0.14	3.2	0.79	0.94	1.29
ZLI 1840	0.14	2.2	0.79	1.05	1.29

[#] Mean volume-weighted diameter of droplets

[&] Dichroic order parameter of dye in nematic host, measured in homogeneously-aligned glass cell

A value of 1.0 for Ψ_{on} indicates near-perfect alignment at high fields. Ψ_{on} is near 1.0 for the E49 and ZLI 3219 systems, but is significantly higher for the ZLI 1840 films. Presently we have no explanation for the higher Ψ_{on} values in the 1840 system, although the results are reproducible; this result might indicate some dye solubility within the polymer matrix, which would increase absorbance at high fields.

In summary, the model of in-plane alignment for unpowered films and out-of-plane alignment for powered films is a reasonably accurate description for the dichroic response of dichroic PDLC films. Film scattering does not significantly increase the absorbance of the dyes in these particular films.

Scattering enhancement of display contrast ratio

In the previous section, we showed that film scattering does not appear to significantly enhance the absorbance of the PDLC devices studied here. That is not to say that film scattering is unimportant in dichroic PDLC devices. For example, if a colored reflector is used behind a PDLC film then film scattering can help mask the color, providing a more neutrally-colored dark state. This ability to hide coloration increases the apparent contrast of the display.⁴

Enhanced contrast can also be achieved by controlling the reflection profile of a reflector. A normal Lambertian reflector (*i.e.*, a diffuse white surface) will uniformly reflect an incident collimated beam in all directions uniformly. In contrast, a *gain* reflector will preferentially reflect a collimated beam into a finite cone of light. To an observer placed within this reflection cone, a gain reflector will appear brighter than a diffuse white reflector placed at the same location. The scattering properties of a PDLC film can modulate the reflectivity of a gain reflector, and make it appear as if it's switching between a diffuse white state (when the film is unpowered and scattering) and a gain state (when the film is powered and transparent). This effect (dark unpowered state, bright powered state) is synergistic with the dichroic response in these films.

To illustrate the sort of enhancement expected, we measured the contrast ratios of a matched set of films (one incorporating a dye, one without) in front of a diffuse reflector and in front of a gain reflector. In our configuration, the gain reflector by itself (with no PDLC) has an apparent luminance of 2.0 relative to a Lambertian reflector. Table 2 shows the results of the contrast ratio measurements for the four different combinations, measured as illustrated in Figure 2.

- For the scattering film with a Lambertian reflector, the contrast is 1.0. This is not unexpected, as the Lambertian reflector diffuses the light the same whether or not the PDLC film is in front of the reflector.
- For the dichroic film in front of the white reflector, the contrast ratio is 7.8. This dichroic effect is independent of film scattering, as described in the previous section.
- For the scattering film with the gain reflector, the contrast ratio is 1.7. This represents the modulation of the gain by PDLC film scattering as described above.

PDLC type	Reflector type	Contrast ratio
No dye	Lambertian	1.0
Dye	Lambertian	7.8
No dye	Gain	1.7
Dye	Gain	13.5

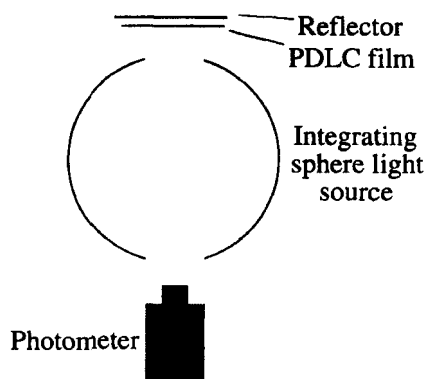


Fig. 2 Apparatus for measuring contrast ratio of dichroic PDLC films.

- For the dichroic film in front of the gain reflector, the contrast ratio is 13.5. The reflected luminance of this display is 0.32, relative to the Lambertian reflector.
- The measured contrast of the dyed film/gain reflector combination is extremely close to the product of the contrast ratios of the dye film/white reflector and the scattering film/gain reflector [measured contrast ratio is 13.5; calculated contrast ratio is $7.8 * 1.7 = 13.4$].

