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FERROELECTRIC SMECTIC C* PHASE WITH SUB-WAVELENGTH HELIX PITCH INDUCED IN A NEMATIC LIQUID CRYSTAL BY CHIRAL NON-MESOGENIC DOPANTS

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We report the development of chiral smectic C* (SmC*) ferroelectric materials with a short helix pitch \( p_0 < 150 \text{ nm} \) obtained by mixing a nematic liquid crystal (NLC) and chiral non-mesogenic dopants. Chiral dopants are optically active lactates based on terphenyldicarboxylic acid, and the NLC is a binary eutectic mixture of phenyl- and biphenylpyrimidines. The appearance of the SmC* phase in mixtures was confirmed by dielectric, optical and electro-optical measurements. The proposed method for the elaboration of smectic C* material makes it possible to create innovative electro-optical media that combine the mechanical stability of NLC and a high switching frequency of ferroelectric liquid crystals. The high twisting power of chiral lactates in the developed nematic matrix made it possible to obtain a satisfactory optical quality of induced SmC* in electro-optical cells that can efficiently operate up to frequency of 3 kHz.

Key words: ferroelectric liquid crystal, chiral dopants, nematic matrix, helix pitch.

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СМЕКТИЧЕСКАЯ C* СЕГНЕТОЭЛЕКТРИЧЕСКАЯ ФАЗА С СУБВОЛНОВЫМ ШАГОМ СПИРАЛИ, ИНДУЦИРОВАННАЯ В НЕМАТИЧЕСКОМ ЖИДКОМ КРИСТАЛЛЕ ХИРАЛЬНЫМИ НЕМЕЗОГЕННЫМИ ДОБАВКАМИ

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Мы сообщаем о разработке хиральных смектических C* (SmC*) сегнетоэлектрических материалов с коротким шагом спирали \( p_0 < 150 \text{ нм} \), полученных путем смешивания нematicического жидкого кристалла (НЖК) и хиральных немезогенных соединений. Хиральные добавки представляют собой оптически активные лактаты на основе терфенилгидрокарбоновой кислоты, а НЖК является бинарной эвтектической смесью фенил- и бифенилпиримидинов. Возникновение SmC* фазы в смесях подтверждено

diэлектрическими, оптическими и электрооптическими измерениями. Предлагаемый способ получения смектических C* материалов позволяет создавать инновационные электрооптические среды, сочетающие механическую устойчивость НЖК и высокую частоту переключения сегнетоэлектрических жидких кристаллов. Высокая закручивающая способность хиральных лактатов в разработанной нематической матрице позволяла получить удовлетворительное оптическое качество индуцированных смектик C* в электрооптических ячейках, которые могут эффективно работать на частотах до 3 кГц.

Ключевые слова: сегнетоэлектрический жидкий кристалл, хиральные добавки, нематическая матрица, шаг спирали.

Introduction

Smectic C* ferroelectric liquid crystals (FLC’s) attract attention of scientists and engineers due to their potential usage in fast display and photonic devices for different applications, operating in the microsecond range [1–3]. The simplest method to create FLC compositions with the requested properties is to add a chiral dopant into a non-chiral smectic C matrix [4, 5]. It is necessary to elaborate a smectic C matrix with the required properties, such as the relevant phase transitions sequence, low rotational viscosity, and appropriate molecular tilt angle. Finally, it is necessary to choose a chiral dopant that provides acceptable values of the spontaneous polarization and the helix pitch of the mixture [6]. For the first time we have induced a chiral smectic C* phase by adding a non-mesogenic chiral dopant – the diester of optical active 2-heptanol and terphenyldicarboxylic acid to the nematic liquid crystal (NLC) 5-hexyl-2-[4-(octyloxy)phenyl]pyrimidine [7]. The smectic C* obtained in such a way can flow, allowing to restore the ferroelectric liquid crystal layer structure in electro-optical cells after the action of mechanical stress, as it happens with the cells filled with NLC. The material developed in [7] can operate only in the surface stabilized ferroelectric liquid crystal (SSFLC) mode since its helix pitch $p_0 > 1 \mu m$.

The main task of this work is the elaboration of the FLC material with a short (sub-wavelength) helix pitch following the procedure described above. Such FLC materials are suitable for using in deformed helix ferroelectric (DHF) electrooptical mode [8], which is favorable for the following applications: field sequential color (FSC) displays [9–11], generation of axial-symmetric vortex light fields [12], light polarization modulation [13, 14], switching of fiber-optic communication channels [15].

