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NEW FERROELECTRIC LIQUID CRYSTALLINE MATERIALS WITH PROPERTIES SUITABLE FOR SURFACE STABILIZED AND DEFORMED HELIX EFFECTS

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Abstract. *Liquid crystals (LC) are widely used in optical devices. New electro-optic effects are still being established. The requirements of such devices increases thus still new materials are elaborated for such purpose. In this review, two electro-optic effects are described, namely Surface Stabilized Ferroelectric LC (SSFLC) and Deformed Helix Ferroelectric LC (DHFLC) effects. New ferroelectric liquid crystal mixtures were formulated which can be used in devices operating on the basis of the mentioned electro-optic effects. Two ways of mixture preparation have been used: mixing of chiral components or mixing of achiral components with addition of a small amount of chiral dopant. The ferroelectric mixtures with very short (less than 200 nm) or very long (more than 1 μm) pitches are discussed. The mixtures meet almost all requirements of SSFLC and DHFLC effects and therefore, have important prospects for applications in optical sensors.*
__Key words:__ liquid crystals, ferroelectric phase, ferroelectric mixtures, SSFLC effect, DHF effect

НОВЫЕ СЕГНЕТОЭЛЕКТРИЧЕСКИЕ ЖИДКОКРИСТАЛЛИЧЕСКИЕ МАТЕРИАЛЫ СО СВОЙСТВАМИ, ПОДХОДЯЩИМИ ДЛЯ ЭФФЕКТОВ СТАБИЛИЗАЦИИ ПОВЕРХНОСТИ И ДЕФОРМАЦИИ СПИРАЛИ

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__Аннотация__. Жидкие кристаллы (ЖК) широко используются в оптических устройствах. Несмотря на это новые электрооптические эффекты все еще устанавливаются для таких материалов. Возрастающие требования к таким устройствам требуют разработки новых материалов для этих целей. В обзоре описываются два электрооптических эффекта, а именно эффект поверхностно-стабилизированного сегнетоэлектрического ЖК (SSFLC) и эффект сегнетоэлектрического ЖК с деформированной спиралью (DHFLC). Сформированы новые смеси сегнетоэлектрических жидких кристаллов, которые могут быть использованы в устройствах, работающих на упомянутых электрооптических эффектах. Эти смеси были приготовлены двумя разными способами, а именно путем

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смешивания хиральных компонентов и путем смешивания ахиральных компонентов с добавлением небольшого количества хиральной добавки. В статье обсуждаются сегнетоэлектрические смеси как с очень коротким (менее 200 нм), так и с очень длинным (более 1 мкм) шагом спирали. Подобные смеси удовлетворяют почти всем требованиям эффектов SSFLC и DHFLC и поэтому имеют большие перспективы применения.

Introduction

Ferroelectric liquid crystals (FLCs) are materials that possess a spontaneous polarisation (P_S) in the absence of an external field and they can be reoriented on the application of electric field. After the ferroelectricity in liquid crystals was discovered in 1975 [1], many books and articles were written about synthesis, studies and application of new compounds having such properties [2–12]. Since then, many compounds have been synthesized and new materials on their basis were prepared and tested [13–21]. FLCs are characterized by fast electro-optical response, low driving voltage and memory effects, which make them suitable candidates for many advanced applications, such as displays, gratings or sensors [22–25]. Different electro-optical modes can be successfully used for these applications: (i) Surface Stabilized (SS) FLC [26, 27]; (ii) Deformed Helix (DH) FLC [28–30]; (iii) Electrically Suppressed Helix (ESH) of FLC [29]; (iv) modulation of light in the diffraction FLC grating [31]; (v) orientational electro-optical Kerr effect [32, 33] and others. This mini-review summarises results on recently prepared ferroelectric liquid crystalline materials and their multicomponent mixtures [34–39].

Electro-optical effects of FLCs

The main electro-optical switching modes of ferroelectric LCs are based on the field-induced director rotation on the "smectic cone" under the torque connected with the coupling of spontaneous polarization and electric field $P_S x E$. It allows obtaining the switching between dark and bright states with much lower energy barrier than that for nematic liquid crystals, hence the electro-optical effects based on FLCs are characterized by considerably shorter switching times. Two effects (SSFLC and DHFLC) are the most popular and they will be discussed here.

DHFLC electro-optical effect

In the DHFLC effect, the helix axis is parallel to the substrate's plane of LC cell, and the helix is partially unwound when the electric field E is applied (which should be smaller than the so-called critical field E_C causing complete helix unwinding). The electric field also changes the optical axis orientation of LC medium relatively to crossed polarizers (Fig. 1). The basic condition for occurrence of DHFLC effect is that the helical pitch p should be much smaller than the thickness d of the LC cell ($p << d$). DHFLC effect is very promising because of tunable, continuous and hysteresis-free optical phase shift at low voltages and short response times (shorter than in other electro-optical effects based on smectic LCs) either in transmission or reflection modes [30, 40, 41].

The parameters characterizing the DHFLC effect: transmission between crossed polarizers (T_n), switching time (τ) and critical electric field (E_C) can be described by the following equations (1–3) [41]:

$$T_n = sin^2 2[\beta \pm \Delta\alpha(E)]sin^2\left(\frac{\pi d \Delta n_{eff}\,(\lambda, f, E)}{\lambda}\right) \quad (1)$$

$$\tau = \frac{\gamma_\varphi p^2}{K 4\pi^2} \quad\quad\quad (2)$$

$$E_C = \frac{\pi^4}{4}\frac{K}{P_S p^2}, \quad\quad\quad (3)$$

where β is the angle between the polarizer axis and helix axis of FLC phase; $\Delta\alpha(E)$ denotes the deviation of optical axis from normal to layer z due to electric field; d is the thickness of LC cell; Δn_{eff} is the effective birefringence of LC; λ is the wavelength; γ_φ is the rotation viscosity; K is the elastic constant. From the equations (1–3) it can be concluded that the helical pitch p is the most important physicochemical parameter of LCs in DHFLC effect as it strongly affects τ and E_C. The pitch should be as low as possible (at least below 200 nm) in order to lead to the

decrease in switching times and increase in the operating voltage range of the described effect. A high tilt angle of the director θ (ideally it should be as close to 45° as possible) promoting high transmission T_n and a moderate spontaneous polarization P_S (ideally it should be within the range 120–180 nC/cm^2) are the other important parameters.

