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Field dependence of the optical activity of a chiral liquid crystal near the isotropic–smectic A transition

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Chiral liquid crystals exhibit molecular optical activity in the isotropic phase. We have studied the evolution of the optical activity as a function of an applied electric field on a 76·2 μm film of the chiral liquid crystal W7, which exhibits an isotropic–smectic A transition at approximately 40°C. We measured the optical activity by recording the rotation of the plane of polarization of an incident linearly polarized ray of light, provided by a He–Ne laser. The applied biasing electric field is parallel to the direction of the incident beam. We find that at 41·0°C, the plane of polarization shifts from −1·1° for an applied voltage of 30 V to a maximum of −4·0° at 70 V. The absolute value of the signal decreases beyond this voltage. These shifts are in the direction of the smectic A phase and are in general larger than those observed as a function of temperature. Close to the isotropic–smectic A phase transition, molecules inside the liquid coalesce to form dynamic coherent groups, which have smectic nature. These groups are randomly oriented with respect to each other in the absence of an electric field. The application of an electric field causes the molecules within these groups to align along the direction of the field and to contribute coherently to the optical activity of the system. The way the molecules align with the field depends on the relative values of the polarizability α, which contributes to the alignment of the long axis of the molecule, and the dipole moment **p**, which contributes to the alignment of the short axis of the molecule. Our preliminary results and calculations suggest that for small fields, the electric field couples with the dipole moment **p**, whereas for fields in excess of 70 V, the field couples with the polarizability of the long axis of the molecule, causing a rotational reorientation of the molecules in the isotropic phase. The value of the field at which this reorientation occurs may be controlled by temperature.

1. Introduction

Chirality is caused by the handedness of the molecules composing the medium and gives rise to optical activity, related to the rotation of the plane of polarization of a wave traversing the medium. The constitutive relations of a chiral medium are

$$\left.\begin{aligned} D &= \varepsilon E + i\zeta_c B, \\ H &= (1/\mu)B + i\zeta_c E, \end{aligned}\right\} \tag{1}$$

where ε is the permittivity, μ is the permeability and ζ_c is the chirality admittance of the chiral material [1]. Inside the isotropic chiral medium, there are two modes of propagation, a left circularly polarized wave (LCP) and a right circularly polarized wave (RCP), with two differing wave numbers

$$\left.\begin{aligned} K_l &= -\omega\mu\zeta_c + \omega\sqrt{(\mu^2\zeta_c 2 + \mu\varepsilon)} \qquad \text{(LCP)}, \\ K_r &= \omega\mu\zeta_c + \omega\sqrt{(\mu^2\zeta_c 2 + \mu\varepsilon)} \qquad \text{(RCP) [2]}, \end{aligned}\right\} \tag{2}$$

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When a linearly polarized wave traverses a chiral material, the plane of polarization experiences a rotation of

$$\delta = \omega\mu\zeta_c z, \tag{3}$$

where ω is the frequency of the wave and z is the thickness of the chiral material. At fixed frequency and thickness, the rotation angle varies by changing the value of ζ_c.

The evolution of the optical activity of chiral liquid crystals in the isotropic phase as a function of temperature has been described in the literature [3]. The basic phenomenological mechanism for the increase of the optical activity close to the transition is the formation in the isotropic phase of dynamic, coherent regions [4]. These regions have liquid crystalline character that adds a structural contribution to the value of the chirality admittance above the molecular contribution [5, 6]. Our purpose is to study and characterize the same effect as a function of applied electric field. If an electric field is applied to the sample, the molecules couple to the field through their polarizability α and permanent dipole moment $\mathbf{p}$. This results in a decrease in the energy of the system, and in the randomness of the molecular distributions of the system, effectively increasing the number and coherence of the ordered regions. Thus, at some critical field E_c a phase transition into an ordered phase may occur.

