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Low Voltage Very Fast Electroclinic Materials. New Molecular Approach

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LOW VOLTAGE VERY FAST ELECTROCLINIC MATERIALS. NEW MOLECULAR APPROACH

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Abstract. The approach to creation of electroclinic materials is proposed, based on mixtures from lamellar matrix and dopants of chiral molecules, having the inclination of long axes even in orthogonal phase of matrix. It is supposed to obtain the transition from collective switching mechanisms (e.g. soft or Goldstone modes) to molecular motions of chiral impurities. Short response times in submicro- and nanosecond range together with low driving voltage as well as the possibility to compensate the temperature dependences of the induced electro-optical angle could be the characteristics of the proposed electroclinic materials. Investigations of mixtures, prepared on the basis of proposed consideration, are described.

INTRODUCTION.

The electroclinic effect[1] in chiral orthogonal smectic phases, e.g. smectic A*, has strong potentials[2] for different applications where the gray scale should be accompanied with short response time. Together with mentioned features the known electroclinic materials as a role have such disadvantages as significant temperature dependence of the electrically induced tilt angle Θ, which usually is explained as a pretransitional behaviour of order parameter Θ at the transition smectic C*-smecticA*[1,3]. Another drowback is the necessarity of relatively high driving voltages if the material exhibits the fast response[3,4]. The attempts to decrease the necessary voltage for inducing the high amplitude of the deviation of optical axis leads to the strong increase of the response time till tens of microseconds[5,6] for one component chiral smectic A compounds, though the temperature independent materials in some temperature interval can be obtained[7].

In this paper we propose to make the electroclinic materials with small response time and low driving voltages on the basis of mixtures, composed from any lamellar (layer) phase, also orthogonal smectic A phase, and chiral dopants with inclination of their long molecular axes from the normal to smectic layers even in orthogonal phase. In this case we can consider, that at relatively small amount of chiral molecules introduced into smectic matrix, the switching and dielectric properties of mixture will be described as a molecular process rather than collective (like soft or Goldstone) modes.

MOLECULAR MODEL OF THE PROPOSED ELECTROCLINIC MATERIALS.

Let us consider the basic properties of mixture, composed from lamellar phase, e.g. smectic A phase with small amount of chiral molecules, having the nonzero angle Θ_m of inclination of long axis **m** from the normal **z** to smectic layers. This inclination can take place for example due to larger length of chiral molecule, Fig. 1, and special mostly zig-zag their shape.

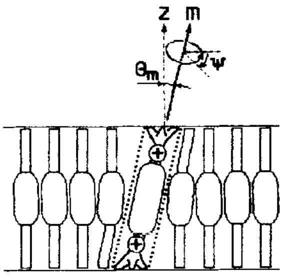


FIGURE I. The asymmetrical hindrance in librations Ψ of inclined chiral molecule, introduced into lamellar phase, around long axis.
⊕ - the transverse molecular dipolar moment
m - the long axis of chiral molecule.

Due to monoclinic environment, created with inclined chiral molecule in smectic phase, the asymmetric hindrance for molecular librations Ψ around long axes takes place and the transverse dipolar moments of inclined chiral molecules will be preferably oriented perpendicular to the inclination planes. Without electric field the inclination planes of chiral molecules are oriented randomly and optical properties of layer are described with optical uniaxial refractive index ellipsoid A with optical axis **n**, directed along the normal **z** to smectic layers, Fig. 2a. The electric field, applied along the layers, does orient the transverse dipole moments of chiral molecules, and the orientation of dipoles is accompanied with the rotation of inclination planes of chiral molecules. The optical properties of material will be described with refractive index ellipsoid with long optical axis **n**(**E**) deviated from the normal **z** in the plane, perpendicular to the direction of electric field. Strongly speaking the electric field will transfer the cylindrical ellipsoid of refractive index to the biaxial one. Such transformation was found even for single component electroclinic materials[8]. The sign of the deviation angle Θ is determined with the sign of electric field, Fig.2 b)c). Corresponding positions of the refractive index ellipsoid are shown in Fig.2 as B and C for two opposite directions of electric field **E** (designated as B in Fig.2 for direction of **E** toward the reader, and as C for direction of **E** backward the reader, resp.).

