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INVESTIGATION OF THE BIASED ROTATION OF CHIRAL MOLECULE AROUND ITS LONG MOLECULAR AXIS IN THE FERROELECTRIC LIQUID CRYSTAL MIXTURE

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Abstract Spontaneous polarization (P_S), tilt angle (θ), helical pitch (p) and densytometric (ρ) characteristics versus temperature and concentration of chiral dopant have been measured for FLC mixture. On the base of computer modelling the molecular dipole moment (μ), transverse (α_t) and longitudinal (α_l) molecular polarizabilities as well as angle (γ and φ_0) between the vector μ and main long n and short l molecular axes of inertia have been calculated. Knowing the molecular parameters μ, α_t, α_l, γ and φ_0 and state parameters θ, p, spontaneous polarization P_S has been calculated as the vector sum of the components of molecular dipole moment $\mu_\perp$ perpendicular to the tilt direction. To do it the Zeks[1] rotational potential modified by us[2] has been used. After comparing spontaneous polarization P_S taken from experimental and obtained from theoretical approximation the biased rotation parameter η has been calculated.

INTRODUCTION

The microscopic origin of the spontaneous polarization P_s arises from chirality - induced broken symmetry of the potential $U(\psi)$ for molecular rotation about the long axis. If the molecule forming ferroelectric S_C* phase carries the effective permanent dipole moment μ_e and mean molecular polarizability $\bar{\alpha}$, the $\mathbf{P_S}$ can be expressed as[3]:

$$P_S = N\mu_e < \cos\delta > +N\bar{\alpha}E_l \qquad (1)$$

where N is the molecular density number, E_l is the local electric field effected on the molecule in the $\mathbf{P_S}$ direction and δ is the angle between the effective dipole moment μ_e and the $\mathbf{P_S}$ vector.

The averaging in $< \cos\delta >$ is carried out by standard statistical methods over the whole sample. This equation shows that the spontaneous polarization is described by a kind and a structure of the molecules which build the S_C * phase and appropriate to these molecules single particle potential $U(\psi)$[1-6]. In the work reported in this paper, we intend to introduce our point of view on this subject and discuss it on the basis of our laboratory results for ferroelectric mixtures presented in Table 2.

THEORY

Let us suppose that in our model a molecule looks like a rigid brick having chirality centre and dipole moment μ built into its integral structure. The main molecular axes of inertia l, m, n of this object are rigidly attached to the local 0x'y'z' system of Cartesian co-ordinates as it is shown in Fig. 1. The mean polarizability $\bar{\alpha}$ is: $\bar{\alpha} = \frac{\alpha_l + 2\alpha_t}{3}$ (2)

where α_l and α_t - polarizabilities along the long axis n and short axis m.

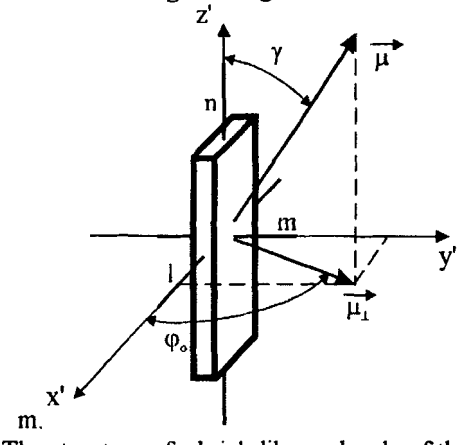

FIGURE 1 The structure of a brick-like molecule of the S_C* phase.

In the 0x'y'z' system of co-ordinates the vector μ can be written as:

$$\mu' = \left[\mu'_x, \mu'_y, \mu'_z\right] = \left[\mu \sin\gamma \cos\varphi_0, \mu \sin\gamma \sin\varphi_0, \mu \cos\gamma\right] \quad (3)$$

where γ is the angle between the vector μ and the molecular director n (0z' axis), φ_0 is the angle between $\mu_\perp$ the projection of the μ on the x'0y' plane and l molecular axis which coincides with 0x' one.

Let us choose the laboratory 0xyz system of co-ordinates with the origin 0 common for 0x'y'z' and 0xyz ones. Let the molecule rotates about the point 0. The position of the moving system (0x'y'z') with respect to the fixed one (0xyz) is described by well-known three Euler's angles θ, φ and ψ. Using the Euler's angles the molecular dipole moment μ in the laboratory 0xyz system is given by expression (4)[2].

