Electro-optic properties of a polymer-dispersed liquid-crystal film: Temperature dependence and phase behavior

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Electro-optic measurements and optical microscopy were used in an investigation into the microscopic properties that determine the switching characteristics of a polymer-dispersed liquid-crystal (PDLC) film. A simple test is demonstrated that provides a necessary condition for the applicability of a previously published formula for the switching voltage [Liq. Cryst. **5**, 1453 (1989); **5**, 1467 (1989)]. This formula is derived from a model that requires droplet asphericity to be the dominant factor determining the switching voltage, and strong anchoring of the liquid crystal texture at the droplet walls. For a commonly studied PDLC film, the formula was found not to be applicable, presumably because of a loss of the strong anchoring boundary condition at the droplet walls, especially at elevated temperatures. Also, a structural transition within droplets of the PDLC film was observed. This transition gives rise to dramatic changes in electro-optic behavior.

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I. INTRODUCTION

A polymer-dispersed liquid crystal (PDLC) consists of micrometer-scale droplets of liquid crystal trapped within a polymeric matrix. An electric field can align the nematic texture in the droplets, resulting in a large change (typically a reduction) in light scattering power. For this reason, PDLC films are candidates for use as the electro-optic material in flat-panel displays. Commercial applicability of PDLC films depends on electro-optic properties such as the switching voltage, response times, contrast between the on and off states, and off-angle haze. These parameters are determined by microscopic properties. The relationship between microscopic properties and macroscopic behavior has been the focus of numerous reports, such as Refs. [1–11]. Because of the complexities of PDLC morphology and dynamics of nematic reorientation, precise relationships between microstructure and macroscopic properties are not yet available. Instead, approximate relationships have been derived and used in the design of PDLC's. The focus of this paper is on the microscopic issues that determine the switching voltage of a PDLC film. In 1989, both Wu, Erdmann, and Doane [5] and Drzaic [3] published derivations and resulting formulas relating the switching voltage of a PDLC film to microscopic parameters. The primary two simplifying assumptions were strong planar anchoring at the droplet walls and that the droplet asphericity is the primary factor in determining the switching voltage. Direct testing of this formula on PDLC films is difficult because the droplet shape cannot be easily measured. On the other hand, this formula, to the knowledge of the author, represents the only attempt to date at a quantitative prediction for the switching voltage of PDLC films.

This paper has two components. First, a simple test is demonstrated that provides a necessary condition for applicability of the above-mentioned formula to any partic-

ular PDLC film. This test is performed on a photocured PDLC film prepared from a commonly used formulation. Second, an internal structural transition is observed inside the droplets at temperatures within ~ 4–$5\,°C$ from the nematic-isotropic phase transition. Accompanying this transition are dramatic changes in electro-optical behavior. The explanation offered for this observation suggests that this behavior should be *qualitatively* general for many PLDC films.

As a starting point, the derivation of a formula for the switching voltage of a PDLC film first published by Drzaic [3] and by Wu, Erdmann, and Doane [5] is reviewed.

Consider a single liquid-crystal-filled cavity as shown in Fig. 1. In the case considered, the boundary condition is planar and the nematic director field adopts a bipolar texture with two characteristic surface point defects [1,7]. The bulk of the electric-field alignment of the liquid-crystal texture can be achieved simply by a rigid-body-like reorientation of the director field pattern within the droplet. If the cavity were perfectly spherical, the various orientations of the texture would be degenerate (in zero field). Alignment could then be achieved in a very small electric field; the anisotropic component of the electric-field energy would only need to exceed Brownian rotation energy. However, asphericity of the cavity breaks the degeneracy in zero field, and certain orientations of the nematic texture are preferred. In the model
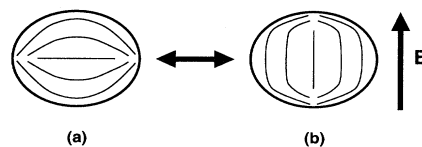

FIG. 1. A single elliptical droplet within a PDLC is shown. The lines follow the director field. The ground state at zero field is represented in (a) and in a strong electric field in (b).

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used here, the cavity is a prolate ellipsoid, with a major radius R_2 and minor radius R_1. The elastic energy density for the orientation where the surface defects lie along a direction with radius R_i is approximated as

$$W_{\text{elastic}} \sim \frac{K}{R_i^2} \, , \tag{1}$$

where K is a Frank elastic constant for distortion of the nematic texture. Here the one-constant approximation is adopted; in actuality, there are constants for both splay and bend distortions. The lowest zero-field energy orientation is the one for which the two surface defects are aligned along the major axis of the cavity.

The switching voltage can be found by equating approximate expressions for the completing elastic- and electric-field energies. The electric field energy density inside the droplet is

$$W_{\text{electric}} \sim \frac{1}{8\pi} \epsilon_{\text{eff}} |\mathbf{E}_{\text{int}}|^2 \, , \tag{2}$$

where ϵ_{eff} is an effective dielectric constant for the liquid crystal, and $\mathbf{E}_{\text{int}}$ is an average electric field inside the droplet. (In this paper, Gaussian units are used, and so the permittivity of free space, ϵ_0, is unity.) $\mathbf{E}_{\text{int}}$ is approximately related to the macroscopic applied field, V/d, by the relation

$$E_{\text{int}} = \frac{3\epsilon_M}{\epsilon_{\text{LC}} + 2\epsilon_M} \frac{V}{d} \, , \tag{3}$$

where ϵ_M is the effective dielectric constant of the matrix, ϵ_{LC} the dielectric constant assigned to the liquid crystal, V the applied voltage, and d the film thickness. This equation comes from the expression for an electric field inside an isolated dielectric sphere embedded in an infinite uniform medium [12]. Because the electric field is generally oscillatory, the dielectric constants must be evaluated at the frequency of the applied field:

$$\epsilon(\omega) = \epsilon' + i \frac{4\pi\sigma_{\text{LC}}}{\omega} \, , \tag{4}$$

where ϵ' is the real component of the dielectric constant, σ the conductivity, and ω the frequency.

