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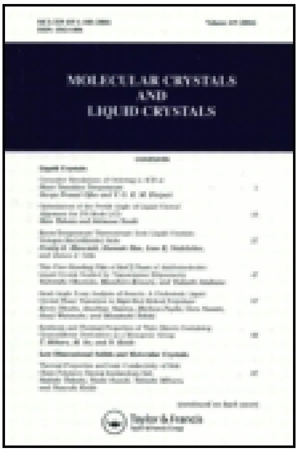

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Investigations on a New Chiral LC Mixture W-22

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INVESTIGATIONS ON A NEW CHIRAL LC MIXTURE W-22

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Abstract The sign and magnitude of spontaneous polarization (P), the tilt angle (Θ), the helical pitch (λ) have been measured for some liquids crystals and their mixtures with the chiral smectic C phases (SmC*). The measurements of P have been performed by two different methods: Diamant bridge and from dielectric permittivity, of Θ by electro - optical technique and of λ by "direct" microscopic observation. The experimental setups as well as two types of cells have been described. All experimental setups and measurement methodes have been tested on the basis of measurements of two well known ferroelectric liquid crystals[1,2]. These parameters (P, Θ, λ) have been determined for a new ferroelectric liquid crystal mixture

Keywords: ferroelectric liquid crystal, spontaneous polarization, tilt angle, helical pitch.

INTRODUCTION

Electro-optic devices based upon the Clark-Lagerwall surface stabilized ferroelectric liquid crystal (SSFLC)

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cell[4] and the Beresnev thin cell[5] have been widely used in all over the world since several years ago. The most important material parameters from an application point of view are the sign and the magnitude of the spontaneous polarization P, the tilt angle Θ and the helical pitch λ[4-6].

The phenomenon of ferroelectricity in the liquid crystal is closely connected with the structure of the tilted smectic phases characterized by a tilt Θ between the director and the normal to the smectic layers, if the constituent molecules are chiral[7-9].

The chiral smectic C phase (SmC^*) develops a helical director structure with the axis perpendicular to the smectic layer . The macroscopic periodicity of this structure is characterized by a helical pitch λ.

The one isolated layer of SmC^* phase posses a two-fold axis of rotation normal to the tilt axis of the molecule and parallel to the layer planes. The spontaneous polarization vector P has a non-zero component only in the direction of this two-fold axis. The macroscopic spontaneous polarization equals zero when the direction of polarization changes from one layer to another with the helix.

So, to obtain the non-zero macroscopic polarization the helical structure has to be unwound by a suffieciently large electrical field[10] or by the surface interactions[11].

The spontaneous polarization of ferroelectric liquid crystal (FLC) is the important parameter because its linear coupling with an applied electrical field is the basis of all applications of these compounds.

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So, from this point of view, the proper material FLC for display should have got the spontaneous polarization, as high as possible.

In order to achieve the maximum optic contrast, the tilt angle θ should be kept about $22,5^{\circ}$ [4,12].
The helical pitch of the SmC^* for devices based upon the SSFLC effect should be rather long ($\lambda > 8\ \mu m$). On the other hand, for displays based on the linear electro-optical Beresnev effect[5] helical pitch is prefered very small ($\lambda \ll 8\ \mu m$).

To facilitate easy and good orientation the FLC for such displays should exhibit the following phase sequence $SmC^* \Rightarrow SmA \Rightarrow N^* \Rightarrow I$ [13] and they should be thermally and photochemically stable in all range of temperatures where the SmC^* phase exists.
Since , it is difficult to obtain the proper ferroelectric, many component mixtures are usualy used[14-15].

To realize FLC mixtures for display application we have to optimize them with respect to the phase transition temperatures, spontaneous polarization, helical pitch and tilt angle. The experimental setups, the cells and some results are reviewed in this paper.

MEASURING CELL

All data in our laboratory concerning P, θ and λ are obtained with two types of cells.
The geometry of each of the cell is the same so-called "bookshelf geometry". in wich the layer normal is parallel to the cell wall and the layers are parallel to each other.

But for one kind of the cells the helical structure isn't perturbed ("thick" sample) and for another it is supressed by surface stabilization ("thin"sample).

To measure the helical pitch we used "thick" sample with helical structure and to measure the tilt angle "thin" samples with the unwound helix were applied.

The sign and the magnitude of the spontaneous polarization were obtained using both "thin" and "thick" samples. For the "thin" samples the helix does not to be unwound by the applied electrical field for the polarization measurements as it would be in a "thick" sample. To achieve this helix-unwinding in a "thick" sample for substances with low polarization and high ionic content is not possible because of electrohydrodynamic effect occuring before the necessary field strength to be achieved. In such cases "thin" sample with unwound helix is advantageous.