Concerning the values of spontaneous polarization P_S [42], it can be mentioned that too low values of P_S can result in a strong decrease of contrast, and too high values of P_S cause the shortening of electric field range, in which the DHFLC effect appears. Additionally, low values of rotational viscosity γ_φ help to achieve short switching times.
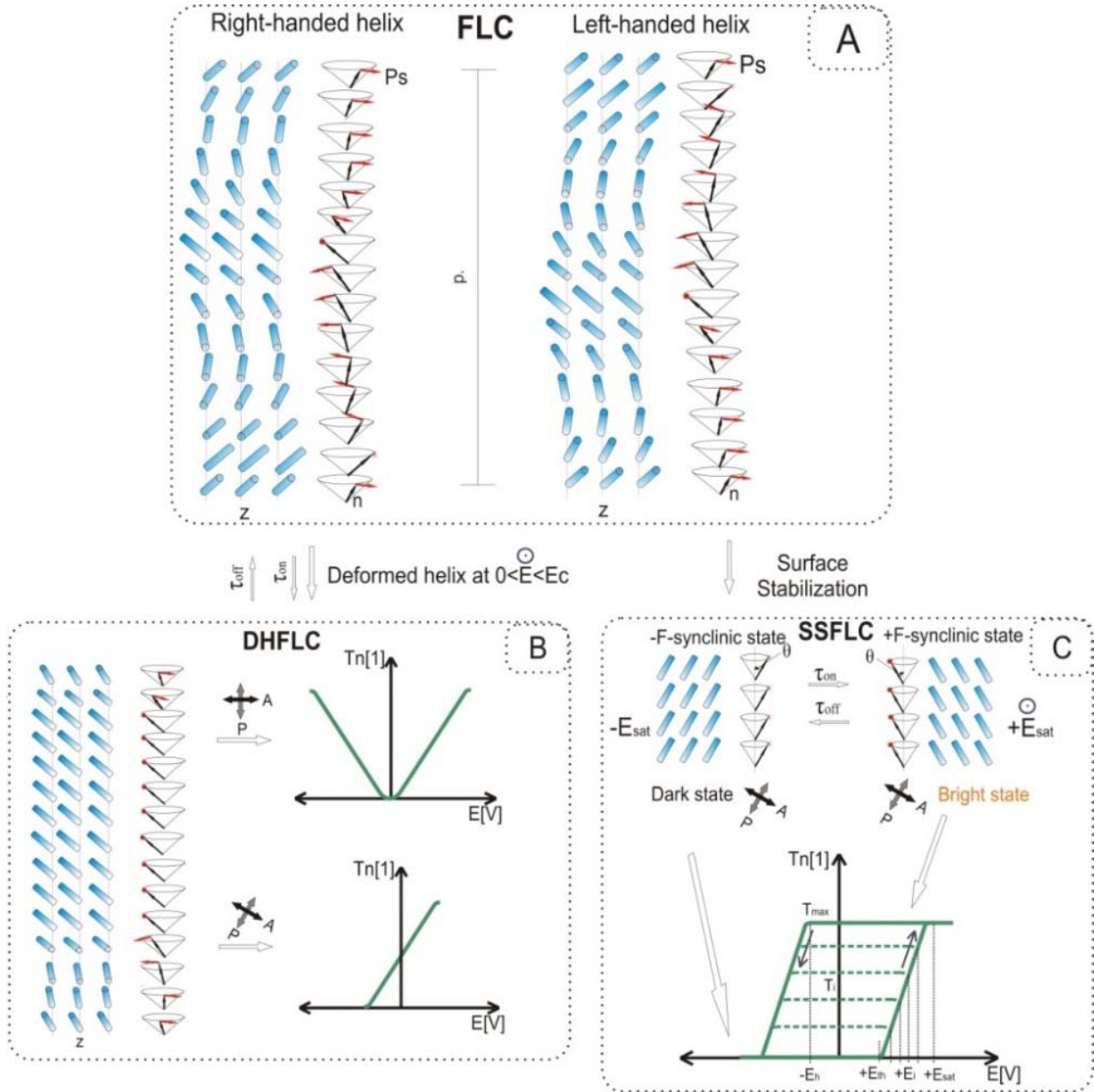

Fig. 1. Arrangement of molecules (blue bars), director *n* (dark arrows) and spontaneous polarization P_S (red arrows) in spontaneously created helical structure in FLCs (*a*). The change in the arrangement of molecules and the resulting change of optical axis vs. crossed polarizers in DHFLC effect with the model shapes of electro-optical response (*b*). The two stable synclinic F-states in SSFLC as well as the model shape of electro-optical hysteresis with marked characteristic electric field and transmission points (*c*). Molecules and directors in four consecutive smectic layers as well as tilt angle θ are indicated

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SSFLC electro-optical effect

In the SSFLC effect, the anchoring surface of LC cell should be strong enough to unwind the SmC* helical structure close to the surfaces. When the LC cell gap d is sufficiently small ($d << p$), the helix is suppressed by the surface action also in the volume. This allows the formation of two possible stable director orientations, simultaneously fulfilling the conditions that the molecules must be parallel to the LC cell surfaces. In the SSFLC effect, two stable states (called synclinic states – F) are energetically equivalent at $E=0$, but can be switched between each other by means of an electric field E that causes the molecules to rearrange in a way that the sense of spontaneous polarization vector of each layer is consistent with that of the electric field (Fig. 1).

The optical indicatrix axis is along to the director of both states. In the SSFLC effect, the switching to the synclinic state is of threshold type and it begins at the threshold electric field E_{th} and ends at the saturation electric field E_{sat}. In order to obtain a dark state between crossed polarizers, one director of two possible synclinic states should be parallel to one polarizer in LC cell.

The parameters characterizing the SSFLC effect are the transmission (T_n) between crossed polarizers and the reorientation time (τ_E) of molecules under electric field are expressed by the following equations (4, 5) [26]:

$$T_n = sin^2(2\alpha)sin^2\left(\frac{\pi d\Delta n_{eff}}{\lambda}\right) \qquad (4)$$

$$\tau_E = \frac{\gamma_\varphi}{P_S E}, \qquad (5)$$

where α is the angle between the polarizer and director axes of FLC.

To assure the maximum contrast in SSFLC effect, the tilt angle θ should be 22.5°. Moreover, the helical pitch p should be as long as possible to obtain a good surface stabilization of smectic layers of FLCs. According to the equation (5), the spontaneous polarization P_S should have moderate values to ensure short time τ_E and reduce the electric current in LC cell as well as the driving electric field used for switching of molecules in LC cell. To obtain short-time switching between the dark and bright states, it is also very important to design FLCs with low rotational viscosity γ_φ. Besides its fast electro-optical response, the SSFLC effect is known possessing a hysteresis of electro-optical switching behaviour. In-plane switching of the

optical axis in LC cell is also observed. According to the equation (5) and Fig. 1, *c*, the SSFLC effect exhibits symmetric switching times because both the rise and fall times (τ_{on} and τ_{off}, correspondgly) are dependent on the electric field E.

The major obstacle for commercialization of SSFLC effect in potential applications is the insufficient contrast of LC cell placed between crossed polarizers due to light leakage in the dark state. This imperfection is mainly caused by the tendencies of smectic layers to fold into a chevron-like structure when transferring from an orthogonal phase (SmA*) to a tilted phase (e.g. SmC*). The appearance of such structure results in an inhomogeneous arrangement of the optical axis of LC medium. The main source of this effect is the decrease of smectic layer thickness d due to the tilt of molecules ($d_{SmC*} \sim d_{SmA*} \cos \theta$). On cooling through the SmA* –SmC* transition, the layers do not slip along the glass surface of LC cell and the smectic periodicity close to this surface corresponds to SmA* phase. The only way for the material to satisfy the new smaller layer thickness of SmC* phase in the bulk of LC cell is to fold in chevron-like structure. Characteristic zig-zag defects appear and cause mentioned light leakage in the dark state of LC cell placed between crossed polarizers in the SSFLC effect. The method to minimize the above mentioned disadvantages is the use of FLCs with the possible smallest layer shrinkage during the transition to a tilted phase. Moreover, the presence of a nematic phase in the phase sequence of LC material affects the improvement of molecule alignment in LC cell.