By equating the electric and elastic energies and using Eqs. (1)–(3), a formula for the switching voltage is obtained:

$$V_{\text{switch}} \approx \frac{1}{c} \frac{d}{R} \sqrt{\mathcal{L}^2 - 1} \left[\frac{4\pi K}{\Delta\epsilon} \right]^{1/2} \, , \tag{5}$$

where R is a characteristic drop radius, $\Delta\epsilon$ is the dielectric anisotropy of the liquid crystal, and L ($\equiv R_2/R_1$) is the droplet aspect ratio. The prefactor c^{-1} represents the field-gathering effect due to the dielectric mismatch or conductivity of the droplets and the surrounding matrix:

$$c = \frac{3\epsilon_M}{\epsilon_{\text{LC}} + 2\epsilon_M} \, , \tag{6}$$

and in two limits can be expressed as

$$c = \begin{cases} \dfrac{3\epsilon_M'}{\epsilon_{\text{LC}}' + 2\epsilon_M'}, & \omega \gg \sigma_M/\epsilon', \sigma_{\text{LC}}/\epsilon' \\[2mm] \dfrac{3\sigma_M}{\sigma_{\text{LC}} + 2\sigma_M}, & \omega \ll \sigma_M/\epsilon', \sigma_{\text{LC}}/\epsilon', \end{cases} \tag{7}$$

where the prime denotes the real component of ϵ.

In a similar manner, the relaxation time of the texture of a droplet within a PDLC film can be approximated by balancing the driving force toward relaxation against viscous dissipation:

$$\tau_{\text{ON}} = \frac{\gamma_1}{\dfrac{\Delta\epsilon E^2}{4\pi} - \dfrac{K(\mathcal{L}^2 - 1)}{R^2}} \, ,$$

$$\tau_{\text{OFF}} = \frac{\gamma_1 R^2}{K(\mathcal{L}^2 - 1)} \, , \tag{8}$$

where γ_1 is a rotational viscosity coefficient.

Equation (5) relates the switching voltage of a PDLC film to microscopic parameters. For this reason, it is a valuable formula, and it is desirable to ascertain its predictive power for various PDLC films. However, it is difficult to test this formula directly because some of the variables are difficult to measure in PDLC films, most notably the aspect ratio of droplets. Previous experiments have qualitatively supported the formula of Eq. (5) in specific cases. Drzaic [1] has shown that the switching voltage scales inversely with the average droplet diameter in similar films made by an emulsion process. Calculations showed that the elastic and electric energy anisotropies differed by a factor of 3 at the switching field, however [3]. In PDLC films that exhibit a radial texture, differences in the calculated switching voltage and experiment were interpreted as due to a weakening of the surface anchoring strength with increasing temperature [8].

The approach described here is to test the applicability of Eq. (5) to a particular PDLC film indirectly. Equation (5) makes a specific claim about the temperature dependence of the switching voltage of PDLC films, and this claim will be tested by comparison to the temperature-dependent Fréedericksz transition. This test will be demonstrated on a PLDC film whose formulation has been widely used by many researchers [13–21].

II. EXPERIMENT

The PDLC film for electro-optic characterization was prepared from a 50:50 (wt %) mixture of $E7$ liquid crystal [22] and Norland Optical Adhesive No. 65 (NOA65) [23]. The mixture was placed between two indium-tin-oxide-coated glass plates along with glass microsphere spacers, then cured for ~ 15 min under irradiation from a mercury arc lamp (~ 3.8-mW/cm^2 intensity, peaked at 365 nm). The film thickness as determined by microscopy was 18 ± 1 μm. The film has a typical PDLC morphology as shown in Ref. [20], with drop sizes on the or-

der of 1–5-μm diameter. The nematic texture in some of the larger drops could be resolved using polarized light microscopy. They exhibit the extinction brushes characteristics of the bipolar texture [1,7], both near room temperature and near the nematic-isotropic phase transition. Configurational transitions across the temperature range studied are considered unlikely because such transitions would be indicated by sudden changes in electro-optical properties. None were found.

Electro-optic properties of the PDLC film were measured by use of the apparatus shown in Fig. 2. Helium-neon laser light, propagating normal to the plane of the PDLC film, first was modulated at 100 kHz by a photoelastic modulator between crossed polarizers, then made circularly polarized by a quarter-wave plate. The collection half-angle for the transmitted light was set to 1° by an iris. The forward-transmitted light was then focused by a lens onto a photodetector. The photodetector signal was amplified and demodulated by a lock-in amplifier, which used the photoelastic modulator signal as a reference. (In this manner, background light was eliminated from the measurement). The signal from the lock-in amplifier was recorded by a digital oscilloscope.

A gated, 1-kHz sinusoidal voltage was applied to the PDLC film. The pulse duration was 500 ms, or longer when dictated by the relaxation time of the film. The voltage amplitude was varied in consecutive experiments; the transmitted light intensity and the response times (both rise and fall) were measured. Rise and fall times are defined as the time for the transmitted light intensity to go from 10% to 90% (or 90% to 10%) of the total change between the on and off states (see Fig. 3).

The sample was heated and cooled in an FP82 Mettler hot stage with cold nitrogen gas flow. To avoid water condensation at low temperatures, the sample area was enclosed in a nitrogen-purged box.

Fréedericksz transition measurements were make on a 42-μm-thick film of $E7$ liquid crystal between indium-tin-oxide-coated glass plates with rubbed polymer coatings for alignment. The liquid-crystal texture appeared well aligned as analyzed by polarized light microscopy. Birefringence measurements were made on this sample using the apparatus shown in Fig. 2, but where the quarter-wave plate was replaced by a Babinet-Soleil com-
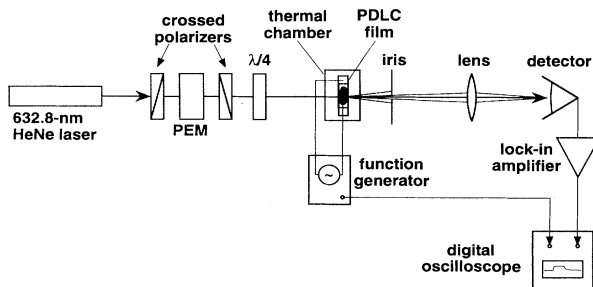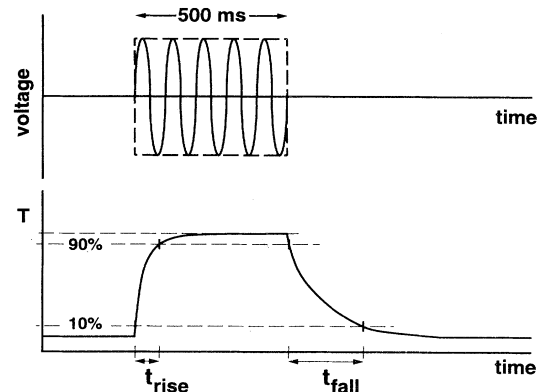

FIG. 3. The applied voltage and the transmitted light intensity (T) as a function of time is represented. The transmitted light intensity recorded is indicated by the upper dashed line. The rise and fall times are taken as time intervals between the 10% and 90% levels of response from baseline to full response.

pensator, and a polarizer was placed in front of the iris, and was crossed to the first polarizer.

