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Invited Article

Experimental techniques for the investigation of ferroelectric liquid crystals

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A review is given of several experimental methods for the measurement of the performance parameters of ferroelectric liquid crystals. We discuss (*a*) the technique for measuring the spontaneous polarization, the elastic modulus and dielectric susceptibility for the tilt of the director (the pyro-electric method), (*b*) the measurement of the tilt angle and the optical anisotropy (the electro-optical method) and (*c*) the determination of the non-linear susceptibility of the chiral smectic C* phase (the optical second harmonic generation technique).

1. Introduction

The electro-optical effect due to the alignment of the director in ferroelectric liquid crystals results from the linear interaction between an external electric field, E, and the spontaneous polarization, P_s, where the associated energy $W_E \propto P_s E$ [1]. These materials have some advantages over nematic liquid crystals where the alignment of the director is due to the quadratic interaction of the field with the dielectric anisotropy ε_a, here the associated energy $W_E \propto \varepsilon_a E^2$. The switching direction for the director of ferroelectric liquid crystals is sensitive to the polarity of the applied voltage and, for high polarizations and relatively low voltages, is faster than that for the nematics. In addition, there is a storage effect for some switching regimes of liquid-crystalline ferroelectrics.

The problem arises of designing new materials having a wide smectic C* range, a spontaneous polarization exceeding $10^{-4}\,\mathrm{C\,m^{-2}}$ and a low viscosity. To solve this problem we should combine the conventional methods of synthetic chemistry with the physico-chemical approach which allows multi-component mixtures with an optimum set of parameters to be prepared. In this case the key problem is the measurement of the most important physical parameters which define the electro-optical behaviour of a given material. In this article we describe several experimental techniques which allow us to characterize ferroelectric liquid crystals to a rather full extent.

2. The pyro-electric experiment for measuring the spontaneous polarization as well as the susceptibility, the elasticity and the viscosity due to the tilt of the director

Initially [2], the pyro-electric experiment was constructed for the measurement of the spontaneous polarization by integrating the pyro-electric coefficient ($\gamma = dP_s/dT$)

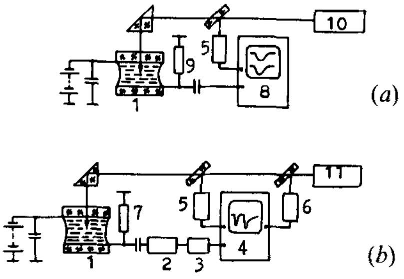

Figure 1. Block diagrams showing the equipment for the measurement of the pyro-electric response to (*a*) a long pulse of the laser (10) in the free-running regime and (*b*) a short giant pulse of the *Q*-switched laser (11). 1, liquid crystal cell; 2, amplifier; 3, delay line; 4, storage oscilloscope; 5, photomultiplier for laser pulse control; 6, photomultiplier for triggering; 7, load resistor (100–300 Ω); 8, two-beam storage oscilloscope; 9, load resistor (100–200 kΩ).

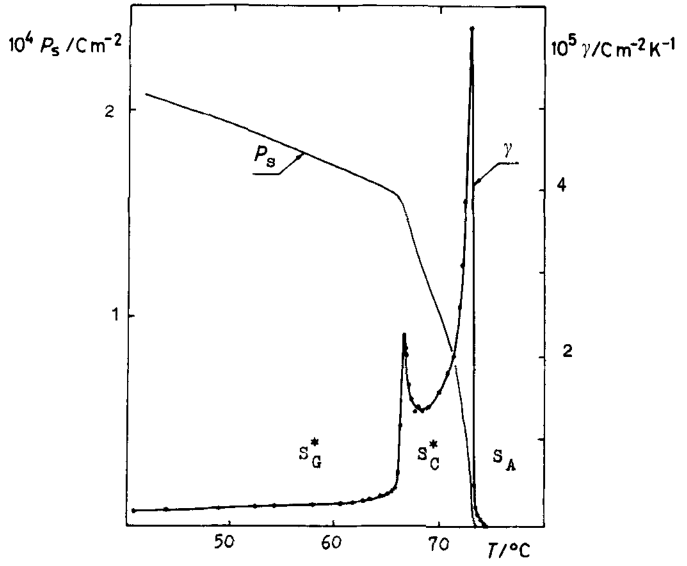

Figure 2. Temperature dependence of the pyro-electric coefficient, γ, and the spontaneous polarization, P_s, for HOBACPC.

