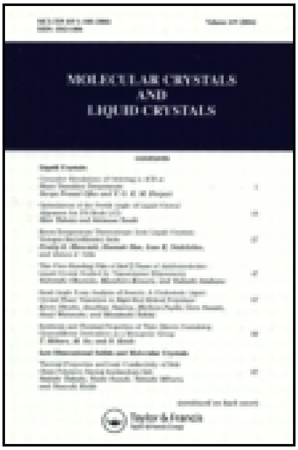

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A Pulsed NMR Study of Molecular Reordering in a Nematic-Cholesteric Mixture

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A Pulsed NMR Study of Molecular Reordering in a Nematic-Cholesteric Mixture†

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The effects of pulsed electric fields on the molecular order in a nematic-cholesteric mixture are reported, and a theoretical discussion of these phenomena is given. The molecular order is determined from the time dependence of the second moment of the proton absorption line shape.

1 INTRODUCTION

In the previous paper we presented a pulsed NMR technique for measuring molecular orientation as a function of time. In the present paper we discuss the application of this technique to the study of nematic-cholesteric mixtures. The effects of applied magnetic and pulsed electric fields are considered, and the average molecular orientation (as reflected in the second moment of the proton resonance absorption line) is outlined. The experimental time dependence of the second moment is interpreted in view of this calculation to obtain a measure of the ratio $\chi_a H_c^2/\gamma_1$, where χ_a is the diamagnetic anisotropy H_c is the critical field for the cholesteric-nematic transition, and γ_1 is the torsional viscosity.

2 EXPERIMENTAL DETAILS

The sample used for this experiment was a mixture of ~ 1.8 wt.% cholesterol-oleyl-carbonate (COC) in Eastman field effect mixture II.[1] The Eastman mixture was chosen because it has a large positive dielectric anisotropy and is nematic at room temperature.

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The sample was vacuum sealed in a pyrex cell of 1 cm × 1 cm cross-section, filled to a depth of 1 cm. The cell contained 9 platinum plates of thickness 0.008 cm supported by slotted teflon spacers, giving an inter-plate spacing of ~0.124 cm. A square NMR coil was wound on the sample cell, providing an r.f. field $H_1 \simeq 30$ G with good homogeneity over the sample volume. Alternate platinum plates were connected to form a parallel plate capacitor. A 5 kHz electric field was produced by applying the output of a high voltage oscillator/amplifier to the capacitor plates. The electric field intensity was 4000 V/cm, which is just above the critical field for the mixture used. As described in the previous paper, the electric field was gated on and off (with rise and fall times of <40 msec) by the data aquisition system.

All measurements were made at 30 MHz using standard pulsed NMR apparatus.[2] The recovery time of the spectrometer for the coil geometry used was <7 μsec.

3 CALCULATION OF REORDERING TIMES

In what follows we shall consider the response of nematic-cholesteric mixtures with positive diamagnetic and dielectric anisotropies to parallel magnetic and electric fields. Let us first consider the response of a typical molecule located at a point z along the cholesteric pitch axis. If we assume that the reordering takes place slowly, then we may write a dynamical equation in terms of the torques on such a molecule as:

$$\gamma_1 \frac{\partial \theta}{\partial t} = K_{22} \frac{\partial^2(\phi - \theta)}{\partial z^2} - \chi_a H^2 \sin\theta \cos\theta, \tag{1}$$

where θ is the angle between $N(t)$ (the preferred direction of local molecular order at time t) and the applied fields, and ϕ is the angle between the applied fields and the equilibrium preferred direction of molecular order (i.e. $N(\infty)$). Note that $\phi = \phi(z)$. Figure 1 shows the coordinate system used.

Now, we make the assumption that the molecular reorientation proceeds in a quasi-static fashion. That is, that the z-dependence of $(\phi - \theta)$ is that which would be assumed by the molecules in an effective field H' such that $H' \leq H_c$, where H_c is the critical field at which the cholesteric pitch length approaches infinity. In equilibrium in such an effective field $\partial\theta/\partial t = 0$, and we may write:

$$\frac{\partial^2(\phi - \theta)}{\partial z^2} = \frac{\chi_a H'^2}{K_{22}} \sin\theta \cos\theta. \tag{2}$$

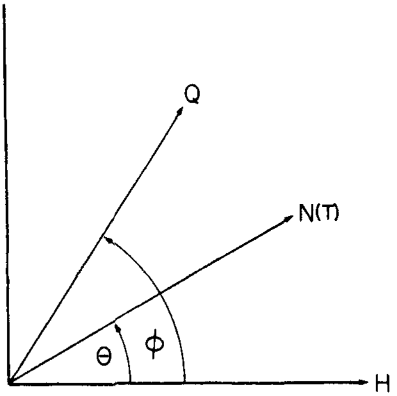

FIGURE 1 Coordinate system showing instantaneous preferred direction of local order N in relation to applied field H and equilibrium order direction Q.

