

Research Article

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**LATERAL SUBSTITUTION AS EFFECTIVE TOOL FOR TUNING
SELF-ORGANISING BEHAVIOUR OF CHIRAL MESOGENS**

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Abstract. Thermotropic liquid crystals belong to an exciting class of self-organising materials, which are broadly utilised now, and, definitely will find advanced applications in future. The combination of fluidity and ordering together with specific electro-optical properties assures their extraordinary practical usefulness. However, the molecular structure – mesomorphic property relationship is still far to be well-established and understood despite more than a hundred years of their existence and intensive study. The design, synthesis and investigation of new liquid crystalline materials with various molecular structure type (rod-like, bend-shaped, disc-like, etc.) and weight (low molar mass, macromolecular) still remain an actual and highlighted task. In this mini-review we discuss relatively broad sub-class of chiral calamitic liquid crystalline materials derived from the lactic acid and give some specific examples on effective tuning of their mesomorphic and electro-optical behaviour using various types of lateral substitution of molecular core. Fluorine, chlorine, bromine and iodine atoms, as well as bulky methyl and methoxy groups are used as lateral substituents on the phenyl ring far from the chiral lactate group. The materials discussed in this work can be potentially used as smart dopants for design of advanced multicomponent mixtures targeted for future applications in opto-electronics and photonics.

Key words: liquid crystals, lateral substitution, chirality, smectic phase, ferroelectric smectic phase, lactic acid, chiral lactate

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Научная статья

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ЛАТЕРАЛЬНОЕ ЗАМЕЩЕНИЕ КАК ЭФФЕКТИВНЫЙ ПОДХОД
К УЛУЧШЕНИЮ ПРОЦЕССОВ САМООРГАНИЗАЦИИ ХИРАЛЬНЫХ МЕЗОГЕНОВВера Хамплова*, Сергей Миронов, Мартин Цигл, Зузана Бёмова,
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Аннотация. Термотропные жидкие кристаллы относятся к впечатляющему классу самоорганизующихся материалов, которые в настоящее время широко используются и несомненно имеют большой потенциал для перспективных практических приложений в будущем. Сочетание текучести и упорядоченности вместе со специфическими электрооптическими свойствами обеспечивает их исключительную применимость в различных областях. Однако взаимосвязь «молекулярная структура – мезоморфные свойства» к настоящему времени еще далеко не установлена и не понята, несмотря на более чем сто летнюю историю их существования и интенсивных исследований. Разработка, синтез и исследование новых жидкокристаллических материалов с различным типом молекулярной структуры (стержнеобразной, изогнутой, дискообразной и пр.) и разной молекулярной массой (низкомолекулярные, высокомолекулярные) по-прежнему остаются актуальной и особо важной задачей. В этом мини-обзоре мы обсуждаем относительно широкий подкласс хиральных каламитных жидкокристаллических материалов, производных молочной кислоты, и приводим некоторые конкретные примеры эффективной настройки их мезоморфного и электрооптического поведения, используя различные типы латерального замещения ядра молекулы. Атомы фтора, хлора, брома и йода, а также объемные метильные и метокси-группы используются в качестве боковых заместителей в фенильном кольце вдали от хиральной группы молочной кислоты. Материалы, обсуждаемые в этой работе, потенциально могут быть использованы в качестве «умных» добавок для дизайна усовершенствованных многокомпонентных смесей, предназначенных для будущих применений в оптоэлектронике и фотонике.

Ключевые слова: жидкие кристаллы, латеральные заместители, хиральность, смектическая фаза, сегнетоэлектрическая смектическая фаза, молочная кислота, хиральный лактат

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Introduction

Thermotropic liquid crystals (LC) belong to an exciting class of self-organising soft materials having high potential for advanced practical applications in future. The field of liquid crystals is truly interdisciplinary as it combines basic features of physics, chemistry, materials science, mathematics, medicine, biology, and engineering [1-4]. The combination of fluidity and ordering together with amazing optical, electro-optical and dielectric properties assures their extraordinary practical usefulness for future technological applications. Among the self-organised supramolecular smart sys-

tems, LCs represent an encouraging class of soft materials, which can exhibit stable supramolecular helical organisations if the mesogens are chiral. Since the discovery of ferroelectric liquid crystalline phase in 1975 [5], its unique physical properties have opened a prospect to a large variety of electro-optical applications in real-time optical processing, computing, control and measuring devices, etc., which stimulated a great progress in the design and investigation of chiral smectic structures [6]. Possible applicability of polar LC phases and structures puts high demands on understanding of the basic and advanced physical properties of new chiral LC materials.