with respect to temperature. The block diagram showing the equipment is given in figure 1. The radiation ($\lambda = 1{\cdot}06\,\mu$m) of a YAG : Nd pulsed laser is absorbed within a liquid-crystalline layer which contains a small amount (< 0·5 per cent) of a soluble light-absorbing dye. A d.c.-external electric voltage is applied to transparent (SnO_2) electrodes to the helical structure of the smectic C* phase and to provide the uniformly polarized sample. A pulse of the pyro-electric voltage caused by sample heating occurs across the same electrodes (the polarizing field may be removed during the sample excitation by a laser pulse). A simple calculation taking the value of the absorbed energy into account allows the pyro-electric coefficient and then the spontaneous polarization to be found. An example of the temperature behaviour of γ and P_s is shown in figure 2.

The pyro-electric technique has a major advantage over a conventional Sawyer–Tower method when measuring the polarization for materials with high viscosity. For example, P_s can be measured for the low temperature smectic G phase of

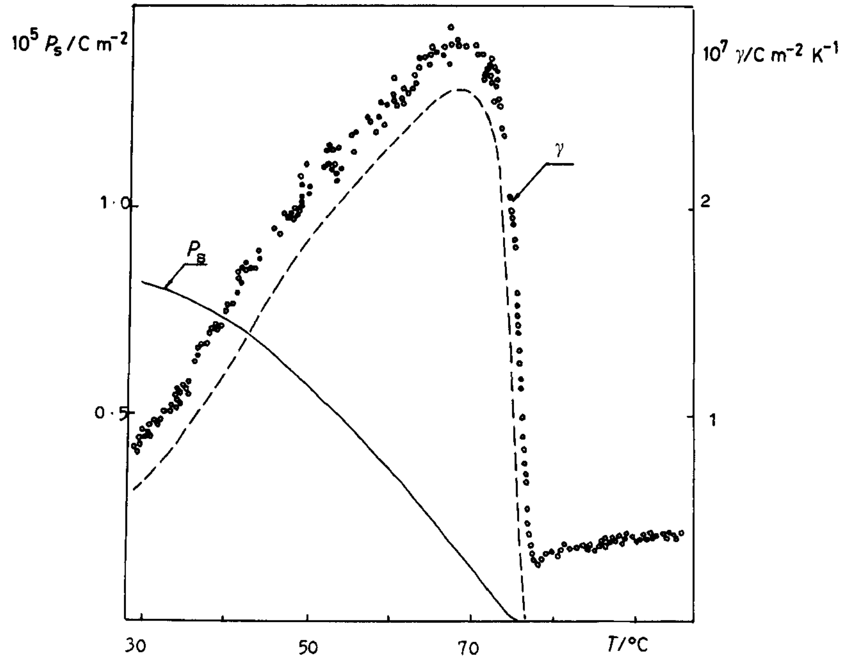

Figure 3. Temperature behaviour of the pyro-electric coefficient, γ, and the spontaneous polarization, P_s, for the ferroelectric liquid-crystalline polymer poly-4-(11-methacryloyloxydecanoytoxy)-phenyl-S-(+)-2-methylbutylterephthalate (P5*M). Cell thickness = 1 mm and the voltage for obtaining monodomains was 300 V. The dashed line shows γ extrapolated to the zero voltage (after subtracting the bolometric effect).

L-4-*n*-hexyloxy-benzylidene-4′-amino-2″-chloro propylcinnamate (HOBACPC) (cf. figure 2). Another example is a recently discovered [3] polymeric ferroelectric liquid crystal. The temperature dependencies of the pyro-electric coefficient and the spontaneous polarization for the polymeric material are shown in figure 3. It should be noted that γ and P_s remain finite even in the glassy state of the substance.