Equation 2 may be written in a more convenient form[3] for our purposes as:

$$\frac{\partial^2(\phi-\theta)}{\partial z^2} = \left[\frac{\kappa}{E(\kappa)}\right]^2 \frac{\chi_a}{K_{22}} H_c^2 \sin\theta\cos\theta \tag{3a}$$

where κ is the argument of a complete elliptic integral of the second kind satisfying

$$\frac{\kappa}{E(\kappa)} = \frac{H'}{H_c}. \tag{3b}$$

Now, substituting Eq. 3a into Eq. 1, we obtain:

$$\frac{\partial\theta}{\partial t} = \frac{\chi_a H_c^2}{\gamma_1}\left\{\left[\frac{\kappa}{E(\kappa)}\right]^2 - \left[\frac{H}{H_c}\right]^2\right\}\sin\theta\cos\theta. \tag{4}$$

Equation 4 then describes the time evolution of the preferred direction of molecular orientation of a typical molecule located at a position z along the cholesteric pitch axis under the assumption that the system evolves slowly from one equilibrium state to another; that is, that the spatial distribution of molecular orientation $\theta(z)$ may always be described by an equation of the form of Eq. 3a, and that κ is a slowly varying function of time. We can now affect an approximate solution to Eq. 4, valid for small time intervals δt, by assuming that $\kappa(t+\delta t) = \kappa(t)$. This solution is given by:

$$\tan\theta(z, t+\delta t) = \tan\theta(z,t)\exp\left\{\frac{\chi_a H_c^2}{\gamma_1}\left(\left[\frac{\kappa}{E(\kappa)}\right]^2 - \left[\frac{H}{H_c}\right]^2\right)\delta t\right\}. \tag{5}$$

This solution may then be used to calculate the time evolution of observable quantities. In particular, we may now calculate the time dependence of the second moment of the proton magnetic resonance in a nematic-cholesteric mixture. Collings, *et. al.*[4] have shown that for nematics of positive diamagnetic anisotropy, the second moment for a nematic-cholesteric mixture in a magnetic field $H \leq H_c$ is given by:

$$M_2^{ch} = \langle P_2(\hat{N} \cdot \hat{H})^2 \rangle M_2^n, \tag{6}$$

where M_2^{ch} is the second moment observed in the cholesteric phase, M_2^n is the second moment observed in the nematic phase (i.e. for $H \geqq H_c$), and the coefficient of M_2^n is the spatial average of the square of the second Legendre polynomial with argument $\cos\theta = \hat{N} \cdot \hat{H}$, $\hat{N}$ and $\hat{H}$ are unit vectors in the direction of N and H respectively. We note that Eq. 6 assumes that the order parameter for the small scale local order in the cholesteric is equal to the nematic order parameter. Hence, we may obtain $\langle P_2^2 \rangle$ directly by measuring M_2^{ch}/M_2^n. Since the minimum value of $\langle P_2^2 \rangle$ for the cholesteric is 11/32 (uniform twist along the optic axis, i.e. $H \ll H_c$), we should expect to measure $11/32 \leqq \langle P_2^2 \rangle \leqq 1$.

Before proceeding further with a determination of the time dependence of $\langle P_2^2 \rangle$ in a transient field, let us consider the field dependence of $\langle P_2^2 \rangle$ in a static field, as reported in Reference 4. In that case, as the field is increased the cholesteric pitch length increases and the molecular orientation becomes nearly parallel to the magnetic field for an increasing fraction of the molecules. That is, the pitch length diverges logarithmicaly, and the preferred direction of molecular order approaches that of a uniformly aligned nematic as H approaches H_c. The latter effect is sketched in Figure 2.

To determine $\langle P_2^2 \rangle$ for equilibrium in a field H, we first obtain the second integral of Eq. 2 as[3]:

$$z = \kappa\xi K(\kappa, \theta), \tag{7}$$

where $K(\kappa, \theta)$ is an elliptic integral of the first kind, z is the distance along the optic axis, ξ is a characteristic length, θ is the angle between N and H at z, and κ is a solution to:

$$\frac{\kappa}{E(\kappa)} = \frac{H}{H_c}, \tag{8}$$

where $E(\kappa)$ is a complete elliptic integral of the second kind. Inverting Eq. 7 numerically, we may then find θ as a function of z and calculate $\langle P_2^2 \rangle$ by integrating $P_2^2(\theta(z))$ over a complete pitch length. The resulting field dependence of $\langle P_2^2 \rangle$ is shown in Figure 3.