Cells were made of two ITO (indium tin oxide) coated glass plates. The ITO conducting layer are etched to define an active cell area of about 16 mm square. The glass plates were separated by special glass spacers and a gap of thickness between them was measured on an epmty cell using an interference method.

The thickness are varied from 2 μm to 50 μm. The cells were filled by capillary action and the "bookshelf" alignment of the sample was achieved using rubbing surface coatings of polyimide [16] and the suitable cooling[17,18]. After filling the sample was heated up to a temperature above the clearing point and then slowly cooled down (0,1°C\min) to the SmC^* phase in presence of an alternating sinusoidal electric field

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(1 Hz, 2V/μm). The sample alignment was checked using an optical polarizing microscope.

MEASURING SETUP

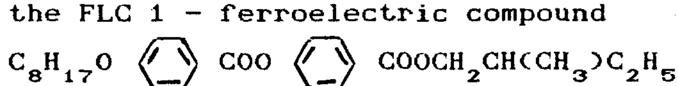
Constructing a system for measuring P,Θ and λ one expected to have a control over parameters determining accuracy of measured material parameters. The solution for us appeared to base all measurements on a principle of a flat cell by different surface coating and special rubbing of them [18,19].

The block diagram of measuring setup is presented in Fig.1. The measuring cell 1 closed in thermal chamber 2 is placed in a hot and rotating stage of a BIOLAR polarizing microscope 3. The chamber 2, shielding electrically the cell, serves the suitable orientation towards the crossed polarizer 4P and analyzer 4A.

The temperature of the sample is stabilized using a precision temperature regulator UNIPAN. To measure the temperature a differential thermocouple copper -constantan 8 placed near the sample is used.

This measuring setup and measuring cells have been tested using two liquid crystals:

- the TKF 8617 - ferroelectric mixture for LCD manufactured BY TEIKOKU CHEMICAL INDUSTRY LTD with the following phase sequence: Cr4SmC*54SmA65I,
- the FLC 1 - ferroelectric compound



with the phase sequence: Cr34SmC*31,5SmA56I synthesized by R.Dąbrowski and tested and described by Pavel et al[1].

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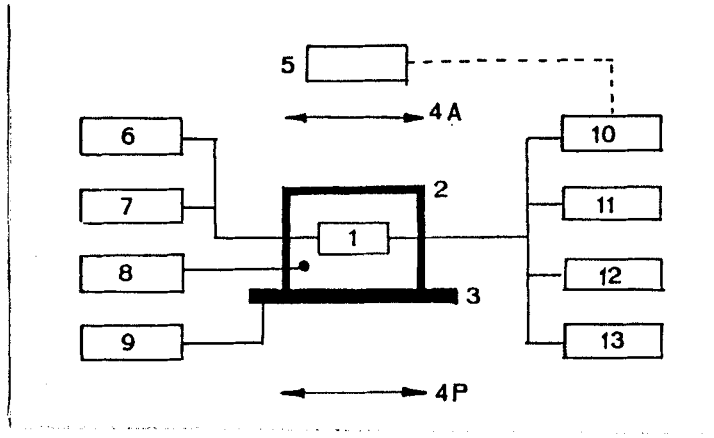

Fig.1. The block diagram of measuring system: 1-measuring cell, 2 - thermal chamber, 3 - the hot and rotating stage of the polarizing microscope, 4P - polarizer, 4A - analyzer, 5 - light detector, 6 - DC power supply, 7 - RC generator, 8 - temperature measuring system, 9-thermostable system, 10 - oscilloscope, 11 -power generator, 12 - Diamant bridge, 13 - R,L,C bridge.

1.SPONTANEOUS POLARIZATION

Measurements of spontaneous polarization are performed of both Diamant ac-bridge technique[20-22] and dielectric technique[23].

The Diamant ac-bridge method is based on a technique of hysteresis compensation. In our case the voltage of the sinus wave form is applied from power generation PO-28 ZOPAN. The amplitude of this can be varied from 0 to 320 V and the frequency from 20 Hz to 20 kHz.

On the other hand, the spontaneous polarization is obtained by dielectric measurement.

For chiral smectic C (SmC^*) in "bookshelf" geometry

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the measuring electric field applied perpendicular to the helix axis disturb the helix in such a way that an average macroscopic polarization P is induced. The disturbance of the helix due to the electric field can be divided into two parts corresponding to two modes of dielectric response[23-25]: the soft mode and the Goldstone mode.