Experimental

Elaboration of the sub-wavelength helix pitch
ferroelectric smectic C*

As an achiral nematic matrix, two-component mixture consisting of 2-(4'-heptylbiphenyl-4-yl)-5-octyl-pyrimidine (I), (BPP-87) [16] and 5-hexyl-2-[4-(octyloxy)phenyl]pyrimidine (II), (PP-608) (commercial available material) was developed:

$$\text{C}_8\text{H}_{17}-\text{N}$$

$$\text{C}_8\text{H}_{17}-\text{N}$$

(I)

(II)

The phase diagram of the mixture is presented on the Fig. 1.

Fig. 1. Phase diagram of the mixtures of pyrimidines (I) and (II). The eutectic mixture of nematic phase is at 20 mol. % of compound BBP-87 and 80 mol. % of compound PP-608.
Transition temperatures were detected using a Mettler-Toledo FP-5 thermo-stage apparatus (Greifensee, Switzerland) with a polarising Leitz microscope (Wetzlar, Germany) and via differential scanning calorimetry (DSC) by means of Perkin-Elmer DSC-7 (Waltham, Massachusetts, USA).

Esters of p-terphenyldicarboxylic acid and (S)-alkan-2-yl-(S)-2-hydroxypropanoates, first described in [17, 18] were chosen as chiral compounds of the smectic C* mixtures. In contrast to the synthesis used in the patent [18], chiral dopants were synthesized in this work according to the following scheme:

![Chemical Structure](attachment:image1.png)

NMR spectra were acquired on Bruker Avance 600 MHz spectrometer at room temperature. High resolution and accurate mass measurements were carried out using Thermo Scientific LTQ Orbitrap XL mass spectrometers. Analytical thin layer chromatography (TLC) was carried out with silica gel 60 (230–400 mesh) and visualized with UV lamp (254 nm). Column chromatography was performed on silica gel 60 (230–400 mesh).

L- (+)-Lactic acid (85% aqueous solution), (2S)-octan-2-ol, (2S)-nonan-2-ol, p-terphenyl-4,4'-dicarboxylic acid are commercially available materials. 1,1':4',1''-Terphenyl-4,4''-dicarboxylic acid was obtained from p-terphenyl-4,4''-dicarboxylic acid according to the procedure, described in [19].

(1S)-1-Methylheptyl (2S)-2-hydroxypropanoate (1a)

A mixture of L-(+)-lactic acid (85% aqueous solution) (ca. 1.54 g, 14.52 mmol), (2S)-octan-2-ol (1.89 g, 14.52 mmol) and p-toluensulfonic acid monohydrate (276 mg, 1.45 mmol, 10 mol.%) in benzene (60 mL) was heated under reflux with 20-mL Dean-Stark trap for 4 h. Reaction mixture was allowed to cool to ambient temperature and concentrated under reduced pressure. The product 1a was purified by column chromatography on silica gel (eluent petroleum ether – ethyl acetate 5:1). Yield 2.20 g (75%); colorless oil. HRMS (ESI) m/z: [M – H] Calculated for C_{18}H_{23}O_{3} 301.1496; Found 301.1494.

(1S)-1-Methyloctyl (2S)-2-hydroxypropanoate (1b)

The substance 1b was synthesized similar to 1a described above. A mixture of L-(+)-lactic acid (85% aqueous solution) (ca. 370 mg, 3.47 mmol), (2S)-nonan-2-ol (500 mg, 3.47 mmol) and p-toluensulfonic acid monohydrate (67 mg, 0.35 mmol, 10 mol.%) were taken into the reaction. The product 1b was purified by column chromatography on silica gel (eluent petroleum ether – ethyl acetate 5:1). Yield 480 mg (64%); colorless oil. HRMS (ESI) m/z: [M – H] Calculated for C_{19}H_{25}O_{3} 315.1653; Found 315.1650. The chemical structure and purity of the substances 1a and 1b were confirmed by 1H NMR and 13C NMR spectroscopy.

Bis[(1S)-1-methyl-2-{[(1S)-1-methylheptyl]oxy}-2-oxoethyl] 1,1':4',1''-terphenyl-4,4''-dicarboxylate (2a)

To a refluxed solution of 1,1':4',1''-terphenyl-4,4''- dicarboxylic dichloride (1.50 g, 4.22 mmol) in dry toluene (50 mL) the solution of (1S)-1-methylheptyl (2S)-2-hydroxypropanoate (2.13 g, 10.53 mmol) in toluene (20 mL) and dry pyridine (5.4 mL) was added dropwise sequentially. The resulting mixture was heated under reflux for 9 h. After cooling to the ambient temperature, the precipitate was filtered off and washed with ethyl acetate (20 mL).
The resulting filtrate was concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent petroleum ether–ethyl acetate 5:1). The eluate was concentrated under reduced pressure. The subsequent recrystallization from petroleum ether afforded the desired product 2b as white crystals. Yield 943 mg (33\%). HRMS (ESI) \text{m/z}: [M + H]^+ Calculated for C_{62}H_{53}O_{8}^+ 687.3891; Found 687.3888.

