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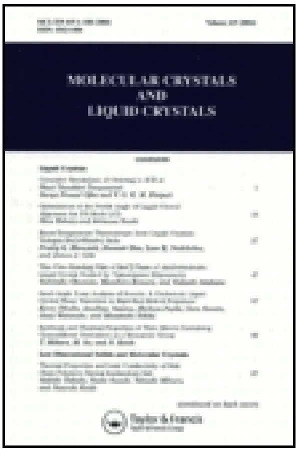

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AC Impedance Spectroscopy (ACIS) Analysis of a Polymer Dispersed Liquid Crystal (PDLC) Film

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AC Impedance Spectroscopy (ACIS) Analysis of a Polymer Dispersed Liquid Crystal (PDLC) Film

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AC impedance spectroscopy is applied to monitoring the chemical–physical condition of polymer dispersed liquid crystals (PDLC). The results define an approach for non-destructive evaluation as the PDLC is designed into informational displays. Response functions are linked to electrical properties of the constituents through mixture relations. Resistivity is established as being much more sensitive than permittivity to the PDLC state. Consideration is given to treating explicitly the large interphasal region found surrounding each liquid crystal droplet in the continuous matrix.

Keywords: mixture relations, PDLC

INTRODUCTION

Polymer dispersed liquid crystals (PDLC) are new composite materials which are being considered for information displays, light shutters and tuneable windows. The PDLC is a mixture of micron-size liquid crystal droplets in a continuous polymer matrix. One type of PDLC films developed by the GMR Physics Department is described in reference 1.

In the information display application, the composite film is activated by an applied electric field (Figure 1), opening the possibility for current flow and chemical changes. As this material makes its way into automotive displays, the engineer must identify ways to monitor the condition of these devices throughout their life cycles. The same probes can also be applied to control quality of future production displays.

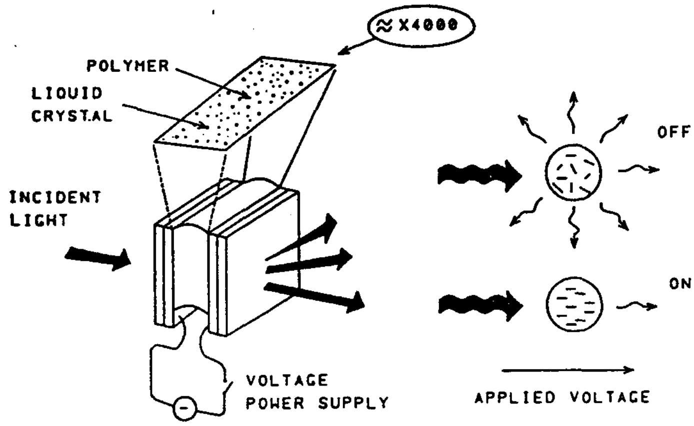

FIGURE 1 Schematic of a PDLC film (courtesy of N. Vaz).

AC impedance spectroscopy (ACIS) offers a natural route to probing the condition of PDLC devices. The response can be interpreted to give the state of regions within the system, in this case, the liquid crystal, the polymer, and both LC–polymer and electrode–polymer interphasal regions. This use of the ACIS transfer function to diagnose liquid crystal-containing systems was previously demonstrated successfully for the layered twisted-nematic design.[2] As with the layered system, response of the PDLC system is represented as a function of permittivities and resistivities associated with the component regions. The simplest possible representation has been identified which simulates PDLC response, and the route to more accurate representations has been sketched.

ELECTRICAL BEHAVIOR OF HETEROGENEOUS SYSTEMS

Electrical properties of the heterogeneous PDLC can be predicted, to a first approximation, by combining properties of the two phases in known relations. We concentrate on analyzing this system as a two-phase mixture, the simplest alternative. But we also touch on the interpretation as a three-phase system, which accounts for the sizeable interphase region seen in photomicrographs of the films. Permittivity and resistivity are treated separately since these quantities are easily isolated in the impedance measurement. The discussion is confined to the PDLC situation: a large volume fraction of

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small liquid crystal spheres (LC) randomly distributed and oriented throughout a polymer matrix.