Experimentally the soft mode is only contributing to P close to transition temperature, but the Goldstone mode on the other hand contributes to P in the entire SmC* phase. The Goldstone mode contribution $\delta\varepsilon_{\perp}$ can be easily eliminated by unwinding the helix with a dc bias voltage. Knowing the Goldstone mode contribution $\delta\varepsilon_{\perp}$ to the measurement permittivity ε, the wanted value of the P can be calculated from the following equation[26, 27].

$$P = \frac{\varepsilon_o \ \delta\varepsilon_{\perp} \ U_{AC}}{d}$$

The low frequency electric permittivity of FLC were measured using a Precision Component Analyzer 642 from 10 Hz to 300 kHz with a measuring voltage from 10 mV to 5V.

Results of the spontaneous polarization for both tested liquid crystals: TKF 8617 and FLC 1 from our different methods: Diamant ac-bridge and dielectric measurement agree well with each other.

In Fig.2 and 3 the temperature dependence of the spontaneous polarization obtained from the Diamant ac-bridge measurements for TKF 8617 and FLC 1 are presented.

In these figures values of spontaneous polarization obtained by dielectric measurement are also shown. To calculate the Goldstone mode contribution $\delta\varepsilon_{\perp}$ to the

$\varepsilon_{\perp}$ was estimated from frequence dependence the dielectric permittivity (Fig.4.).

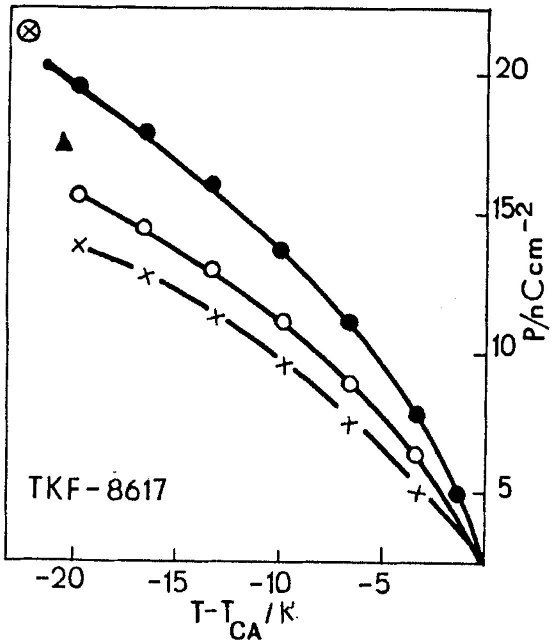

Fig.2. Temperature dependence of the P for TKF 8617: × d=3,6μm o d=9μm, ● d=15,8μm. ▲ - a point from dielectric measurement ⊗ - a point from[2].

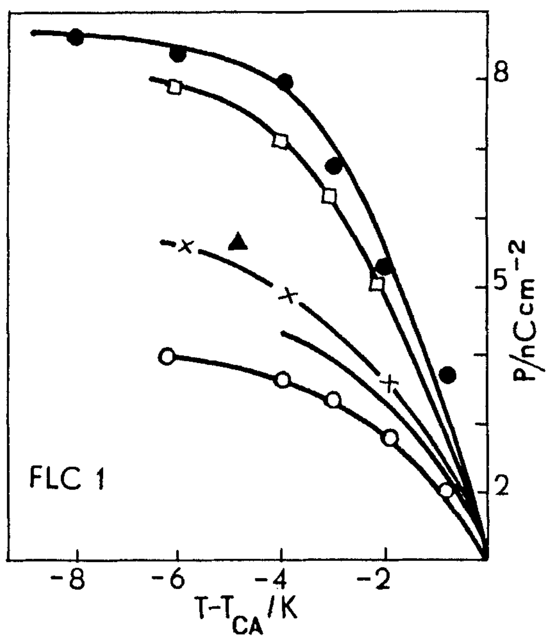

Fig.3. Temperature dependence of the P for FLC 1: ● ν = 20Hz, □ ν =50Hz, × ν =150Hz, o ν =200Hz, —— - the curve from[1] for d=25μm and ν=100Hz, ▲ - a point from dielectric measurement