2. Experimental methods and results

We measured the rotation δ of the plane of polarization in a 76·2 μm thick sample of the liquid crystal W7, which has an isotropic–smectic A transition at 40°C. We measured the rotation of the plane of polarization of incoming linearly polarized light provided by a He–Ne laser after traversing the sample. A sketch of the experimental apparatus appears in figure 1. To do this, a plot was taken of the intensity as an analyser

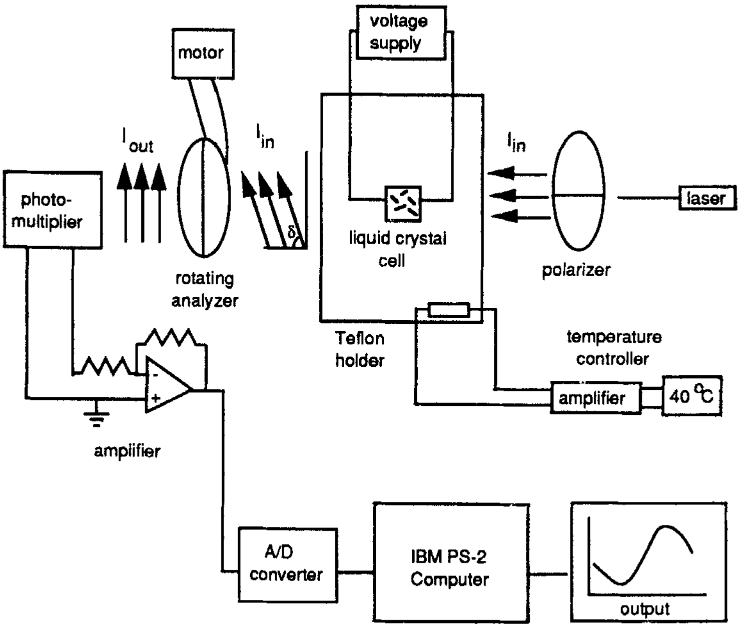

Figure 1. Sketch of the experimental apparatus used in the experiment.

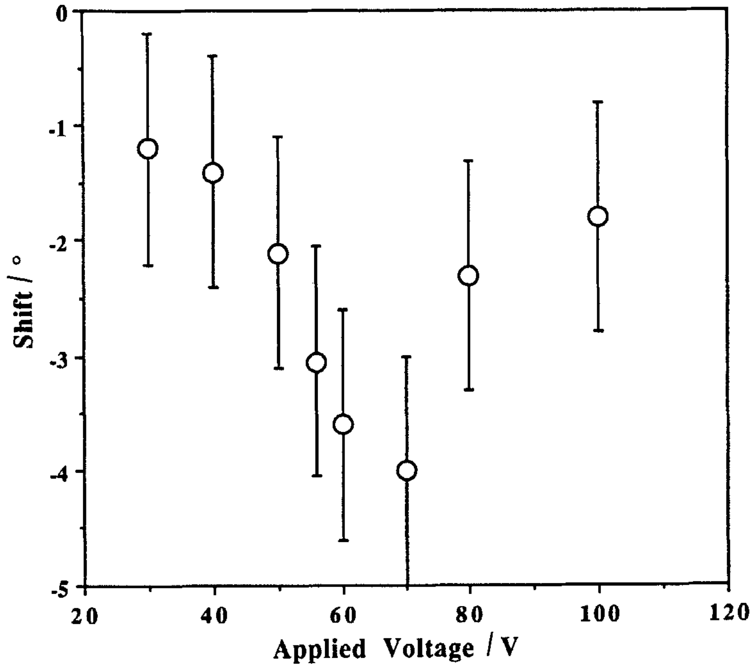

Figure 2. Rotation of the angle of polarization as a function of applied voltage for a 76·2 μm thick cell containing W7 at 41°C.

was rotated through 360°. By comparing the output intensity at 0 applied voltage to that measured at a finite voltage, the rotation in the plane of polarization, δ, was determined.