Resistivity

Assuming one phase to be completely dispersed in another leads to the following relation[3]:

$$\rho = \rho_1 \left\{ \frac{1 - \nu_2[(1 - (\rho_2/\rho_1))/(2(\rho_2/\rho_1) + 1)]}{1 + 2\nu_2[(1 - (\rho_2/\rho_1))/(2(\rho_2/\rho_1) + 1)]} \right. \tag{1}$$

where

ρ_i = resistivity of solvent 1 or solute 2
ν_i = volume fraction of solvent 1 or solute 2
ρ = resistivity of system.

However, interaction effects in some systems can be quite pronounced, and the resistivity is affected by temperature and humidity variations.

A second resistivity model, which includes interactions and is based on geometric averaging of the component resistivities, is given by[4]:

$$\log(\rho) = \nu_1 \log(\rho_1) + \nu_2 \log(\rho_2) - \alpha \nu_1 \nu_2 \log(\rho_2) \tag{2}$$

where α is a constant and the last term is used to compensate for differences between theory and experiment. For the ideal case, $\alpha = 0$.

Permittivity

Permittivity of the liquid crystal phase in the PDLC depends on the magnitude of the applied electric field because there is a competition between surface alignment (at low field) and field alignment (at high field). The liquid crystal molecules orient at the surface of each droplet, giving it an electrical polarity. When the spheres are randomly oriented, the (zero-field) permittivity of the collection of spheres can be expressed as:

$$\overline{\varepsilon} = (2\varepsilon_\perp + \varepsilon_\parallel)/3 \tag{3}$$

where $\varepsilon_\perp$ and $\varepsilon_\parallel$ are the respective permittivities normal and parallel to the director.[5]

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Three models for the PDLC impedance response will be considered, and the influence of a third distinct region—an interface between polymer and liquid crystal—will be discussed.

The simplest model is obtained by *volumetric averaging*. Here, the total relative permittivity is given by the volume-weighted average of the relative permittivities of the components of the system.

$$\varepsilon = \nu_1\varepsilon_1 + \nu_2\varepsilon_2 \tag{4}$$

where ν_1 is the volume fraction of medium 1 or sphere 2, and ε_i is the permittivity of medium 1 or spheres 2. In the PDLC system, ε_2 represents liquid crystal permittivity. ε_2 equals to $\bar{\varepsilon}$ at the zero-field, and shifts towards $\varepsilon_{\parallel}$ as the applied voltage exceeds the critical voltage V_c.

A second simple model which is useful in many situations is derived from the *logarithmic mixing rule*.[6]

$$\log(\varepsilon) = \nu_1\log(\varepsilon_1) + \nu_2\log(\varepsilon_2) \tag{5}$$

Finally, a third alternative is available in *Bottcher's mixture formula*. The relation is obtained by calculating the polarization field and induced dipole moments created by an electric field applied to the system under consideration[7]:

$$\varepsilon - \varepsilon_1 = 3\nu_2\,(\varepsilon_2 - \varepsilon_1)\,\varepsilon'/(2\varepsilon' + \varepsilon_2) \tag{6}$$

A simple schematic of the system is shown in Figure 2, where

ν_i = volume fraction of medium 1 or spheres 2
ε_i = permittivity of medium 1 or spheres 2
ε' = permittivity of interphase region about spheres
ε = permittivity of entire system.

Since we are considering a system with a large volume fraction of spheres, the permittivity of the region surrounding the spheres can be approximated by the permittivity of the entire system. (Conversely, if one had only a small volume fraction of spheres, the interphasal regional permittivity would be better represented by the permittivity of the continuous medium.) Replacing ε' by ε in Eq. 6, we get:

$$\varepsilon - \varepsilon_1 = 3\nu_2\,(\varepsilon_2 - \varepsilon_1)\,\varepsilon/(2\varepsilon + \varepsilon_2) \tag{7}$$