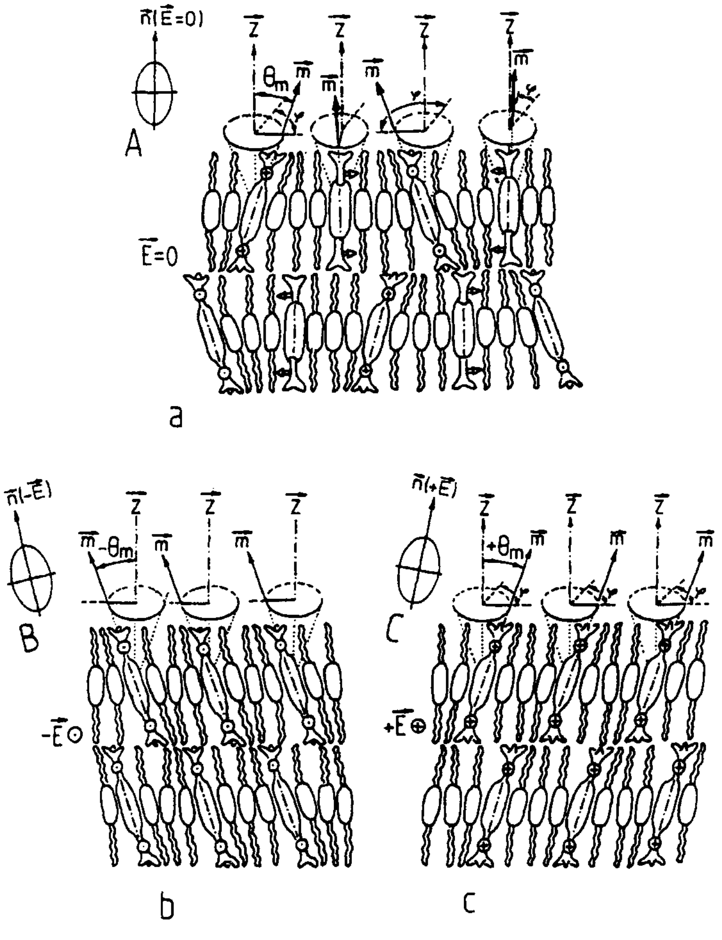


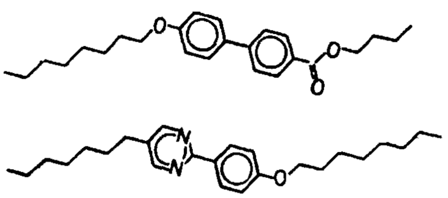
FIGURE.2. The drive of refractive index indicatrix of material, composed from lamellar matrix and chiral inclined molecules, by means of electric field E, applied along the layers.

A: E=0 ; B: E<0 ; C: E>0.

EXPERIMENT.

Substances.

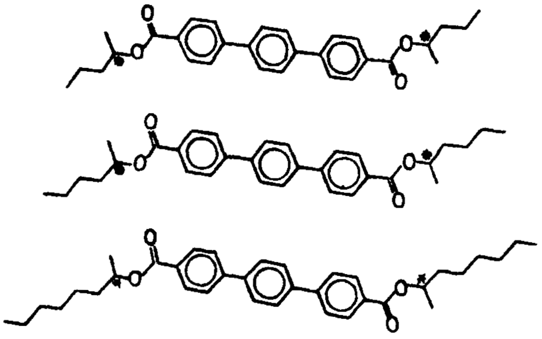
The model mixtures were prepared from compounds, exhibiting the achiral smectic A and smectic C phases, Fig.3, and chiral dopants, having two chiral fragments with large enough transverse dipole moments from class of double esters of the terphenyl - bis - carboxilic acid[9], Fig.4 .



8OBPh4

8OPhPm7

FIGURE 3. The chemical structures of molecules 80BPh4 and 80PhPm7, compousing the lamellar matrix. Here the orthogonal smectic A phase takes place in the interval from room temperature to 75° C.



"3"

"4"

"6"

FIGURE 4. The chemical structure of molecules "3", "4" and "6" used as chiral inclined compounds. Note, please, the significant length difference of molecules.

Tilt angle Θ in dependence on concentration of chiral compounds.

In Fig.5 electrically controlled tilt angle increases significantly with the increase of c_d , for mixtures of the same achiral matrix and chiral compound "4" in dependence on the concentration of "4" . Another well pronounced feature is the unexpectably high induced tilt angle $\Theta \sim 10^{\circ}$ in the smectic A phase at very small voltage 10V. The first fact we explain with the additive nature of optical properties of two subsystems: 1) achiral smectic A matrix and 2) chiral impurity. We consider, that the small angle $\Theta \approx 5^{\circ}$ for small concentration $c_d = 2\%$ is connected with almost orthogonal state of molecules of smectic A matrix but simultaneously with large angle Θ_m of molecules of "chiral subsystem", Fig.6.