Preparation of mixtures

Considering such a complex research task of simultaneous tailoring of several parameters in DHFLC and SSFLC effects, it is clear that those requirements cannot be reached in a single smectogenic compound, but the only possible solution is to design and prepare specific multicomponent LC mixtures. There are at least two main approaches to design and obtain desirable FLC mixtures. The first one is based on doping an achiral base smectic C mixture with a chiral dopant or dopants, to produce chiral smectic C* mixture possessing the optimal physico-chemical and electro-optical properties. The advantage of this FLC mixtures concept is the ability of controlling the values of spontaneous polarization P_S and helical pitch p in a broad range. Additionally, this approach consists in

keeping the rotational viscosity of the final material as low as in the basic smectogenic mixture and providing the possibility to obtain phase sequence with nematic phase at higher temperature. However, the director tilt angle in mixtures developed by this method is rather low ($\theta < 35°$). Such mixtures can also exhibit strong instability when the concentration of chiral dopant is high. The instability often occurs in LC mixtures consisting of compounds significantly differing in chemical structure. It can cause precipitation of some components, mainly of chiral dopant.

The second approach relies on the mixing of chiral LC compounds promoting chiral tilted phases. This method provides advanced LC materials with high stability and allows to obtain high director tilt angle θ in SmC* phase.

All above information about the requirements and drawbacks of LC materials dedicated to the DHFLC and SSFLC effects have become motivation for the Military University of Technology research team to design and develop new generation of FLCs. In this paper, we demonstrate summary of these efforts.

*FLCs prepared from achiral SmC basic mixture and chiral dopants*

In order to obtain FLCs material according to the idea of doping achiral mixture with chiral dopant, the bicyclic pyrimidine compounds with alkyl or/and alkoxy terminal chain (based on a general structure **1**, where: R_1 and R_2 are $C_nH_{2n+1}-$ or $C_nH_{2n+1}O-$; $n = 4 \div 11$) were chosen and an achiral base mixture (denoted here as **W**) was prepared [37].
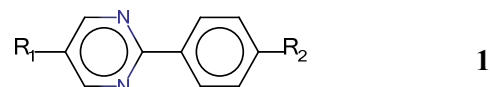
The prepared eutectic base mixture **W** exhibits the following phase transitions at heating:
Cr 7.9 °C SmC 68.8 °C SmA 82.8 °C N 87.0 °C Iso.

To induce ferroelectric properties in the tilted SmC phase, the base mixture **W** was doped with several low-melting, non-mesogenic, terphenyl-based dopants having two homo-chiral terminal chains (**A**, **F**, **G** (mixture), **I**, **J**). Thus, five FLC mixtures were obtained containing 5.0 wt. % of each dopant. The general structure **2** and acronyms of dopants along with their phase transition temperatures are presented below.
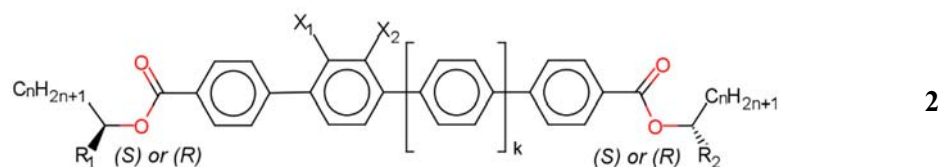
A: *(S, S)*; $n = 6$; $k = 0$; $X_1, X_2 = H$; $R_1, R_2 = CH_3$;   Cr 81.1 °C Iso [43]

F: *(S, S)*; $n = 4$; $k = 0$; $X_1, X_2 = H$; $R_1, R_2 = CH_3$;   Cr 75.7 °C Iso [43]

G: 84 wt. %.: *(R, R)*; $n = 6$; $k = 0$; $X_1, X_2 = H$; $R_1, R_2 = CH_3$ [by analogy to 43];
16 wt. %.: *(R, R)*; $n = 6$; $k = 1$; $X_1, X_2 = H$; $R_1, R_2 = CH_3$; Cr 82.7 °C Iso [unpublished results]

I: *(S, S)*; $n = 6$; $k = 0$; $X_1, X_2 = H$; $R_1, R_2 = CF_3$;   Cr 42.9 °C Iso [44]

J: *(S, S)*; $n = 6$; $k = 0$; $X_1, X_2 = F$; $R_1, R_2 = CH_3$;   Cr 34.3 °C Iso [43]

All prepared chiral mixtures exhibit the ferroelectric SmC* phase in very broad temperature ranges and their melting points are below 10 °C (crystallisation temperatures are below 0 °C). Almost all mixtures exhibit the desired phase sequence: Cr – SmC*– SmA* – N* – Iso. The exception is the mixture containing terphenyl and quaterphenyl chiral dopants (mixture **W_G**), which does not form a chiral nematic phase. It may be the evidence that the presence of long and flat molecular core in the base mixture hinders the

molecular movements along the director and promotes layered ordering. Surprisingly, in the case of **W_G** mixture, the lack of nematic phase allows to obtain nearly perfect, almost defectless surface stabilized geometry of smectic layers in LC cell. Such almost perfect alignment was obtained for all prepared mixtures and the dark state without light leakage exhibits beneficial properties for application. This is an uncommon feature in comparison to FLC materials reported previously (i.e., see ref. [15]).

This fact can be explained by the properties of multicomponent base mixture **W**, which forms smectic layers with a small layer contraction and shows low viscosity values. Such properties that hinder formation and support relaxation of emerging defects, can be connected with the structural similarity of mixture **W** components. Moreover, the helical pitch *p* obtained for the mixtures with 5.0 wt. % of chiral dopants is higher than 1.5 μm (the thickness of the used electro-optical cell is lower) and it also contributes to a better ordering of mixture molecules in LC cell.

From the obtained results [37], many interesting conclusions regarding the influence of the chiral dopants structure on the properties of final multicomponent FLC mixtures can be highlighted. Some of the physicochemical and electro-optical parameters of prepared mixtures described in Ref. [37] are presented in Table 1.