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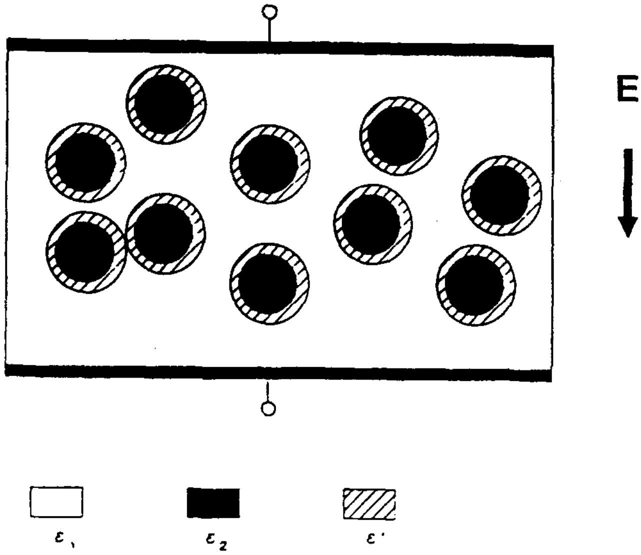

FIGURE 2 The *Bottcher's mixture formula* dielectric model.

or, rearranging:

$$2\varepsilon^2 + [(3\nu_2 - 2)\varepsilon_1 + (3\nu_1 - 2)\varepsilon_2]\varepsilon - \varepsilon_1\varepsilon_2 = 0 \quad (8)$$

The Bottcher model is more complicated than the volumetric (linear or logarithmic) averaging versions. But it has a theoretical basis, by virtue of its derivation from electrical principles. One notes that this model still does not include several factors, such as the effects of non-spherical globules and of molecular shape and length.

Extension of models to three components

Photomicrographs of the PDLC film show a halo about each sphere of liquid crystal suspended to the polymer.[1] The models for resistivity and permittivity can then be expanded to account for this halo. For example, the simpler averaging models would become:

$$\log(\rho) = \nu_1\log(\rho_1) + \nu_2\log(\rho_2) + \nu_3\log(\rho_3) \quad (2a)$$

$$\varepsilon = \varepsilon_1\nu_1 + \varepsilon_2\nu_2 + \varepsilon_3\nu_3 \quad (4a)$$

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$$\log(\varepsilon) = \nu_1\log(\varepsilon_1) + \nu_2\log(\varepsilon_2) + \nu_3\log(\varepsilon_3) \tag{5a}$$

$\varepsilon_3, \nu_3, \rho_3$ = permittivity, volume fraction and resistivity of the halo, respectively.

To test and apply these relations, one needs to know the extent, composition, resistivity and permittivity of the halo region. The volume fraction of the halo material, relative to that of the liquid crystal, can be easily estimated from the photomicrographs of the film. The other quantities (or relations) have yet to be determined.

EXPERIMENTAL

Test cells for determining dielectric properties of the liquid crystal materials were fabricated with the following configuration:

Glass/SiO_2/In-SnO_x/Polyimide/LC/Polyimide/In-SnO_x/SiO_2/Glass.

Polyimide surfaces are microgrooved to align the LC molecular axes parallel to the substrates at the field-off state (homogeneous surface alignment). The LC material is added by a vacuum-fill; a description of the test samples is given in Table I.

The computer-controlled ac impedance measuring system has been described earlier.[2] Impedance measurements are carried out by superimposing, at a zero-volt dc bias voltage, a sinusoidal voltage across

TABLE I

Test samples

Material	Area (cm^2)	Cell Gap (μm)
E7	1.00	11 ± 1
7CB	1.00	11 ± 1
NOA65	6.27	25 ± 5
PDLC	6.27	25 ± 5

E7: Commercial mixture of cyanobiphenyls and a cyanoterphenyl from EM Chemicals, Hawthorne, NY.

7CB: 4-cyano-4'-*n*-heptylbiphenyl

NOA65: Norland Optical UV-curable Adhesive #65 from Norland Products, Inc., New Brunswick, NJ.

PDLC: 50 v/0 E7, 50 v/0 NOA65

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two terminals of the test cell, and measuring the current response of the system. From the excitation-response ratio, the transfer function (impedance) of the system being tested is determined over a wide range of frequencies (60 kHz to 1 mHz).

The upper ac voltage limit of our present instrument is 10 V_{RMS}. The dielectric responses of pure liquid crystal in both "off" (surface-aligned) and "on" (field-aligned) states can be recorded within this voltage limit. However, a typical turn-on voltage for PDLC films is 30 volts; therefore, the impedance of the PDLC film was measured only for its "off" state.