III. OBSERVATIONS

A. PDLC film electro-optic behavior

Steady-state light transmission as a function of the applied voltage is shown in Fig. 4 for the PDLC film at various temperatures. The light intensity was normalized to the light transmission through an identical cell containing only cured NOA65 acrylate instead of the acrylate/liquid crystal mixture. Three characteristics of the transmission curves are plotted in Figs. 5(a) and 5(b): transmission at zero applied voltage and at high voltages for which the transmission shows no further change, and V_{50}, the voltage at which the mean of these two transmissions was obtained. Below 0 °C, the film could not be fully switched before the dielectric breakdown limit was approached. For these temperatures, V_{50} was estimated by determining the scaling factor for the abscissa necessary to superimpose the available data onto the data taken at 30 °C. These calculated values are indicated by the open data points in Fig. 5(a). Agreement between V_{50} values obtained with this method and by direct measurement for data taken above 30 °C is excellent.

The response times of the PDLC film are shown in Fig. 5(c). The rise time is evaluated at the applied voltage V_{50}. The fall time is measured after the film is fully switched. Below 0 °C the film could not be fully switched, and the fall time could not be measured.

B. Fréedericksz transition

At voltages below the Fréedericksz transition threshold voltage V_{th}, the uniform liquid-crystal texture remains undistorted. Above V_{th}, the director pattern becomes distorted [24], and the effective birefringence of the cell is reduced. The change in the birefringent phase shift as a function of the applied field for the $E7$ liquid

FIG. 2. Electro-optic apparatus for measuring light transmission through PDLC films. Light scattered outside a 1° half angle cone is blocked by the iris.

crystal film at 30 °C is shown in Fig. 6. The onset of distortion is given by the intercept between the straight line through the low-field data and the line through the data just above the threshold voltage. The sharp transition at the threshold voltage, seen at all temperatures studied, is evidence of low pretilt at the surfaces [25,26]. Figure 7 shows the threshold voltage as a function of temperature. The measured value at 20 °C is within 11% of 0.85 V, the value calculated from Eq. (9) (see below) using data provided by EM Industries [27]. This supports the assump-

tion of strong anchoring and low pretilt angles at the surfaces of the Fréedericksz transition cell.

IV. DISCUSSION

A. Trends

The magnitude of the switching voltage for the PDLC film is consistent with the magnitude one calculates assuming that asphericity of the droplets is the dominant

FIG. 4. Light transmission vs the rms applied voltage at various temperatures.
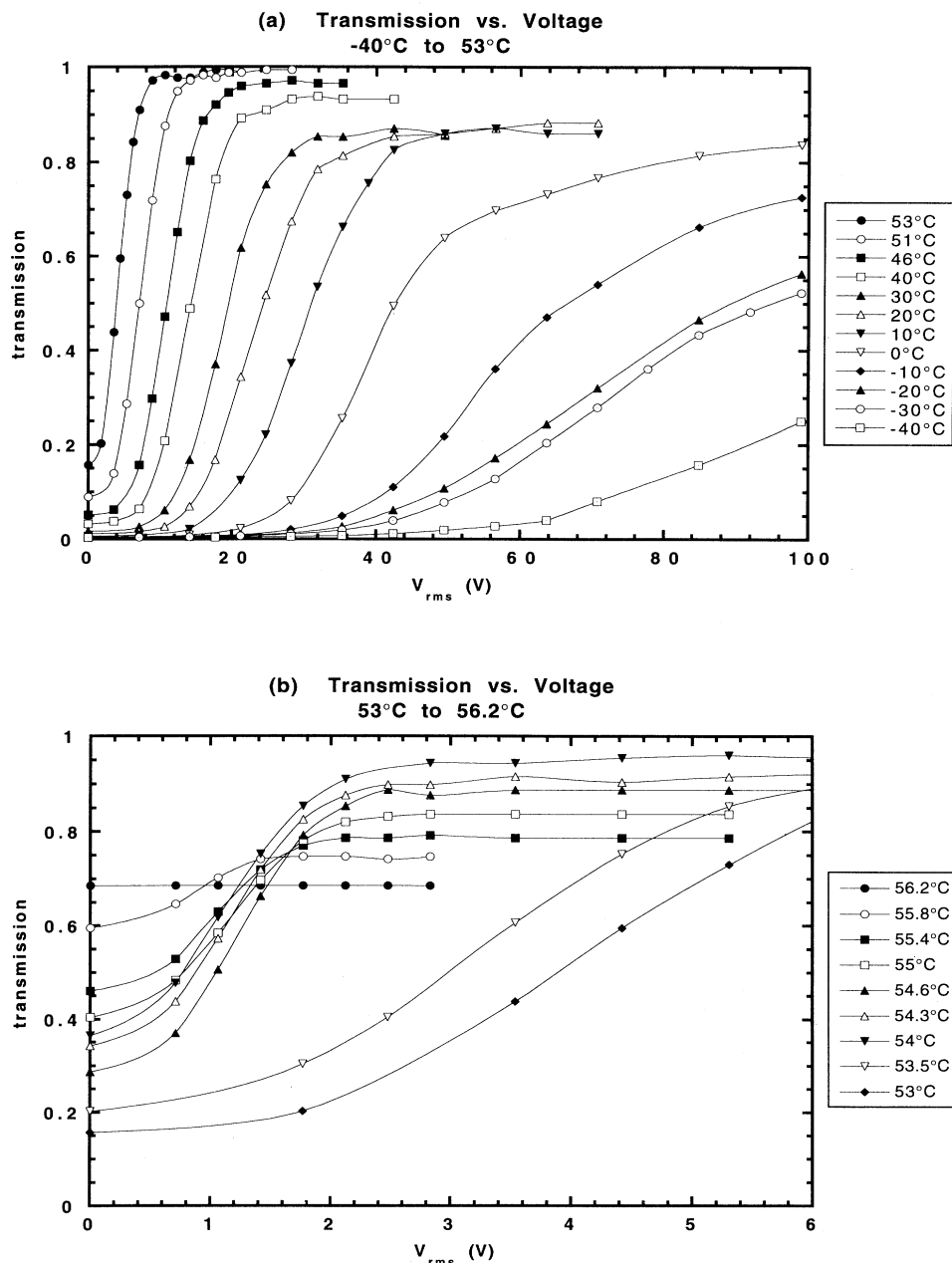
factor in determining the switching voltage, at least at lower temperatures. From Eq. (5), the ambient temperature switching voltage is consistent with aspect ratios of droplets in the range 1.1 to 1.5, which is similar to what is observed.

