Manifestation of ferroelectricity in a lyotropic liquid crystal with a chiral impurity: a structural analog of a biological membrane

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A ferroelectric effect has been observed in a nonaqueous lyotropic liquid crystal doped with a chiral impurity by a method involving an acoustically induced deformation.

1. The appearance of a spontaneous polarization in a lyotropic liquid crystal was predicted in Ref. 1 on the basis of a symmetry analogy with thermotropic liquid crystals. This effect has not previously been seen experimentally, primarily for two reasons. The first reason is that lyotropic liquid crystals generally have a high electrical conductivity, $\sigma \gtrsim 10^{-5}$ S/cm, which is five orders of magnitude greater than the typical conductivities of thermotropic ferroelectric phases. This high conductivity prevents the use of the two basic methods which are used to study ferroelectricity in liquid crystals: the pyroelectric method and the Sawyer-Tower method. The second reason is the difficulty in producing a single-domain sample with a uniform molecular orientation, since the average spontaneous polarization over the volume is zero in the case of an unoriented sample.

We know that sufficient conditions for the existence of a spontaneous polarization in a liquid crystal are that there be a layer structure, that the long molecular axes be tilted toward the normal to the layer, and that the molecules having a nonzero dipole moment be of a chiral nature (the chirality and the dipole moment can be imparted to the system by a dopant[2]). If these conditions are met, the liquid crystal has the symmetry of a pyroelectric (a twofold polar axis[3]).

The same symmetry characteristics can be realized in a lyotropic liquid crystal if one starts with membrane-forming phospholipids (in particular, lecithin) as a basis and dopes them with optically active cholesterol. We selected for the present study this system, not in an aqueous medium but in ethylene glycol, which is a poor conductor in comparison with water.

2. We studied one manifestation of ferroelectricity in a liquid crystal: the piezoelectric effect. In the experiment we studied the acoustically induced piezoelectric effect as a function of the temperature, using an oscillating-drop method which we had developed previously.[4] As the object of the study we used synthetic dipalmethoyl lecithin ($\mathrm{DPL}_{\beta,\gamma}$, molecular mass $M = 734.06$ g/mole, a Fluka product) in a mixture with cholesterol ($M = 386.67$ g/mole, a Merck product) in concentrations ranging from 0 to 15% by weight. Nonaqueous lyotropic lamellar phases[5] were produced by adding ethylene glycol ($M = 62.09$ g/mole, a Loba Fein Chemie product) in concentrations of about 30%.

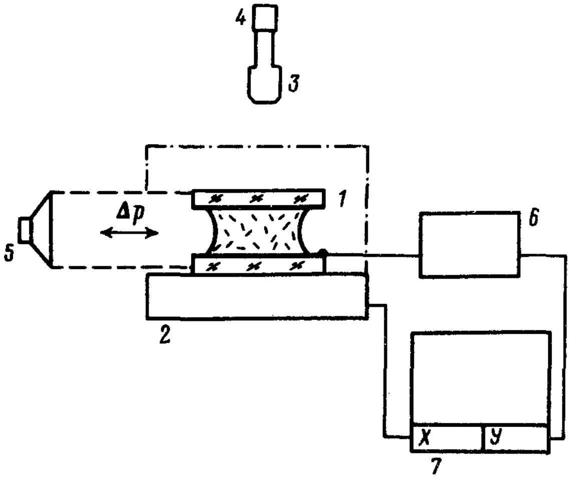

FIG. 1. Experimental layout. 1—Liquid-crystal cell, which is a plane capillary filled with a lyotropic liquid crystal; 2—Linkam programmable temperature-control stage; 3—Meodta polarizing microscope; 4—FÉU-68 photomultiplier; 5—10GD-34 compressional electrodynamic speaker; 6—tuned nanovoltmeter with a 232 V synchronous detector; 7—Endin *x*, *y* chart recorder.

Lyotropic layered phases without cholesterol are characterized by sharp phase transitions from the tilted phase L_β to the folded phase P_β and then to the normal phase L_α. The temperatures of these transitions were found by measuring the intensity of depolarized light as a function of the temperature.[6] Adding cholesterol spread these phase transitions out over $\Delta T \sim 5$–10 °C.

The experimental layout is shown in Fig. 1. The liquid-crystal cell is placed in a programmable constant-temperature chamber (2). To observe textures and to detect the intensity of transmitted light, we use a polarizing microscope (3), a photomultiplier (4), and an *x*, *y* chart recorder (7).

A change in spontaneous polarization is induced by an oscillating air pressure at the edge of a drop of the lyotropic liquid crystal in a plane glass capillary ($d = 110$ μm) with semitransparent conducting electrodes (SnO_2). The sample is not deliberately oriented, but the piezoelectric response from the nonuniform texture is not averaged out completely, so its temperature dependence can be studied. A static external field can be used to polarize the sample, putting it in a single-domain state in the presence of a ferroelectric phase. The alternating pressure is produced by a compression electrodynamic speaker (5) at the resonant frequency of the mechanical oscillatory circuit ($f = 74$ Hz, $l = \lambda/4$, where l is the length of the acoustic line, and $\lambda = 4.4$ m is the length of the sound wave). The acoustic power at the sample is 12.5 kPa. The piezoelectric signal is detected at the frequency of the applied sound by a tuned amplifier with an input resistance of 100 MΩ, followed by synchronous detection (6).