If the long axes of molecules n are assumed to be parallel to the y0z plane, then the spontaneous polarization $\mathbf{P_S}$ is induced perpendicularly to the tilt plane, i.e. direction of $\mathbf{P_S}$ coincides with 0x one. In this case we obtain:

$$\mu_x = \mu \cos\delta = \mu(\cos\psi \cos\varphi_0 \sin\gamma - \sin\psi \sin\varphi_0 \sin\gamma) \quad (4)$$

Since φ_0 and γ are constants for a given kind of a molecule, the average of $\cos\delta$ for a whole sample takes form:

$$<\cos\delta> = \sin\gamma(\cos\varphi_0 <\cos\psi> - \sin\varphi_0 <\sin\psi>) \quad (5)$$

where the angle ψ describes the orientation of the molecular axis l (0x' axis) with respect to the $\mathbf{P_S}$ direction (0x axis).

The following form of the rotational potential[2] is proposed when the $\mu_\perp$ forms the angle φ_0 with the l axis:

$$U(\psi) = -a_1 \sin\theta \cos(\psi - \varphi_0) - a_2 \sin^2\theta \sin 2\psi - a_3 q \sin\theta \sin\psi \qquad (6)$$

where $q = 2\pi p^{-1}$ parameters a_1, a_2 and a_3 are different for various kind of a ferroelectric liquid crystal. Using this potential, considering only the first term the exponential in potential a theoretical expression for $<\cos\delta>$ can be obtained as:

$$<\cos\delta> = \sin\gamma \frac{\sin\theta}{2kT}(a_1 + a_3 q \sin\varphi_0) \qquad (7)$$

In the Lorentz local field approximation: $\mu_e = \mu$ and $E_1 = \frac{P_S}{3\varepsilon_0}$ (8)

where ε_0 is electric permittivity of free space and then the required theoretical relation for the spontaneous polarization P_{SL} is:

$$P_{SL} = \frac{N\mu \sin\gamma \frac{\sin\theta}{2kT}(a_1 + a_3 q \sin\varphi_0)}{1 - \frac{N}{3\varepsilon_0}\bar{\alpha}} \qquad (9)$$

On the basis (7), (8), (9) the following functions $F_L(T)$ can be defined:

$$F_L(T) = \frac{P_{SL}(1 - \frac{N}{3\varepsilon_0}\bar{\alpha})2kT}{N\mu \sin\gamma \sin\theta} = a_1 + a_3 \frac{2\pi}{p(T)} \qquad (10)$$

Knowing the temperature dependence of spontaneous polarization $P_S(T)$, thermal dielectric and densytometric characteristics as well as μ, γ and $\bar{\alpha}$ we can calculate the a_1, a_3 and $<\cos\delta'>$ defined as: $<\cos\delta'> = \frac{<\cos\delta>}{\sin\gamma}$ (11)

If we know a_1, a_2 and a_3 factors in eq. (6) we would find the ψ_M angle for that rotational energy takes minimum value. If we neglect the quadrupolar term a_2, the ψ_M can be calculated from:

$$\psi_M = \arctan\left[\frac{a_3 q + a_1 \sin\varphi_0}{a_1 \cos\varphi_0}\right] \qquad (12)$$

The above results of calculations of $\delta_M = \psi_M - \varphi_0$ we can see in Table 2.

The rotational orientation of molecules can be described by $<\cos\delta'>$. In the first approximation we can image that the N hindered rotational molecules characterised by $<\cos\delta'>$ consist of M molecules with stopped rotation with orientation defined by $<\cos\delta_M>$ and (N-M) with free rotation. Taking into account the above one can see that $N<\cos\delta'> = M<\cos\delta_M>$. The hindered rotational parameter η is the following:

$$\eta = \frac{M}{N} = \frac{<\cos\delta'>}{<\cos\delta_M>} \qquad (13)$$

When all molecules are stopped η must be 1 and for free rotation: $\eta = 0$.

EXPERIMENTAL, RESULTS AND DISCUSSION

Two kinds of ferroelectric mixtures with different LC matrix have been studied. One of them have been examined while various concentration of chiral dopant have been introduced with gradually increasing concentration.

