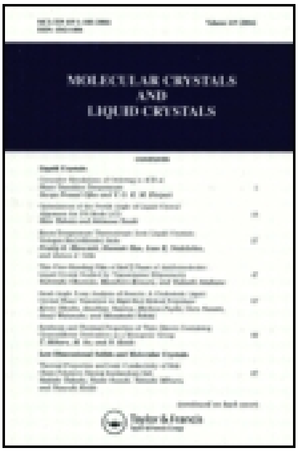

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STUDY OF THE IONIC DYNAMICS IN A POLYSILOXANE FERROELECTRIC LIQUID CRYSTAL POLYMER USING OPTICAL CONTRAST AND DIELECTRIC SPECTROSCOPY

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Abstract The real and imaginary parts of the optical transmittance and the relative permittivity have been measured for a polysiloxane ferroelectric liquid crystal polymer (FLCP) subjected to a weak alternating electric field. A simple dynamical model of the collective switching has been adopted for describing the director motion and the transport of ions through a FLCP cell. Numerical solution of a set of equations governing the director dynamics allows us to explain the transmittance and dielectric response of a FLCP cell. The model is shown to reproduce the experimental dielectric and optical transmittance response quite satisfactorily.

INTRODUCTION

Ferroelectric liquid crystals are known to display a complex dielectric behaviour below 1 MHz frequency range with two relaxation modes corresponding to the magnitude and the phase fluctuations of the director. Below 10 Hz however, the ionic impurities can contribute to the dielectric spectra. In anology to the dielectric measurements, the optical response of a FLCP cell subjected to an alternating electric field, with the cell placed under crossed polarisers, can be measured. For sufficiently low alternating voltages applied across the cell, both the real and imaginary parts of the optical transmittance show striking similarities to the dielectric spectra. This spectroscopy termed as the optical contrast spectroscopy together with the dielectric spectroscopy can provide extremely valuable information about the dynamical processes in a FLC cell. The optical contrast spectroscopy has so far been only sparingly used [1,2]. Furthermore, no theoretical model to-date has been given which explains both the collective director dynamics as well as the transport of ions through a FLC cell.

In this paper, we show how a simple equation for the director dynamics combined with the diffusion equation for the charge transport can be used to predict the dielectric and optical response of a FLC cell subjected to a sinusoidally varying voltage. Using this model, we can analyse contributions of the ions to the collective modes in the dielectric and the optical contrast spectra.

THEORETICAL DESCRIPTION

The dielectric response and transmittance of a FLC cell subjected to a sinusoidal alternating voltage is manifested in a small perturbation of the helical superstructure of this cell. The study of the switching dynamics, in the literature so far, is based on using square wave voltages and no serious attempt has been made to analyse the corresponding case of a sinusoidal voltage. To study the dynamical response of a FLC system, we consider a typical tilted-layer FLC cell. Each of the two electrodes of the cell is coated with an alignment layer of thickness d_l and dielectric permittivity ε_l The thickness of the FLC material is assumed to be d and its permittivity ε.

The equation governing the director dynamics can be expressed as follows [3,4].

$$\gamma \sin^2\theta \frac{\partial\phi}{\partial t} = P_S\, E(t)\cos\delta\, \sin\phi + K_\phi \sin^2\theta \frac{\partial^2\phi}{\partial z^2} \qquad (1)$$

where P_S is the spontaneous polarisation, γ is the rotational viscosity, K_ϕ is the mean elastic constant, θ is the tilt angle, δ is the smectic layer tilt angle, ϕ is the azimuthal angle defined as the angle that the C director makes with the y axis and z is directed along the helical axis, E(t) is the time-dependent local electric field acting on P_s.