RESULTS AND DISCUSSION

The impedance spectra have sufficient structure for comparing the predictions of models with the measured electrical response. We concentrate on the simpler response models, but sketch the direction for deriving more accurate, and also more complicated, versions.

Polymer matrix

The dielectric behavior of the polymer-only (NOA 65, Figure 3) can be represented by an RC parallel circuit. Resistance was calculated from the low frequency impedance plateau (<0.01 Hz), and capac-

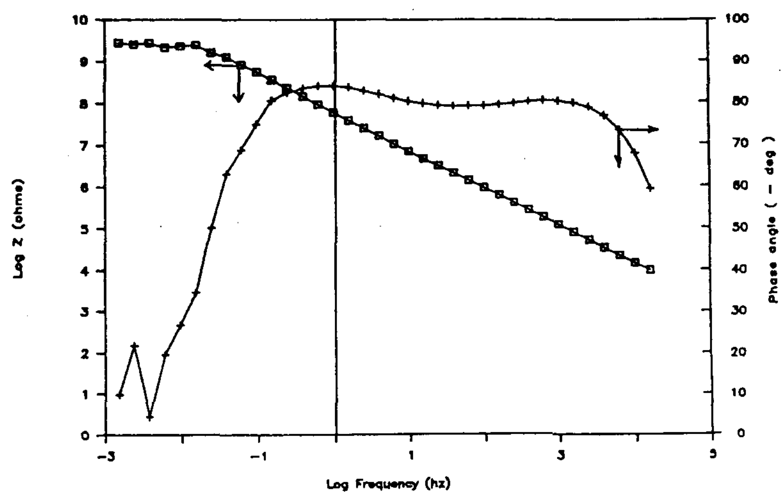

FIGURE 3 Bode plot of the UV-cured polymer film, NOA65, 1.0 V_{RMS}.

itance was determined from the intercept of the high frequency linear region with $f = 1$. These values were then converted to resistivity (ρ) and relative permittivity (ε) using an electrode area of 6.27 cm^2 and an electrode separation of 25 μm (± 5 μm). Due to this thickness variation across the film, the data spread can be $\pm 20\%$.

Liquid crystal

Two LC materials were investigated; the impedance spectrum of E7 measured at 0.2 V is shown in Figure 4. The impedance response can again be represented by an RC parallel circuit. Electrode area of this test cell is 1 cm^2 and electrode separation is 11 $\pm$ 1 μm; therefore, a $\pm 10\%$ spread can be assigned to the data. Nematic liquid crystals interact with electric fields through the anisotropy of the permittivity. In a homogeneously aligned cell, such as we have here, the permittivity measured below the threshold voltage is the normal permittivity ($\varepsilon_\perp$). Above the threshold, the orientation of the director gradually distorts toward the direction parallel to the field.

The effect of applied voltage on the impedance spectra in the frequency region 60 kHz to 100 Hz is shown in Figure 5. For measuring voltages below the threshold, a frequency- and voltage- independent capacitance value was obtained and the $\varepsilon_\perp$ was calculated accordingly. For $V > V_t$, there exist three frequency regions: (1) > 40 kHz—In this region orientation polarization can no longer follow

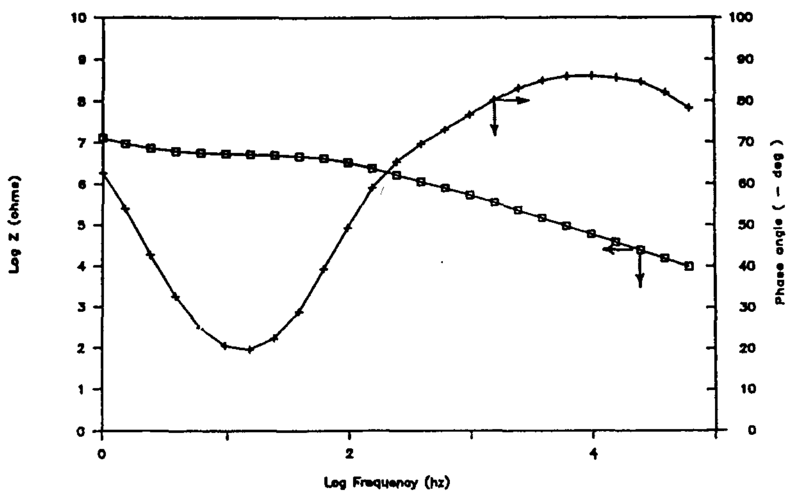

FIGURE 4 Bode plot of E7 LC material, homogeneous alignment, 0.2 V_{RMS}.