The results of these initial measurements at 41°C appear in figure 2 [7]. In this work, we found that the plane of polarization shifts from $-1{\cdot}1°$ at 30 V to $-4°$ at 70 V. The absolute value of the signal decreases beyond this point. These changes suggest that ordering toward the smectic A phase occurs inside the sample as a result of the application of the electric field. We present one possible mechanism which may describe the decrease in the absolute value of the phase shift.

3. Analysis

As mentioned above, the molecules in the liquid crystal couple to the applied electric field $\mathbf{E}$ through their polarizability α and permanent dipole moment $\mathbf{p}$. The permanent dipole moment is provided by the chiral substituent, and its value depends on the relative electronegativity of the substituent. The polarizability of the long axis of the molecule gives rise to an induced dipole. If $U_0(T)$ is the potential energy due to the interaction between charges in the molecule, in the presence of an applied electric field this energy will be reduced by

$$U_{\mathrm{total}} - U_0(T) = U_{\mathrm{induced}} - U_{\mathrm{permanent}}, \tag{4}$$

where the subscripts 'induced' and 'permanent' refer to the induced and permanent dipoles respectively, $U_{\mathrm{induced}} = \mathbf{p}_{\mathrm{ind}} \cdot \mathbf{E}$, $U_{\mathrm{permanent}} = \mathbf{p} \cdot \mathbf{E}$. If θ and ϕ are the tilt and azimuthal angles of the long axis of the molecule with respect to the z axis of the

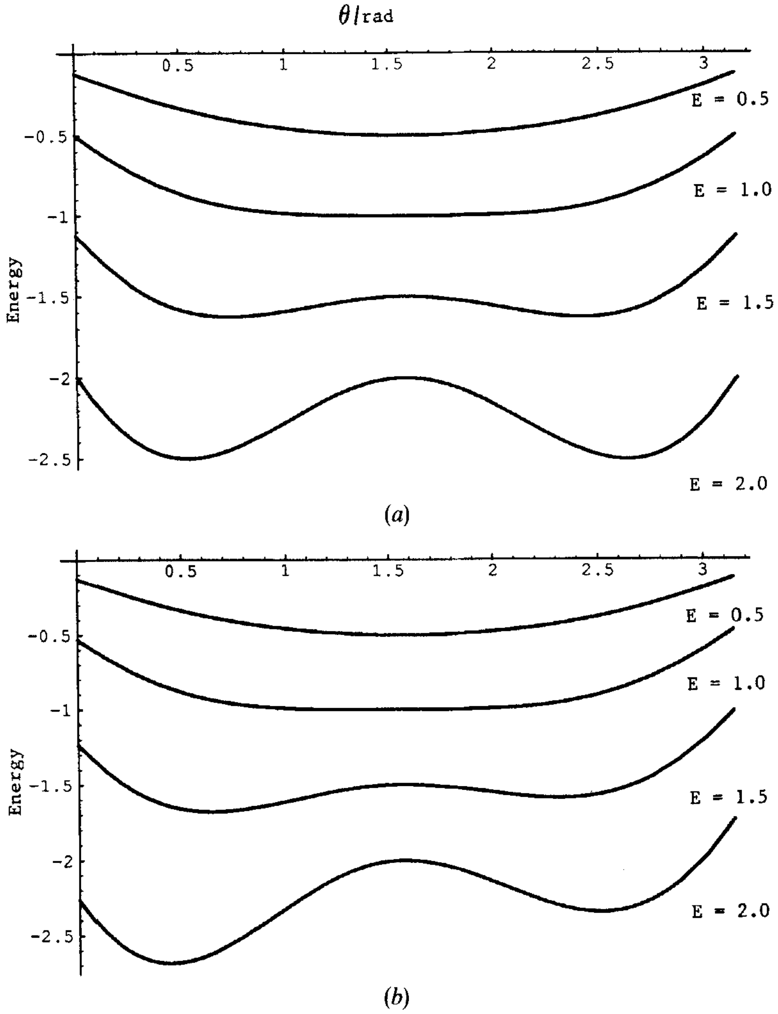

Figure 3. Plot of the total energy of the liquid crystal as a function of tilt angle θ, according to equation (6). The solid lines correspond to different values of the electric field. (*a*) Symmetrical polarizability term case; (*b*) asymmetrical polarizability term case.