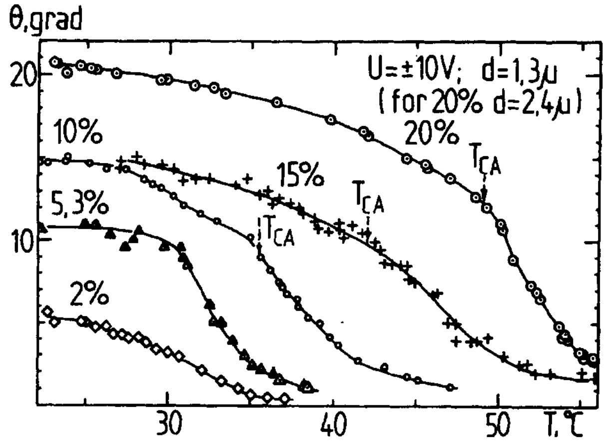


FIGURE 5. The temperature dependence of electrically controlled angle Θ in mixture of achiral smectic matrix and chiral dopant "4" for variable concentration of dopant.

FIGURE 6.
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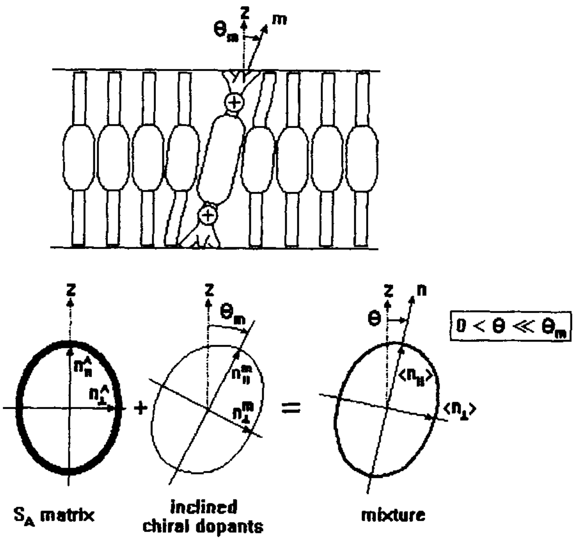


FIGURE.6. The optical index indicatrix of mixture, composed from orthogonal smectic A matrix and inclined chiral dopants as a superposition of indicatrices of matrix "subsystem" and dopant "subsystem", at small concentration of dopants. The measured value of the electrically induced tilt angle Θ can be much less than the inclination angle Θ_m of chiral molecules, $\Theta << \Theta_m$.

We suppose also that angle Θ_m is aproximately the same for fixed voltage, if the concentration c_d is small (less 10%). In this case the more the c_d the more the average tilt angle Θ of superposition of smectic A matrix and chiral inclined "subsystem". In Fig.7 we can see that electrooptical response time τ(10-90%) of these mixtures for small concentrations c_d in smectic A phase practically doesn't increase with the increase of c_d and decreases at high temperatures to 1.5-2 μs.

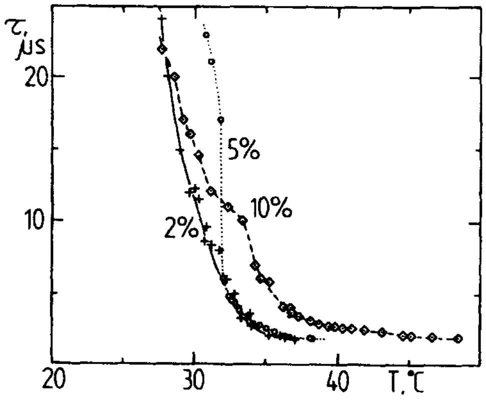


FIGURE7. Temperature dependences of switching time τ for mixtures with small concentration of chiral compound. Cell thickness d=1.3-1.4 μm. Driving voltage ±10V.

This behaviour of τ was tested from the point of view of characteristic relaxation frequencies ν_R, obtained from dielectric spectra, Fig.8.