3. The experimental results are shown in Figs. 2 and 3. Curve 1 in Fig. 2 shows the electrical response to the applied sound of pure $DPL_{\beta,\gamma}$ with ethylene glycol (without the cholesterol impurity). The three characteristic temperature regions on this curve correspond to the $L_{\beta'}$, P_β, and L_α phases, which are also shown (schematically) in this figure. Polarizing this sample by means of an external field in either the tilted or normal phase had essentially no effect on the magnitude of the piezoelectric

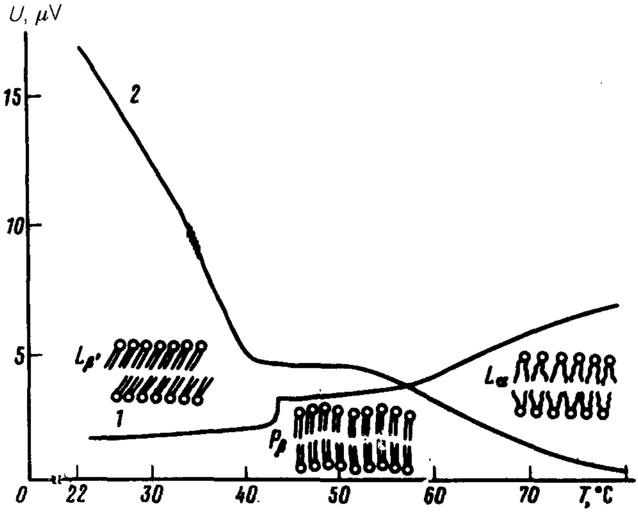

FIG. 2. Temperature dependence of the piezoelectric effect. 1—Pure $\mathrm{DPL}_{\beta,\gamma}$; 2—$\mathrm{DPL}_{\beta,\gamma}$ with a 15% cholesterol impurity.

signal. Curve 2 shows the temperature dependence of the piezoelectric effect in a $\mathrm{DPL}_{\beta,\gamma}$ sample doped with 15% cholesterol, in an experiment in which an electric field was not applied; curve 1 in Fig. 3 shows the corresponding results after polarization of the sample in an electric field $E \sim 2 \times 10^3$ V/cm for a minute (the sample was polarized in the folded P_β phase).

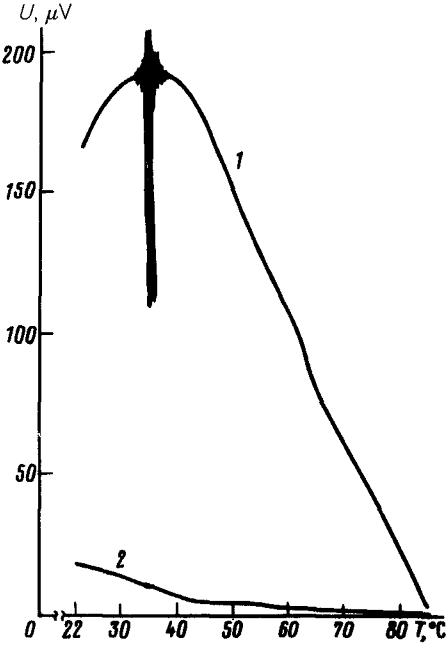

FIG. 3. 1—Temperature dependence of the piezoelectric effect for $\mathrm{DPL}_{\beta,\gamma}$ with a 15% cholesterol impurity after preliminary polarization in a static electric field $E \sim 2 \times 10^3$ V/cm; 2—the same sample, but without polarization in an electric field. A structural instability is observed near the temperature $T = 36°$ C.

4. Two facts verify that the piezoelectric effect in the tilted L_{β}, and P_{β} phases of the chiral lyotropic liquid crystal is of a ferroelectric nature: a) in the lyotropic liquid crystal doped with the chiral impurity, the piezoelectric effect increases with decreasing temperature (while the viscosity increases, and the deformation decreases). This behavior can be explained on the basis of a pronounced increase in spontaneous polarization. The undoped lyotropic liquid crystal exhibits the opposite tendency; the absolute maximum of the signal in the $L_{\beta'}$ phase is much lower than that for the doped lyotropic liquid crystal. The small piezoelectric effect in the pure $\mathrm{DPL}_{\beta,\gamma}$ at room temperature is probably a consequence of a slight deviation of the mixture composition from the racemic composition and thus the induction of a slight spontaneous polarization. The subsequent increase in the signal with the temperature is determined by an electrokinetic effect: a flow potential. b) The polarization of a chiral lyotropic liquid crystal in the tilted phase by a static electric field changes the texture of the liquid crystal and increases the piezoelectric response by more than an order of magnitude, in contrast with the results for an achiral lyotropic liquid crystal. This fact can be linked with a field-induced rotation of individual domains, i.e., the conversion of the sample to a single-domain state by an external field.

5. Biological phospholipid membranes are known to be bilayers which are structurally analogous to lyotropic phases. In addition, they contain a significant amount of cholesterol.[7] A matched tilting of the molecules in a bilayer, on the other hand, can be induced by external agents (mechanical deformation, electrical effects, steric factors resulting from the introduction of protein molecules in the membranes, etc.). Our experiments thus give us every reason to expect that ferroelectric effects should occur in membranes, and the spontaneous-polarization vector should lie in the plane of the membrane. If this proves to be the case, then this point must be taken into consideration in interpretations of ion transport and other electrical phenomena in membranes.

In summary, we have shown that chiral impurities induce a piezoelectricity in tilted lyotropic phases and that various manifestations of ferroelectricity should be expected in twisted lyotropic systems, including biological membranes, on the basis of the structural analogy with thermotropic liquid crystals.

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