Basic base:

(23.35% wt.) C_8H_{17}-O-⟨⟩-COO-⟨⟩-O-C_6H_{13}

(18.80% wt.) $C_{10}H_{21}$-O-⟨⟩-COO-⟨⟩-O-C_6H_{13}

(25.41% wt.) $C_{10}H_{21}$-O-⟨⟩-COO-⟨⟩-C_5H_{11}

(32.44% wt.) C_8H_{17}-⟨⟩-COO-⟨⟩-C_2H_4-⟨⟩-O-C_6H_{13}

Smectogenic dopant: $C_{10}H_{21}$-⟨⟩-⟨⟩-CO-⟨⟩-C_9H_{19}

Chiral dopant: C_6H_{13}-C*H(CH_3)-OOC-⟨⟩-⟨⟩-⟨⟩-COO-C*H(CH_3)-C_6H_{13}

TABLE 1 Investigated mixtures.

Notation	Amount of smectogenic dopant in base	Amount of chiral dopant in mixtures	Temperatures of phase transition (Celsius degree)
A1	3%	30%	SmC* 70 SmA 76 Ch 81 Iso
A	7%	30%	SmC* 69 SmA 82 Ch 85 Iso
B	7%	20%	SmC* 70 SmA 84 Ch 93 Iso
C	7%	10%	SmC* 71 SmA 85 Ch 107 Iso

The spontaneous polarization was measured by a Diamant bridge method and the tilt angle θ was derived from the optical switching angle of the sample. Both of these measurements were performed on the same sample using commercially available Linkam cells. The cell spacing was directly measured by interference method for each sample and it was kept between 6 and 7 μm. The cells were filled with the isotropic phase of studied mixtures and then the samples were cooled slowly from isotropic phase to smectic C* phase in the presence of low frequency electric AC field. In this way we obtained the bookshelf geometry without chevron structures. During the alignment process and the measurements the temperature was controlled with Linkam TMS 92 hot stage.

The helical pitch of phase S_{C^*} of studied mixtures was measured by Grandjean-Cano[7,8] method using the samples with homeotropic alignment[9]. Liquid crystal was kept between flat and spherical surfaces. Both of them were coated of surfactant HTAB and the standard method of rubbing was used[10]. Determination of the helix handedness in the smectic C* phase of the investigated mixtures was performed by conoscopic method. It was assumed that the handedness of ferroelectric helix is in the agreement with the handedness of Airy helix. It was determined that the helix is right -handed for all mixtures. It was denoted as (+).

The density as a function of temperature for all phases I, N*, S_A and S_C* was determined employing a Paar DMA 602.

For ferroelectric properties the most important is chiral molecule. After computer calculations and some experiment we have got molecular parameters of this molecule: $\mu = 1.585\ 10^{-29}$ Cm, $\gamma = 85°$, $\varphi_0 = -10°$, $\overline{\alpha} = 7.751\ 10^{-39}\ C^2m^2J^{-1}$.

The spontaneous polarization P_S, the tilt angle θ, the helical pitch p and the density ρ were measured for studied mixtures as a function of temperature. The results of our measurements are presented in figures 2, 3, 4.

On the basis of the above experimental results the following parameters were established. First the values of a_1 and a_3 factors in eq. (6) were determined. From our

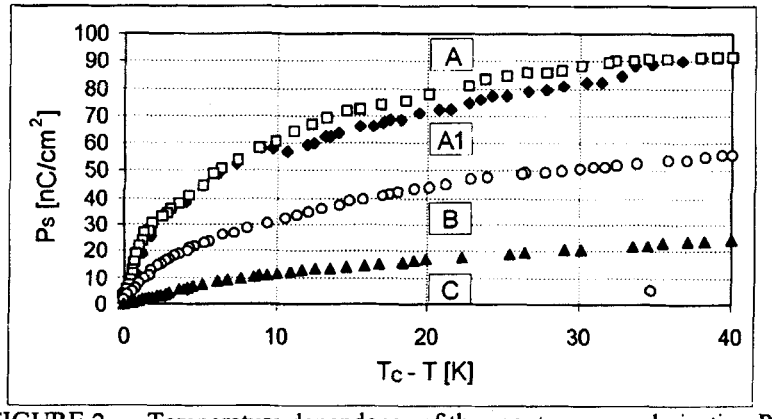

FIGURE 2 Temperature dependence of the spontaneous polarization $P_S(T)$ for all investigated mixtures.