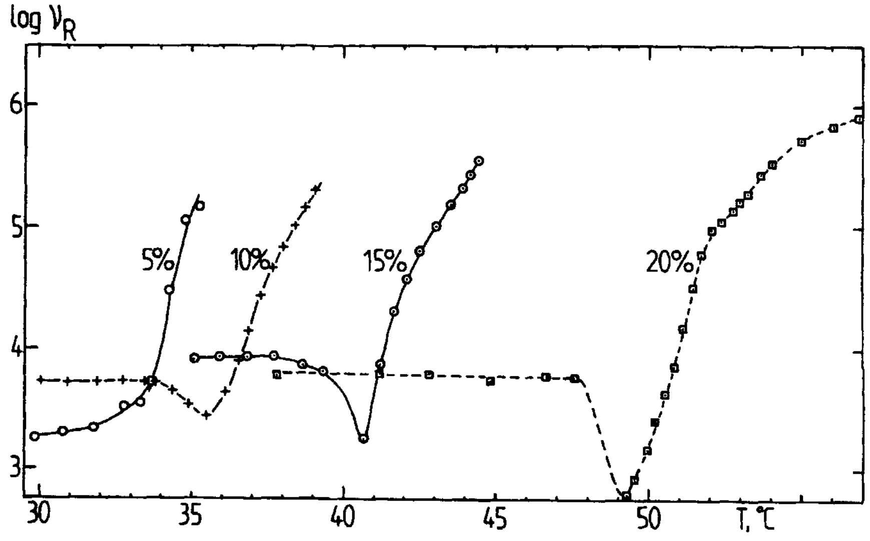
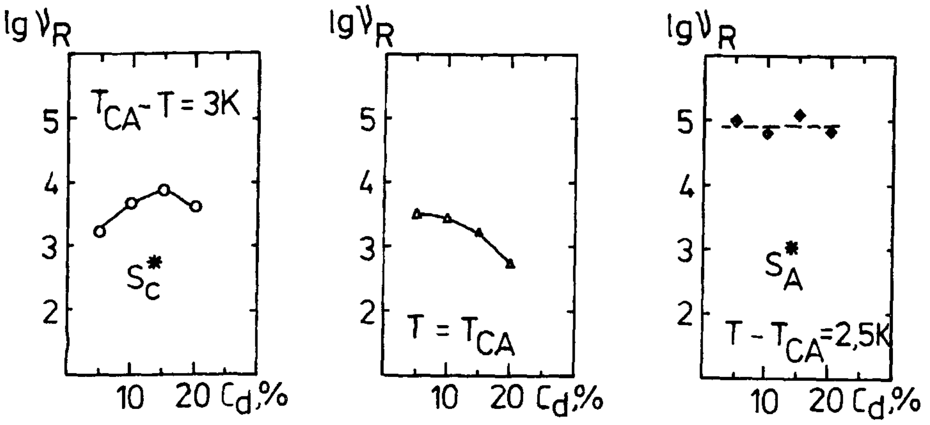


FIGURE 8. Temperature dependences of the relaxation frequencies ν_R in dependence on the concentration of chiral compound "4".

As it follows from the concentration dependences of ν_R for chiral smectic C* and A* phases as well as for the transition temperature T_{CA} between them, Fig.9, the relaxation frequency ν_R (factually, the inverse time τ^{-1} for A* phase) does not depend on the concentration c_d in smectic A phase, Fig.9c, though the decrease of ν_R takes place for the transition temperature T_{CA} , Fig.9b.



a **b** **c**

Fig.9. Concentration dependences of the relaxation frequency ν_R at some temperatures.

a) in smectic C phase, b) transition temperature T_{CA} , c) in smectic A phase.

The electroclinic coefficient μ_e determines the value of voltage, necessary for inducing the tilt Θ: $\Theta \sim \mu_e E$, hence, we can reduce the amplitude of driving voltage by means of increase of concentration of chiral components without increase of switching time.

Estimation of inclination angle of chiral molecules in smectic A phase.

We estimated the angle $\Theta(0) \approx 1.5^{\circ}$ of the deviation of averaged optical axis **n**, extrapolated to zero voltage, Fig.10, curve $\Theta(U)$ = 45.4°C. In Fig.11 the temperature dependences of the induced tilt angle Θ and spontaneous polarization P_s are presented. From these data the extrapolation of curve $P_s(\Theta)$ to zero value of P_s gives us similar value of $\Theta(0)$, Fig.12a)b). Taking into account the concentration of chiral molecules 10% and superposition of approximately equal refractive indices for matrix and dopant "subsystems", discussed earlier, Fig.6, we estimate the inclination angle $\Theta_m \approx 15^{\circ}$ of chiral molecules in orthogonal smectic A phase.