Table 1. **Electro-optical and physicochemical properties of the compositions prepared on the basis of mixture *W* at T ≈ 30 °C in SmC* phase. The table prepared on the basis of the data from [37]**

Properties	*W_A*	*W_F*	*W_G*	*W_I*	*W_J*
$\theta[°]$	21.4	24.1	21.1	25.0	21.9
Smectic layer thickness [Å]	27.8	27.7	28.6	28.2	28.3
The difference of the layer thickness between SmC* and SmA* phases [Å]	1.8	1.9	1.7	1.9	1.7
τ_E [μs]	80	71	88	88	104
P_S [nC/cm^2]	9.5	21.4	14.0	28.4	16.0
γ_φ [mPa·s]	28	53	45	92	61

The smectic layer spacing for both mixtures **W_A** and **W_F** is near equal. Compound **F** with shorter terminal chain in comparison with dopant **A** causes a greater increase of spontaneous polarisation P_S, the director tilt angle θ and rotational viscosity γ_φ and decrease the switching time τ_E in the final FLC mixture. Dopants **I** and **J** differ from each other in the location of fluorine atoms – in the terminal chain of dopant **I** and in the core of dopant **J**. The higher values of spontaneous polarisation P_S, optical tilt angle θ and rotational viscosity γ_φ are observed in the mixture with dopant **I**. It suggests that the presence of the heavy and electronegative fluorine atoms close to the chiral centre reflects in a hindrance of molecular rotation and, hence, results in a higher value of the spontaneous polarization P_S. Apparently, the location of the fluorine atom in chiral molecules, as studied in work [37], does not affect the layer spacing in the final FLC mixture. It can also be noted, that fluorine substitution in dopants causes an increase in the rotational viscosity γ_φ of the resulted mixtures.

Among prepared materials, the mixture **W_A** exhibits a set of parameters that altogether make it the best candidate for applications in SSFLC mode (Table 1).

Here, the most uniform and defectless surface stabilized geometry, the director tilt angle θ approximated to the required one, the lowest spontaneous polarisation P_S and short switching time τ_E observed are of the highest importance.

Furthermore, we also designed and prepared a series of mixtures consisting of an excessive amount of chiral dopant in the base mixture **W** (up to 30.0 wt. %) [37]. At the chiral dopants concentration above 20.0 wt. %, the values of helical pitch *p* are very low (in some cases being lower than 150 nm at the room temperature). Such mixtures show high application potential in DHFLC effect.

FLCs prepared from chiral compounds

FLC mixtures consisted of "all chiral" compounds were formulated according to the procedure based on mixing of selected chiral compounds with ferroelectric and antiferroelectric properties. The proper composition allows the competition between the synclinic and anticlinic order, leading to appearance of frustrated ferroelectric phase, which provides the V-shape electro-optical switching [45]. This method allows to optimize the physicochemical and electro-optical properties of FLC materials beneficial in DHFLC effect.

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In the first step of these studies, we selected compounds with the identical chiral terminal chain but different structure of rigid molecular core and achiral opposite chain (see compounds *3b-e* and *4a-d* in Table 2). Those compounds were added to the basic high tilted ferroelectric compound (see compound *3a* in Table 2)

[34]. The aim of the preparation of such bicomponent systems was to establish the miscibility of phases, especially ferroelectric phase, and to determine the temperature dependence of the helical pitch *p* and the tilt angle of the director *θ* in the mixtures.
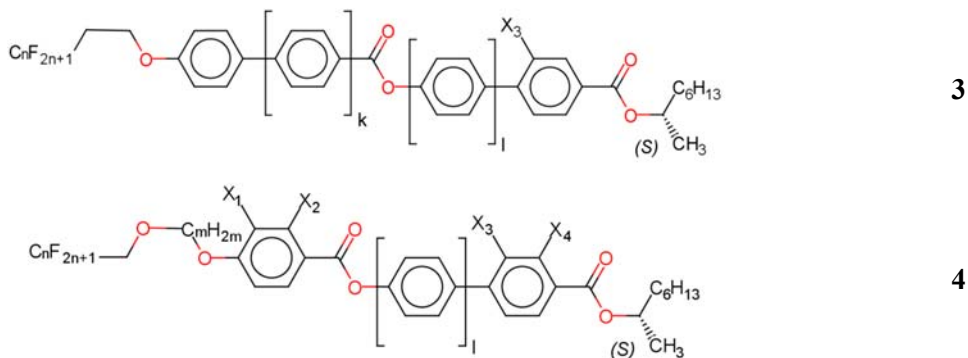

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Table 2. **Compounds selected for miscibility investigation and their phase transition temperatures suitable for DHFLC effect**

Compound acronym	n	m	X_1	X_2	k	l	X_3	X_4	Phase transition temperatures determined on heating, °C
3a	6	–	–	–	1	0	H	–	Cr_{II} 80.7 Cr_I 98.9 SmC* 141.4 SmC_α* 149.0 SmA* 184.0 Iso [46,47]
3b	6	–	–	–	0	1	H	–	Cr_{II} 94.3 Cr_I 97.9 SmC* 155.6 SmA* 184.6 Iso [46]
3c	6	–	–	–	1	0	F	–	Cr 89.7 SmC* 133.6 SmCα* 134.8 SmA* 154.7 Iso [46]
3d	6	–	–	–	0	0	H	–	Cr 60.0 SmA* 63.4 Iso [by analogy to 46]
3e	8	–	–	–	0	0	H	–	Cr 82.2 SmA* 90.7 Iso [48]
4a	1	5	H	H	–	0	H	H	Cr 43.4 Iso [49]
4b	3	6	H	H	–	0	H	H	Cr 36.2 Iso [by analogy to 50]
4c	3	6	F	H	–	0	H	H	Cr 32.8 Iso [by analogy to 50]
4d$^\$$	3	0	H	H	–	0	H	F	Cr 14.9 Iso [49]
4e	3	5	H	F	–	1	H	H	Cr 28.1 SmC_A*99.0 SmC* 101.0 Iso [50]
4f	3	7	F	H	–	1	H	H	Cr 37.4 SmC_A* 103.1 SmC* 104.3 SmA* 109.1 Iso [50]

$ – compound without oxygen atom between olighomethylene group $(CH_2)_m$ and rigid core

Results of studies [34] show that two-ring compounds, which do not form ferroelectric phase, destabilize it in the mixtures with compound *3a*. Among them, compounds *3d* and *3e*, showing SmA* phase, cause the smallest destabilization. They have the longest fluorinated part of achiral terminal chain, similar to that of the basic compound *3a*. Among compounds without liquid crystalline phase, the compound *4b* having the longest achiral terminal chain without lateral substitution of fluorine atom gives the smallest phase destabilization in mixtures with the base compound *3a*. Systems containing compounds *4a*, *4c* and *4d* show the phase coexistence area (SmC* and Iso) without stable SmC* phase above 0.3 molar fraction in the mixture with compound *3a* at room temperature. Almost all investigated compounds cause small decrease of a helical pitch length in the ferroelectric phase of basic compound *3a* except compounds with SmA* phase (compounds *3d* and *3e*). The tilt angle of mixtures with 0.2 molar fraction of the two-ring

compounds is still relatively high (above 30° at lower temperatures). Among biphenyl compounds, the compound **3d** causes the lowest reduction of tilt angle in mixture with compound **3a**. Based on the analysis of the above results [34], it can be concluded that compounds **3b**, **3c**, **3d**, **3e** and **4b** seem to be the most promising components for creation of ferroelectric mixtures with compound **3a**. They should be characterized by broad temperature range of SmC* phase, short helical pitch *p* and high director tilt angle *θ*.

In the next step of preparation of the FLC mixtures with the properties appropriate for DHFLC effect and consisting of compounds having ferro- and/or antiferroelectric phase, the multicomponent mixtures based on compounds presented in Table 2 were designed and characterized [35, 36]. The compositions of the developed mixtures and their phase transition temperatures are presented in Tables 3 and 4, respectively.