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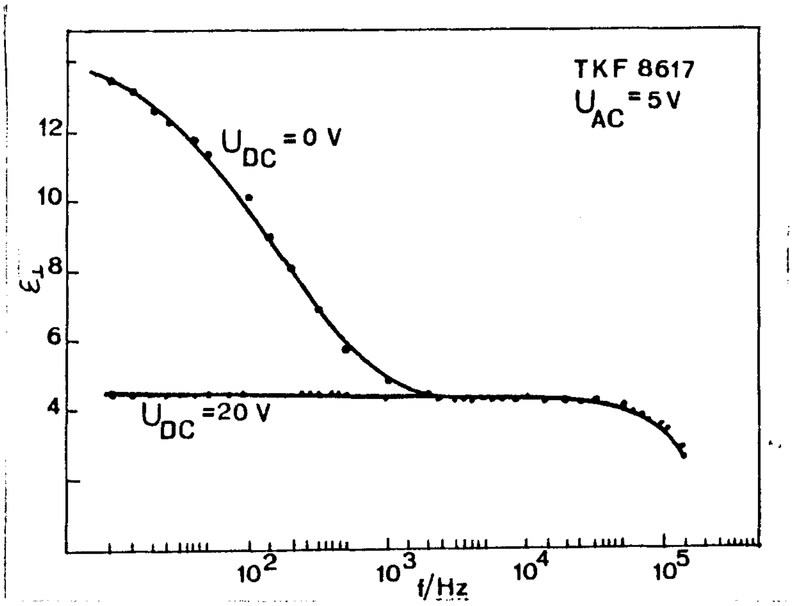

Fig.4. Frequency dependence of the perpendicular dielectric constant $\varepsilon_\perp$ for TKF 8617 at 22°.

Our values of spontaneous polarization for FLC 1 and TKF 8617 agree with data presented in[1,2], respectively.

2 THE SIGN OF SPONTANEOUS POLARIZATION

According to the proposal put forward by[28,29] the direction of the spontaneous polarization vector P is given by the formula:

$$\mathbf{P} = P(\mathbf{z} \times \mathbf{n})$$

where **P** is the polarization vector, **z** the normal to the smectic layers and **n** the director such that the angle between **z** and **n** is less than 90°.

The signs of the spontaneous polarizations were determined directly from electric field studies[30,31] using "thin" samples with unwoud helix.

The above method was tested on the base of the measurement for FLC 1[30]. The sign of spontaneous polarization for both FLC 1 and TKF 8617 is negative.

3 TILT ANGLE

To measure the tilt angle Θ we used a "thin" sample in the "bookshelf" geometry with unwound helix and applied the electro-optic method[32,33] based on the observation of the switching effect.

The measurements for TKF 8617 and FLC 1 were made in the 2 μm thickness cell with dc voltage of 20V. The results for them are presented in Fig.5.

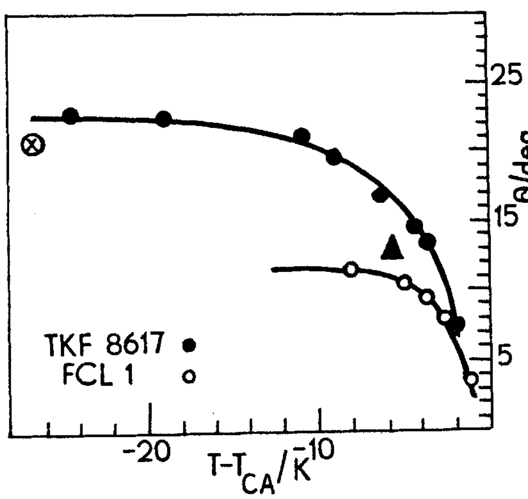

Fig.5. Temperature characteristics of the tilt angle for TKF 8617 (• , ⊗ - the point from[2]) and for FLC 1 (o , ▲ - the point from[1]).

4 HELICAL PITCH

To measure the helical pitch λ we used a "thick" sample in a "bookshelf" geometry with helical structure and used the technique of "direct" microscopic observation of the strips spacing[34-36]. Fig.6 presents the photo of the typical linear texture of a "thick" sample of TKF 8617 in the

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"bookshelf" geometry with the helical structure. The distance between two lines equals helical pitch λ.

The temperature dependence of helical pitch for TKF 8617 is shown in Fig.7. The obtained results entirely correspond to [2].