The numbers listed in this section are in a sense arbitrary, as the exact contrast and brightness will depend strongly on dye concentration, dye order parameter, film thickness, external lighting, and the choice of gain reflector. The point to remember is that the presence of a controllable scattering can improve the contrast of dichroic PDLC films.

Photostability of dyes in PDLC films

The stability of dichroic dyes is an important factor in applications of PDLC devices. Dichroic dyes for liquid crystals tend to be of the azo or anthraquinone types.⁷ Decomposition of these dyes have been found to follow⁸ a standard rate law for unimolecular photoprocesses in a well-stirred medium⁹

$$\log(10^{A(t)} - 1) = -Rt + \log(10^{A_0} - 1), \quad (10)$$

where $A(t)$ is the absorbance at time t , A_0 is the initial absorbance, I is the light intensity, and R is a rate constant which includes contributions from the quantum yield, extinction coefficient, and path length.

Typically, dichroic dye fading is tested using dyes placed in glass cells, often with degassing of the solution before filling. However, PDLC devices are often used and tested on plastic substrates. Plastic substrates allow for diffusion of oxygen into the system, whereas glass substrates do not. Thus, dye photoreactions in glass cells takes place under anaerobic conditions, while photoreactions in plastic cells usually take place under aerobic conditions. We have found that in many cases the stability of dichroic dyes can differ significantly under aerobic and anaerobic conditions.

To demonstrate these differences, we illustrate the fading rate constant R for two dichroic PDLC systems in plastic cells, with one set of cells irradiated in air and the other under nitrogen. Approximate light intensity was 40,000 lux, and a 380 nm long pass filter was used to remove ultraviolet light. Table 3 shows the rate constants measured for these samples; a smaller R indicates a slower reaction and a more stable dye. It is apparent that for these particular systems the fading rate with oxygen present is much faster than in the absence of oxygen. These different rates must be accounted for when predicting the long-term lifetime of dichroic displays.

Table 3. Fading rates of select dyes in PDLC films			
Dye	Type	R (in air)	R (in nitrogen)
M-137	Anthraquinone	3×10^{-8}	$< 3 \times 10^{-10}$
SI-426	Azo	2×10^{-8}	9×10^{-10}

Dyes obtained from Mitsui Toatsu, Ltd. Rate constants in $\text{lux}^{-1} \text{hours}^{-1}$. A lower rate constant corresponds to a more stable dye.

Current status of dichroic PDLC devices

Reduction in the operating voltage of PDLC devices is an important goal for compatibility with high-performance drive electronics. Dichroic PDLC materials with 7 V operation ($1 \text{ V}/\mu\text{m}$ reorientation field, $7 \mu\text{m}$ coating thickness) have been demonstrated in the laboratory. This low voltage material is suitable for use in active matrix display applications.

The photostability of dyes is a limiting factor for many applications. We have developed a black mixture where the average fading rate constant is $4 \times 10^{-10} \text{ lux}^{-1} \text{ hour}^{-1}$ under aerobic conditions. This stability is suitable for indefinite indoor operation and several years of outdoor application.

The requirements for dyes in active matrix displays are somewhat different, as it is important that the liquid crystal system maintains a high impedance over time. If the photoproducts of dyes are ionic in nature the impedance of the system drops and contrast in active matrix applications suffers. We have developed dichroic PDLC systems with sufficiently good charge holding and stability for several years of operation in active matrix devices.¹⁰

Currently, dichroic PDLC films can be found in many control panel applications for office equipment and appliances. The ability to make large area displays with plastic substrates allows for designs where touch switches are incorporated behind the pixels in the PDLC display. Thus, the user actually pushes through the display pixel to access the switch, which can be used to control both device and display functions.

There is still much room for improvement for dichroic PDLC materials. In particular, more stable dyes are of great interest, as would enable widespread use of PDLC displays outdoors, as well as improve their suitability in active matrix applications.

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