

First nonhelical ferroelectric liquid crystal

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A nonhelical liquid crystal, which polarizes spontaneously in the absence of external effects, has been produced experimentally.

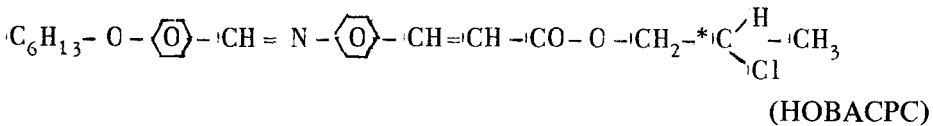
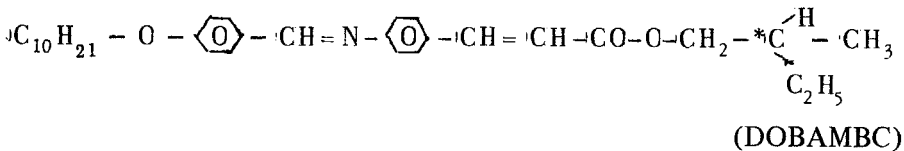
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1. Spontaneous polarization in liquid crystals (LC) has been realized in tilted, layered phases [for example, the smectic *C* phase (S_C^*)] comprised of mirror-asymmetric (chiral) molecules.¹ The only symmetry element of such phases is the twofold axis which is directed along the layers and which is perpendicular to the slope plane of molecules. This twofold axis accounts for the existence of a macroscopic dipole moment in the layer which is parallel to the axis and which can be realized because of the presence of a transverse dipole moment in chiral molecules.

The chiral nature of these molecules, as a rule, gives rise to the formation of a spiral or helicoidal structure in liquid crystals, which has been detected in all ferroelectric liquid crystals. The direction of spontaneous polarization of smectic layers precesses from layer to layer around the normal to the surfaces of the layers with $< 10\text{-}\mu\text{m}$ -pitch of the helix,² so that the macroscopic polarization in the bulk of a LC, whose dimensions are commensurable with this pitch, is compensated for by the helicoidal twist. A volume polarization can be accomplished in such phases by applying an external electric field which untwists the helix and which directs the total dipole moments of the smectic layers in such a way that the net polarization is oriented in the direction of the field. A volume polarization can also be produced by other external effects, for example, by a mechanical displacement of smectic layers³ as well as by the directive action of solid surfaces that are in contact with an LC.⁴

Meyer *et al.*¹ indicated, however, that a macroscopic polarization can occur in mixtures of left- and right-handed, chiral, smectic LC whose molecules have different transverse dipole moments. The twist, but not the local dipole moment, therefore, can be compensated for at a certain concentration. Such a compensation in terms of theory⁵ accounts for the fact that dipole ordering in pseudo-natural, liquid, ferroelectric materials has a secondary nature, whereas the primary nature is the orientational order, which arises in the tilted, smectic phases as a result of slowed-down rotation of chiral molecules around the long axes.

2. A nonhelical, ferroelectric, liquid crystal was obtained by us experimentally for the first time in a mixture of left- and right-handed, chiral, smectic LC (DOBAMBC and HOBACPC, respectively)



The pitch L_0 of the helicoidal helix was determined from the diffraction angle of a helium-neon laser beam. The spontaneous polarization P_s of the mixtures was determined by integrating the temperature dependence of the pyrocoefficient $\gamma(T) = dP_s/dT$, measured from the volt-watt sensitivity to the radiation pulses from a neodymium laser.⁶

The nonhelicoidal ferroelectric LC shown in Fig. 1 (for a cell of thickness $d = 200 \mu\text{m}$) corresponds to a concentration range of HOBACPC of 50–60 wt.% for which the wave vector of the helix $q_0 = 2\pi/L_0$ is equal to zero. It should be mentioned that the q_0 dependence on temperature at $T_{CA} - T > 1^\circ \text{C}$ for all mixtures in the S_s^* phase is rather weak and is analogous to that measured in Refs. 2 and 7 for single-component, chiral, smectic liquid crystals. The choice of temperature, for which the wave vectors are given in Fig. 1, is therefore nonessential: for the other differences in temperature $T_{CA} - T$ the concentration dependence q_0 is completely analogous to that illustrated in Fig. 1, except for a small (within the limits of the coefficient 2) variation of the scale along the q_0 axis. The helicoid is untwisted in the entire temperature range of the S_s^* phase in mixtures with a 50–60% HOBACPC concentration for $d = 200 \mu\text{m}$ and 35–75% concentration for $d = 20 \mu\text{m}$.