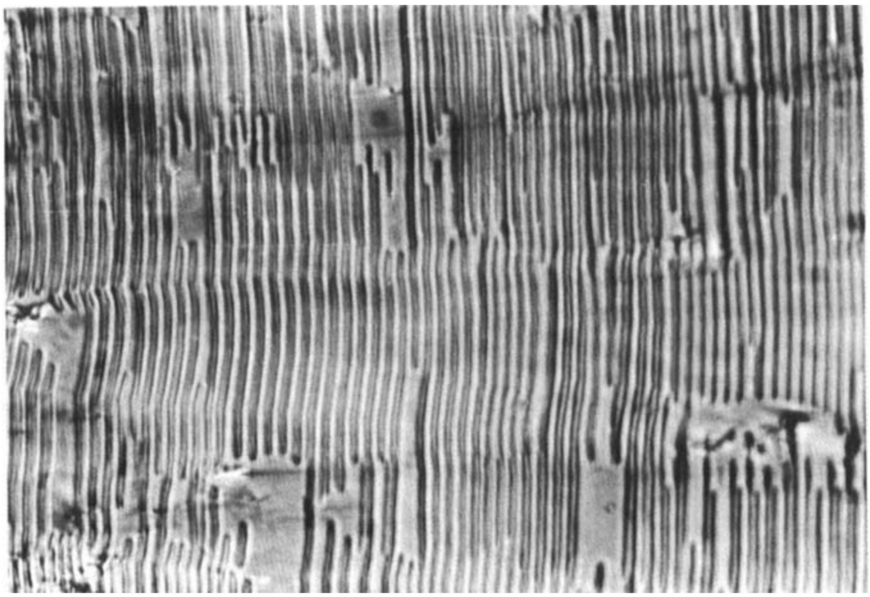

Fig.6. Photo of the linear texture of planar sample
See Color Plate I.

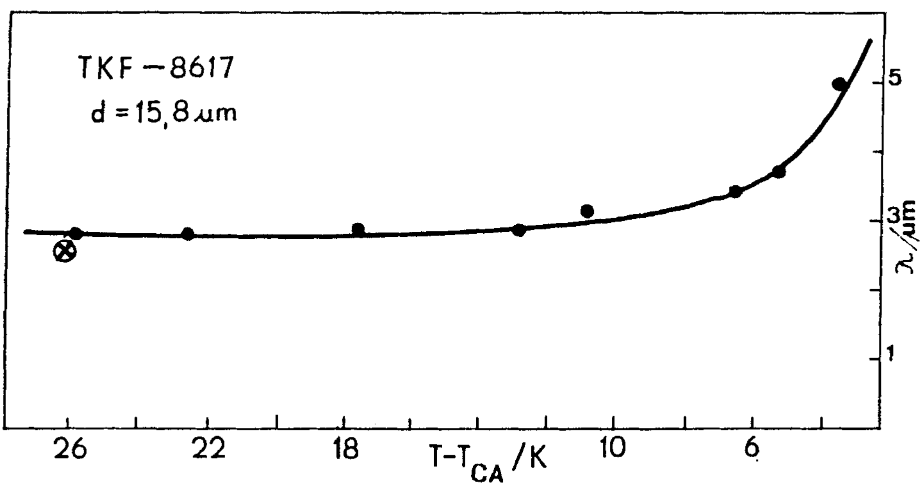

Fig.7. Helical pitch variation in TKF 8617 versus the temperature, ⊗ – the point from[2].

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PHYSICAL PROPERTIES OF A FLC MIXTURE FOR DISPLAY APPLICATION

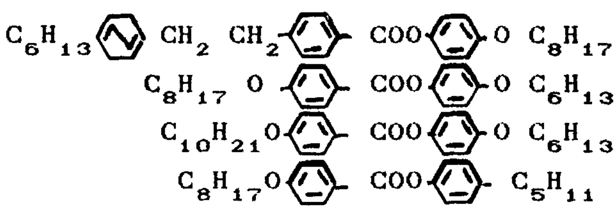
In[37] it have been shown that alkylbicyclo(2,2,2) octylethylphenyl alkoxybenzoates (formula 3) are mesogened with the SmC phase which may be used as components of ferroelectric mixtures.


3

Compound 3 mixed with alkoxyphenyl alkoxybenzoates yield mixtures with a wide range of the SmC phase and the phase sequence SmC⇒N or when suitable chiral dopants are used also SmC*⇒Ch or SmC*⇒SmA⇒Ch⇒I or else SmC*⇒SmA⇒I[3].

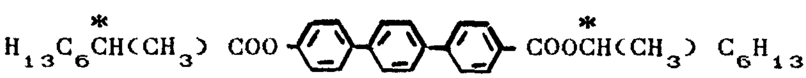
When compound 3 (with n=6, m=8 and X=H) is mixed with four esters, the four component eutectic mixture B is obtained.