The first prepared mixture **W-212B** [35] was an eutectic mixture consisting of three-ring ferroelectric compounds (**3a-c**) and two low melting two-ring compounds **3d** and **3e**, forming the SmA* phase. In order to decrease melting point as well as a helical pitch length of this mixture **W-212B** (see Table 4 and Fig. 2, *a*), three modified mixtures have been developed.

The second mixture **W-212B2** additionally contains compound **4e** possessing a wide-temperature range of antiferroelectric phase. This modification allows to decrease melting point and helical pitch (see Table 4 and Fig. 2, *a*) but at the same time, antiferroelectric phase is induced at lower temperatures in this mixture.

The third mixture **W-212B3** was prepared on the base of two eutectic mixtures: the first developed one with acronym **W-212B** and the antiferroelectric one with acronym **W-1000** [51, 52] (consisting of compounds **4e** and **4f**). Using the phase diagram of the system of these two mixtures, we chose the composition of the final **W-212B3** mixture with the frustrated ferroelectric phase at a broad temperature range.

Table 3. **Compositions of the studied mixtures [35, 36]**

Component acronym	Mixtures acronyms						
	W-212B	*W-212B2*	*W-212B3*	*W-212B3A*	*W-212C*	*W-212C2*	*W-212C3*
	Concentration (wt. %)						
3a	11.88	7.97	7.72	8.22	8.35	7.52	7.52
3b	12.13	8.14	7.88	8.39	8.31	7.48	7.48
3c	24.29	16.30	15.79	16.81	18.54	16.69	16.69
3d	38.80	26.04	25.22	26.85	29.75	26.77	26.77
3e	12.90	8.66	8.39	8.93	–	–	–
4b	–	–	–	–	35.05	31.54	31.54
4e	–	32.89	18.38	11.47	–	10.00	5.25
4f	–	–	16.63	10.37	–	–	4.75
A		–	–	8.97	–	–	–

Table 4. **Mesomorphic behaviour of the studied mixtures (on cooling) [35, 36]**

Mixture acronym	**Cr**	T, °C	**SmC$_A$***	T, °C	**SmC***	T, °C	**SmA***	T, °C	**Iso**
W-212B	•	11.4	–	–	•	83.9	•	118.0	•
W-212B2	•	<–20.0	•	–4.8	•	91.0	•	111.0	•
W-212B3	•	<–20.0	–	–	•	85.2	•	105.0	•
W-212B3A	•	<–20.0	–	–	•	71.2	•	98.9	•
W-212C	•	<–20.0	–	–	•	61.8	•	97.0	•
W-212C2	•	<–20.0	–	–	•	61.7	•	71.0	•
W-212C3	•	<–20.0	–	–	•	64.4	•	74.7	•

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The **W-212B3** mixture exhibits the Cr – SmC* – SmA* – Iso phase sequence with low melting point and short helical pitch (see Table 4 and Fig. 2, *a*). Moreover, it is characterized by similar values of spontaneous polarization P_S (Fig. 2, *c*) and the director tilt angle θ lower only by 3° than the mixture **W-212B2** (Fig. 2, *b*). It is worthy to notice that **W-212B3A** differs from **W-212B3** by an additional chiral component **A** and has the smallest value of the helical pitch length – around 150 nm – suitable for DHFLC effect (Fig. 2, *a*).

Unfortunately, the mixture **W-212B3A** has one disadvantage, i.e. too high values of spontaneous polarization P_S (higher than 200 nC/cm^2, Fig. 2, *c*). According to equation (3), high P_S considerably decreases the value of E_C and, thereby, reduces the voltage range, over which the mixture **W-212B3A** could be driven in DHFLC effect. Therefore, we have modified the composition of the base mixture **W-212B** and the newly designed mixture **W-212C** [36] was formulated. Instead of compound **3e** with the SmA* phase, the mixture **W-212C** contains a non-mesogenic compound **4b** having much lower melting point and possessing strong tendency to decrease the helical pitch p [34]. Due to that, the SmA*–SmC* phase transition, as well as the melting point of **W-212C** mixture became much lower than those of **W-212B** mixture. Furthermore, and importantly, the helical pitch length of **W-212C** is lower than 180 nm (Fig. 2, *a*), thus, it was possible to avoid the use of compound **A**, which significantly increases spontaneous polarization P_S. We used again the procedure of blending compounds with ferroelectric and antiferroelectric compounds at proper concentrations. For this purpose, we chose compounds **4e** and **4f** to tune the features of **W-212C**. Two systems, namely **W-212C** + compound **4e** as well as **W-212C** + mixture of compounds **4e** and **4f** (in the proportion corresponding to mixture **W-1000**), were prepared in order to find a material with a broad temperature range of frustrated ferroelectric phase and with the shortest possible helical pitch p. Based on the analysis of phase diagram and temperature dependence of helical pitch lengths p for both systems, we have chosen two mixtures consisting of 10.0 wt. % of compound **4e** or **W-1000** blended with the mixture **W-212C**, these mixtures have been denoted with the acronyms **W-212C2** and **W-212C3**, respectively. These mixtures are characterized by low melting points and relatively broad temperature ranges of the ferroelectric phase (over 70 °C). The values of their helical pitch lengths p are lower than 180 nm (see Fig. 2, *a*), similar as for **W-212C** mixture. As the values of helical pitch length p for **W-212C2** mixture are the highest from all three discussed mixtures, the studies of temperature dependence of the director tilt angle θ, spontaneous polarization P_S, switching times τ and rotational viscosity γ_φ were performed for **W-212C** and **W-212C3** mixtures only. The lowest values of spontaneous polarization P_S were detected for the base **W-212C** mixture, which contains the highest quantity of ferroelectric compounds and no components with antiferroelectric phase (see Table 3). On the other hand, antiferroelectric components of **W-1000** mixture cause saturation of the tilt angle values θ (about 40°) at a broader temperature range in **W-212C3** mixture (Fig. 2, *b*)**.** It is worthy to notice that both mixtures **W-212C** and **W-212C3** exhibit lower values of spontaneous polarization P_S and comparable values of tilt angle θ in comparison with the mixtures based on **W-212B** series (Fig. 2, *b, c*). Taking into account the basic information from Introduction section, the designed **W-212C** and **W-212C3** mixtures fulfilled almost all material requirements for DHFLC effect, including not too high spontaneous polarization P_S. Thanks to this, the basic disadvantage of the previously prepared **W-212B3A** mixture was eliminated. On the other hand, **W-212C** and **W-212C3** mixtures exhibit two times higher rotational viscosity γ_φ but also much lower melting point than the reported FLC materials for DHFLC effect [41]. So, it means that they can extend the switching times τ, while allowing to work in DHFLC mode at lower temperatures. Furthermore, some mixtures of the designed binary systems (**W-212B**+**W-1000**, **W-212C**+**W-1000** and **W-212C**+compound **4e**) described in Refs. [35, 36] possess antiferroelectric phase with a very short and simultaneously, temperature independent helical pitch p. That fact makes them potentially applicable and useful for DHAFLC effect [53].
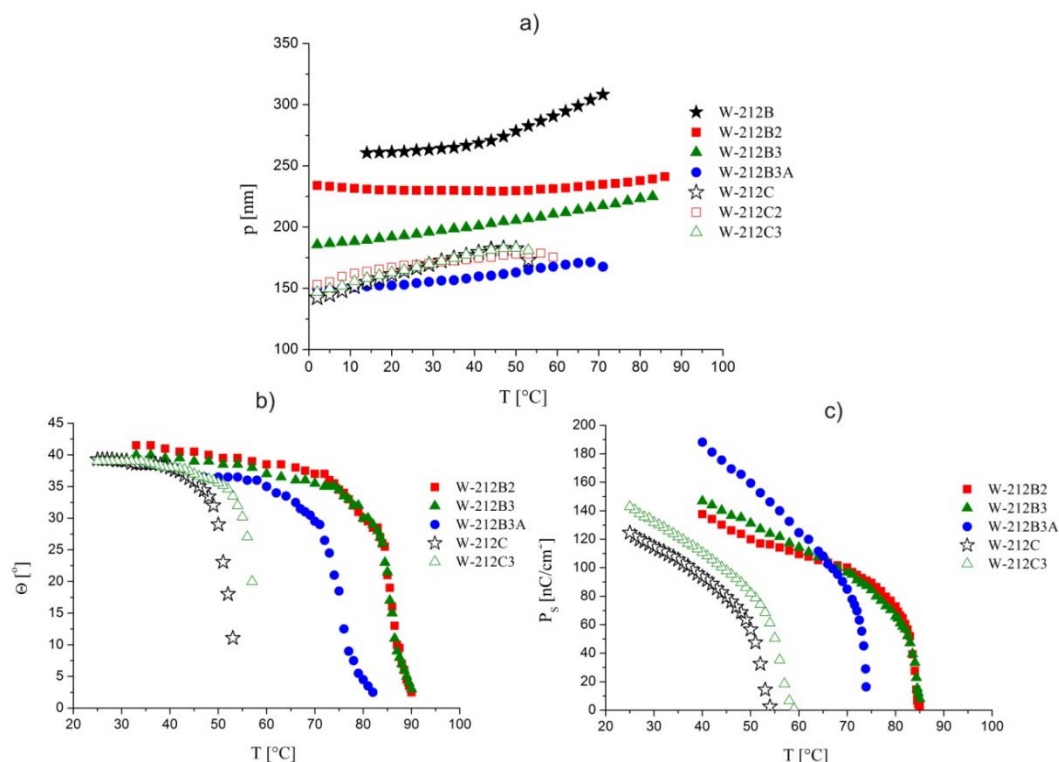
Fig. 2. Temperature dependences of the helical pitch length *p* (*a*), the director tilt angle *θ* (*b*) and spontaneous polarization *P_S* (*c*) of the mixtures belonging to **W-212** series