The steady-state value of the pyro-coefficient is measured using a relatively long laser pulse of duration $t_L = 3 \times 10^{-4}$ s. This time exceeds the characteristic time for the director tilt (i.e. the soft mode) but is short enough to provide the adiabatic regime for samples with thickness $\geqslant 200\,\mu$m. When we use a short pulse of the same laser in the Q-switching regime, $t_s = 3 \times 10^{-8}$ s, we can perform independent measurements of the relaxation times for the tilt angle of the director (i.e. the soft mode). With this purpose in mind the form of the time oscillations of the pyro-electric coefficient signal should be analysed [4] (cf. figure 4).

Other important properties of ferroelectric liquid crystals may be investigated if the dependence of the pyro-electric coefficient on an external field is utilized. In this case, the field must be higher than the threshold necessary to unwind the helix of the smectic C* phase. We have found a surprisingly simple but, as far as we are aware, an unknown equality which relates the *field dependence* of the pyro-coefficient to the *temperature dependence* of the dielectric susceptibility, $\chi = (\varepsilon - 1)4\pi$ [5]

$$\frac{\partial \gamma}{\partial E} \equiv \frac{\partial}{\partial E}\left(\frac{\partial P}{\partial T}\right) \equiv \frac{\partial}{\partial T}\left(\frac{\partial P}{\partial E}\right) \equiv \frac{\partial \chi}{\partial T}. \tag{1}$$

Here, P is the total (spontaneous and field-induced) polarization.

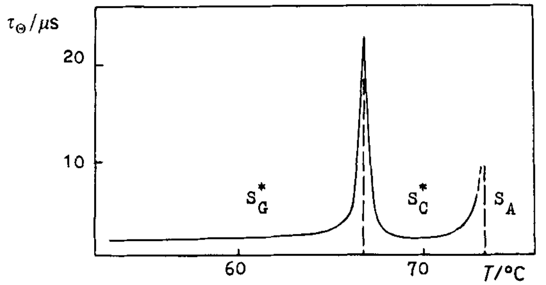

Figure 4. Temperature dependence of the relaxation time, τ, for the spontaneous polarization (and tilt angle) of HOBACPC.