The transport properties of the ionic impurities under a weak electric field can satisfactorily be described by the charge transport equation which in the simplest form can be written as

$$\frac{dn(t)}{dt} = -n(t)E(t)\frac{\mu}{d} \qquad (2)$$

The charge density $\sigma(t)$ that accumulates on the interface between the alignment layer and the FLC medium is given by

$$P = \sigma(t) = \int_0^t q\, n(t')\mu\, E(t')dt' + P_S \cos\delta\left[\cos\phi(t) - \cos\phi(0)\right] \qquad (3)$$

In Eqs. 2 and 3, n(t) is the number density, μ is the mobility of ions and q is charge per ion. The number density n(t) is assumed to be uniform throughout the cell. The field acting on a particular molecule within the FLC called the local field, E(t), is the sum of the field induced by the external voltage, $E_e = E_0$ Sinωt and the depolarisation field created by the spontaneous polarisation and the space charge collected at the interfaces of the two alignment layers and the sample.

$$E(t) = -\frac{V(t)\varepsilon_1}{2d_1\varepsilon + d\varepsilon_1} + \frac{2\sigma(t)d_1}{2d_1\varepsilon + d\varepsilon_1} \qquad (4)$$

The coupled equations (1-4) can be numerically solved and the solution yields E(t), $\phi(t)$, and $\sigma(t)$ as functions of time.

Once the functional dependence of the azimuthal angle $\phi(t)$ is known, the optical transmittance, T, through a FLC cell kept in between the crossed polarisers can be calculated as in ref. [5]. The total optical transmittance, T, through a cell in such a case is given by

$$T = \sin^2 2\Theta \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \qquad (5)$$

where Θ is the angle between the projection of the director on the glass plate and the polariser direction, the angle Θ can be expressed as

$$\Theta = \Omega - \tan^{-1}\left[\sin\theta\cos\phi / (\sin\delta\sin\theta\sin\phi + \cos\theta\cos\delta)\right] \tag{6}$$

Ω is the angle between the polariser direction and the projection of the layer-normal on the glass plate, Δn is the effective refractive index anisotropy and is given by

$$\Delta n = \frac{n_o n_e}{\sqrt{(n_o^2\cos^2\theta' + n_e^2\sin^2\theta')}} - n_o \tag{7}$$

where θ' is the angle between the director and the substrate interface and is given by

$$\sin\theta' = \cos\delta\sin\delta\sin\phi - \cos\theta\sin\delta \tag{8}$$

To compare the experimental results in the frequency domain with those predicted by the model, we calculate the Fourier coefficient, for the fundamental frequency of the applied field, of the charge density σ(t) in order to obtain the dielectric susceptibility, χ*(ω)

$$\chi^*(\omega) = \frac{\sigma(\omega)}{\varepsilon_0 E_0} \tag{9}$$

and similarly the Fourier coefficient of the optical transmittance gives the real and imaginary parts of the optical transmittance in the frequency domain, $T^*(\omega)$

Figs. 1a and 1b show the typical spectra of the real and imaginary parts of the complex susceptibility and of the optical transmittance for a system with the following parameters:

$\varepsilon=10\varepsilon_0$, $\varepsilon_1=5\varepsilon_0$, d=5 μm, d_1= 0.1μm, V_o=1 V, μ= 2.10^{-9} m^2/V.s, P_s =2 mC/m^2, γ= 5.0 mPa.s, ε_o is the permittivity of free space.

Two peaks in χ'' can easily be identified. The peak centred at a higher frequency f_P can be identified with the polarisation switching mode, whereas the lower frequency peak centred at f_I seems to corrspond to the relaxation of ions. We find from eqs. 1-4 that the amplitude and the frequency of the ionic peak depends on the number density of the ions whereas that for the polarisation peak depends on the spontaneous polarisation of the FLC material.