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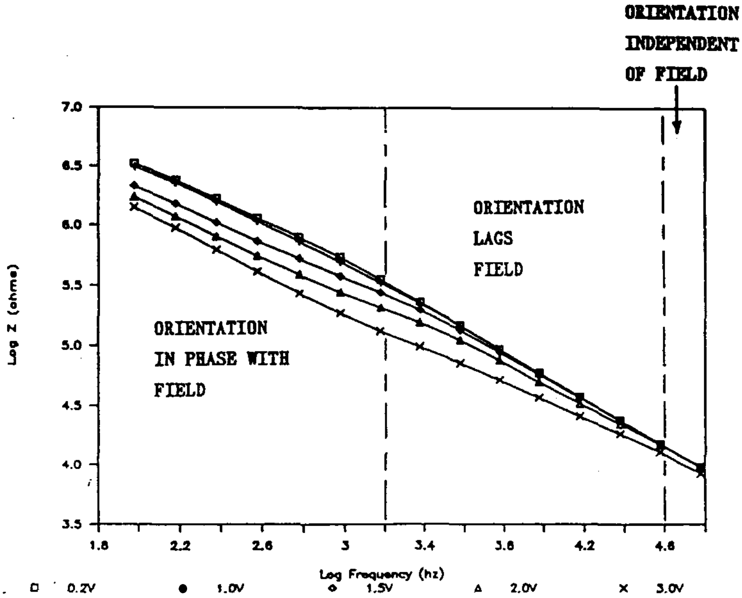

FIGURE 5 Effect of applied voltages on the impedance spectra for E7 LC material.

the variation of the field, and the capacitance values are independent of both the applied voltages and the measuring frequency; (2) 40 kHz $> f >$ 2 kHz—The measured capacitance values are dependent on both the applied voltages and the measuring frequency; and (3) $<$ 2 kHz—The capacitance values are independent of the measuring frequency, but dependent on the applied voltages. Similar behavior was observed for 7CB liquid crystal material; the impedance plot at 0.2 V measuring voltage is shown in Figure 6, and the effect of the applied voltage on the impedance spectra is shown in Figure 7. Being a single component LC material, 7CB shows a much narrower transition region (region 2).

Both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ can be determined in a single cell by an extrapolation technique.[8] Permittivities at 1 kHz were calculated as a function of applied voltages. Permittivity values were then plotted against 1/V, and the plots are shown in Figure 8. Initially, ε_{meas} is independent of the applied voltages and is a measure of $\varepsilon_{\perp}$; as the voltages exceed the threshold, ε_{meas} increases linearly with the reciprocal of the applied voltages. The linear relationship is:

$$\varepsilon_{meas} = \varepsilon_{\parallel} - k\ (1/V), \text{ where } k \text{ is a constant.}$$

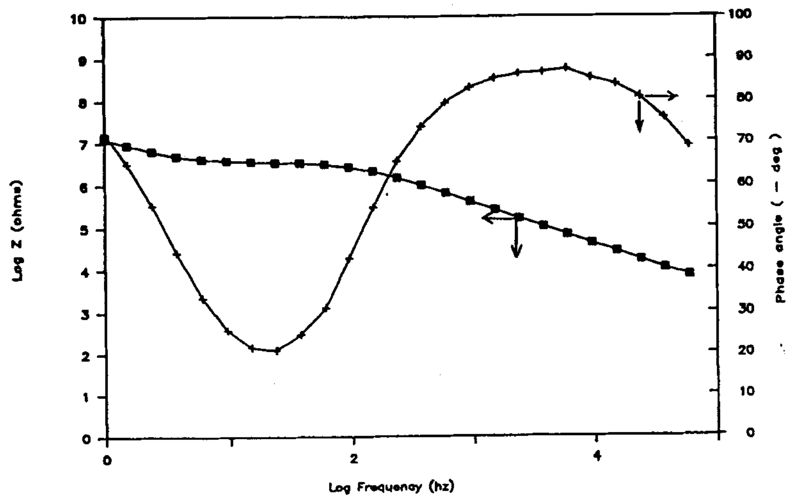

FIGURE 6 Bode plot of 7CB LC material, homogeneous alignment, 0.2 V_{RMS}.