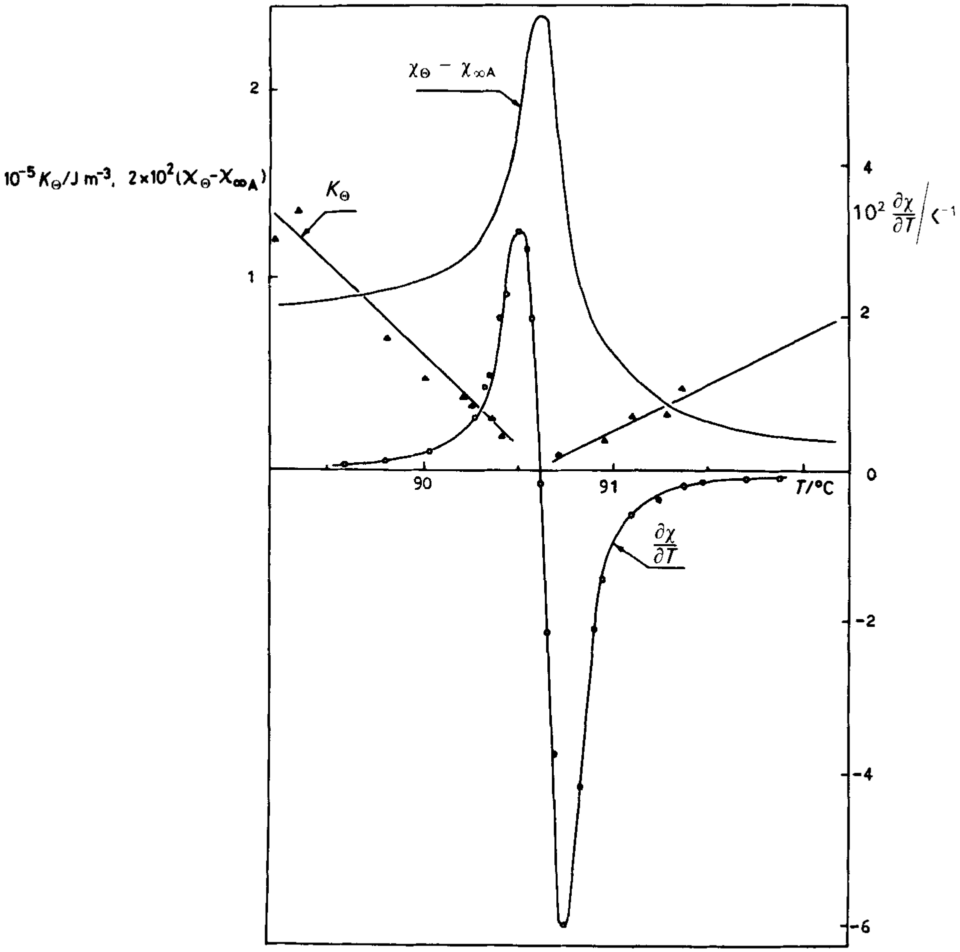

Figure 5. Temperature dependence of the static dielectric susceptibility in the soft mode ($\chi_\Theta - \chi^A_\infty$), its temperature derivative and the elastic modulus K_Θ near the smectic C*–smectic A phase transition for DOBAMBC under a strong electric field, $E > E_c$.

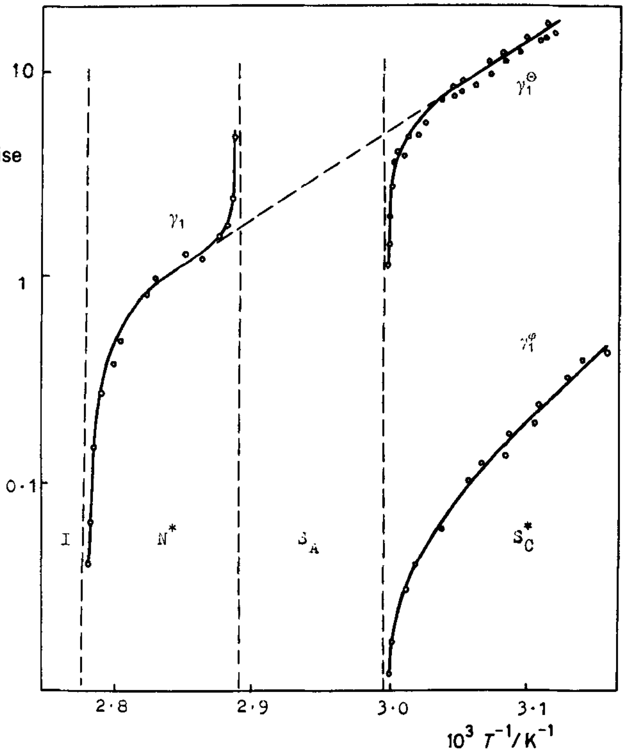

Figure 6. Temperature behaviour of the twist viscosity coefficient for the nematic and smectic C* phases of 4-*n*-hexyloxyphenyl ester of 4′-*n*-octyloxybenzoic acid (HOPEOOBA). γ_1^{Θ} was obtained from pyro-electric measurements in the strong field limit ($E > E_c$) and γ_1^{φ} was found from electro-optical measurements.

Since these measurements are carried out with an unwound helix, the susceptibility, χ, is the component which is due to a change in the tilt angle of the director, Θ, with respect to the layer normal (a soft mode). In the smectic A phase similar information may be obtained from measurements of the electro-clinic effect [6]. An example of measuring $\partial\chi/\partial T$ via $\partial\gamma/dE$ and calculating the $\chi(T)$ function is shown in figure 5. Furthermore, the elastic modulus K_{Θ} related to a change in the tilt angle Θ may be calculated from [5]

$$K_{\Theta} = \alpha^2/\chi_T, \tag{2}$$

where χ_T is the temperature dependent part of the susceptibility in the soft mode and α is a proportionality constant between the tilt angle and the spontaneous polarization;

$$P_s = \alpha\Theta. \tag{3}$$

Here $P_s(T)$ is calculated from the pyro-coefficient $\gamma(T)$ and $\Theta(T)$ is measured by a pyro-electro-optical method (see later). As a result, we obtain the temperature behaviour of $\alpha(T)$ and $K_{\Theta}(T)$.