Let us now return to the problem of the time dependence of $\langle P_2^2 \rangle$ in response to a transient field. Consider the effect of an electric field applied parallel to a magnetic field. The total torque exerted by the two fields is:

$$\left(y_a H^2 + \frac{\varepsilon_a}{4\pi}\right)\sin\theta\cos\theta\left[\chi_a H^2 + \frac{\varepsilon_a}{4\pi}E^2\right]\sin\theta\cos\theta, \tag{9}$$

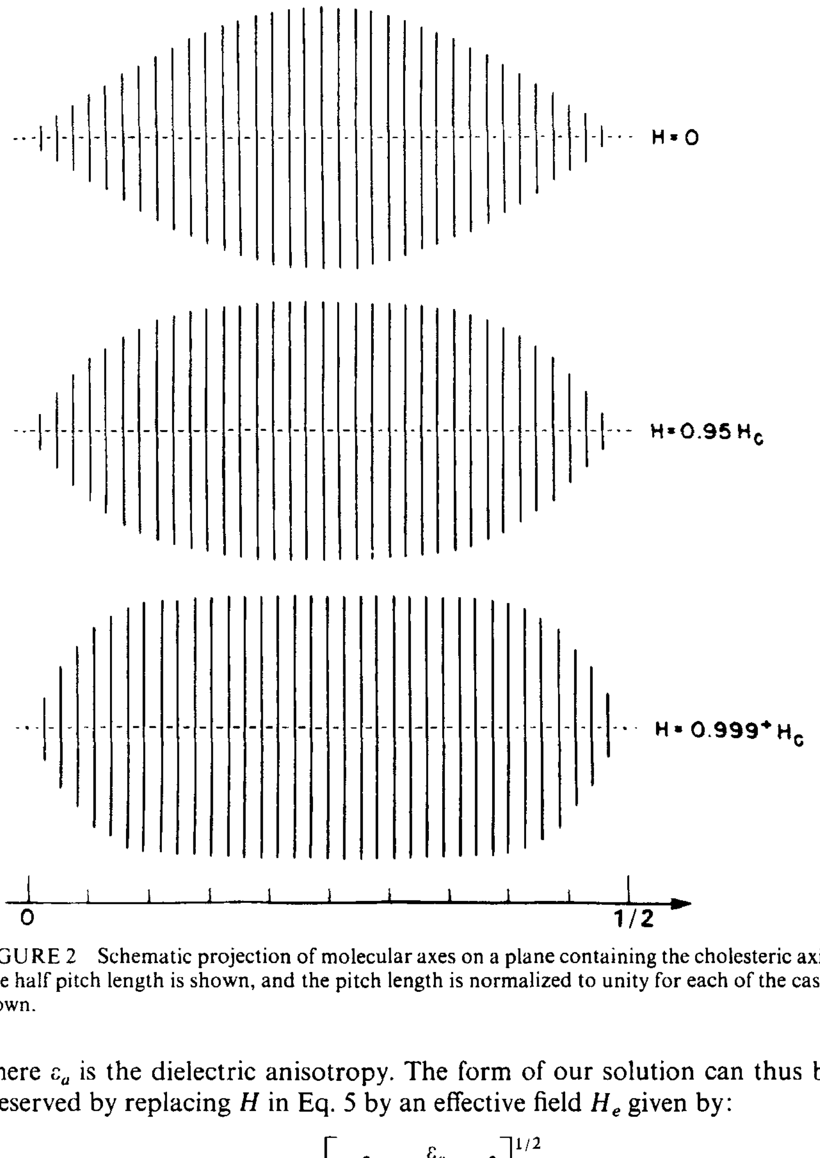

FIGURE 2 Schematic projection of molecular axes on a plane containing the cholesteric axis. One half pitch length is shown, and the pitch length is normalized to unity for each of the cases shown.

where ε_a is the dielectric anisotropy. The form of our solution can thus be preserved by replacing H in Eq. 5 by an effective field H_e given by:

$$H_e = \left[H^2 + \frac{\varepsilon_a}{4\pi\chi_a} E^2 \right]^{1/2}. \tag{10}$$

We shall now consider two cases of a transient electric field applied parallel to a constant magnetic field H_0, such that $H_0 < \simeq \frac{1}{2} H_c$ so that the equilibrium molecular orientation in the magnetic field alone is a nearly uniform twist about the optic axis.

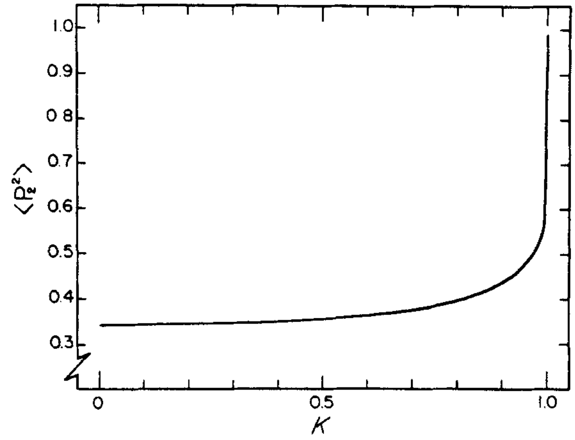

FIGURE 3 $\langle P_2^2 \rangle$ vs. κ.