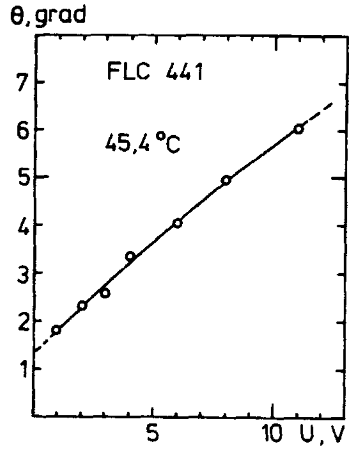


FIGURE 10. The voltage dependences of the tilt angle Θ for material FLC-441 at fixed temperatureT=45.4°C in smectic A phase.

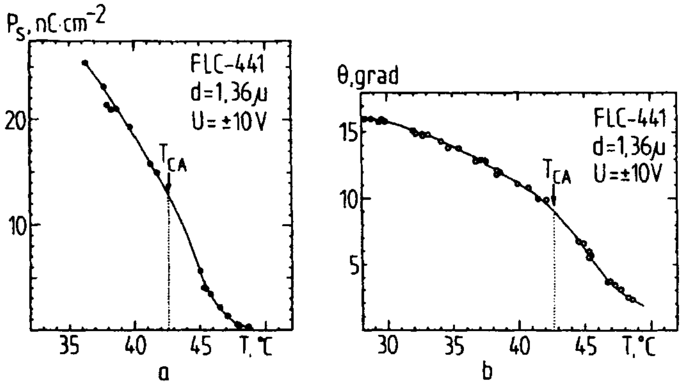


FIGURE 11. The temperature dependences a) of spontaneous polarization P_S and b) of tilt angle Θ for material FLC-441. Cell thickness d=1.36μm, driving voltage ±10V.

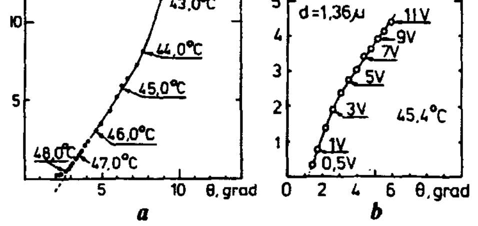


FIGURE 12. The dependence of the spontaneous polarization P_S on tilt angle Θ for FLC-441.
a - the voltage 10 V, variation of temperature;
b - variation of voltage at temperature 45.4°C.

Voltage dependence of response time in smectic A phase. Frequency dispersion in dielectric response.

As follows from Fig.13, the response time τ(10-90)% in smectic A decreases from 15 μs to 2 μs for increase of voltage from 1 to 10 V, whereas in common smectic A* phase the electroclinic response time depends weakly on voltage[3].

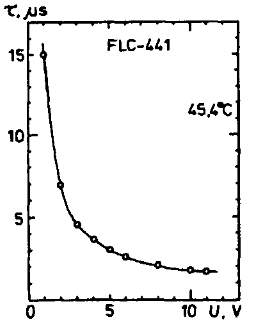


FIGURE 13. The voltage dependences of the switching time τ(10-90%) for material FLC-441 at fixed temperature T=45.4° C in smectic A phase.

We suppose that this behaviour is connected with the reorientation of chiral molecules on cone surface, shown in Fig.2, rather than with collective change of polar angle of the director in smectic A phase. This suggestion is confirmed with the significant decrease of relaxation frequency ν_R of investigated smectic A material near the transition S_C*-S_A* as well as in chiral smectic C phase if the geometrical length of chiral molecules increses, Fig.14.

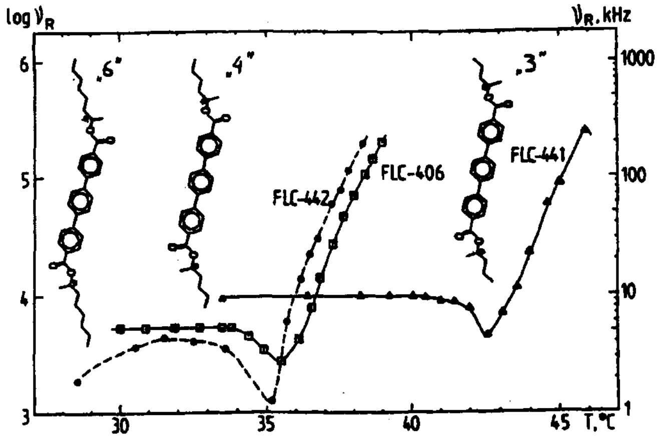


FIGURE 14. Temperature dependences of relaxation frequencies ν_R for materials FLC-442, FLC-406 and FLC-441, having 10 wt.% of chiral compounds "6", "4" and "3", resp.,with different molecular length.