Finally, using the independent measurements of relaxation times of the director in the soft mode, $\tau(T)$, we can calculate the twist viscosity coefficient $\gamma_1^{\Theta}(T)$ associated with the energy dissipation due to the relaxation of the tilt angle Θ after an external excitation (a temperature jump or an electric pulse). The curve of $K_{\Theta}(T)$ is shown in figure 5 in the vicinity of the S_C^*–S_A transition. The temperature behaviour of the viscosity $\gamma_1^{\Theta}(T)$ is given in figure 6.

3. The electro-optical experiment for the measurement of the director tilt angle and the optical anisotropy in the smectic C* phase

The spontaneous polarization is directly proportional to the tilt angle (cf. equation (3)). Moreover, both the angle Θ and the optical anisotropy of the smectic C* phase define the electro-optical response of thin cells (we consider a smectic C* to be optically uniaxial, $\Delta n \simeq n_e - n_0$ where n_e and n_0 are the refractive indices $\|$ and $\perp$ to the director). The block-diagram of the equipment [7] for measuring these important parameters (Θ and Δn) is shown in figure 7. A change in the polarity of an external pulsed voltage across optically transparent electrodes of a sandwich-type liquid crystal cell results in the switching of the director from left to right along the surface of a cone whose axis coincides with the normal to the smectic layer. Thus the layer of a ferroelectric liquid crystal behaves as a uniaxial plate with an optical axis switched by an angle 2Θ when the field is changed from, say, $-E$ to $+E$. Hence, the angle 2Θ would be measured if the cell is turned around the field direction and the difference is taken between the two angular positions corresponding to the minima in the optical transmission of the cell placed between crossed nicols normal to the beam of a He–Ne laser.

In order to measure the optical anisotropy Δn a cell is excited by a sequence of alternating square-wave pulses with a frequency between 100 and 10 Hz. The cell is fixed between crossed nicols at the angular position $\alpha = \Theta$, where the intensity of the outgoing beam passes through a minimum for a negative polarity of the pulses (the corresponding oscillograms are shown in [7]). In this case, the direction of the director for the field $(-E)$ coincides with the light polarization vector, (cf. figure 7). Then, rotating the analyser by the angle $\gamma = 2\Theta + \beta$ the other minimum of the intensity is found which corresponds to the positive polarity of the pulses. The new position of the analyser coincides with the direction of the principal axis of the polarization

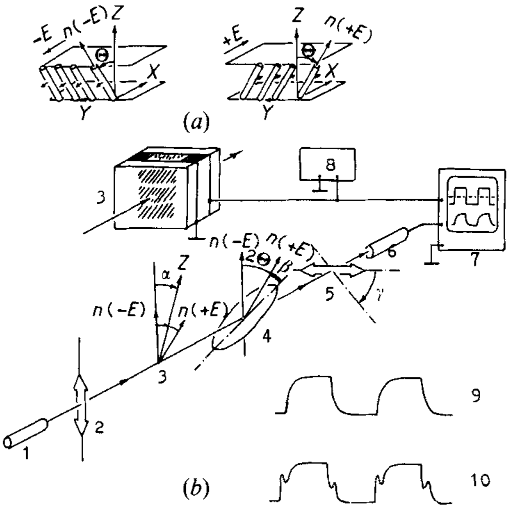

Figure 7. (*a*) Switching the director **n** caused by a change in polarity of an external electric field applied along the X axis. (*b*) The equipment for measuring the tilt angle Θ, the optical anisotropy Δn and the director switching times in the smectic C* phase. 1, a He–Ne laser; 2, polarizer; 3, liquid crystal cell; 4, the polarization ellipse for outgoing light; 5, analyser; 6, photomultiplier; 7, oscilloscope; 8, pulse generator; 9, 10, oscillograms of the cell response for $N = 0$ and $N = 1$, respectively.