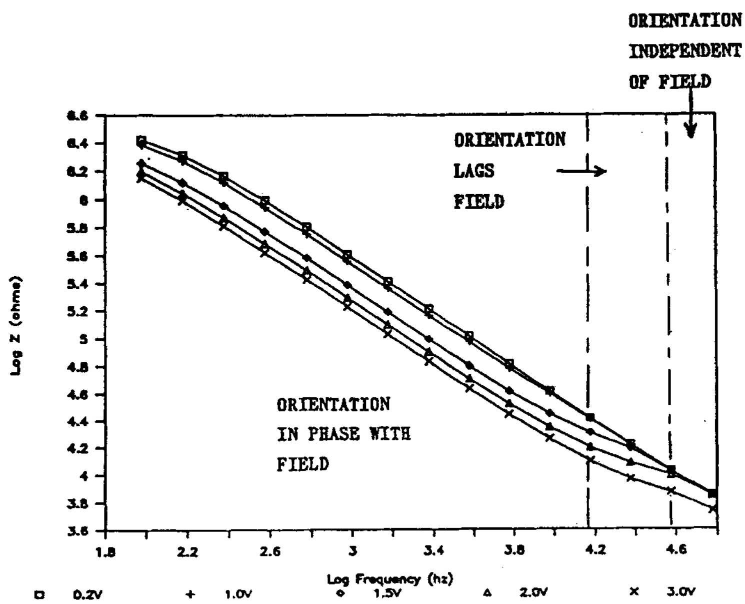

FIGURE 7 Effect of applied voltages on the impedance spectra for 7CB LC material.

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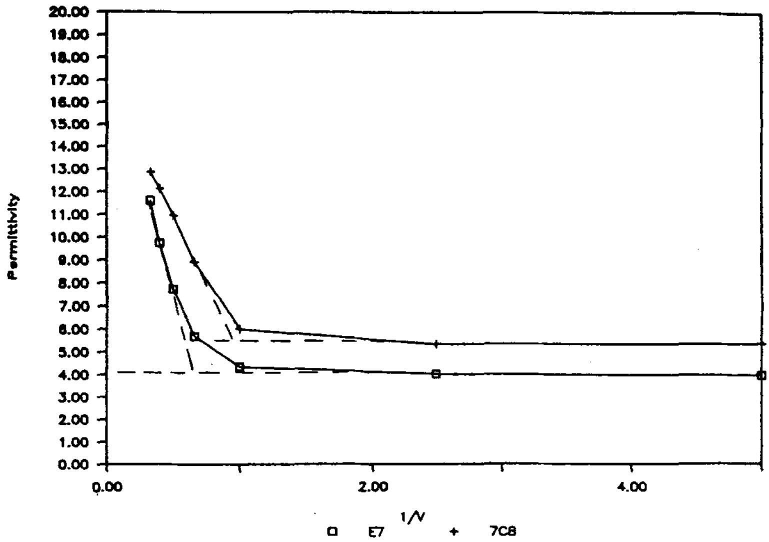

FIGURE 8 Measured permittivity at 1 kHz for E7 and 7CB at 25°C plotted against 1/V.

The linear region was extrapolated to the low voltage $\varepsilon_{\perp}$ plateau, where the intercept gives the threshold voltage.

Polymer dispersed liquid crystal film

The impedance spectrum of the PDLC film is shown in Figure 9. Up to 10 V_{RMS} applied voltage (limit of the present instrumentation), the spectra are independent of the applied voltage. Electro-optic results indicated that the turn-on voltage for this film was 30 V[1]; therefore, the impedance measured here represents the electrical characteristics of the PDLC film at the "off" state. The impedance response can be represented by an RC parallel circuit, and the permittivity and the resistivity can then be calculated.

The electrical characteristics of the component materials and the PDLC film are summarized in Table II.

Comparison of model predictions with test data

Using the data found in Table II and the equations outlined previously, the resistivity and permittivity of the PDLC sample were calculated (see Table III) to test the models.