Melting point detected by microscopy is 92.4–93.0 °C. Melting point detected via DCS is 91.86 °C, melting heat is J/g = 68.32

**Bis[(1S)-1-methyl-2-[[[(1S)-1-methyloctyl]oxy]-2-oxoethyl] 1,1':4',1''-terphenyl-4,4''-dicarboxylate (2b)**

![Chemical structure of 2b](image)

The substance 2b was synthesized similar to 2a described above. To a refluxed solution of 1,1':4',1''-terphenyl-4,4''-dicarboxyl dichloride (298 mg, 0.84 mmol) in dry toluene (10 mL) the solution of (1S)-1-methyloctyl (2S)-2-hydroxypropanoate (416 mg, 1.93 mmol) in toluene (5 mL) and dry pyridine (1.0 mL) was added dropwise sequentially, etc. The subsequent recrystallization from petroleum ether afforded the desired product 2b as white crystals. Yield 206 mg (34\%). HRMS (ESI) \text{m/z}: [M + H]^+ Calculated for C_{42}H_{52}O_{8}^+ 715.4204; Found 715.4213.

The chemical structure and purity of the substances 2a and 2b were confirmed by \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectroscopy. Melting point detected by microscopy is 91.5–92.3 °C. Melting point detected via DCS is 90.79 °C, melting heat is J/g = 68.32.

**Techniques for preparation and investigations of SmC* cells.**

The FLC cells with homogeneous planar alignment were fabricated using rubbed polyimide PMDA-ODA [20, 21] as aligning layers that cover indium tin oxide (ITO) layers deposited onto glass substrates. The cell gap of assembled experimental cells was formed with glassy spacers and then fixed by epoxy glue. The cells were filled with FLCs in isotropic phase by capillary action.

Measurements of the helix pitch were performed with the cells that were aligned homeotropically (the helix axes of the mixtures in SmC* phase were aligned perpendicular to the substrates). The homeotropic alignment of the mixtures has been accomplished by spin-coating glass plates with 40-nm-thick layer of stearic acid chromium salt followed by heating at temperature 100 °C for 10 min [22]. The helix pitch was measured due to angular dependence of selective reflection from the SmC* phase [23].

Phase transition temperatures were determined using differential scanning calorimetry (DSC) and polarizing microscopy (POM), which also allows to take micro-photographs of liquid crystal textures. For this purpose, a polarizing microscope POLAM-P-312 was used.

Spontaneous polarization \( P_s \) was measured using the field-reversal method [24], and rotational viscosity \( \gamma_\phi \) was evaluated from the measurements of the electrooptical response time and \( P_s \), as it has been reported in [25].

**Results and discussion**

A variety of mixtures have been developed containing a binary eutectic nematic matrix (ENLC) and the synthesized chiral dopants of various concentrations. All such mixtures, which have been used to construct the phase diagram at mixing of ENLC with (2a) or (2b) compounds (Fig. 2), were investigated by DSC, POM, dielectric and electro-optical methods.

![Phase diagram of ENLC matrix and chiral dopants](image)
The phase diagram shows that at the dopant 2b concentration of 3.2 mol. % the eutectic mixture exists and the enantiotropic smectic C* is induced at the temperature higher than 22.3 °C. At the dopant 2a the phase diagram is very similar, but the eutectic mixture occurs when the concentration of 2a equals to 9.1 mol. %.

Evidently, at concentrations of the chiral dopant 2b different from the eutectic one, there is a wide temperature range of the two-phase region Cr + SmC* (Fig. 2). However, when mixtures are cooled from isotropic phase, the SmC* phase exists in a supercooled state (without the two-phase region) till +15 °C usually within several days. This property allowed us to measure the main parameters of the induced SmC* phase in a wide temperature range: the helix pitch, spontaneous polarization, rotational viscosity, and the tilt angle of molecules in smectic layers.

We have measured the temperature dependencies of the SmC* mixtures helix pitch at various concentrations of the chiral dopant 2b (Fig. 3). In particular, for the ENLC eutectic mixture with chiral dopant 2b the helix pitch exceeds 150 nm at any temperature. Note that helix pitch $p_0 = 100$ nm was measured at the concentration of 2b equal to 9.1 mol. % and at temperature 17 °C.

\[
HTP = \frac{1}{p_0c}, \quad (1)
\]

where $c$ is a chiral dopant concentration. For the chiral dopant 2b, at $c = 9.09$ mol. % and temperature 17 °C HTP $\approx 109$ μm$^{-1}$ that can be calculated by the formula (1) and the data shown in Fig. 3. For a comparison, the maximum HTP known before for chiral dopants was estimated as 46 μm$^{-1}$ [16]. Thus, in this work, a chiral dopant with the highest HTP known to date was synthesized.