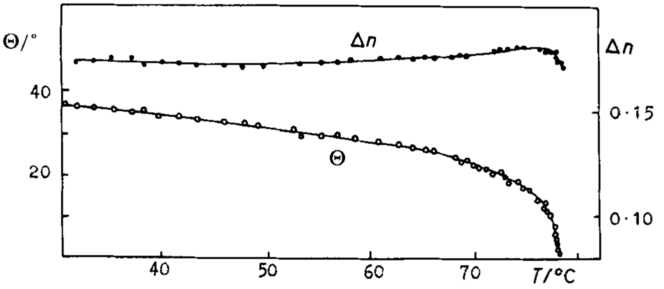

Figure 8. Temperature dependence of the tilt angle Θ and the optical anisotropy Δn (at $\lambda = 0{\cdot}632\,\mu\mathrm{m}$) for the smectic C phase of 4-*n*-hexyloxy-4′-*n*-hexylsalicylidene-aniline doped with the chiral additive L-4-*n*-hexyloxy-benzylidene-4′-amino-2″-cyano-propylcinnamate (HOBACNPC) (5 per cent weight), cell thickness = 8·6 μm, pulse voltage = ±50 V.

ellipse at the exit of the cell which, in turn, depends on the phase delay of the transmitted light ϕ. So, the phase delay may be found by the formula derived for a uniaxial plate:

$$\cos\phi = \tan 2\beta/\tan 4\Theta; \qquad (4)$$

the optical anisotropy is calculated from the known values for ϕ, thickness d, and wavelength $\lambda = 0{\cdot}632\,\mu\mathrm{m}$: $\phi = 2\pi\Delta n d/\lambda + 2\pi N$. As usual, the cell thickness is about 3–7 μm and typical values for Δn are 0·1–0·2. Thus, the integer N is equal to either 0 or 1. Its exact value may be found by analysing the form of the oscillogram edges; the number of minima at, say, the front edge is exactly equal to N (cf. figure 7). Examples of the temperature dependence for the tilt angle and the anisotropy are shown in figure 8.

The calculated values for Δn allow the prediction of precise values for the cell thickness which satisfies the condition when the cell becomes a uniaxial *half-wave* plate with a maximum contrast of optical switching

$$d = \lambda(N + \tfrac{1}{2})/\Delta n, \quad N = 0, 1, 2, \ldots . \qquad (5)$$

The relaxation time for the director moving around the cone surface with constant Θ, $\tau = \gamma_1^{\varphi}/P_s E$, can be determined by studying the kinetics of the cell optical response after switching the polarity of the electric field. For a known P_s value the twist viscosity coefficient γ_1^{φ} associated with changes in the azimuthal angle φ can be calculated [8]. In figure 6 the two viscosity coefficients (for tilt and azimuthal angles) are compared. It is remarkable that γ_1^{φ} is nearly two orders of magnitude lower than γ_1^{Θ} which, in turn, is comparable with the twist viscosity coefficient γ_1^{N} extrapolated from the nematic phase [5].

The electro-optical technique may also be used to study the response of the *helical* structure of a ferroelectric liquid crystal to a weak ($E \ll E_c$) sinusoidal electric field. Here the response is due to the interaction of the field with the total spontaneous polarization including both the piezo-electric and the flexo-electric terms. (Note that the P_s measured by the pyro-electric technique for the unwound helix does not contain the flexo-electric contribution; however it is the same polarization which defines the electro-optical behaviour of thin cells.) From the electro-optic response to the weak field we have evaluated the piezo- and the flexo-contributions to the total value of the spontaneous polarization in L-4-*n*-decyloxy-benzylidene-4′-amino-2″-methylbutylcinnamate (DOBAMBC) and other materials [9, 10].

