

# Liquid-crystal ferroelectric with a record high spontaneous polarization

L. A. Beresnev, E. P. Pozhidaev, L. M. Blinov, A. I. Pavlyuchenko, and N. B. Étingen

*Scientific-Research Institute of Organic Semifinished Products and Dyes*

(Submitted 6 April 1982)

Pis'ma Zh. Eksp. Teor. Fiz. **35**, No. 10, 430–432 (20 May 1982)

A spontaneous polarization has been obtained in a smectic *C* liquid crystal over a broad temperature range. This polarization is 1.5 times that which has been obtained elsewhere for the best liquid-crystal ferroelectrics.

PACS numbers: 77.30. + d, 77.80. – e, 61.30. – v

1. The search for ferroelectric liquid crystals with a high spontaneous polarization ( $P_s$ ) is of fundamental interest for the physics of liquid crystals and the physics of ferroelectrics, and it is also of much practical interest, primarily because of the use of ferroelectric liquid crystals in fast, linear electro-optic devices with low control voltages.<sup>1</sup> The highest value of  $P_s$  which has been reported to date is that of the liquid crystal hexyloxybenzylidene *p*'-amino 2 chloropropyl cinnamate (HOBACPC)<sup>2</sup>:  $P_s \cong 2 \times 10^{-8}$  C/cm<sup>2</sup> in the chiral smectic *H* phase ( $S_H^*$ ) at  $T \geq 45^\circ\text{C}$  (Ref. 3). In the chiral smectic *C* phase ( $S_C^*$ ), however,  $P_s$  does not exceed  $1.5 \times 10^{-8}$  C/cm<sup>2</sup>, and the narrow interval corresponding to this  $S_C^*$  phase is at quite high temperatures,<sup>3,4</sup> (67–73°C; this is the phase which exhibits a linear electro-optic effect, which is suitable for practical use in linear electro-optic devices).

The problem in raising  $P_s$  further, and also the problem in choosing the appropriate working temperatures (including low temperatures) for single-component ferroelectric liquid crystals, is that the molecules must simultaneously meet the following conditions, which are necessary and sufficient conditions for the occurrence of spontaneous polarizations<sup>5</sup>: 1) The molecules must form a layered smectic structure. 2) The long axes of the molecules (the director) must make some angle  $\theta \neq 0$  with the normal to the surfaces of the layers. 3) The molecules must be chiral (optically active). 4) They must have a transverse dipole moment. Requirements 2) and 4) are conflicting, since in order to achieve a high value of  $P_s$ , it is necessary to increase the dipole moment of the chiral end fragment of the molecule, but an increase in this dipole moment will result in the contraction or even disappearance of the temperature interval in which the  $S_C^*$  phase exists (this happens, for example, when the chlorine atom in the HOBACPC molecule is replaced by the dipole group  $-C \equiv N$ ).

2. In this letter we will show that a high polarization of a ferroelectric liquid crystal can be achieved in a mixture of two components; conditions 1) and 2) are satisfied by an inclined smectic, e. g., nonchiral smectic  $C$ , while conditions 3) and 4) are satisfied by a chiral impurity dissolved in this smectic. The molecules of the impurity are to contain a dipole moment in their chiral fragment. In the first attempt along this line,<sup>3,6</sup> the value of  $P_s$  induced by chiral impurities in smectics  $C$  did not exceed  $10^{-9}$  C/cm<sup>2</sup>.

It follows from our studies that the value of  $P_s$  induced by a chiral impurity in a smectic  $C$  (the "matrix") is roughly proportional to the impurity concentration, the angle made by the matrix molecules with the normal to the surfaces of the smectic layers, and the rigidity of the molecular skeleton of the impurity. Our results also show that the optimum ratio of the length of the matrix and impurity molecules promotes an increase in  $P_s$ .

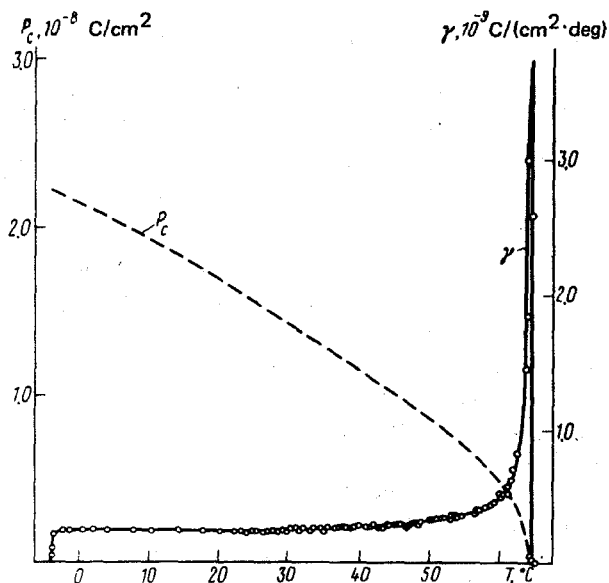


FIG. 1. Temperature dependence of the pyroelectric coefficient ( $\gamma$ ) and that of the spontaneous polarization ( $P_s$ ) for a mixture of a smectic  $C$  liquid crystal (ZhK-1246 with a chiral impurity (ZhK-1239, 12.5% by weight).

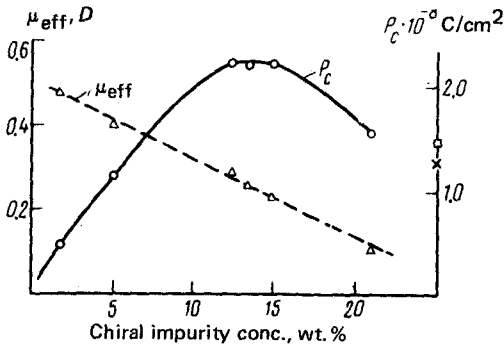


FIG. 2. Dependence of the maximum spontaneous polarization ( $P_s$ ) and of the effective dipole moment ( $\mu_{\text{eff}}$ ) per molecule of the ZhK-1239 chiral impurity on the concentration of this impurity.  $\square$ ,  $\times$ —The maximum values of  $P_s$  for HOBACPC in the chiral smectic  $C$  phase obtained in Refs. 3 and 4, respectively.