Trends in the electro-optic properties of the PDLC film with temperature can be qualitatively rationalized using Eq. (5). With increasing temperature, the order parameter S of the liquid crystal decreases. Accompanying this is a decrease in the Frank elastic constants, which are expected to scale as $K \sim S^2$, and the dielectric constant anisotropy $\Delta \epsilon \sim S$ [28]. The birefringence will also decrease with decreasing order parameter. The decreasing contrast between the on and off states upon heating the PDLC film [cf. Fig. 4(b)] is an expected consequence of the decrease in the liquid-crystal birefringence. Ultimate-
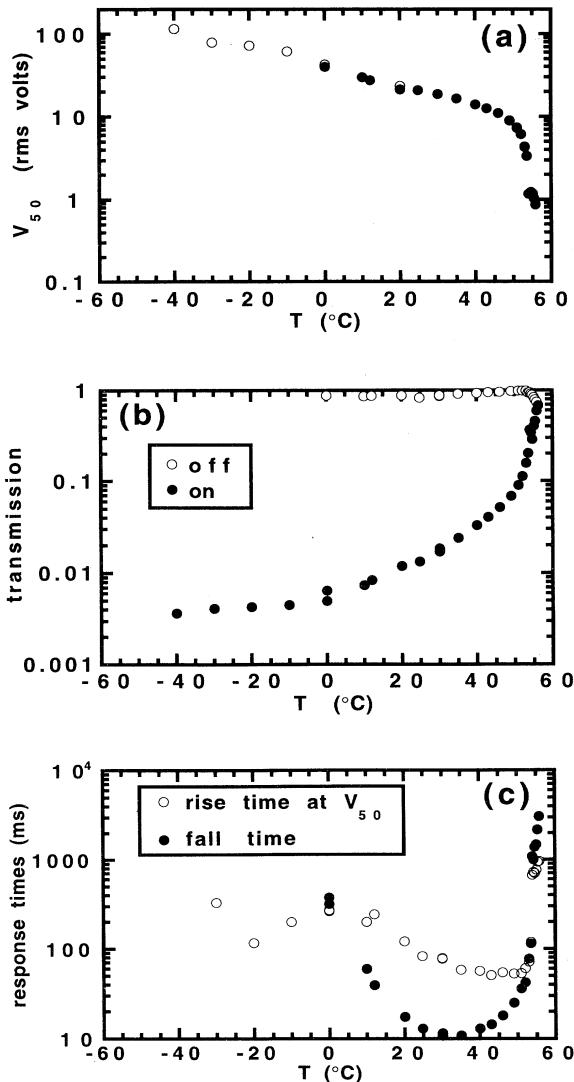

FIG. 6. Birefringent phase shift ϕ between two light polarizations passing through the $E7$ liquid crystal as a function of the applied voltage. The phase shift is proportional to the effective birefringence of the liquid crystal film. The value in the absence of an electric field is subtracted from the ordinate. The Fréedericksz transition threshold voltage is taken as the intercept of the two lines as shown.

ly, above 56 °C, the nematic state is lost and there is no contrast.

The relaxation (fall) time depends upon several physical properties, including the scattering cross section of droplets, the number density of droplets, and the film thickness. It is also proportional to the relaxation time of the liquid-crystal texture within the droplets, which scales with a rotational viscosity of the liquid crystal divided by an elastic constant (γ_1 / K). Far from the nematic-to-isotropic transition, the dependence of K on temperature is slight, and so the drop in the fall time is presumably a reflection of the decreasing viscosity with temperature, which has a much stronger, Arrhenius-type temperature dependence. As the nematic-to-isotropic phase transition is approached, the elastic constant decreases more rapidly. This is presumably why the fall time ultimately reverses its trend and increases with increasing temperature. The behavior of the rise and fall times is influenced by changes in the internal droplet structure that is described later in this paper.

The focus of this paper, however, is on the trend of the switching voltage with temperature. According to Eq.

FIG. 5. Electro-optic specifications of the PDLC film are shown as a function of temperature. V_{50} is shown in (a), the transmission in the on and off states in (b), and the rise time (evaluated at V_{50}) and fall time from saturation in (c).
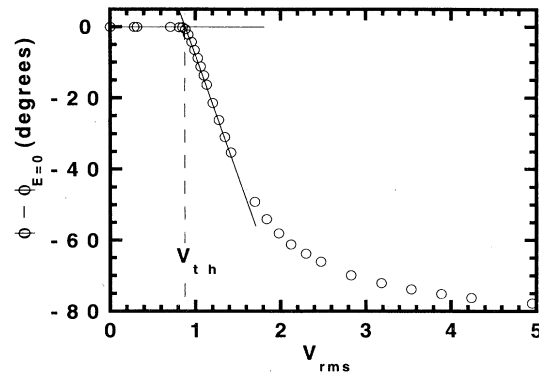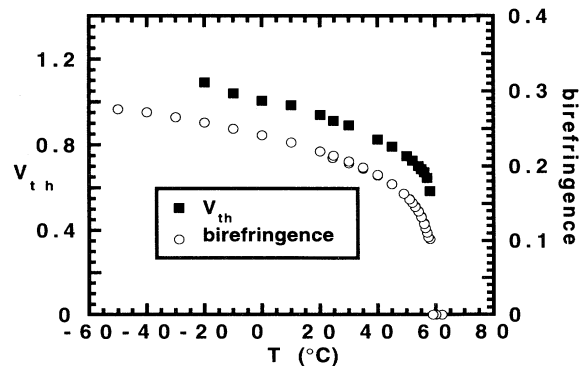

FIG. 7. Threshold voltage and the birefringence of the $E7$ liquid crystal as a function of temperature.

(5), the switching voltage is a product of a prefactor c^{-1}, times a grouping of geometric parameters, times a term that depends upon properties of the bulk liquid crystal: $(K/\Delta\epsilon)^{1/2}$. From dielectric measurements detailed in the Appendix, it was determined that the prefactor is at most only weakly dependent on temperature. The geometric terms will exhibit only minute changes with temperature, in accordance with thermal expansion of the PDLC materials [29]. Therefore, to a good approximation, the temperature dependence of the switching voltage ought to be carried only in the term $(K/\Delta\epsilon)^{1/2}$.