4. Investigation of the flow-induced piezo-electric effect in the smectic C* phase

A study of the piezo-electric effect is based on the measurement of the electric charge resulting from the distortion of a ferroelectric liquid crystal by shear flow [11]. In contrast with earlier experiments by Pieranski *et al.* [12] where Couette flow was obtained using the mechanical shift of one plate of the liquid crystal cell, we use Poiseuille flow in a planar capillary excited by periodically changing air pressure (cf. figure 9). Such a technique allows us to avoid any moving mechanical parts and to increase the sensitivity for charge detection.

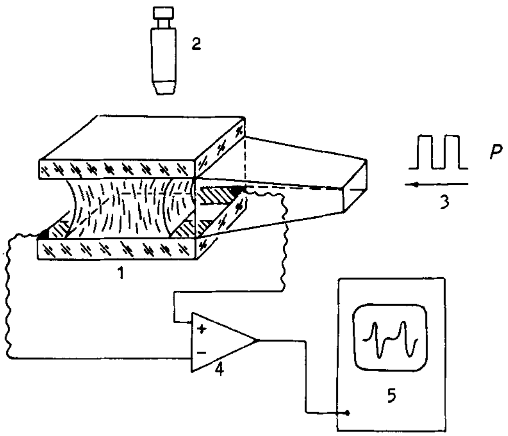

Figure 9. An arrangement for the investigation of the piezo-electric effect in ferroelectric liquid crystals. 1, liquid crystal cell in a thermostat; 2, polarizing microscope; 3, micro-compressor; 4, charge amplifier; 5, oscilloscope.

In the experiment with ferroelectric liquid crystals, unlike nematics [11], the electrodes were parallel to the flow direction; this is due to the symmetry of the ferroelectric phase. The periodic shear with a velocity gradient $\partial v/\partial Z$ results in the distortion of the director in the XZ plane (X is the direction of air flow). Initially the director is oriented homeotropically (i.e. parallel to the Z axis) for its interaction with an a.c. electric field resulting from the quadratic dielectric torque (i.e. $W_E = \varepsilon_a E^2$, $\varepsilon_a > 0$). Then the electric field is switched off and the air pressure is applied.

The periodic flow of a liquid crystal caused by the pressure results in a charge q_y across the electrodes which is proportional to the spontaneous polarization P_s (within a smectic layer) and a change in $\langle \cos \varphi \rangle$ for one period of pressure. The azimuthal angle φ is measured from the X axis and the macroscopic polarization $\langle P_Y \rangle = P_s \Delta \langle \cos \varphi \rangle$ occurs in the Y direction. The value of the spontaneous polarization may, in principle, be calculated using independent optical measurements of the angle φ from the phase delay of the transmitted light. In the case of high pressure and large distortions the angle φ saturates, $\Delta \langle \cos \varphi \rangle = 1$ and $P_s = q_y/S$ where S is the lateral surface area of the layer. The piezo-electric response for a relatively weak distortion, $\Delta \langle \cos \varphi \rangle \ll 1$, is shown in figure 10.

5. Measurement of the second-order non-linear susceptibility

The polar structures of ferroelectric liquid crystals open up possibilities for the investigation and potential application of the effects which are due to the non-zero value of the second-order dielectric susceptibility $\chi_{(2)}$. In particular, optical second harmonic generation [13] can be observed in these materials. Moreover, this generation

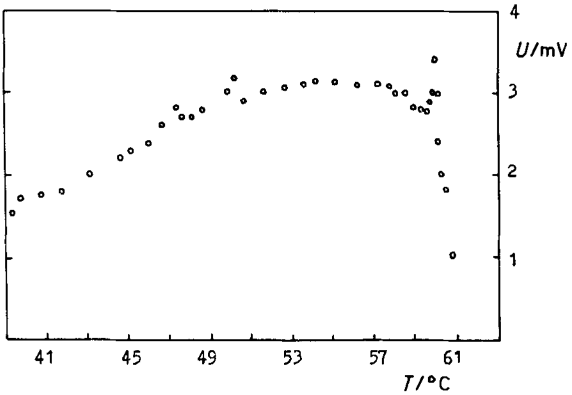

Figure 10. The piezo-electric response as a function of temperature for the smectic C* phase of the 4-*n*-hexyloxyphenyl ester of 4′-octyloxybenzoic acid doped with 5 per cent of HOBACNPC, cell thickness = 110 μm, pressure amplitude = 70 Pa.