Case I The nematic-cholestric mixture is initially in equilibrium at $H_e = H_0$. At time $t = 0$ an a.c. electric field of constant r.m.s. amplitude E is suddenly switched on. Here E is such that $H_e > H_c$. Thus, the molecular orientation will change from a nearly uniform twist about the cholesteric axis to a nearly uniform nematic alignment with the preferred direction of orientation parallel to the applied fields. In this case, the field term in Eq. 5 will be H_e, where H_e is as given in Eq. 10 with $H = H_0$, and the initial angular distribution will be $\theta(z, 0) = \alpha z$ and $\phi(z) = 0$.

Case II The sample is initially in equilibrium in the effective field $H_e > H_c$ defined above. At time $t = 0$ the electric field is switched off. Thus, the field term in Eq. 5 is $H_e = H_0$, where $H_0 < H_c$, and the initial angular distribution is $\theta(z, 0) \simeq 0$ and $\phi(z) = \alpha z$.

It should be noted that the derivation above is somewhat similar to that reported by Pieranski, *et. al.*[5] for the case of a Freedericsz transition. In the present case, however, we use rather different approximations appropriate to the cholesteric geometry.

4 EXPERIMENTAL DETERMINATION OF $\chi_a H_c^2/\gamma_1$

An approximation technique is used to obtain the time dependence for each of the special cases noted above. We begin by computing tables of $\langle P_2^2 \rangle$ vs. κ and $\theta(z)$ vs. κ from the numerical inversion of Eq. 7. Appropriate initial values of $\tan \theta(z, 0)$ and κ are selected and substituted into Eq. 5 with $\gamma_1/\chi_a H_c^2$ taken to be a constant τ to be determined later. The time is incremented by an amount $\delta\tau$ (i.e. by a small fraction of τ), and new values of tan $\theta(z, \delta\tau)$ are determined. From these new values of $\theta(z)$ a new value for $\langle P_2^2\rangle$ is calculated and the corresponding value of κ is determined from the $\langle P_2^2\rangle$ vs. κ table. The distribution of tan θ vs. z is then corrected by interpolating in the $\theta(z)$ vs. κ table, and the process is iterated using the corrected κ and $\theta(z)$ values. In this manner we obtain $\langle P_2^2\rangle$ vs. time in units of τ. The time constant τ is then determined by least squares fitting the calculated values of $\langle P_2^2\rangle$ vs. time to the experimental results, and thus $\chi_a H_c^2/\gamma_1$ is derived. The results are shown in Figures 4 and 5 where the value obtained for $\chi_a H_c^2/\gamma_1$ is 1.11 sec^{-1}.

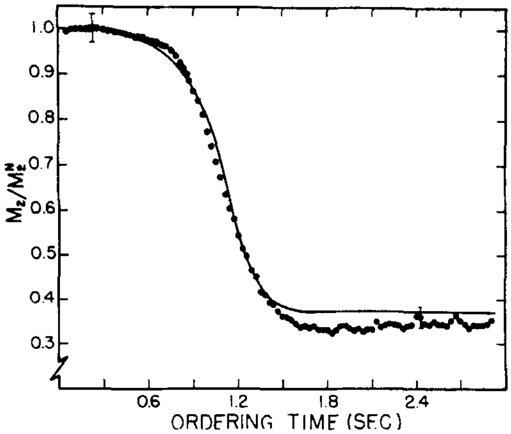

FIGURE 4 $M_2^{ch}/M_2^n = \langle P_2^2\rangle$ vs. time following turn *off* of electric field. Solid line is calculated from Eq. 5.

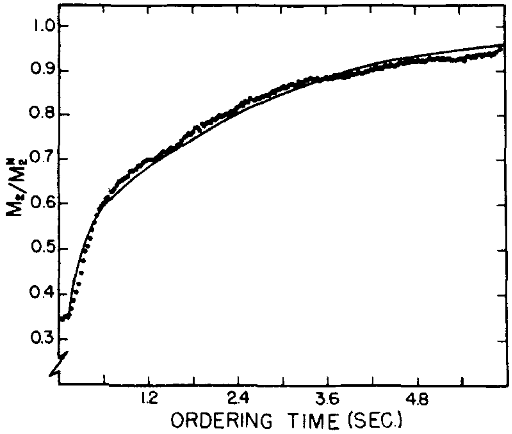

FIGURE 5 $M_2^{ch}/M_2^n = \langle P_2^2\rangle$ vs. time following turn *on* of electric field. Solid line is calculated from Eq. 5.

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