The temperature dependence of the materials grouping $(K/\Delta\epsilon)^{1/2}$ is tracked by the Fréedericksz transition, as the threshold voltage is given by [24]

$$V_{th} = \pi \left[\frac{K_1}{\Delta\epsilon} \right]^{1/2} , \tag{9}$$

where K_1 is the elastic splay constant. The temperature dependence of V_{50} for the PDLC film and V_{th} for the Fréedericksz transition ought to be similar, as they both scale as $(K/\Delta\epsilon)^{1/2}$. A couple of caveats are appropriate at this point. The Fréedericksz transition threshold voltage V_{th} depends upon the *splay* elastic constant K_1, while both splay and bend distortions are present in the PDLC film. However, both splay and bend elastic constants ought to scale approximately as $K \sim S^2$, and thus have a similar temperature dependence [28]. Therefore, since we are interested only in the temperature dependence, the fact that V_{th} depends upon one elastic constant and V_{50} depends upon a grouping of elastic constants is not very important. Second, Eq. (9) assumes a strong surface anchoring of the director at the cell wall, and no pretilt. Certainly, these are only approximately achieved in the cell used in this study. However, only the temperature trend in the threshold voltage, not the absolute value is of interest here. The temperature dependence is quite insensitive to *weak* violations of these assumptions, and were these assumptions *strongly* violated they would be reflected in the nature of the Fréedericksz transition and the birefringence of the sample. The measured birefringence agrees well with data provided by EM Industries [27].

The two voltages are shown together on a semilogarithmic plot in Fig. 8. The decrease in V_{50} with temperature is much greater than the decrease of the materials grouping $(K/\Delta\epsilon)^{1/2}$ (tracked by V_{th}). As Eq. (5) predicts that the curves in Fig. 8 would be parallel, this equation fails to predict the temperature dependence of the switching voltage of the PDLC film. As a corollary, the majority of the decrease in V_{50} with increasing temperature cannot be ascribed to changes in bulk properties inside the PDLC droplets. A reasonable speculation is that the reduction in V_{50} is due primarily to weak surface anchoring ($W_0 R/K$ not large) and W_0 decreasing with temperature.

Several previous reports show examples where the anchoring energy of $E7$ liquid crystal at a polymeric interface decreases with increasing temperature [8–10]. Erdmann, Zuman, and Doane [8] report such a trend for $E7$ in contact with a polyurethane, and West *et al.* [9] and
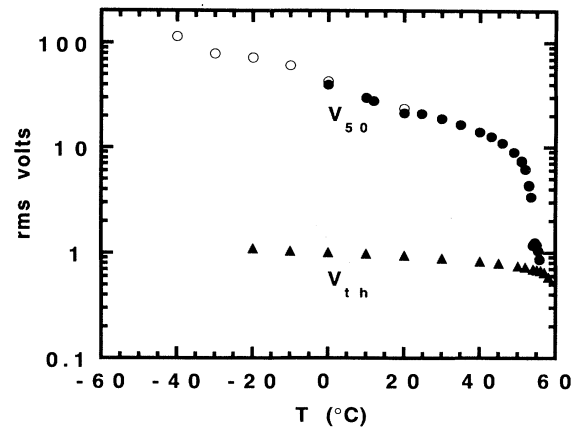
FIG. 8. V_{50} for the PDLC film and the Fréedericksz transition threshold voltage for the $E7$ liquid crystal, V_{th}, are both shown as a function of temperature.

Ji, Kelly, and West [10] report the same trend for $E7$ in contact with poly(vinyl formal). It is likely that the decrease in switching voltage with increasing temperature reported here reflects a similar trend, and one where the surface anchoring strength is sufficiently small that the strong anchoring condition is lost. When the assumption of strong anchoring behind Eq. (5) is violated, Eq. (5) will not predict switching voltages. For the case of the PDLC film, surface anchoring is weak when its strength is similar to or less than K/R, which is on the order of 10^{-2} erg/cm^2. Values of this magnitude were reported for $E7$ in contact with poly(vinyl formal) and a polyurethane [8–10], especially as the nematic-isotropic transition is approached.

The effect on V_{50} of a weakening surface anchoring strength can be understood from the progression represented in Fig. 9. As the surface anchoring strength
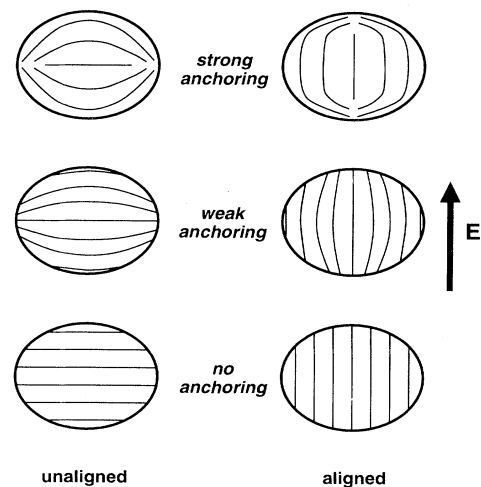
FIG. 9. Depiction of the nematic texture in an elliptical cavity in the absence of an electric field (left column) and in the presence of a strong electric field (right column). Strong anchoring, weakening anchoring, and the limiting (ideal) case of no anchoring are shown.

decreases, the nematic director at the surface can tilt away from the planar orientation in order to reduce the energy of nematic distortion [Fig. 9(b)]. With the reduction of the elastic energy, the electric field required to overcome elastic distortion forces decreases, and so the switching voltage decreases. In the extreme, consider the case of zero anchoring strength [Fig. 9(c)]. Here there is no preferred direction for the director at the surface, and so the lowest energy director configuration is uniform, as in this configuration there is no distortion energy. In this case, all director field orientations are degenerate, and the voltage required to switch the texture is only that required to overcome Brownian reorientation.

### B. Behavior near the nematic-isotropic transition

Let us now focus on the electro-optic behavior within 4–5 K of the nematic-to-isotropic transition. Over this range, the switching voltage decreases by over an order of magnitude to values below 1 V (< 0.1 V/μm), and the response times of the film rise by 1.5–2 orders of magnitude (cf. Fig. 5). These rapid changes are due to a change in the internal structure of the PDLC film cavities.

The internal structure of PDLC cavities was observed by microscopy of a PDLC film made the same way as the one used in the electro-optical studies, but with a reduced UV light intensity during curing (but same total UV light dose). In this second PDLC film the cavities were significantly larger (often > 5 μm) and the internal structure with the cavities could be readily identified by polarized light microscopy. (Microscopy reveals similar behavior in both PDLC films, but microphotographs lack the resolution required to demonstrate the phenomenon discussed in this section except for the larger drops.)