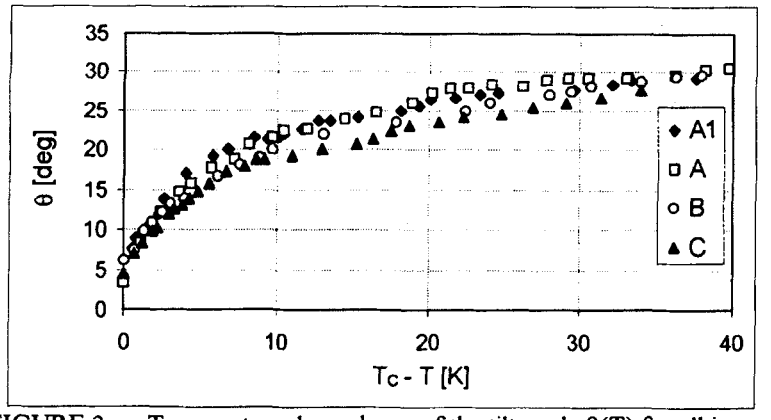

FIGURE 3 Temperature dependence of the tilt angle θ(T) for all investigated mixtures.

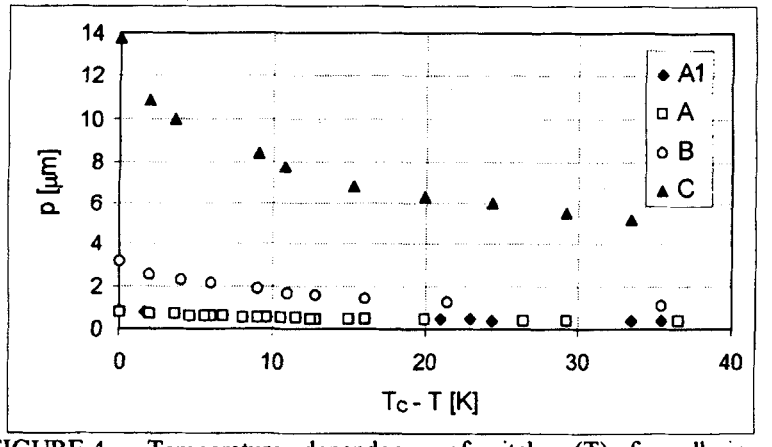

FIGURE 4 Temperature dependence of pitch p(T) for all investigated mixtures.