laboratory frame of reference and θ' and ϕ' are the tilt and azimuthal angles of the chiral substituent with respect to the long axis of the molecule, we can write equation (4) as

$$U_{\text{total}} - U_0(T) = -\frac{\sum_i C_i(\mathbf{E}\cdot\mathbf{e}_1)^{i+1}}{(i+1)} - \mathbf{E}\cdot\mathbb{M}_{\theta\phi}\mathbf{p}, \tag{5}$$

where, $\mathbf{e}_1 = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, $\mathbf{p} = p(\sin\theta'\cos\phi', \sin\theta'\cos\phi', \cos\theta')$, and $\mathbb{M}_{\theta,\phi}$ is the rotational matrix relating the angles θ and ϕ, and θ' and ϕ'. Note that θ' is determined by the nature of the bonds in the molecule and is considered fixed. If the z axis is defined such that $\mathbf{E} = E\mathbf{e}_z$, equation (5) becomes, without loss of generality,

$$U_{\text{total}} - U_0(T) = -\frac{\sum C_i(E\cos\theta)^{i+1}}{(i+1)} - pE(-\sin\theta\sin\theta'\cos\phi' + \cos\theta\cos\theta'). \tag{6}$$

The energy will have minima when $\phi' = 180°$. Figure 3 shows plots of the total energy as a function of angle θ for different values of the applied electric field magnitude, E. Figure 3 (*a*) shows the energy obtained when only the symmetrical polarizability term in equation (6), C_1, is considered: $C_2, C_3 \ldots = 0$. For simplicity, θ' is taken as 90°. The minimum of the energy shifts as a function of increasing electric field from a 90° tilt to a 10° or 170° tilt of the long axis of the molecule with respect to the direction of the electric field. Note that the energy is bimodal in this case. Figure 3 (*b*) shows the results obtained considering a finite polarizability asymmetrical term, $C_2 > 0$. The minima at high fields favour a tilt of 10°.

We now relate the results shown in figure 3 with the experimental results in figure 2. At low fields, the molecules tilt at 90° with respect to the electric field direction. This electric field direction coincides with the direction of the wavevector of the incoming linearly polarized light, as can be seen from figure 1. The incoming light thus interacts with the asymmetric cross-section of the optical ellipsoid, producing a large, structurally related rotation of the plane of polarization. This effect increases with increasing field, since the electric field tends to reduce the randomness of the molecular orientations inside the isotropic crystal. For large fields, the contribution to the energy of the system due to the polarizability of the long axis of the molecules dominates, and the molecules tend to align along the electric field. The incoming light interacts with the symmetric cross-section of the optical ellipsoid, and the main contribution to the rotation of the plane of polarization is the molecular optical activity. Finally, we note that our results give values for the angular shift that are higher than those observed as a function of temperature [8]. We propose that this is caused by the aligning effect of the electric field which produces a structural contribution to the optical activity, not present in the temperature studies.

4. Summary

We have introduced a mechanism to describe our preliminary experimental observations on the shift of the angle of polarization of light incident on an isotropic chiral liquid crystal. This mechanism suggests the presence of a rotational transition in the isotropic phase of a chiral liquid crystal as a function of electric field just above the smectic A transition. In addition, equation (6) implies that for sufficiently large electric fields, the energy of the isotropic phase can decrease below that of the smectic A phase, inducing a phase transition, which may be preceded by the rotational transition described above.

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