An optical micrograph showing the droplet structure of the PDLC film with the larger drops is shown in Fig. 10. Below ~52 °C the droplets appear fully nematic, as revealed by their birefringence, which gives brightness between crossed polarizers. Above ~52 °C the droplets appear biphasic. An optical micrograph of the same region at 54 °C is shown in Fig. 10(b). Here a quarter-wave plate was inserted between the crossed polarizers. In this manner, interfaces between optically distinct regions are apparent, and birefringence gives rise to interference colors (or greyscale in the black and white photograph). Each cavity contains a nematic sphere (it appears bright between crossed polarizers) surrounded by an isotropic (nonbirefringent) fluid shell. Each cavity can be likened to an egg, where the egg yolk corresponds to the nematic component and the egg white to the isotropic fluid. The volume fraction of the nematic component appears to be roughly the same in all the drops, and it persists over the time of observation (several hours) with no sign of hysteresis. The size of the nematic component decreases continuously from the size of the cavity below ~52 °C until it vanishes at around 56 °C. Between crossed polarizers, the droplets flicker in zero field—a consequence of Brownian reorientation of the nematic texture. The flickering is on the one-second time scale.

From these observations, the cause of the rapid changes in electro-optic behavior is apparent. For one thing, the nematic component is no longer in contact with the matrix, but instead with its own isotropic phase (which wets the wall of the cavity). Therefore, the surface anchoring energy has changed. A more important factor is the fact that the nematic drops reside within a fluid medium and adopt a spherical shape (to the resolution of optical measurements). Below ~52 °C the nematic texture in the droplets experiences a "local force" because they conform to irregular cavity shapes. Once a significant fraction of the cavity is composed of isotropic material, the droplets take a spherical shape, and these local forces are greatly reduced or eliminated. (It should be noted that the spherical shape is not *a priori* apparent. Surface tension drives isotropic fluid drops suspended in a second fluid to a spherical shape. In the case of nematic fluid drops, elastic distortion energy can be reduced by adopting a nonspherical shape. The spherical shape is
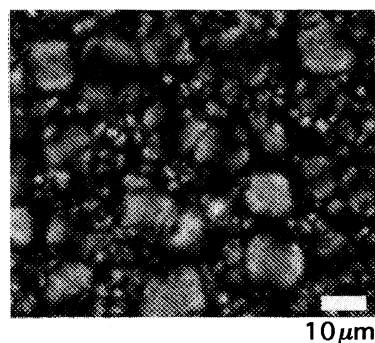
(a) 50 °C
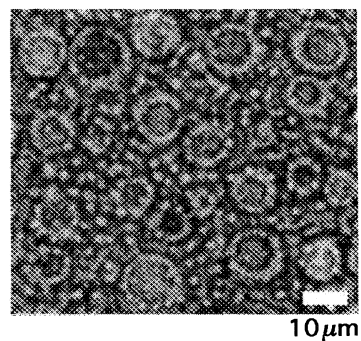
(b) 54 °C

FIG. 10. (a) Microscopic view of a PDLC film at 52 °C between crossed polarizers. In (b) the same region is shown but at 54 °C. Here a quarter-wave plate was inserted between the crossed polarizers, so that various regions can be distinguished. The central, spherical region within each cavity is birefringent, the surrounding region is not. The white bars correspond to 10 μm.

observed because $\sigma R / K \gg 1$, presuming a typical magnitude for the surface tension, σ [30].) Regardless of the droplet shape, the Brownian reorientation at zero field is evidence that orientational energies due to local forces are smaller than even thermal energy, $k_B T$.

The high-temperature electro-optic properties of the PDLC film can be rationalized in light of the above observations. In the absence of local forces, Brownian reorientation is responsible for relaxation of the nematic droplets. Upon cessation of an electric field, the relaxation time for the PDLC film ought to be on the order of the inverse of the rotational diffusion coefficient. This can be estimated by considering the forces on the droplet: viscous drag from the isotropic fluid surrounding the droplet, and Brownian forces. Although the orientation of the sphere is described by two degrees of freedom, an analogous one-dimensional problem is considered for simplicity. The equation of motion can be expressed in the form of a Langevin equation

$$\frac{1}{2} I \ddot{\theta} + 8 \pi \mu R^3 \dot{\theta} = \Gamma(t) \ , \tag{10}$$

where θ is the (arbitrary) polar angle of the drop orientation, I is the moment of inertia, and R the sphere radius. $\Gamma(t)$ represents Brownian forces. As an approximation, the nonturbulent viscous drag torque for a rigid sphere in an infinite medium of viscosity μ was used. The angular diffusion coefficient resulting from this equation is [31]

$$D = \frac{k_B T}{16 \pi \mu R^3} \ , \tag{11}$$

where k_B is Boltzmann's constant, and T is the absolute temperature. Using $\mu \sim 10^{-2}$ P and $R \sim 0.5$ μm, $D \sim 0.7$ s^{-1}. Measured fall times of 1–3 s are on the order of the inverse of the angular diffusion coefficient. The Brownian reorientation observed by microscopy (Brownian flickering) has a time scale on the order of a second, which is also consistent with this estimate for the diffusion coefficient.

The voltage required to align the droplets against thermal energy can be estimated by balancing the anistropic component of the electric energy density times the volume of a drop against thermal energy:

$$\frac{1}{8 \pi} \Delta \epsilon | \mathbf{E}_{\text{int}} |^2 \frac{4}{3} \pi R^3 \sim k_B T \ . \tag{12}$$

The internal field E_{int} can be roughly approximated as V / d, the applied voltage divided by the film thickness (18 μm), to give

$$V_{\text{switch}} \approx d \left[\frac{6 k_B T}{\Delta \epsilon R^3} \right]^{1/2} . \tag{13}$$

$\Delta \epsilon \sim 3.5$ at 55 °C, as determined by scaling the reported value of 13.8 at ambient temperature to the square root of the elastic constant for $E7$ (data provided by EM Industries) [27]. Equation (13) gives a switching voltage of ~ 0.0014 statvolt (Gaussian units), or ~ 0.4–0.5 V. This value is close to V_{50} values measured at temperatures approaching the nematic-isotropic transition.

Next, an explanation is presented for the phase behavior within the PDLC film cavities. First, it should be noted that pure $E7$ liquid crystal is biphasic over a 1.5-K temperature range, as observed using polarized light microscopy. This biphasic temperature range could be increased to the 4–5 K range observed in the PDLC films because of impurities in the droplets, such as uncured components from the optical adhesive, photoinitiator fragments, or oligomers.