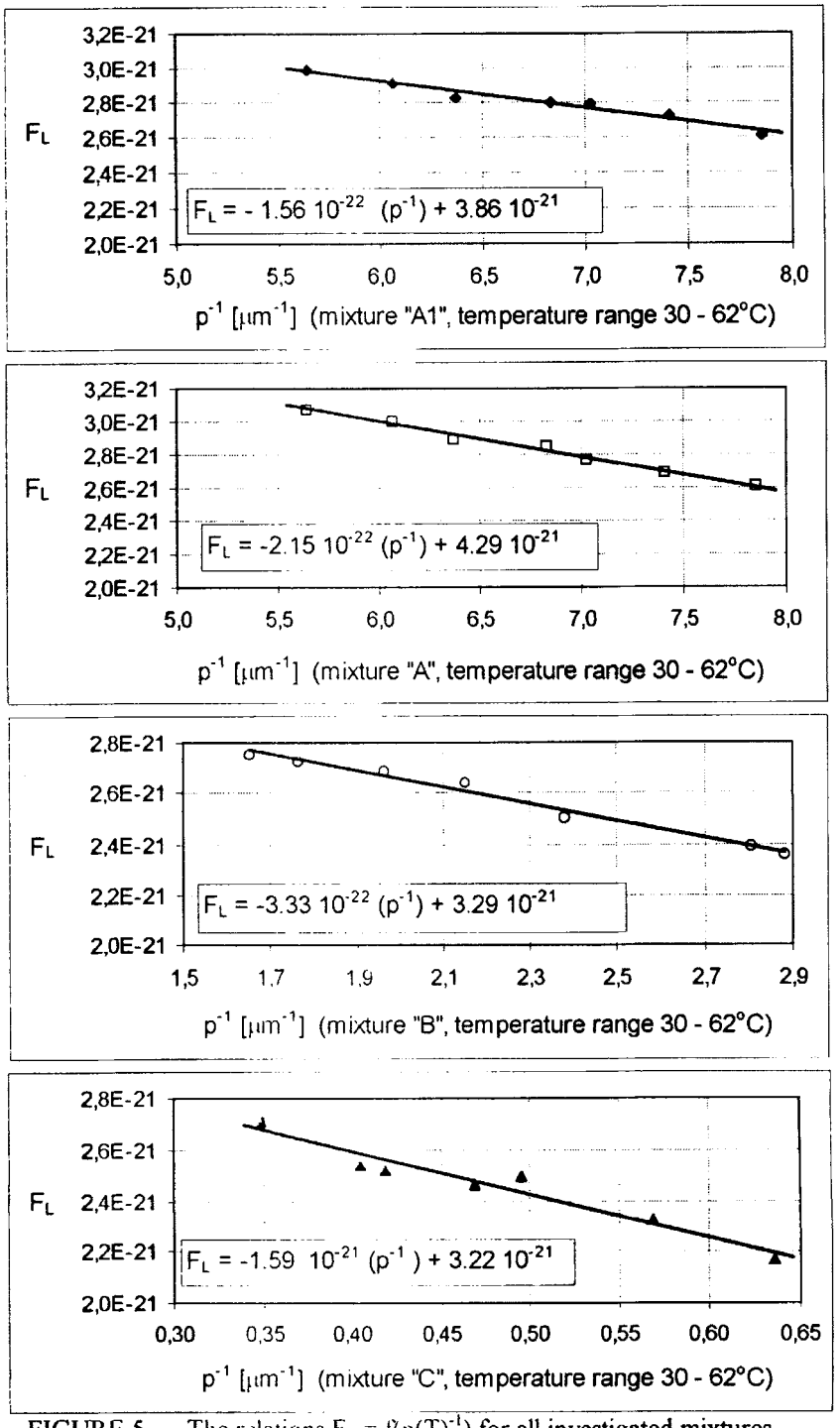

FIGURE 5 The relations $F_L = f(p(T)^{-1})$ for all investigated mixtures.

results presented in Figure 5 it can be seen that potential factors a_3q and a_1 are smaller for C mixture than for all remaining mixtures B, A, A1. So, on this ground, it can be concluded that rotational potential must be deeper for mixtures with larger amount of chiral dopant.

TABLE 2 Results of calculations.

	Mixture A1		Mixture A		Mixture B		Mixture C	
Temperature [°C]	δ_M [deg]	η	δ_M [deg]	η	δ_M [deg]	η	δ_M [deg]	η
30	5.1	0.154	6.4	0.153	4.7	0.137	5.1	0.124
40	4.8	0.148	6.0	0.148	4.5	0.126	4.5	0.117
50	4.5	0.132	5.7	0.132	3.8	0.114	3.9	0.109
54	4.4	0.125	5.5	0.124	3.5	0.110	3.7	0.099
58	4.1	0.114	5.1	0.108	3.1	0.098	3.3	0.090
60	3.9	0.104	4.9	0.101	2.7	0.091	3.2	0.084
62	3.6	0.091	4.5	0.088	2.5	0.078	2.9	0.076

Second from the values of δ_M and of η eq. (13) gathered in Table 2 it can be seen that the values of $<\cos\delta'>$ for C mixture are smaller than for B, A and A1 mixtures. It is well-known that the rotational orientation of the molecule is described by $<\cos\delta'>$, so it can be assumed that rotation is more hindered in mixtures with more concentration of chiral dopant. Because of values of $<\cos\delta'>$ in A and A1 mixtures are similar the hindered rotation does not depend on the amount of smectogenic compound.

From the results given in Table 2 for each temperature parameter η seems to be proportional to the concentration of the chiral dopant. It means that according to our model amount of molecules with stopped rotation increases with increasing of concentration of chiral molecules. Presented values of parameter η for investigated mixture are much larger (about 100 times) than values for CE8[2]. It can be understood by means of different molecular structure of CE8 molecule and studied chiral molecule, specially presence of two chiral centres in the chiral molecule under discussion compared with one chiral centre in CE8 molecule. It is worth to mentioned that for each concentration of chiral dopant amount of stopped molecules (parameter η) decreases for higher temperatures.

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