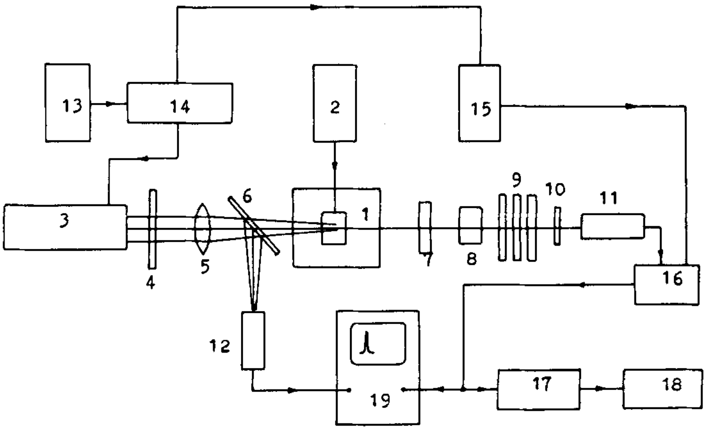

Figure 11. A block diagram of the equipment for measuring the intensity of the second harmonic generation. 1, liquid crystal cell in a thermostat; 2, d.c. voltage supply; 3, laser (λ = 1·06 μm), 4, filter; 5, lens (F = 43 cm); 6, semi-transparent mirror; 7, attenuator; 8, analyser; 9, filter; 10, interference filter for λ = 0·53 μm; 11, 12, photomultipliers; 13, triggering pulse generator; 14, amplifier; 15, strobing pulse generator; 16, analogue switch; 17, integrator; 18, digital meter; 19, oscilloscope.

may be observed in the phase-matching regime and there is a correlation between the values of the non-linear susceptibility and the spontaneous polarization [14].

In the equipment shown in figure 11 [15] the second optical harmonic (λ = 0·53 μm) is excited by a YAG:Nd laser (λ = 1·06 μm) with a peak pulse power of 200–300 kW. The sensitivity of the photo-electric circuit corresponds to nearly 30 photons of second harmonic per laser pulse. A d.c. electric field may be applied to the cell to unwind the helical structure of the smectic C* phase. The initial homeotropic orientation in the smectic A phase (before cooling) is achieved with the help of chromium stearyl chloride.

On decreasing temperature the tilt angle Θ and the optical anisotropy change and, as a result, at a certain temperature phase-matched second harmonic generation may be observed (cf. figure 12). However, the temperature dependence of the susceptibility is usually calculated from the data obtained for the asynchronous regime. The $\chi_{(2)}(T)$

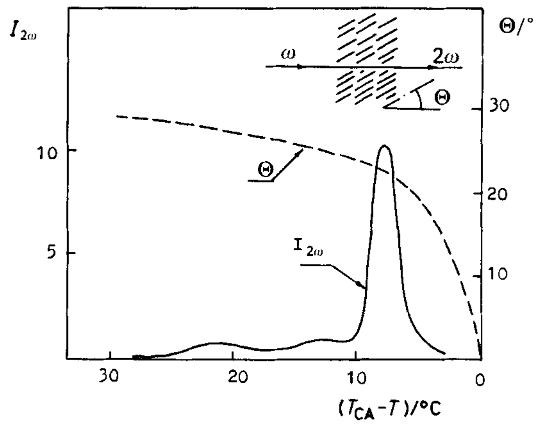

Figure 12. The director tilt angle θ and the intensity of the phase-matched second harmonic generation $I_{2\omega}$ as a function of temperature for DOBAMBC (cell thickness 90 μm, d.c. field strength = 3 kV cm^{-1}).

function is found to correlate with the temperature behaviour of the spontaneous polarization $P_s(T)$ [14].

6. Conclusion

In conclusion, a variety of the experimental techniques which we use for studying ferroelectric liquid crystals allows us to measure virtually all the physical parameters which are essential for the development of ferroelectric liquid-crystalline materials for fast displays and optical processing devices.

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