It is useful to understand this phenomena by use of pseudobinary phase diagram. Figure 11(a) shows a qualitative phase diagram of a liquid crystal and a small-molecule material with limited solubility in the liquid crystal (in this case a UV-curable small molecule). Use of this pseudobinary phase diagram presumes that the liquid crystal and prepolymer material can both be considered as single components. The phase diagram is not quantitative, but its general structure agrees with phase measurements. The general features can be rationalized: at elevated temperature the two components are soluble, while a two-phase region is found at lower temperature. At high liquid-crystal fractions the solution is nematic. The single-phase isotropic and nematic regions are separated by an extension of the two-phase envelope.

The temperature-composition coordinate characterizing the pre-PDLC mixture resides in the one-phase isotropic region [e.g., the point marked in Fig. 11(a)]. Upon UV irradiation, the molecular weight of the UV-curable component increases. The range of immiscibility, indicated by the two-phase region, grows as represented in Fig. 11(b). After the expanding two-phase region envelopes the temperature-composition coordinate for the solution, the mixture phase separates into a polymer-rich matrix and liquid-crystal-rich droplets, whose coordinates are denoted M and D, respectively, on the phase diagram.

Consider heating the film after the PDLC structure is formed, and the matrix exhibits solidlike or elastic behavior. The trajectories of the two components will not follow the coexistence curve, as would be the case for simple liquids, because the elastic energy of the matrix opposes remixing. In the limit of high elastic constant, the trajectories will be vertical, as represented in Fig. 11(b). The coordinate representing the state of the droplets passes through the single-phase nematic region, then enters the two-phase region at an elevated temperature. Above this temperature, the droplets are biphasic, and the nonmesogenic elements (monomer and oligomer) segregate preferentially to the isotropic component. The volume of the nematic component shrinks with increasing temperature, in accordance with the lever rule for phase behavior.

This construct points out a couple of important features. First, one may expect biphasic behavior to be general for PDLC systems. The temperature range over which biphasic behavior is exhibited depends upon the degree of cure, and more specifically on the width of the two-phase region at the composition of the droplets. It also shows how the impurities in the droplets will be concentrated in the isotropic component of the cavities. This could possibly be exploited to improve PDLC properties.

(a)

1-phase, isotropic

59°C

T

23°C

Nem.

N + I

0   liquid crystal fraction   1

(b)

1-phase, isotropic

59°C

M'

D' D"

T

Nem.

23°C

M   D

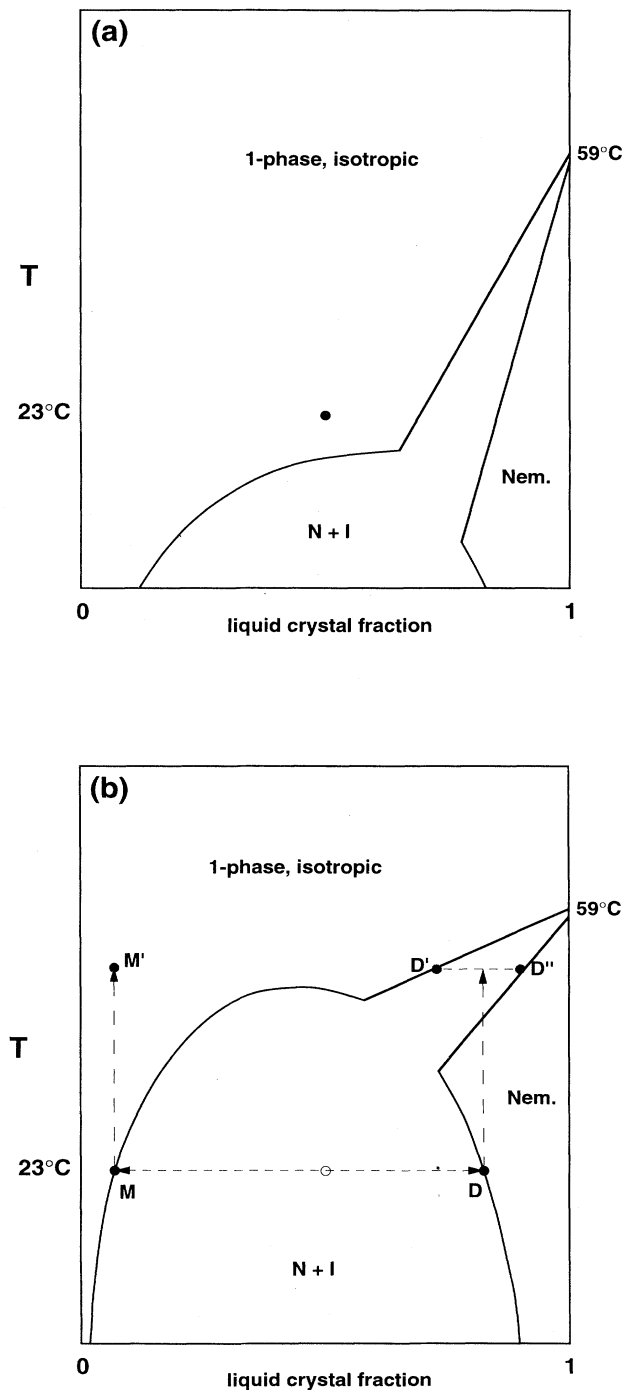N + I

0   liquid crystal fraction   1

FIG. 11. (a) The character of the pseudobinary phase diagram for the PDLC mixture prior to curing is illustrated. The temperature-composition coordinate for the mixture is superimposed. In (b), a (hypothetical) evolution of the phase diagram after cure is shown. The material phase separated into a matrix and droplets, the coordinates are indicated by the points labeled M and D, respectively. Upon heating, the coordinate for the matrix moves vertically to M', and the droplets can enter the biphasic region and further separate into an isotropic component (D') and a nematic component (D'').

At the same time, it must be kept in mind that the pseudobinary approximation has shortcomings. Once the polymerization has proceeded to a fair degree, the impurities within the nematic droplets are presumably only the lowest molecular weight components and are not representative of the matrix material. Such aspects have no representation on the pseudobinary phase diagram.

V. CONCLUSIONS

The temperature-dependent electro-optic properties of a photocured PDLC film made from $E7$ liquid crystal and Norland Optical Adhesive No. 65 were explored. To the awareness of the author, there is only one previously published formula that makes a quantitative prediction for the switching voltage of PDLC films. A simple test was demonstrated that provides a necessary condition for the applicability of this formula *toward any particular* PDLC film. This test involves a comparison of the temperature dependence of the switching voltage and a Fréedericksz threshold voltage of the liquid crystal of composition, along with dielectric measurements. For a PDLC film made from a commonly studied formulation, it was shown that the formula is not applicable. A likely cause is violation of the assumption of a strong-anchoring boundary condition ($W_0 R / K \gg 1$). Trends in the electro-optic behavior are then understood in terms of an expected weakening of the anchoring strength with increasing temperature. Also, an interesting biphasic behavior within nematic droplets was reported over a 4–5-K temperature range just below the nematic-isotropic transition temperature. The electro-optic properties of the PDLC film are strongly influenced by the change in droplet structure over this temperature range. From a consideration of the phase behavior of mixtures with a nematic component, an explanation for this phenomenon was given.