In the same time in smectic A phase we don't see the appreciable dependence of ν_R versus the length of chiral molecules, Fig. 15

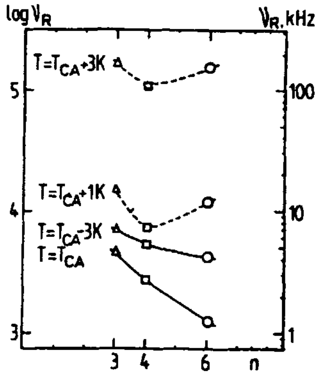


FIGURE 15. Relaxation frequencies ν_R of materials, differing only with the length of alkyl tails in molecules of chiral component, for smectic C*, smectic A* phases and for the transition temperature T_{CA} between them.

This result together with data in Fig.9 gives us the possibility to design the fast operating materials with low driving voltage by means of increase of concentration of chiral dopant. The another evidence of molecular nature of electric response rather than of collective one follows from exponential dependence of the relaxation frequency ν_R on temperature (see, for instance Fig.14, curve FLC-441), in smectic A phase instead of Curie-Weiss low, describing the soft mode of common electroclinic materials[3,10].

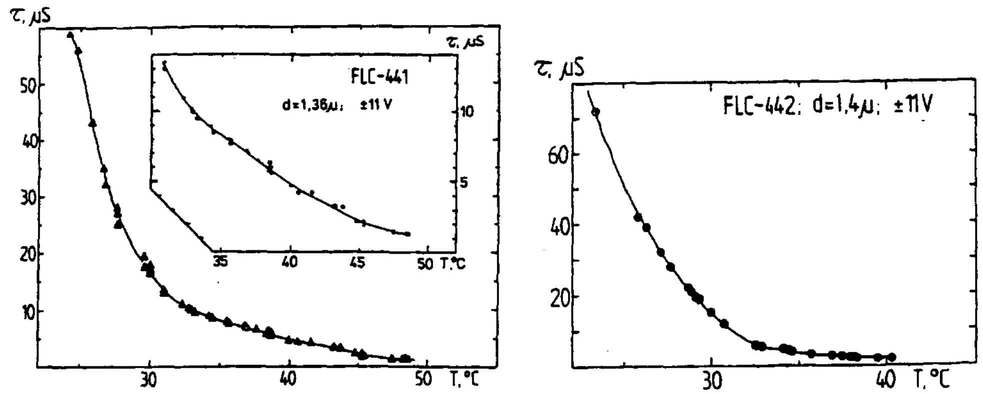
The influence of size of chiral molecules on rotational viscosity of electroclinic mixtures.

For accurate characterization of performance of developed FLC materials the rotational viscosity, describing the relaxation process of investigated mode, is very usable characteristic. We have measured the rotational viscosity γ_φ using the relationship between electrooptical response time τ(10-90%) and another FLC parameters[11] :

$$\tau = \frac{1.76\,\gamma_\varphi \sin^2\Theta}{P_s E}$$

where P_s is the spontaneous polarization, and E - electric field of driving voltage, determined from the amplitude U and cell thickness d, E= U/d . Using the temperature dependences of spontaneous polarization P_s (T), tilt angle Θ(T) and response time τ(T), Fig. 16, measured for mixtures FLC-441 and FLC-442, having the different lengthes of chiral molecules "3" and "6", see Fig. 4, the temperature dependences of γ_φ are obtained,

Fig.17.



a *b*

FIGURE 16. Temperature dependences of the response time τ(T), obtained from the oscillograms of electrooptical response between levels 10-90%, a) for mixture FLC-441 and b) for mixture FLC-442.

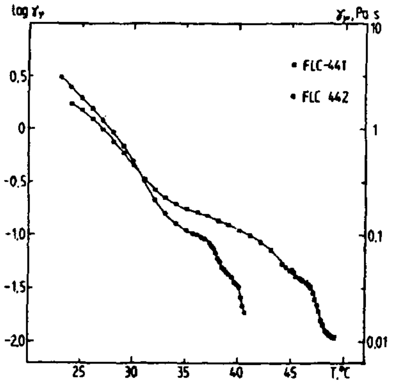


FIGURE 17. The temperature dependences of the rotational viscosity γ_{φ} for materials FLC-441 and FLC-442.