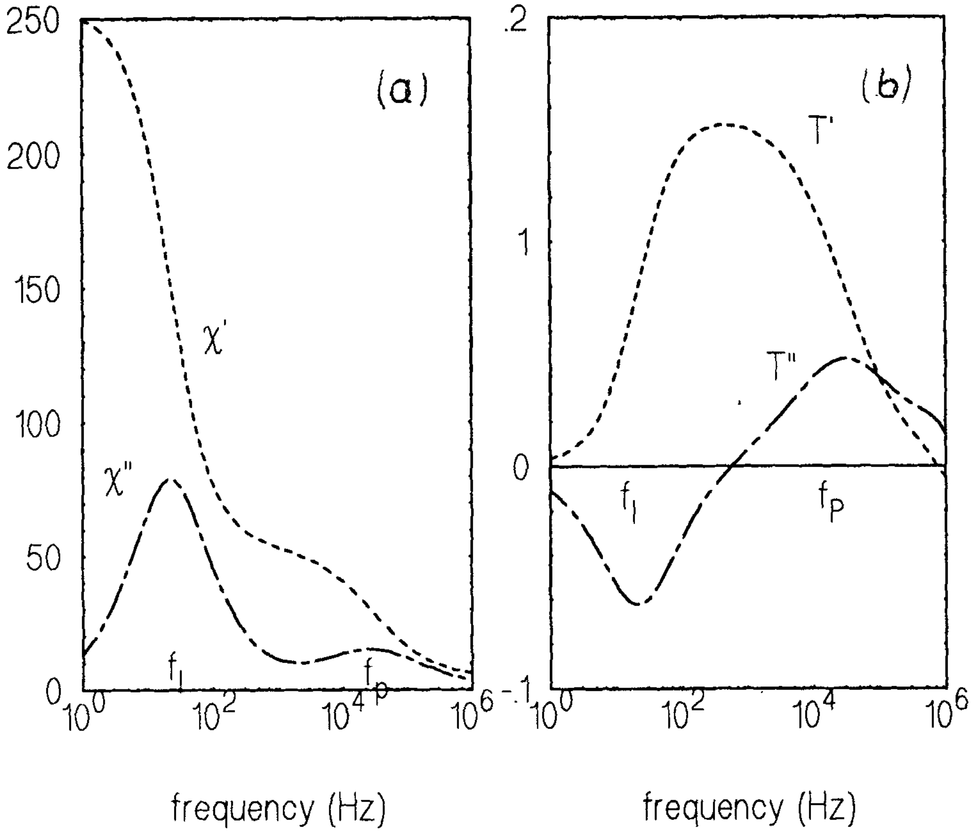

Fig. 1 Theoretical optical contrast and dielectric spectra for a system with parameters given in the text.

We define the characteristic relaxation time, τ_P of the spontaneous polarisation as

$$\tau_P = \frac{\gamma \sin^2\theta}{P_S E_0} \qquad (10)$$

and the relaxation time of the ionic charge, τ_I, is given by

$$\tau_I = \frac{d}{\mu E_0} = \frac{d^2}{\mu V_0} \qquad (11)$$

where V_0 is the voltage applied across the cell, since $d_I \ll d$, d effectively corresponds to the cell-thickness. From Figs 1a and 1b we find that for the case $\tau_P \ll \tau_I$, two peaks are observed in both χ'' and T", and these are centred at frequencies of

$$f_I \cong \frac{1}{2\pi\tau_I} \quad \text{and} \quad f_P \cong \frac{1}{2\pi\tau_P} \qquad (12)$$

On examining the spectra of T"(ω) in Fig. 1b, we identify three regions in the frequency spectrum. A negative peak in T" is due to the ionic relaxation at low frequencies.

(a) for $f \gg f_P$, the spontaneous polarisation cannot follow the alterations of the electric field, hence we do not observe any optical response.

(b) for $f_P > f > f_I$ the ions are too slow to follow the alterations of the electric field and hence these cannot contribute to the depolarisation field and so the optical response in T' is observed.

(c) for $f \ll f_I$ frequency is low enough and the ions can follow the external field and these consequently reduce the local field in FLCP, hence we do not observe any optical switching.

EXPERIMENTAL

FLC cells of various thicknesses ranging from 2μm to 40 μm containing polysiloxane [6] have been prepared. These consist of ITO coated glass plates separated by mylar foil. The plates were spin coated with polyimide (E. Merck ZLI-2650), annealed for 1 hour at a temperature of 300° C and then rubbed in antiparallel directions. The real (ε') and imaginary (ε'') parts of the complex permittivity ($\varepsilon^*=\varepsilon'-i\,\varepsilon''$) were measured in the frequency range 10 Hz to 1 MHz using a 1255A Schlumberger frequency response analyser (FRA) and a Chelsea dielectric interface. The latter is used as an impedance buffer between the sample and the FRA. The sample was placed in the hot stage of the polarising