However, during last decades of intense research, it has been shown that to reach the desired specific mesomorphic and electro-optical properties in a single molecular structure is almost impossible. This problem can be solved by the design of binary and multicomponent mixtures composed by structurally similar [7–10] or structurally different [11–14] molecules mixed-up in a definite quantity. Incorporation of various polymerisable groups, for example vinyl [15–16], acrylate [17–21], methacrylate [22–24], or various functional photo-active moieties (azo group [16–17, 25–25], cinnamoyl group [27], hydrazone [28], spiropyran [29], etc.) assures the induction of supplementary functionality and may results in extraordinary mesomorphic and electro-optical behaviour. During last years, various nanocomposite materials exhibiting liquid crystalline behaviour attract a lot of attention, for example: (i) nanocomposites, in which liquid crystalline matrix is doped by nano-sized objects (for example, various nanoparticles [30], single/multiwall carbon nanotubes [31–33], etc.); (ii) nanocomposites, in which liquid crystal is used as an active component (for example, photo-active [34] or ferroelectric LC [35] filled in the porous polyethylene film, or photo-controllable photonic crystals based on porous silicon filled with photochromic LC mixture [36], etc.); (iii) nanocomposites, in which LC materials are used as dopants for increasing the power conversion efficiency of organic photovoltaic solar cells [37–39].

Design and synthesis of new chiral liquid crystalline materials with definite mesomorphic and electro-optical properties [10–11, 40–41] still remain a crucial challenge for certain advanced applications. It requires a deep knowledge of the molecular structure – resulted property correlation to assess their impact on mesomorphic behaviour [6]. Every specific part of a molecule, namely the type of molecular core, the type and place of lateral substituent, the structure and length of chiral as well as achiral part of terminal alkyl chain, plays a crucial role and strongly influences the mesomorphic, electro-optical and dielectric properties of chiral liquid crystals [25]. Design of new chiral LC materials and keeping under control their molecular structure is an effective tool to tune the resulting material properties and also supply new materials for development of advanced mixtures. Last years, many conventional techniques used for establishing the mesomorphic and electro-optical behaviour of chiral smectic LC materials were modified and extended, but also complemented by advanced investigations using the deuterium ^2H -NMR spectroscopy to study orientational order pa-

rameter [42–46] and the neutron spin-echo spectroscopy [46] to evaluate the dynamics and conformational properties of chiral LC phases.

The type of chiral centre is very important while designing chiral LC materials. In this term, the chiral lactate group is one of the exceptional possibilities. There are several substantial advantages of the lactic acid derivatives [7, 41, 47–51], as a subclass of chiral self-assembling materials, that makes them very attractive [52]. Specifically, their attractiveness consists of the following:

- (i) the occurrence of a broad variety of basic LC phases, including cholesteric, paraelectric, ferroelectric and antiferroelectric smectic phases as well as a number of frustrated phases, like the twist grain boundary – TGBA* and TGBC* phases [53], cubic SmQ* phase [54] and re-entrant orthogonal and tilted phases [42, 55–56];
- (ii) the utilisation of the lactic unit as a precursor of chiral centre considerably minimises the synthetic costs with respect to the most commonly used chiral precursors (e.g., (S)-2-octanol or (S)-2-methylbutan-1-ol);
- (iii) the melting points in the range of 5–70 °C are often desirable for application purposes and the LC phases can easily be supercooled below the room temperature;
- (iv) the lactic acid derivatives usually show no aging and are highly thermally as well as chemically stable and, finally,
- (v) good miscibility with LC materials of different chemical structure makes the lactic acid derivatives truly smart materials with high application potential. Due to all above mentioned properties, and especially the last one (v), lactic acid derivatives demonstrate their high ability to be used as functional dopants for the design and tailoring of advanced multicomponent LC mixtures [9, 11–12, 57–58] and various LC composite materials [31–34, 37–38]. They are also effective for controllable tuning of properties.