Conclusions

The mixtures showing broad temperature range of ferroelectric phase have been prepared. Both methods of mixture preparation, namely the mixture formulation from chiral as well as from achiral components with addition of chiral dopant, have specific advantages. The former method is better suitable for preparation of the mixtures with classic ferroelectric phase having the director tilt angle around 22.5º. The latter method is good for the mixtures with orthoconic ferroelectric phase having the director tilt angle around 45º. The properties of presented mixtures satisfy the requirements of SSFLC as well as DHFLC electro-optic modes and by that have opened the possibility of using them for some optical sensors and other devices.

References

1. Meyer R., Liebert L., Strzelecki L., Keller P. Ferroelectric liquid crystals. *J. Phys. Lett.*, 1975, **36** (3), L69–L71. **DOI**: 10.1051/jphyslet:0197500360306900.
2. Lagerwall S.T. Ferroelectric and antiferroelectric liquid crystals. Weinheim: Wiley-VCH, 1999. 427 p. **DOI**:10.1002/9783527613588.
3. Takezoe H. Ferroelectric, antiferroelectric, and ferrielectric liquid crystals: applications. *Encyclopedia of Materials: Science and Technology*. Oxford: Elsevier, 2001, 3063–3074. **DOI**: 10.1016/B0-08-043152-6/00546-5.
4. Fukuda A., Ouchi Y., Arai H., Takano H., Ishikawa K., Takezoe H. Complexities in structures of ferroelectric liquid crystal cells. The chevron structure and twisted states. *Liq. Cryst.*, 1989, **5** (4), 1055–1073. **DOI**: 10.1080/02678298908026410.

===

5. Rieker T.P., Clark N.A. The layer and director structures of ferroelectric liquid crystals. *Phase Transitions in Liquid Crystals* / ed. by S. Martellucci and A.N. Chester. New York: Plenum Press, 1992, 287–341. **DOI**: 10.1007/978-1-4684-9151-7_21.

6. Lagerwall S.T., Matuszczyk M., Matuszczyk T. Old and new ideas in ferroelectric liquid crystal technology. *Proc. SPIE.*, 1998, **3318**, 2–38. **DOI**: 10.1117/12.299943.

7. Bubnov A., Novotná V., Hamplová V., Kašpar M., Glogarová M. Effect of multilactate chiral part of liquid crystalline molecule on mesomorphic behaviour. *J. Mol. Struct.*, 2008, **892**, 151–157. **DOI**: 10.1016/j.molstruc.2008.05.016.

8. Novotná V., Hamplová V., Bubnov A., Kašpar M., Glogarová M., Kapernaum N., Bezner S., Giesselmann F. First photoresponsive liquid-crystalline materials with small layer shrinkage at the transition to the ferroelectric phase. *J. Mater. Chem.*, 2009, **19**, 3992–3997. **DOI**: 10.1039/b821738f.

9. Tykarska M., Dąbrowski R., Czerwiński M., Chełstowska A., Piecek W., Morawiak P. The influence of the chiral terphenylate on the tilt angle in pyrimidine ferroelectric mixtures. *Phase Transitions*, 2012, **85** (4), 364–370. **DOI**: 10.1080/01411594.2011.646274.

10. Ziobro D., Dąbrowski R., Tykarska M., Drzewiński W., Filipowicz M., Rejmer W., Kuśmierek K., Morawiak P., Piecek W. Synthesis and properties of new ferroelectric and antiferroelectric liquid crystals with a biphenylyl benzoate rigid core. *Liq. Cryst.*, 2012, **39** (8), 1011–1032. **DOI**: 10.1080/02678292.2012.691560.

11. Węgłowska D., Dąbrowski R. Highly tilted ferroelectric liquid crystals with biphenylyl benzoate rigid core. *Liq. Cryst.*, 2014, **41**(8), 1116–1129. **DOI**: 10.1080/02678292.2014.907454.

12. Kula P., Herman J., Perkowski P., Mrukiewicz M., Jaroszewicz L.R. On the influence of the chiral side linking bridge type upon the synclinic vs. anticlinic balance in the case of 2′,3′-difluoroterphenyl derivatives. *Liq. Cryst.,* 2013, **40** (2), 256–266. **DOI**: 10.1080/02678292.2012.738311.