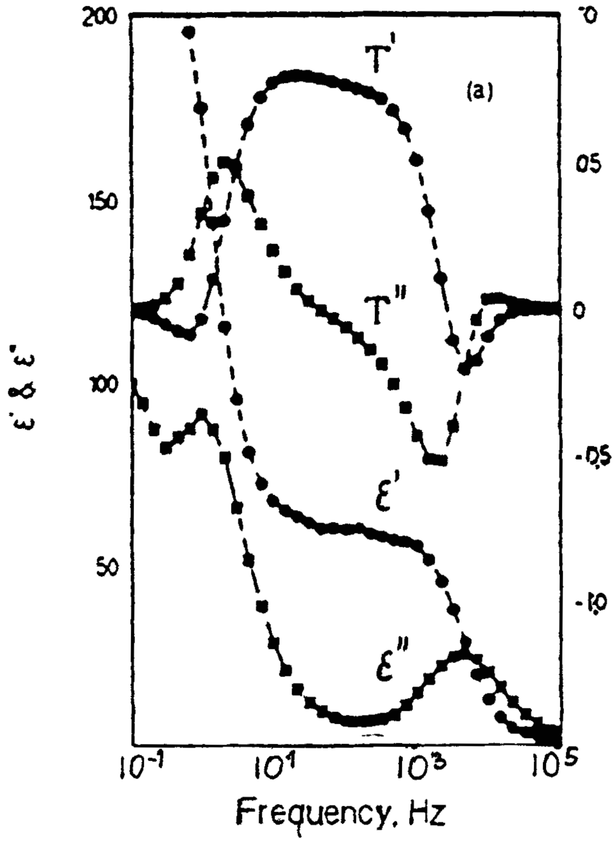

Fig.2. Optical contrast spectra(T'(ω) and T''(ω)) and dielectric spectra(ε'(ω) and ω)) for ZHKS-311 at 59° C (SmC* phase) in the frequency range 10 Hz to 100 kHz

microscope so that the transmission as well as the dielectric measurements can simultaneously be made on the same arrangement The hot stage of the polarising microscope and its temperature controller are supplied by INSTEC, Boulder, CO, USA. The temperature stability of the arrangement is better than 0.01° C. The accuracy in the measurements of ε' was better than 1% and of ε" better than 2%.

RESULTS and DISCUSSION

Fig. 2 shows the dielectric and the optical contrast spectra for a low molar mass ferroelectric mixture ZHKS-311 at a temperature of 59° C (SmC*phase). The