The type and place of lateral substitution in molecular core play a crucial role [59–60] as the π -electron density of substituted aromatic rings, which is strongly influenced by the character of atom used for substitution, affects the intermolecular interactions (packing) in smectic layers of ferroelectric SmC* phase due to donor–acceptor coupling. However, in the cases, when the lateral substitution is placed far from a chiral centre, the direct influence upon the chiral centre is not expected. The most functional lateral substituents placed in various positions of phenyl and biphenyl aromatic rings of molecular core [25, 61–63], which are broadly used

for the design of liquid crystalline materials, are the halogen atoms (fluorine [64–69], chlorine [67, 70], bromine [68, 71–72], iodine [73–75]) and also bulky methyl [15, 43, 61–62, 76] and methoxy [15, 61, 63] groups.

However, double substitution might suppress smectic behaviour and cholesteric phase starting to be favourable, as for example in the case of dimethyl substitution [77–78]. There is no doubt that the type of lateral substitution results in various effects but unluckily there is no general rule as the place of lateral substitution also plays a major role on the resulting mesomorphic, electro-optic and dielectric behaviour even of the molecules with the same molecular core and flexible terminal chains.

The *main objective* of this work is to establish the effect of lateral substitution in molecular core on

mesomorphic behaviour of the specific class of chiral calamitic lactic acid derivatives. An overall target is to contribute to better understanding of the molecular architecture – self-organising property relationship of this class of liquid crystalline materials and to summarise the results obtained during several years of intense investigations.

Materials

Two specific series of chiral liquid crystalline materials were selected to demonstrate the effect of lateral substitution far from the chiral lactate group on fine tuning of mesomorphic and electro-optical properties (see Table 1 and 2).

Table 1. General chemical structure of the *H*-subseries with the indication of lateral substitution in *ortho*-position to the non-chiral alkoxy chain

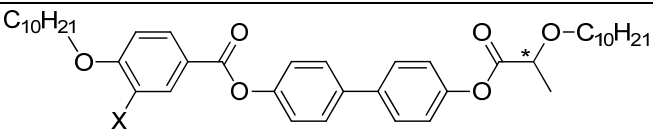
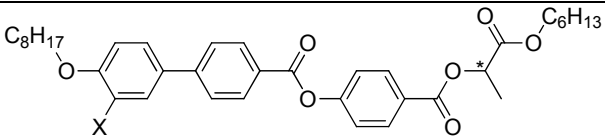
			
	Full compound name:	Substituent X	References
H 10/10	4'-((2-(decyloxy)propanoyl)oxy)-[1,1'-biphenyl]-4-yl-4-(decyloxy)benzoate	Hydrogen atom	[46, 61, 78–80]
F 10/10	4'-((2-(decyloxy)propanoyl)oxy)-[1,1'-biphenyl]-4-yl-3-fluoro-4-(decyloxy)benzoate	Fluorine atom	[68]
Cl 10/10	4'-((2-(decyloxy)propanoyl)oxy)-[1,1'-biphenyl]-4-yl-3-chloro-4-(decyloxy)benzoate	Chlorine atom	[81–83]
Br 10/10	4'-((2-(decyloxy)propanoyl)oxy)-[1,1'-biphenyl]-4-yl-3-bromo-4-(decyloxy)benzoate	Bromine atom	[68]
M 10/10	4'-((2-(decyloxy)propanoyl)oxy)-[1,1'-biphenyl]-4-yl 4-(decyloxy)-3-methylbenzoate	Methyl group	[43, 61, 76, 78]
MO 10/10	4'-((2-(decyloxy)propanoyl)oxy)-[1,1'-biphenyl]-4-yl 4-(decyloxy)-3-methoxybenzoate	Methoxy group	[61, 78, 84]

Table 2. General chemical structure of the *ZL*-subseries with the indication of lateral substitution (chlorine, bromine and iodine atoms) in *ortho*-position to the non-chiral alkoxy chain

			
	Full compound name:	Substituent X	References
ZL 8/6	4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl-4'-(octyloxy)-[1,1'-biphenyl]-4-carboxylate	Hydrogen atom	[7, 85]
BCl 8/6	4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl-3'-chloro-4'-(octyloxy)-[1,1'-biphenyl]-4-carboxylate	Chlorine atom	[85–86]
BBr 8/6	4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl-3'-bromo-4'-(octyloxy)-[1,1'-biphenyl]-4-carboxylate	Bromine atom	[53, 85, 87]
BI 8/6	4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl-3'-iodo-4'-(octyloxy)-[1,1'-biphenyl]-4-carboxylate	Iodine atom	[88]