13. Węgłowska D., Perkowski P., Piecek W., Mrukiewicz M., Dąbrowski R. The effect of the octan-3-yloxy and the octan-2-yloxy chiral moieties on the mesomorphic properties of ferroelectric liquid crystals. *RSC Adv.*, 2015, **5**, 81003–81012. **DOI**: 10.1039/c5ra14903g.

14. Pramanik A., Das M.K., Das B., Hamplová V., Kašpar M., Bubnov A. Self-assembling properties of lactic acid derivative with several ester linkages in the molecular core. *Phase Transitions*, 2015, **88**, 745–757. **DOI**: 10.1080/01411594.2015.1025782.

15. Gaładyk K., Piecek W., Czerwiński M., Morawiak P., Chrunik M., Raszewski Z. An effect of chiral dopants on mesomorphic and electro-optical properties of ferroelectric smectic mixture. *Liq. Cryst.*, 2019, **46** (15), 2134–2148. **DOI**: 10.1080/02678292.2019.1613689.

16. Dardas D. Tuning the electro-optic and viscoelastic properties of ferroelectric liquid crystalline materials. *Rheologica Acta*, 2019, **58**, 193–201. **DOI**: 10.1007/s00397-019-01129-z.

17. Fitas J., Marzec M., Kurp K., Żurowska M., Tykarska M., Bubnov A. Electro-optic and dielectric properties of new binary ferroelectric and antiferroelectric liquid crystalline mixtures. *Liq. Cryst.*, 2017, **44** (9), 1468–1476. **DOI**: 10.1080/02678292.2017.1285059.

18. Nataf G.F., Guennou M., Scalia G., Moya X., Wilkinson T.D., Lagerwall J.P.F. High-contrast imaging of 180° ferroelectric domains by optical microscopy using ferroelectric liquid crystals. *Appl. Phys. Lett.*, 2020, **116** (21), 212901-1-5. **DOI**: 10.1063/5.0008845.

19. Żurowska M., Dziaduszek J., Szala M., Morawiak P., Bubnov A. Effect of lateral fluorine substitution far from the chiral center on mesomorphic behaviour of highly titled antiferroelectric (S) and (R) enantiomers. *J. Mol. Liq.*, 2018, **267**, 504–510. **DOI**: 10.1016/j.molliq.2017.12.114.

20. Barman B., Das B., Das M.K., Hamplová V., Bubnov A. Effect of molecular structure on dielectric and electro-optic properties of chiral liquid crystals based on lactic acid derivatives. *J. Mol. Liq.,* 2019, **283**, 472–481. **DOI**: 10.1016/j.molliq.2019.03.071.

21. Herman J., Aptacy A., Dmochowska E., Perkowski P., Kula P. The effect of partially fluorinated chain length on the mesomorphic properties of chiral 2',3'-difluoroterphenylates. *Liq. Cryst.,* 2020, **47** (14–15), 2332–2340. **DOI**: 10.1080/02678292.2020.1811410.

22. Iwasaki Y., Yoshino K., Uemoto T., Inuishi Y. Colour switching in ferroelectric smectic liquid crystal by electric field. *Jpn. J. Appl. Phys.*, 1979, **18** (12), 2323–2324. **DOI**: 10.1143/JJAP.18.2323.

23. Pozhidaev E., Chigrinov V.G., Li X.H. Photoaligned ferroelectric liquid crystal passive matrix display with memorized gray scale. *Jpn. J. Appl. Phys.*, 2006, **45**, 875–882. **DOI**:10.1143/JJAP.45.875.

24. Fan F., Srivastava A.K., Chigrinov V.G., Kwok H.S. Switchable liquid crystal grating with sub millisecond response. *Appl. Phys. Lett.*, 2012, **100** (11), 111105-1-4. **DOI**: 10.1063/1.3693601.

25. Brodzeli Z., Silvestri L., Michie A., Guo Q., Pozhidaev E.P., Chigrinov V.G., Ladouceur F. Reflective mode of deformed-helix ferroelectric liquid crystal cells for sensing applications. *Liq. Cryst.*, 2013, **40**, 1427–1435. **DOI**: 10.1080/02678292.2013.807942.

26. Clark N.A., Lagerwall S.T. Submicrosecond bistable electro-optic switching in liquid crystals. *Appl. Phys. Lett.*, 1980, **36** (11), 899–901. **DOI**: 10.1063/1.91359.

27. Clark N.A., Handschy M.A., Lagerwall S.T. Ferroelectric liquid crystal electro-optics using the surface stabilized structure. *Mol. Cryst. Liq. Cryst.*, 1983, **94**, 213–233. **DOI**: 10.1080/00268948308084258.

===

28. Beresnev L.A., Chigrinov V.G., Dergachev D.I., Poshidaev E.P., Fünfschilling J., Schadt M. Deformed helix ferroelectric liquid crystal display: A new electrooptic mode in ferroelectric chiral smectic C* liquid crystals. *Liq. Cryst.*, 1989, **5**, 1171–1177. **DOI**: 10.1080/02678298908026421.

29. Chigrinov V.G., Pozhidaev E., Srivastava A., Qi G., Kwok H.S. Fast ferroelectric liquid crystal modes for field-sequential-color and 3D displays. *SID Symp. Dig. Tech. Pap.*, 2012, **43** (1), 117–120. **DOI**: 10.1002/j.2168-0159.2012.tb05725.x.

30. Guo Q., Brodzeli Z., Pozhidaev E.P., Fan F., Chigrinov V.G., Kwok H.S., Silvestri L., Ladouceur F. Fast electrooptical mode in photo-aligned reflective deformed helix ferroelectric liquid crystal cells. *Opt. Lett.*, 2012, **37**, 2343–2345. **DOI**: 10.1364/OL.37.002343.

31. Srivastava A.K., Hu W., Chigrinov V.G., Kiselev A.D., Lu Y-Q. Fast switchable grating based on orthogonal photo alignments of ferroelectric liquid crystals. *App. Phys. Lett.*, 2012, **101**, 031112-1-4. **DOI**: 10.1063/1.4737642.

32. Pozhidaev E.P., Kiselev A.D., Srivastava A.K., Chigrinov V.G., Kwok H.S., Minchenko M.V. Orientational Kerr effect and phase modulation of light in deformed-helix ferroelectric. *Phys. Rev. E*, 2013, **87** (5), 052502-1-8. **DOI**: 10.1103/PhysRevE.87.052502.

33. Kiselev A.D., Kesaev V.V., Pozhidaev E.P. Orientational Kerr effect in liquid crystal ferroelectrics and modulation of partially polarized light. *J. Phys.: Conf. Ser.*, 2018, **1092**, 012056-1-4. **DOI**: 10.1088/1742-6596/1092/1/012056.

34. Kurp K., Czerwiński M., Tykarska M. Ferroelectric compounds with chiral (S)-1-methylheptyloxycarbonyl terminal chain – their miscibility and a helical pitch. *Liq. Cryst.*, 2015, **42** (2), 248–254. **DOI**: 10.1080/02678292.2014.982222.