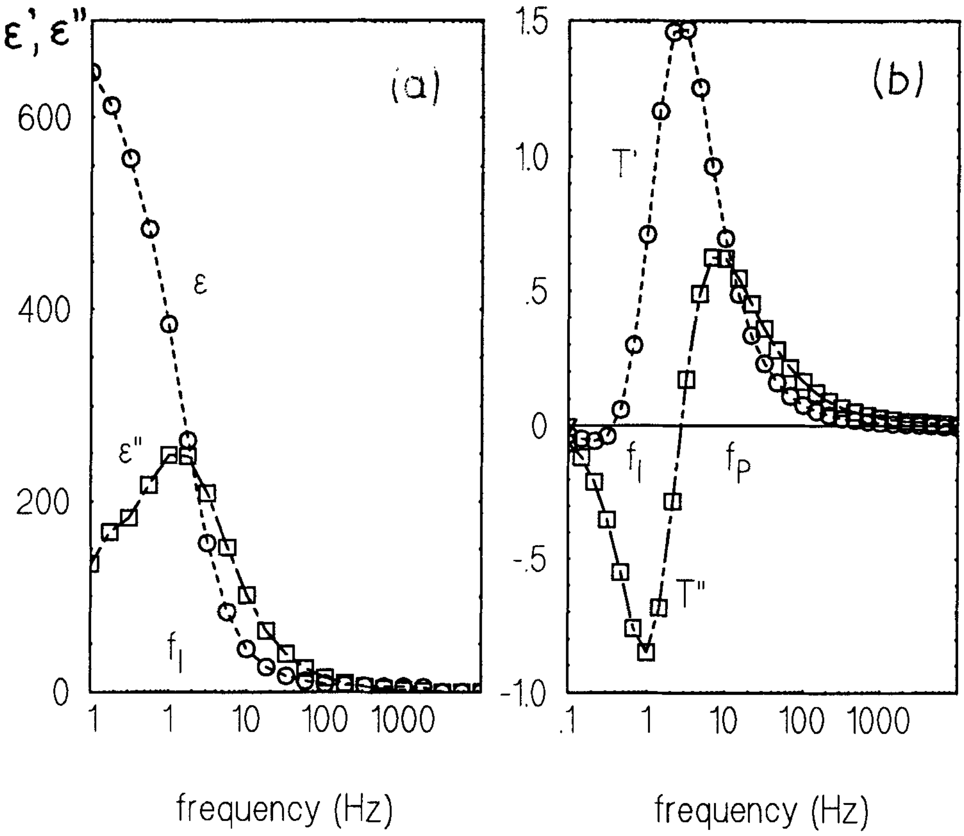

Fig.3a and Fig.3b: Optical contrast spectra (T'(ω) and T"(ω) and dielectric spectra $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$) for polysiloxane at a temperature of 82°C in the frequency range 0.1Hz to 1kHz (Polysiloxane in SmC* phase) model reproduces the experimental data reasonably well. For the case of the dielectric spectra, ε" goes to a extremely high value at low frequencies because of the dc conductivity, the latter was not included in the model.The results for a FLC cell containing polysiloxane are shown in Figs. 3a and 3b. Surprisingly, only one peak has been observed in the dielectric spectra of polysiloxane as seen in Fig. 3a. In order to find the origin of the process, we extended the measurements of the spectra to the SmA phase; no critical behaviour for this peak was found in terms of both its frequency and its relaxation strength at the SmC*-SmA phase transition temperature. The relaxation time corresponding to this peak for FLC cells containing polysiloxane with different thicknesses follows the equation

$$\tau \propto \frac{d^2}{V_0} \qquad (13)$$

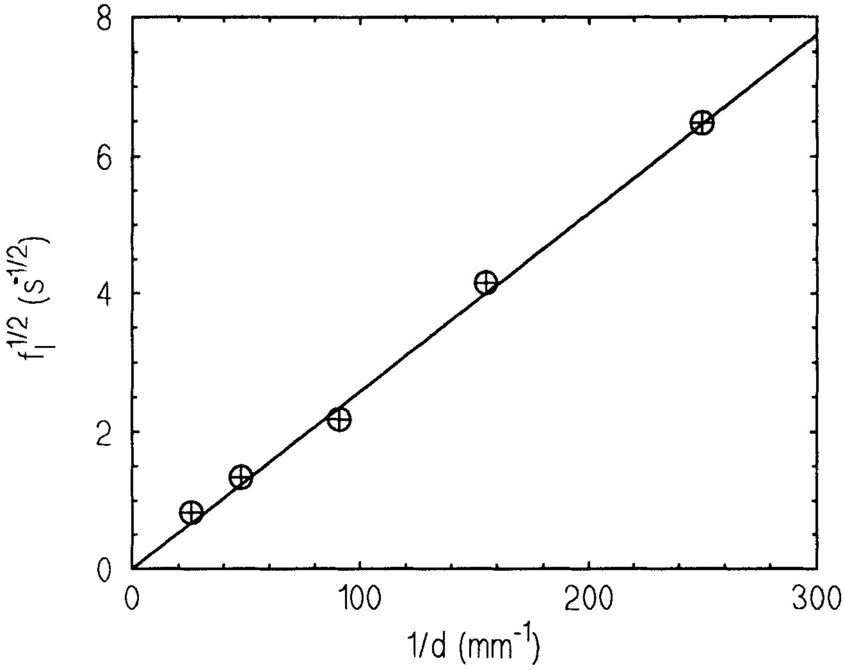

Fig.4. Plot of $(f_l)1/2$ vs. 1/d for polysiloxane at a temperature of 88^0 C in the SmC*phase.

as shown by a linear plot of $(f_l)^{1/2}$ versus 1/d in Fig. 4. Eq. 13 is the same as Eq.11 and this proves that the peak under discussion is due to the ionic motion, hence the polarisation peak can hardly be seen. The mobility of ions, μ, at a temperature of 140° C found from Eq.11 is about 10^{-8} m^2/Vs This decreases by an order of magnitude at 70° C and becomes zero at the glass transition temperature.