The chiral dopant 2a exhibits HTP smaller than the dopant 2b. HTP of 2a calculated at $c = 9.1$ mol. % (eutectic point) is equal to 78 μm$^{-1}$. This value is confirmed by the data presented in Fig. 4, where $p_0 = 140$ nm at temperature 18 °C.

Fig. 4. Dependencies of the spontaneous polarization of the eutectic mixture (ENLC matrix and chiral dopant 2a) at heating from crystal to isotropic phase and cooling down. The helix pitch of the same mixture FLC-661 was measured on cooling.

Fig. 4 also presents the temperature dependencies of spontaneous polarization upon heating and cooling of the eutectic mixture of the non-chiral nematic matrix ENLC and the chiral non-mesogenic compound 2a. Let us emphasize that this mixture (FLC-661) is the eutectic of three compounds: BPP-87, PP-608 and 2a. The eutectic of the mixture FLC-661 is confirmed both by a very narrow temperature interval of the phase transition from crystal to SmC* phase (1.8 °C) and the absence of the temperature hysteresis of the spontaneous polarization (Fig. 4). FLC-661 has the maximum spontaneous polarization in enantiotropic Sm C* phase near 32 nC/cm$^2$. The $P_s$ value is approximately 1.5 times greater than the spontaneous polarization of the mixture NFLC-1, previously induced in the NLC matrix by a chiral non-mesogenic dopant [7].
The alignment quality of FLC-661 is illustrated in Fig. 5. It is obvious that the defects density is rather low, what characterizes the quite satisfactory optical quality of the SmC* layer in the electro-optical cell.

Fig. 5. Microphotographs of planar aligned FLC-661 6.7 μm thick layer textures taken by the polarizing microscope at 23 °C with crossed polarizer and analyzer. Rubbed 20 nm polyimide PMDA-ODA were used as aligning layers. a – The helix axis is parallel to the polarizer plane, b – the angle between the helix axis and the polarizer plane is 45 deg.

Thus, FLC-661 developed by us combines all the necessary properties that allow it to be used in electro-optical devices operating on the basis of the DHF-electrooptical mode [8]. This SmC* material provides the electrooptical modulation up to the frequency of 3 kHz (see Fig. 6) with the contrast ratio of about 45:1 in the white light.

Fig. 6. Modulation of the white light intensity passing through the DHF cell filled with FLC-661 and placed between two crossed dichroic polarizers (bottom curve) under the electric field (top curve) applied to the cell. The cell gap is 6.7 μm, the temperature is 23 °C.

The eutectic mixture of ENLC with the chiral dopant 2b contains a very low concentration of the dopant (3.2 mol. %). In order to compare the influence of the dopants 2a and 2b on the FLC mixtures properties, we prepared a mixture with the same content of dopant 2b equal to 9.1 mol. % (FLC-661/7) as in FLC-661. Temperature dependences of the rotational viscosity γ₀ and the tilt angle θ of molecules in smectic layers for the mixture FLC-661/7 are presented in Fig. 7.

Fig. 7. Temperature dependences of tilt angle θ and rotational viscosity γ₀ for the mixture FLC-661/7 in the cooling mode.

It turned out that these dependencies on cooling from the isotropic phase are practically equivalent for the mixtures FLC-661/7 and FLC-661. The same can be said about the temperature dependencies of spontaneous polarization in the cooling regime from the isotropic phase (Pᵣ of FLC-661 is presented in Fig. 4). On the other hand, the helical twisting power of the chiral dopant 2b is essentially higher with respect to 2a. Due to this, the helix pitch of the induced SmC* mixture FLC-661/7 reaches 100 nm (Fig. 3), while for FLC-661 it is 140 nm (Fig. 4).

Conclusion

In this work, two new chiral compounds were synthesized: bis(1S)-1-methyl-2-[(1S)-1-methylheptyl]oxy]-2-oxoethyl)-1,1′:4′,1″-terphenyl-4,4″-dicarboxylate (2a) and bis(1S)-1-methyl-2-[(1S)-1-methylcyclooctyl]oxy]-2-oxoethyl]-1,1′:4′,1″-terphenyl-4,4″-dicarboxylate (2b). These compounds were used as chiral dopants to induce a chiral SmC* phase by introducing them into a specially designed eutectic nematic matrix. As a result, for the first time, we suc-
ceeded to induce a ferroelectric SmC* phase with a subwavelength helix pitch of the order of 100–150 nm in a nematic matrix. It was experimentally proved that dopants 2a and 2b possess the highest known helical twisting power: 78 μm⁻¹ and 109 μm⁻¹, respectively. The electro-optical cells based on the elaborated mixtures manifest a satisfactory optical quality of the induced SmC* and can efficiently operate at frequencies up to 3 kHz in DHF mode.

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