The q_0 dependence on the concentration of each component is close to a linear

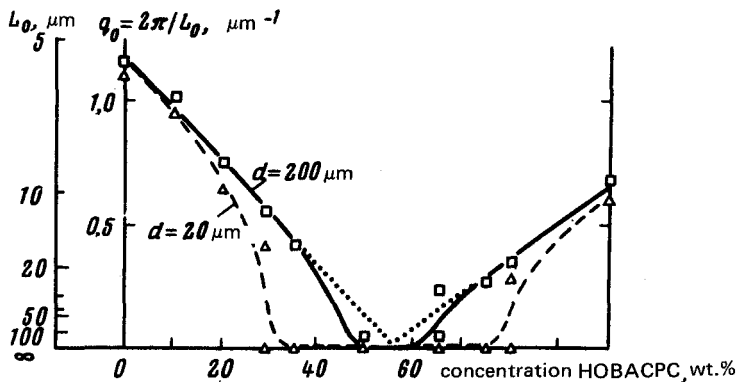


FIG. 1. Dependence of the wave vector of a helicoid $q_0 = 2\pi/L_0$ for different thicknesses d of a liquid-crystal cell on the concentration of HOBACPC mixed with DOBAMBC. $T_{CA} - T = 4^\circ \text{C}$. T_{CA} is the temperature of the transition between a smectic C phase and a smectic A phase.

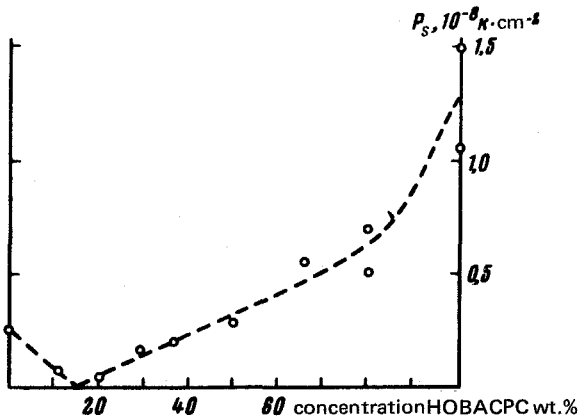


FIG. 2. Dependence of spontaneous polarization P_s on the concentration of HOBACPC mixed with DOBAMBC. $T_{CA} - T = 20^\circ \text{ C}$.

dependence, as predicted by the theory,⁸ until the helix pitch L_0 becomes commensurable with the sample's thickness. It can be seen in Fig. 1 that the concentration range, in which the helicoid becomes untwisted, expands with decreasing thickness of the cell. This effect is attributable to the untwisting action of the solid walls in a cholesteric LC.⁹ As illustrated in Fig. 2, the spontaneous polarizations of a nonhelicoidal mixture exceeds the polarization of the well-known, helicoidal, ferroelectric LC DOBAMBC. At the same time, the polarization is compensated for at $\approx 15\%$ concentration and the helicoidal structure, which cannot be untwisted by external elec-

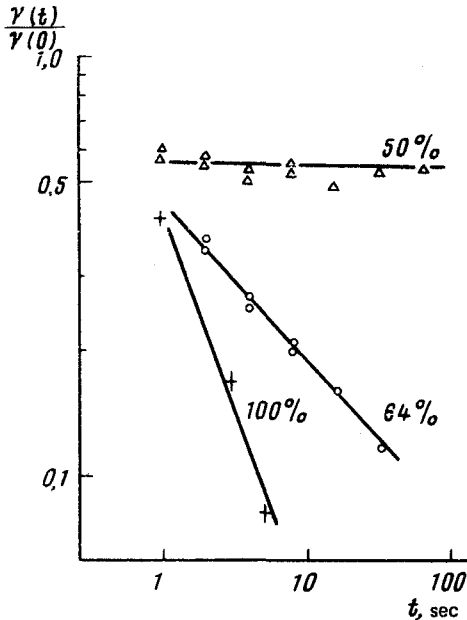


FIG. 3. Kinetics of decay of the pyrocoefficient for three concentrations of HOBACPC mixed with DOBAMBC after the polarization voltage has been turned off; the value of the pyrocoefficient before turning off the polarization voltage is assumed to be unity. $T_{CA} - T = 2^\circ \text{ C}$.

tric field, is conserved. This is consistent with the fact that the local dipole moment of a single molecule of pure HOBACPC in the S_3^* phase is 5 to 6 fold larger than the dipole moment of a single molecule of pure DOBAMBC,¹⁰ whereas the twisting capacities of these materials are approximately the same.²

3. The most characteristic property of a nonhelical, ferroelectric LC is the conservation of macroscopic polarization in the sample after the external voltage is turned off and the electrodes of the cell are short circuited. It must be noted that the field is used here to obtain single domains in the sample, rather than to untwist the helix. This is done in the case of conventional, solid, ferroelectric materials. Under these conditions the rate of decrease of the polarization of a mixture with a helical twist depends on the magnitude of the wave vector of the helical helix.

The kinetics of pyroelectric response of the three different concentrations of HOBACPC mixed with DOBAMBC after switching off the polarization voltage are illustrated in Fig. 3. The pyrocoefficient γ in a compensated, nonhelical mixture (50% HOBACPC concentration) remains the same for several minutes, whereas it decreases an order of magnitude in helical mixtures in less than a minute (64%) and even in seconds (100%). A fast decrease of γ in all three mixtures during the first second, in our opinion, is attributable to the polycrystalline structure of the samples and to a fast relaxation of the kink of those smectic layers whose planes were parallel to the surfaces of the electrodes before the application of the external electric field and whose total polarization was perpendicular to the field.

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