The temperature dependence of τ_I follows a typical Arrhenius behaviour. This is shown in Fig.5 by a plot of $f_I=1/2\pi\tau_I$ as a function of temperature over the SmA and SmC* phases, except at temperatures below 69° C. For lower temperatures, τ_I is governed by a slowing-down process on approaching the glass transition temprature of 59° C. This is an extremely interesting result which shows that the frequency of ions, similar to that for the permanent dipoles, follows a critical behaviour with temperature and goes to almost zero

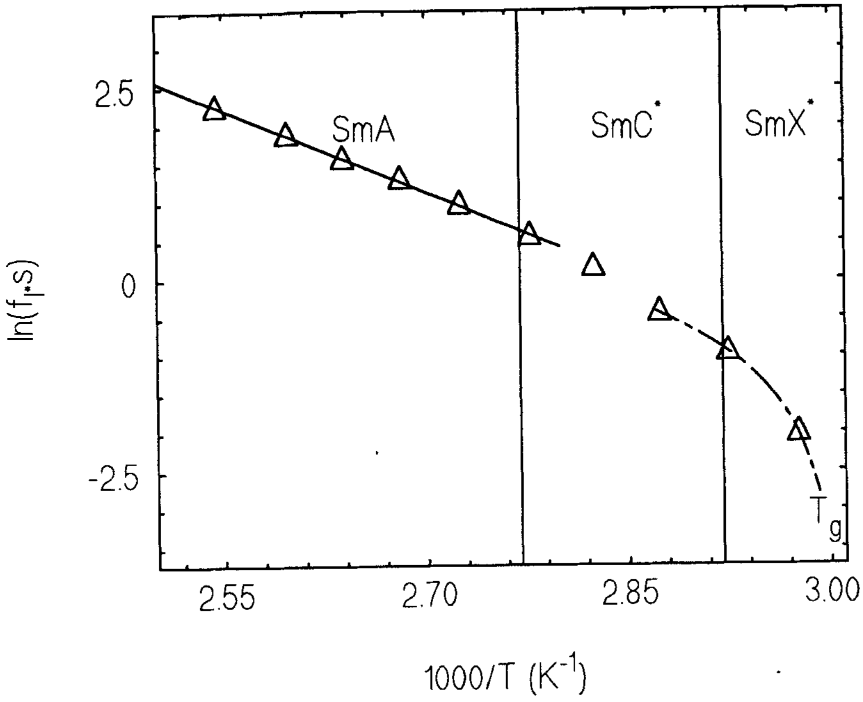

FIG. 5 Plot of $\log_e(f_I/Hz)$ vs. 1000/T (K^{-1}) for polysiloxane, △ experimental points continuous line shows linear fit; discontinuous line shows fitting to critical behavior for T close to T_g

for $T=T_g$. This indeed is the characteristic of the α relaxation of polymers just above the glass transition temperature. The optical transmittance spectra, Fig 3b, is more suitable for observing these two processes, since both polarisation and the ionic contributions to this spectra are comparable to each other in this case. The ionic peak appears in $T''(\omega)$ spectra at low frequencies and shows the same temperature dependence as for the dielectric spectra. The high frequency peak is assigned to the polarisation process and shows a typical critical behaviour both in terms of the frequency and the inverse relaxation strength at the SmC*-SmA transition temperature. Both $\varepsilon''(\omega)$ and $T''(\omega)$ spectra can be reproduced reasonably well by the model except for the dc conductivity part of the dielectric spectra.

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REFERENCES

1. R.J.Cava, J.S.Patel, J.W. Goodby and E.A.Rietman, Phys.Rev., 35, 4378 (1987).
2. J.Pavel and M.Glogarova, Ferroelectrics, 121,45-53 (1991).
3. K.H.Yang and T.C.Chieu, Ferroelectrics, 85, 153 (1988).
4. K.H.Yang, T.C.Chieu and S.Osofsky, Appl.Phys.Lett. 55, 155 (1989).
5. H. Xu, S.T. MacLughadha, A. Kocot and J. K. Vij, Ferroelectrics, in the press.
6. A. Kocot, R. Wrzalik, J. K. Vij and R. Zentel, J. Appl. Phys. 75, 728 (1994).