B


32,44 wt.%
23,35 wt.%
18,80 wt.%
25,41 wt.%

This mixture has the following phase transition: Cr8SmC58,8N119,5I and its viscosity is 536 mPa at 40°C

To lower the high clearing temperature of the wanted mixture and to introduce a chirality, the chiral compound 4 (Cr78I)[39] is added to the B mixture.


4

In Fig.8a the fragment of the phase diagram is presented for the mixtures obtained by adding to the base mixture B the compound 4. We see that compound 4 lowers the clearing point of the B mixture and gives the effect of the stability of the SmC phase. The maximum SmC⇒Ch transition temperature is observed for

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the C mixture of 20 per cent of compound 4 with 80 per cent of the B mixture. Both B and C mixtures show a high value of tilt angle Θ^3.

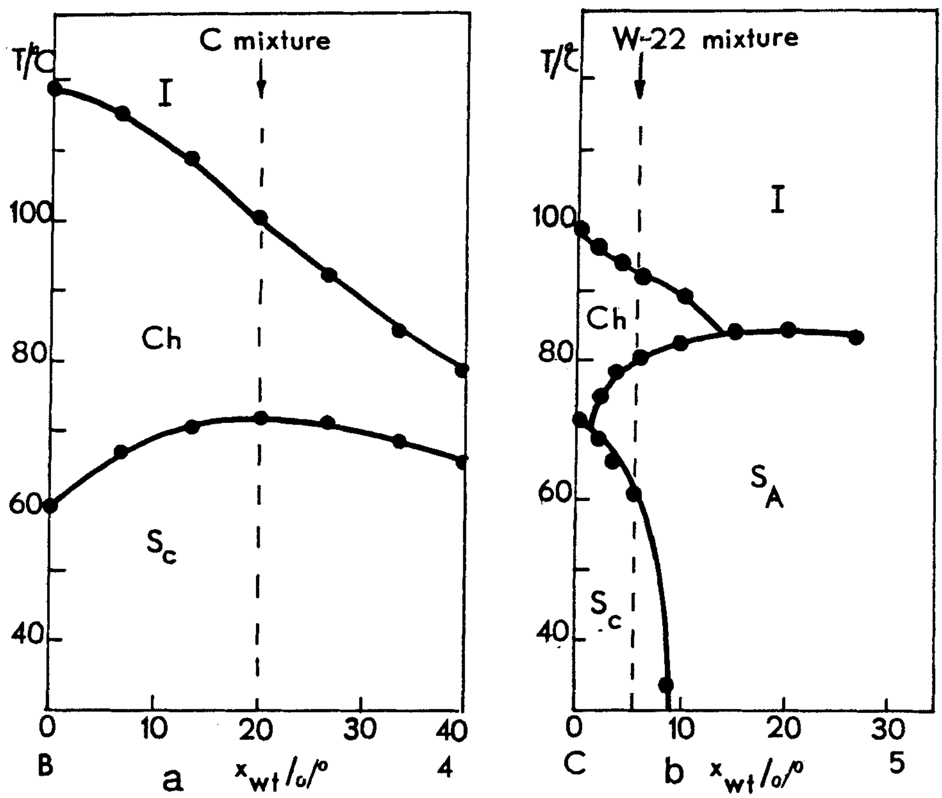
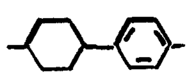


Fig.8. a – the phase diagram for the B – 4 mixture,
b – the phase diagram for the C – 5 mixture.

To induce phase SmA and to change the tilt angle Θ, the achiral compound 5 (Cr76I)[40] is added to the C mixture.

trans – $H_{21}C_{10}$  $COCH_3$ 5

In Fig.8b the fragment of the phase diagram is plotted for the mixture consisting of the C mixture into which compound 5 is added. We can see that compound 5 added to the C mixture strongly destabilizes the SmC phase and induces SmA phase.

The W-22 mixture consists of the C mixture into which 6,9% compound 5 is added. The W-22 mixture has the following phases and transition temperatures: Cr4SmC*51SmA82Ch92I.

Spontaneous polarization P and helical length λ for the W-22 mixture are plotted versus the reduced temperature in Fig.9 and 10, respectively.