Due to appreciable difference in the temperature intervals of smectic A and smectic C phases of discussed materials it is more convenient to compare the parameters γ_{φ} , reduced to the tilt angle Θ. In Fig. 18 it is seen the strong increase of rotational viscosity γ_{φ} at increase of length of chiral molecule. In the vicinity of the transition temperatures T_{CA} the value of γ_{φ} for "longer case" (chiral molecular "6") is about 2 times larger than for "shorter case" (chiral molecular "3"). We conclude, that approximately equal response times of mixtures, containing chiral molecules with different length, can be explained with simultaneous increase of both parameters, determining the value of response time: γ_φ and P_S.

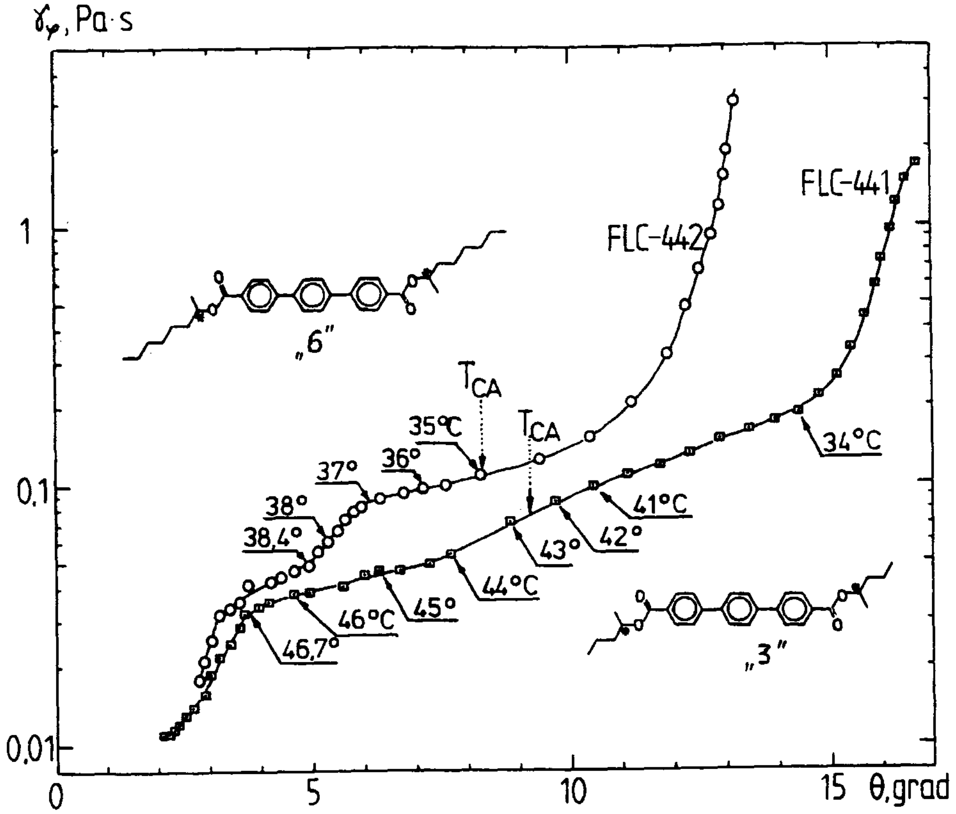


FIGURE 18. The rotational viscosity γ_φ of materials FLC-441 ("short" chiral compound "3") and FLC-442 ("long" chiral compound "6") in dependence on tilt angle Θ. Voltage ±10V, cell thickness 1.4 μm. Appreciable increase (2 times) of rotational viscosity in case of longer chiral molecule "6" is well pronounced.

The strong increase of maximum value of spontaneous polarization, extrapolated to 100% of chiral compounds, with increase of length of chiral molecules, is presented in Table 1.

TABLE 1. Spontaneous polarization, induced with chiral compounds in achiral smectic A matrix, extrapolated to 100 mol.% and reduced to different angles: apparent (measured) switchable angle Θ of mixture, and supposed inclination angle $\Theta_m=30^o$ for chiral molecules.