Taking these factors into account, we have achieved the value  $P_s \cong 2.2 \times 10^{-8} \text{ C/cm}^2$  in a mixture of a nonchiral smectic  $C$  with a chiral nonmesogenic impurity. This value is nearly 1.5 times the polarization achieved in HOBACPC in the  $S_C^*$  phase. This record value of  $P_s$  corresponds to a temperature of  $-4^\circ \text{C}$ . Even at such a low temperature, the switching time for the director in a cell  $8 \mu\text{m}$  thick upon a change in the polarity of the control voltage, with an amplitude of 50 V, is less than 2 ms (such a short switching time is unattainable in nematic liquid crystals). Figure 1 shows the temperature dependence of the spontaneous polarization,  $P_s(T)$ , and that of the pyroelectric coefficient  $\gamma(T) \neq dP_s/dT$  of the mixture of a smectic  $C$  liquid crystal (ZhK-1246) with a chiral impurity (ZhK-1239). The impurity concentration was  $c = 12.5\%$  by weight. The measurements of  $P_s(T)$  and  $\gamma(T)$  were carried out by a pulsed pyroelectric method,<sup>7</sup> and the experimental geometry used to measure the director switching time was similar to that of Ref. 1.

In the dependence of the maximum spontaneous polarization on the impurity concentration (Fig. 2) there is a maximum, which results from the pronounced decrease in the angle  $\theta$  which we observed upon an increase in the impurity concentration. The decrease in  $\theta$  also explains the decrease in the maximum dipole moment  $\mu_{\text{eff}}$  per chiral molecule which was calculated from the maximum spontaneous polarization (Fig. 2; here  $\mu_{\text{eff}} = P_s M / N_0 \rho$ , where  $M$  is the molecular weight of the chiral molecule,  $N_0$  is Avogadro's number, and  $\rho \cong 1 \text{ g/cm}^3$  is the density of the liquid crystal).

3. According to the present understanding,<sup>5,8</sup> ferroelectric liquid crystals are pseudoproper ferroelectrics, in which the dipole order is a secondary effect; the primary ef-

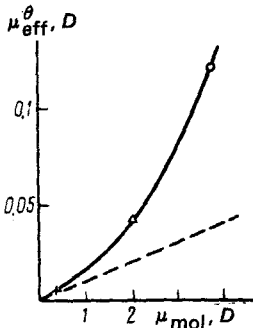


FIG. 3. Superlinear dependence of the effective dipole moment, normalized to the angle  $\theta$  ( $\mu_{\text{eff}}^\theta$ ), in the smectic  $C$  phase on the dipole moment in the chiral fragment ( $\mu_{\text{mol}}$ ) of the molecules.  $+$ —DOBAMBC;  $\triangle$ —HOBACPC;  $\circ$ —ZhK-1239.

fect is the orientational order of the chiral molecules in the inclined smectic layers. The spontaneous polarization results primarily from the piezoelectric and flexoelectric interactions (the angle  $\theta$  serves as the transition parameter). The dipole-dipole interactions are negligibly weak.<sup>8</sup>

In a comparison of the effective dipole moments  $\mu_{\text{eff}}^{\theta}$  normalized to the same angle between the chiral molecules and the normal to the surfaces of the smectic layers, however, we observe a pronounced deviation from a linear dependence  $\mu_{\text{eff}}^{\theta}$  on the dipole moment  $\mu_{\text{mol}}$  of the chiral fragment of the molecule [Fig. 3; this comparison was carried out for three materials, DOBAMBC (decyloxybenzylidene *p'*-amino 2 methyl butyl cinnamate), HOBACPC, and ZhK-1239)].

Since the steric factors for the molecules of these substances are approximately the same, because of the similar structures of the molecular skeletons and the chiral fragments, we suspect that the reason the dependence  $\mu_{\text{eff}}^{\theta}(\mu_{\text{mol}})$  is stronger than linear may be an increase in the contribution of the dipole-dipole interactions to the dipole order upon an increase in the dipole moment in the chiral fragment of the molecules.

In summary, by choosing the appropriate chiral impurity in an inclined smectic, it is possible to simulate a transition from a pseudoimproper orientation ferroelectric order to a proper (dipole-dipole) ferroelectric order.

We wish to thank V. A. Baikalov for carrying out the electro-optic measurements.

1. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
2. P. Keller, S. Juge, L. Liebert, and L. Strzelecki, *C. R. Acad. Sci. C-282*, 639 (1976).
3. L. A. Beresnev and I. M. Blinov, *Ferroelectrics* **33**, 129 (1981).
4. L. Petit, P. Pieranski, and E. Guyon, *C. R. Acad. Sci. B-284*, 535 (1977).
5. R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. (Paris) Lett.* **36**, L-69 (1975).
6. W. Kuszynski and H. Stegemeyer, *Chem. Phys. Lett.* **70**, 123 (1980).
7. I. M. Blinov, L. A. Beresnev, N. M. Shtykov, and Z. M. Elashvili, *J. Phys. (Paris)* **40**, C3-269 (1979).
8. S. A. Pikin and V. L. Indenbom, *Usp. Fiz. Nauk* **125**, 251 (1978) [*Sov. Phys. Usp.* **21**, 487 (1978)].

Translated by Dave Parsons  
Edited by S. J. Amoretty