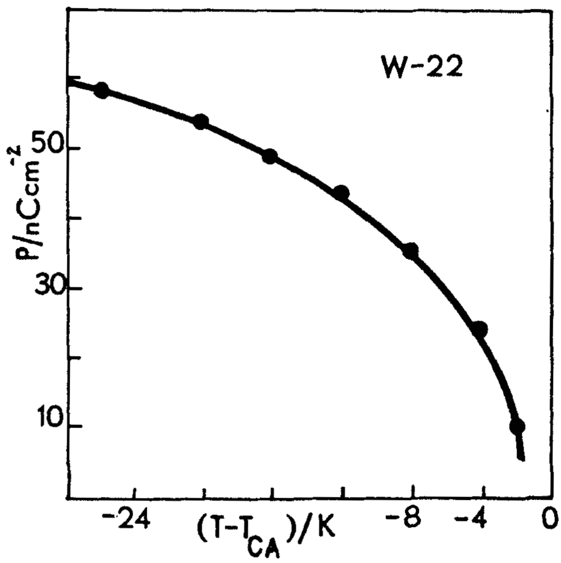


Fig.9. Temperature dependence of the P for W-22: d=8μm, ν=20Hz.

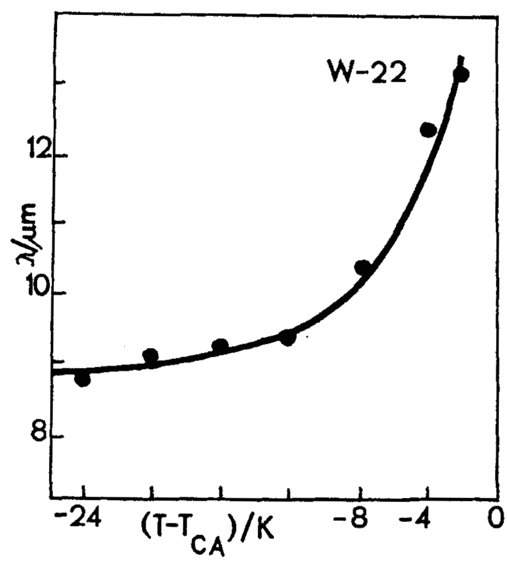


Fig.10. Temperature dependence of the helical pitch λ for W-22.

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The sign of the spontaneous polarization for W-22 seems to be P(+).

The decreasing of the tilt angle Θ of mixture B after adding of compound 4 (mixture B becomes mixture C) and then of mixture C after adding of compound 5 (mixture C becomes mixture W-22) is shown in Fig.11. By varying the concentration of compound 4 and 5 in the mixture W - 22 one can vary the angle Θ into more optimal value.

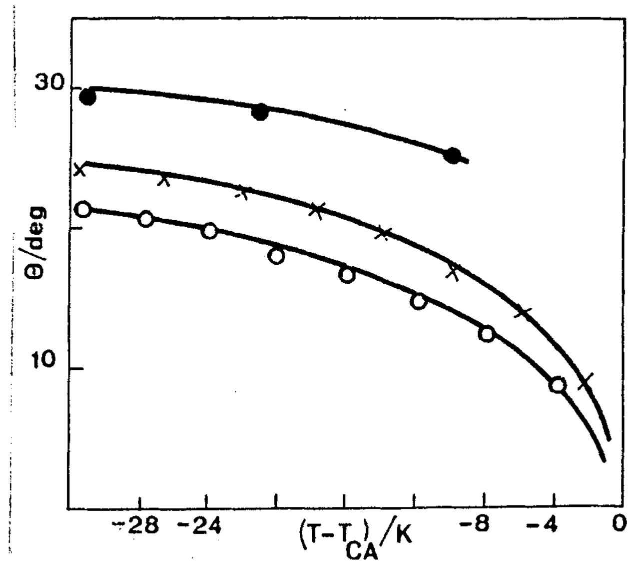

Fig.11. Tilt angle Θ of molecules in smectic C layer versus the reduced temperature: ● - the mixture of B[3], × - the mixture of C[3], ○ - the mixture of W-22

CONCLUSION

The mixture of W-22 including esters of alkoxybenzoic acids and compounds 4 and 5 exhibits the phase sequence Cr⇒SmC*⇒SmA⇒Ch⇒I suitable for a good orientation of FLC in the SSFLC thin cells. The mixture W-22 is thermally and photochemically stable Such parameters as P,Θ and λ were adjusted in order to make the mixture suitable for practical use.

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REFERENCES

[1] J.Pavel,M.Glogarowa,R.Dąbrowski,Ferroelectrics,81, 413(1988).

[2] Commercial certificate of Teikoku Chemical Industry Co.,LTD for Ferroelectric Smectic Mixture TKF 8617.