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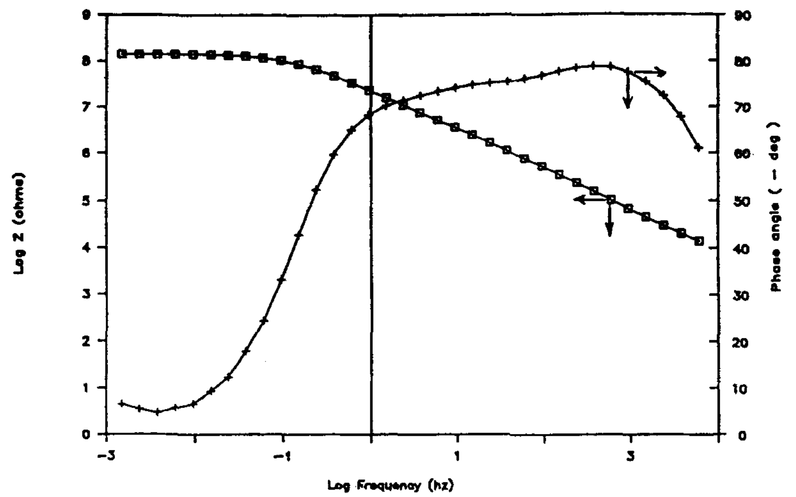

FIGURE 9 Bode plot of PDLC (50 v/o E7 + 50 v/o NOA65).

For a PDLC film, the resistivity seems to be expressed well by Eq. (2), assuming a modest correction factor; Eq. (1) gives an incorrect prediction. Looking at the problem from another perspective, Eq. (2) and Eq. (1) were used to compute volume fractions from the measured system resistivity. Eq. (2), even with $\alpha = 0$, gives a prediction of 43 v/o, acceptably close to the empirical 50 v/o. This supports the conclusion that Eq. (2) is a useful tool to model resistivity of a PDLC film.

TABLE II

Electrical Characteristics of Component Materials and PDLC Film at 25°C

Materials	ε_{meas}	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	ρ (Ω.cm)	V_t (volt)[a]	f_t (KHz)[b]
NOA65	11.89			6.8×10^{12}		
E7	8.97[c]	4.00	18.92	5.0×10^{9}	1.16	40
7CB		5.35	16.86	3.1×10^{9}	0.92	40
PDLC	12.48			3.0×10^{11}	30.00[d]	

[a]Threshold voltage
[b]Threshold frequency
[c]Average permittivity = $(2\varepsilon_{\perp} + \varepsilon_{\parallel})/3$
[d]Electro-optic measurement data from N. Vaz, GM Research

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TABLE III

Calculated values for ε, ρ, and ν_2 from models

Equation No.	ρ (Ω.cm)	ε	ν_2
4		10.43	
5		10.33	
7		10.36	
1	1.7×10^{12}		
2 ($\alpha = 0$)	1.8×10^{11}		
2 ($\alpha = -.08$)	3.0×10^{11}		
1			.88
2 ($\alpha = 0$)			.43

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The experimental permittivity results ($\varepsilon = 12.48 \pm 2.50$) agree reasonably well with all these theoretical predictions. The permittivities of the E7 (liquid crystal) and NOA65 (epoxy) components differ by 2.92 when the PDLC is probed in the "off" state. This is close to the uncertainty (± 2.50) of the PDLC film permittivity measurement. Therefore, permittivity of PDLC in the "off" state is difficult to interpret unambiguously. However, if the permittivity of the PDLC film in the "on" state can be measured, the sensitivity can be improved since permittivity of the components differ then by 7.03. Another possible method to improve the sensitivity is to have a better control of the PDLC film thickness.

SUMMARY

- AC impedance spectroscopy can be applied in straightforward manner to the PDLC to isolate system resistivity and permittivity.
- Resistivity is an extremely sensitive probe of chemical–physical changes within the PDLC. A mixture model with interaction included gives the best representation.
- Permittivity is of marginal use in probing PDLC films in the "off" state.
- The halo often observed around each liquid crystal droplet in SEM micrographs of the PDLC can be accounted for in response models. However, the composition and electrical properties of this interphasal region must be measured before any model response functions can be confirmed.

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