Materials (chiral molecules)	Concentration, weight %	Apparent tilt angle Θ, grad	$\frac{P_s(100\%)}{\sin\Theta}$, nCcm^{-2}rad	The same, but reduced to $\Theta_m=30^o$	Reference
FLC-441("3")	10	16.4	2100	1185	this study
FLC-446("4")	10	14.7	2200	1117	this study
FLC-442("6")	10	13.2	2700	1233	this study
FLC-288 (AK-113)	15.5	31	2260		11
FLC-363	50	31	738		12

It is also seen from this table the very high absolute value of the extrapolated spontaneous polarization $P_s(100\%)$, reduced to the measured value of tilt angle Θ. Mentioned ratio is in the range of record data[11]. We explain this phenomenon as an apparent increase of ratio $P_s(100\%)/\sin\Theta$ due to the fact, that calculated spontaneous polarization is related to the inclined chiral molecules, having much larger tilt angle Θ_m than the measured angle Θ of whole mixture, Fig.6. This explanation is valid also for smectic C phase, where the inclination angle of molecules of matrix can be significantly less than inclination angle Θ_m of chiral molecules, and the measured angle Θ of electrooptical switching of mixture is less than Θ_m. Supposing the angle $\Theta_m = 30^o$ we obtain the corrected value of the reduced P_s about 1100-1200 nCcm^{-2}rad, which is close to data for mixtures with high concentration of chiral compounds[12], like FLC-363, Table1.

Thus, we propose the detail molecular approach to the development of electroclinic materials based on lamellar liquid crystal phase, containing inclined chiral molecules.

Even in presented case the switching time can be reduced to 1 μs at low voltage about 20V with switchable angle Θ of the order of 5^o-10^o. Starting from this consideration, we developed fast working electroclinic FLC materials with small driving voltage less 20V with response time less 5 μs at room temperature, Fig's.20,21.

Having in mind the results of investigation of dynamical properties of ferroelectric liquid crystals[13,14] we should expect the possibility to obtain the low voltage electroclinic materials with response time in range of tens and units of nanoseconds by means of choice of low viscous smectic matrix, also polymer one, and chiral molecules of special kinds, e.g. dyes with strongly inclined central core of small size and with chiral fragments, containing large dipole moments.We consider also that such disadvantage of fast electroclinic materials as a temperature dependence of the induced tilt angle can be ovecamed by means of choice of lamellar matrix, composed also from chiral molecules, but having the temperature dependence of electroclinic response of inverse sign and stronger temperature dependence near the transition SmC-SmA in comparison with contribution from inclined chiral "subsystem".

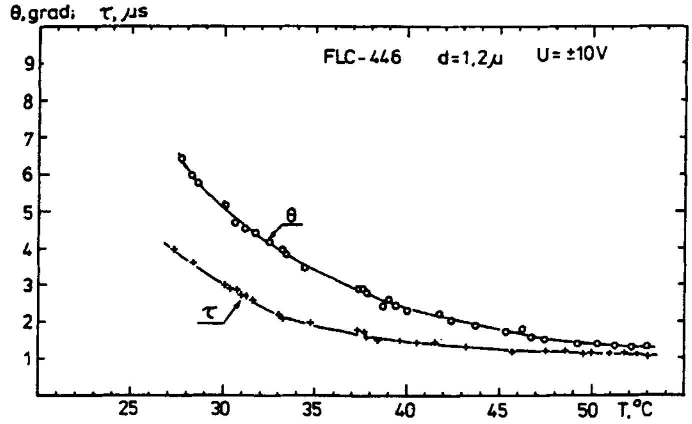


FIGURE 20. The temperature dependences of time switching τ and induced angle Θ for electroclinic material FLC-446 at driving voltage ±10 V.

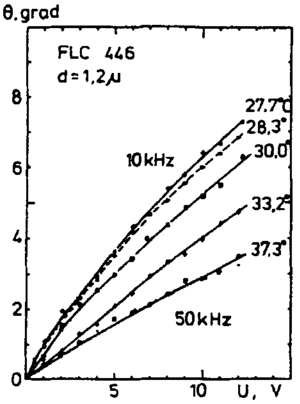


FIGURE 21. The voltage dependences of the electrooptical response of material FLC-446 for some temperatures. Cell thickness 1.2 μm.

CONCLUSION.

The special kind of molecular organization in mixtures of lamellar matrix with chiral molecules is discussed for development of high performance electroclinic materials, setting the transition from collective switching mechanism to molecular one. Further material search (synthesis and compositions) can give us electrooptical media with submicrosecond and nanosecond response and low driving voltages, also with temperature compensation of the induced tilt angle.

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