[3] R.Dąbrowski,J.Dziaduszek,J.Szulc,K.Czupryński, B.Sosnowska,Z.Raszewski, The 13^{th} International Liq.Cryst.Conf.;Mol.Cryst.Liq.Cryst.,1990 in press

[4] N.A.Clark,S.T.Lagerwall,Appl.Phys.Lett.,36,899 (1980).

[5] L.Beresnev,L.Blinov,D.I.Dergachev,Ferroelectrics, 85,173 (1988).

[6] J.Dijon, Proceedings of The 9^{th} International Display Reasearch Conference, Kyoto,October 1989.

[7] R.Meyer,L.Liebert,L.Strzelecki,P.Keller,J.Physique Lett.,36,L-69 (1975)

[8] K.Skarp,M.A.Handschy,Mol.Cryst.Liq.Cryst.,165,439 (1988).

[9] G.W.Gray,J.W.Goodby,"Smectic Liquid Crystals: Textures and Structures",Leonard Hill,Glasgow (1984).

[10] R.B.Meyer, Mol.Cryst.Liq.Cryst.,40,33 (1977).

[11] N.A.Clark,S.T.Lagerwall.Appl.Phys.Lett.,36,899 (1980)

[12] M.Born,"Optik",New York (1972)

[13] C.Escher,H.Dubal,W.Hemmerling,I.Muller, D.Ohlendorf,R.Winger,Ferroelectrics,84,89 (1988).

[14] T.Geelhar,Ferroelectrics,85,329, (1988).

[15] I.Sage,J.Jenner,M.Chambers,Ferroelectrics,85,351 (1988).

[16] M.Bradshaw,B.Brimell,E.Raynes,Liq.Cryst.,2,107 (1987).

[17] J.Hoffman,W.Kuczyński,Ferroelectrics,84,253 (1988)

[18] E.Jastrzębska,J.Rutkowska,J.Kędzierski,Z.Raszewski J.Zmija to be published in Biul.WAT.

[19] E.Jastrzębska,J.Rutkowska,J.Kędzierski,Z.Raszewski J.Żmija to be published in Biul.WAT.

[20] C.Sawyer,C.H.Tower,Phys.Rev.,35,269 (1930)

[21] H.Diamant,K.Drenck,R.Pepinsky,Rev.Sci.Instr.,28,30 (1957).

[22] J.Hoffman,W.Kuczyński,J.Małecki,Mol.Cryst.Liq. Cryst.,144,287 (1987)

[23] A.Levstik,T.Carlsson,C.Filopic,I.Levstic,B.Zeks, Phys.Rev.A,35,3527 (1987).

[24] J.P.Parneix,C.Legrand,Ferroelectrics,84,199(1988)

[25] C.Legrand,J.Parneix,A.M'kadmi,Ferroelectrics,84, 249 (1988)

[26] Z.Raszewski,J.Rutkowska,J.Kędzierski,J.Żmija, to be published in Biul.WAT.

[27] Z.Raszewski, Electron Tech.,20,99 (1987).

[28] J.Goodby, Science,231,350 (1986)

[29] R.Eidenschink et al.,Ferroelectrics,84,167 (1988).

[30] J.Goodby,E.Chin,T.Leslie,J.Geary,J.Pater, J.Am.Chem.Soc.,108,4729 (1986).

[31] J.Goodby,E.Chin,J.Am.Chem.Soc.,108,4736 (1986)

[32] Ph.Martinot-Lagarde,R.Duke,G.Durand,Mol.Cryst.Liq. Cryst.,75,249 (1981).

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[33] V. A. Baikalov, L. A. Beresnev, Mol. Cryst. Liq. Crystal., 127,397 (1985)

[34] Ph. Martinot-Lagarde, J. Physique, 37, C3-129 (1976).

[35] K. Kondo, H. Takezoe, A. Fukuda, E. Kuze, Jap. J. Appl. Phys. 21,224 (1982).

[36] M. Brunet, N. Isaert, Ferroelectrics, 84, 25 (1988).

[37] R. Dąbrowski, J. Dziaduszek, B. Sosnowska, J. Przedmojski The 2nd International Symposium of Ferroelectric, Goteborg, June 1989, Ferroelectrics, 1990 in press

[39] A. Rasbinovich, M. Loseva, N. Chernova, E. Pozhidaev, The 8th Liq. Conf. of Socialist Countries, Cracow, August 1989, Mol. Cryst. Liq. Cryst., 1990 in press

[40] T. Szczuciński, R. Dąbrowski, Mol. Cryst. Liq. Cryst., 88, 55 (1982).

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