35. Kurp K., Czerwiński M., Tykarska M., Bubnov A. Design of advanced multicomponent ferroelectric liquid crystalline mixtures with submicrometre helical pitch. *Liq. Cryst.*, 2017, **44** (4), 748–756. **DOI**: 10.1080/02678292.2016.1239774.

36. Kurp K., Czerwiński M., Tykarska M., Salamon P., Bubnov A. Design of functional multicomponent liquid crystalline mixtures with nano-scale pitch fulfilling deformed helix ferroelectric mode demands. *J. Mol. Liq.*, 2019, **290**, 111329-1-10. **DOI**: 10.1016/j.molliq.2019.111329.

37. Czerwiński M., Gaładyk K., Morawiak P., Piecek W., Chrunik M., Kurp K., Kula P., Jaroszewicz L.R. Pyrimidine-based ferroelectric mixtures–The influence of oligophenyl based chiral doping system. *J. Mol. Liq.*, 2020, **303**, 112693-1-14. **DOI**: 10.1016/j.molliq.2020.112693.

38. Węgłowska D., Perkowski P., Chrunik M., Czerwiński M. The effect of dopant chirality on the properties of self-assembling materials with a ferroelectric order. *Phys. Chem. Chem. Phys.*, 2018, **20** (14), 9211–9220. **DOI**: 10.1039/C8CP01004H.

39. Lalik S., Deptuch A., Fryń P., Jaworska-Gołąb T., Węgłowska D., Marzec M. Physical properties of new binary ferroelectric mixture. *J. Mol. Liq.*, 2019, **274**, 540–549. **DOI**: 10.1016/j.molliq.2018.11.010.

40. Kotova S.P., Samagin S.A., Pozhidaev E.P., Kiselev A.D. Light modulation in planar aligned short-pitch deformed-helix ferroelectric liquid crystals. *Phys. Rev. E*, 2015, **92** (6), 062502-1-13. **DOI**: 10.1103/PhysRevE.92.062502.

41. Mikhailenko V., Krivoshey A., Pozhidaev E., Popova E., Fedoryako A., Gamzaeva S., Barbashov V., Srivastava A.K., Kwok H.S., Vashchenko V. The nano-scale pitch ferroelectric liquid crystal materials for modern display and photonic application employing highly effective chiral components: Trifluoromethylalkyl diesters of p-terphenyldicarboxylic acid. *J. Mol. Liq.*, 2019, **281**, 186–195. **DOI**: 10.1016/j.molliq.2019.02.047.

42. Malik P., Raina K.K., Bubnov A., Chaudhary A., Singh R. Electro-optic switching and dielectric spectroscopy studies of ferroelectric liquid crystals with low and high spontaneous polarization. *Thin Solid Films*, 2010, **519** (3), 1052–1055. **DOI**: 10.1016/j.tsf.2010.08.042.

43. Kula P, Herman J, Chojnowska O. Synthesis and properties of terphenyl- and quaterphenyl-based chiral diesters. *Liq. Cryst.*, 2013, **40** (1), 83–90. **DOI**:10.1080/02678292.2012.733033.

44. Pozhidaev E.P., Torgova S.I., Molkin V.M., Minchenko M.V., Vashchenko V.V., Krivoshey A.I., Strigazzi A. New chiral dopant possessing high twisting power. *Mol. Cryst. Liq. Cryst.*, 2009, **509** (1), 300–308. **DOI**: 10.1080/15421400903054667.

45. Matsumoto T., Fukuda A., Johno M., Motoyama Y., Yui T., Seomun S.S, Yamashita M. A novel property caused by frustration between ferroelectricity and antiferroelectricity and its application to liquid crystal displays-frustoelectricity and V-shaped switching. *J. Mater. Chem.*, 1999, **9**, 2051–2080. **DOI**: 10.1039/A903273H.

46. Drzewiński W., Czupryński K., Dąbrowski R., Neubert M. New antiferroelectric compounds containing partially fluorinated terminal chains. Synthesis and mesomorphic properties. *Mol. Cryst. Liq. Cryst.*, 1999, **328**, 401–410. **DOI**: 10.1080/10587259908026083.

47. Mandal P.K., Jaishi B.R., Haase W., Dąbrowski R., Tykarska M., Kula P. Optical microscopy, DSC and dielectric relaxation spectroscopy studies on a partially fluorinated ferroelectric liquid crystalline compound MHPO(13F)BC. *Phase Transitions*, 2006, **79** (3), 223–235. **DOI**: 10.1080/01411590500500724.

48. Murashiro K., Kikuchi M., Inoue H., Fukushima M., Saito S. Dopant effect on threshold electric field of anti-ferroelectric liquid crystal switching. *Liq. Cryst.*, 1993, **14** (2), 371–380.
DOI: 10.1080/02678299308027652.

49. Sokół E., Drzewiński W., Dziaduszek J., Dąbrowski R., Bennis N., Otón J. The synthesis and properties of novel partially fluorinated ethers with high tilted anticlinic phase. *Ferroelectrics*, 2006, **343**, 41–48.
DOI: 10.1080/00150190600962051.

50. Żurowska M., Dąbrowski R., Dziaduszek J., Garbat K., Filipowicz M., Tykarska M., Rejmer W., Czupryński K., Spadło A., Bennis N., Oton J.M. Influence of alkoxy chain length and fluorosubstitution on mesogenic and spectral properties of high tilted antiferroelectric esters. *J. Mater. Chem.*, 2011, **21** (7) 2144–2153.
DOI: 10.1039/C0JM02015J.

51. Piecek W., Perkowski P., Raszewski Z., Morawiak P., Żurowska M., Dąbrowski R., Czupryński K. Long pitch orthoconic antiferroelectric binary mixture for display applications. *Mol. Cryst. Liq. Cryst.*, 2010, **525**, 160–172. **DOI**: 10.1080/15421401003796223.

52. Piecek W., Bubnov A., Perkowski P., Morawiak P., Ogrodnik K., Rejmer W., Żurowska M., Hamplová V., Kašpar M. An effect of structurally non-compatible additive on the properties of a long-pitch orthoconic antiferroelectric mixture. *Phase Transitions*, 2010, **83** (8), 551–563. **DOI**: 10.1080/01411594.2010.499496.

53. Pozhidaev E.P., Vashchenko V.V., Mikhailenko V. V., Krivoshey A.I., Barbashov V.A., Shi L., Srivastava A.K., Chigrinov V.G., Kwok H.S. Ultrashort helix pitch antiferroelectric liquid crystals based on chiral esters of terphenyldicarboxylic acid. *J. Mater. Chem. C,* 2016, **4**, 10339–10346. **DOI**: 10.1039/C6TC04087J.

Contribution of the authors:
*[1]**Czerwiński Michal** – development of the research concept and planning of the experiment, including the compositions of the developed mixtures; performing measurements of the parameters of the helicoid structure, director angle, spontaneous polarization, switching times and rotational viscosity of chiral phases of chiral mixtures; participation in collecting and analyzing the results; participation in the preparation of the manuscript.*
*[2]**Tykarska Marzena** – complicity in development of the research concept, including the compositions of the developed mixtures; participation in the preparation of the manuscript; carrying out the publication process.*
*[3]**Kula Przemyslaw** – participation in the preparation of the manuscript.*

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