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APPENDIX: ON THE ISSUE OF CONDUCTIVITY IN THE PDLC FILM

Here it is shown that the prefactor c of Eqs. (5) and (6) is at most only weakly dependent upon temperature and, for the purposes of this paper, can be regarded as a constant. This prefactor, as defined in Eq. (6), is expressed as

$$c = \frac{3\epsilon_M}{\epsilon_{LC} + 2\epsilon_M} \tag{A1}$$

where the dielectric constants of the matrix and liquid crystal are given by

$$\epsilon_M(\omega) = \epsilon'_M + i\frac{4\pi\sigma_M}{\omega},$$

$$\epsilon_{LC}(\omega) = \epsilon'_{LC} + i\frac{4\pi\sigma_{LC}}{\omega}. \tag{A2}$$

The prime denotes the real component, and σ is the con-

ductivity. The subscripts M and LC refer to the matrix and liquid-crystalline components, respectively. This prefactor characterizes how the electric field is magnified or diminished by the dielectric mismatch between the droplets and their environment. A low magnitude corresponds to shielding of the electric field from the drop interior by dielectric polarization or conductive charges. A large magnitude for c corresponds to the case where the electric field is magnified in the droplets.

If both components of the film are in the dielectric regime ($\epsilon' \gg 4\pi\sigma/\omega$), then the prefactor is on the order of unity, and will not change much with temperature. If one or both components are in the conductive regime ($4\pi\sigma/\omega \gg \epsilon'$) then the absolute magnitudes of the complex dielectric constants can differ greatly and the prefactor c can take on a wide range of values. Dielectric measurements were made to demonstrate that neither component of the PDLC film is in the conductive regime.

The magnitude and phase of the complex impedance for the PDLC film at several temperatures are shown in Fig. 12. The values were computed from phase-sensitive current-voltage measurements at several frequencies. If the matrix were in the conductive regime, then the real (resistive) component of the PDLC film would be greater than the reactive component, and the phase of the impedance would be close to zero. The phase of the impedance is closer to 90° (although somewhat below 90° at 55 °C). The PDLC film therefore performs much more like a capacitor than a resistor, and the possibility $4\pi\sigma_p/\omega \gg \epsilon'_p$ can be ruled out.

Because the liquid-crystalline component of the PDLC film does not form complete paths between electrodes, conductivity in the droplets can increase the effective *capacitance* of the PDLC film, while the film itself may be nonconductive. From the dielectric data, the effective capacitance (at 1 kHz) is between 1 and 4 nF, while from the cell geometry and dielectric constants of materials (assuming no conductivity), the calculated value is on the order of 20 nF. Although the discrepancy between the measured and calculated value is not understood, clearly the capacitance of the PDLC film is not anomalistically large. Therefore, both the matrix and liquid-crystal com-
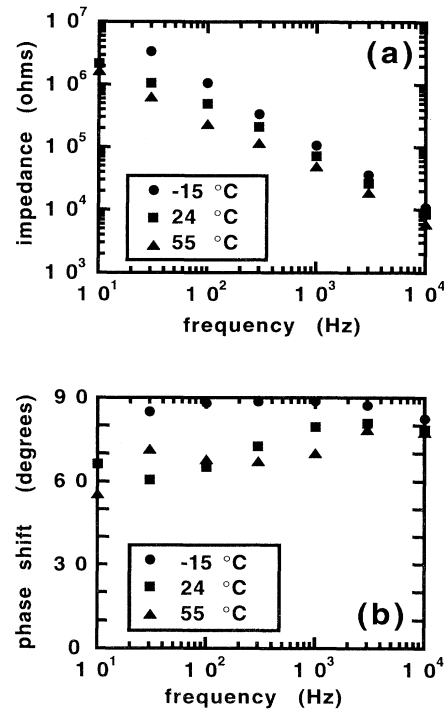

FIG. 12. Magnitude (a) and phase (b) of the complex impedance of the PDLC film as a function of frequency are shown for several sample temperatures.
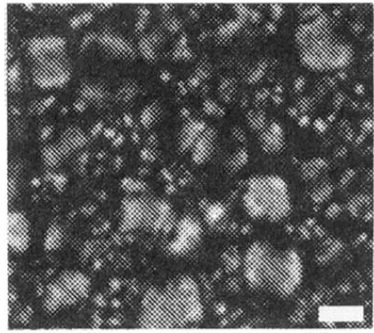
ponent are not in the conductive regime.

From these determinations, the prefactor must be close to the value for purely dielectric components,

$$ c = \frac{3\epsilon'_M}{\epsilon'_{LC} + 2\epsilon'_M} , $$
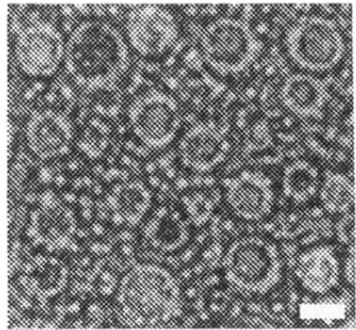
which is on the order of unity. Had this prefactor c changed significantly with temperature, it would have certainly been accompanied by a change in the dielectric behavior much greater than what was observed.

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[29] If the linear expansion coefficient is on the order of 10^{-4}/K, then a sphere would develop at most an asphericity on the order of 10^{-2} over a 100-K temperature change. This is far less than the asphericity of the droplets, and so it is not a significant factor. It is for this reason that I am able to ignore thermal expansion effects on drop shape.

[30] The surface tension approaches zero at a critical point. However, the birefringence data shown in Fig. 7 indicate that the nematic-to-isotropic phase transition is strongly first order. For this reason, the surface tension is presumed to remain large even near the phase transition temperature.

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(a) 50 °C

(b) 54 °C

FIG. 10. (a) Microscopic view of a PDLC film at 52 °C between crossed polarizers. In (b) the same region is shown but at 54 °C. Here a quarter-wave plate was inserted between the crossed polarizers, so that various regions can be distinguished. The central, spherical region within each cavity is birefringent, the surrounding region is not. The white bars correspond to 10 μm.