Both series possess three phenyl ring molecular core. The ***H-subseries*** has a biphenyl benzoate core with a 2-alkoxy-propionate chiral part. The ***ZL-subseries*** has the molecular core derived from the 4-hydroxybiphenyl-4'-carboxylic acid and the chirality is introduced by the chiral lactate group. Quite a large variety of lateral substituents is used, specifically the fluorine, chlorine, bromine and iodine atoms, as well as the methyl and methoxy groups. The general chemical structures of both sub-series are presented in Table 1 and Table 2, respectively, together with the specific references related to the design, synthesis and self-organising properties of these materials structures (in some cases, the length of alkyl chains might be different).

Experimental

The *sequence of mesophases* was determined by the observation of characteristic textures and their changes in a polarising optical microscope (POM) – Nikon Eclipse E600POL (Nikon, Tokyo, Japan). Planar cells (bookshelf geometry) of 5 μm and 12 μm thickness (glasses with Indium Tin Oxide transparent electrodes ($5 \times 5 \text{ mm}^2$)) were supplied by Military University of Technology (Warsaw, Poland). The cells were filled with the studied material in isotropic phase by means of capillary action. The heating/cooling stage Linkam LTS E350 (Linkam, Tadworth, UK) with a TMS 93 temperature programmer was used for temperature control, which allows temperature stabilisation within $\pm 0.1 \text{ K}$.

Phase transition temperatures were determined by differential scanning calorimetry (DSC) using Perkin-Elmer DSC8000 calorimeter (PerkinElmer, Shelton, CT, USA). The samples of about 4–8 mg, hermetically sealed in aluminium pans, were placed into the calorimeter chamber filled with nitrogen. For the precise evaluation of phase transition temperatures, the calorimetric measurements were performed on cooling/heating runs at a rate of 5 K min^{-1} . The temperature and enthalpy change values were calibrated on the extrapolated onset temperatures and enthalpy changes of the melting points of water, indium and zinc.

Spontaneous polarisation values, P_s , were determined from the polarisation current peak at driving of the sample with a triangular electric field at a frequency of 30 Hz and an electric field magnitude of $10 \text{ V}/\mu\text{m}$.

The driving voltage was supplied from an Agilent 33210A (Agilent Technologies, Santa Clara, CA, U.S.A.) function generator amplified with a linear amplifier providing the maximum amplitude of about $\pm 100 \text{ V}$. The Tektronix DPO4034 digital oscilloscope (Tektronix Co., Beaverton, Oregon, U.S.A.) provided information about the switching current profile versus time. The experiments were driven by the specific homemade software [11]. **Spontaneous tilt angle** values, θ_s , have been determined optically using well aligned samples at a bookshelf-like surface stabilised structure, and observing the difference between extinction positions at crossed polarisers under opposite d.c. electric fields $\pm 40 \text{ kV}\cdot\text{cm}^{-1}$. The tilt angle is an angle between the long molecular axis and the smectic layer normal.

Results and discussion

In this section, the results on mesomorphic behaviour as well as electro-optical characteristic of two selected subseries of lactic acid derivatives with different molecular core and various types of lateral substituents placed far from chiral molecular chain (see Table 1 and Table 2) will be presented and discussed. Specifically, we discuss the effect of lateral substitution on sequence of mesophases, phase transition temperatures, values of spontaneous polarisation and tilt angle of the selected materials.

Mesomorphic behaviour

The mesomorphic behaviour of compounds of the ***H-subseries*** determined by POM and DSC is summarised in Table 3. The characteristic microphotographs of textures of different mesophases detected for individual compounds of ***H-subseries*** are presented in Fig. 1. It has been found that materials with such chemical structure possess quite high melting points and a considerable temperature range of the mesophase possess the monotropic character (monotropic means that the whole phase, or its part, is observed on cooling only). All compounds of this subseries form the tilted ferroelectric smectic C^* phase (SmC^*) over a broad temperature range before the onset of crystal phase (Cr).

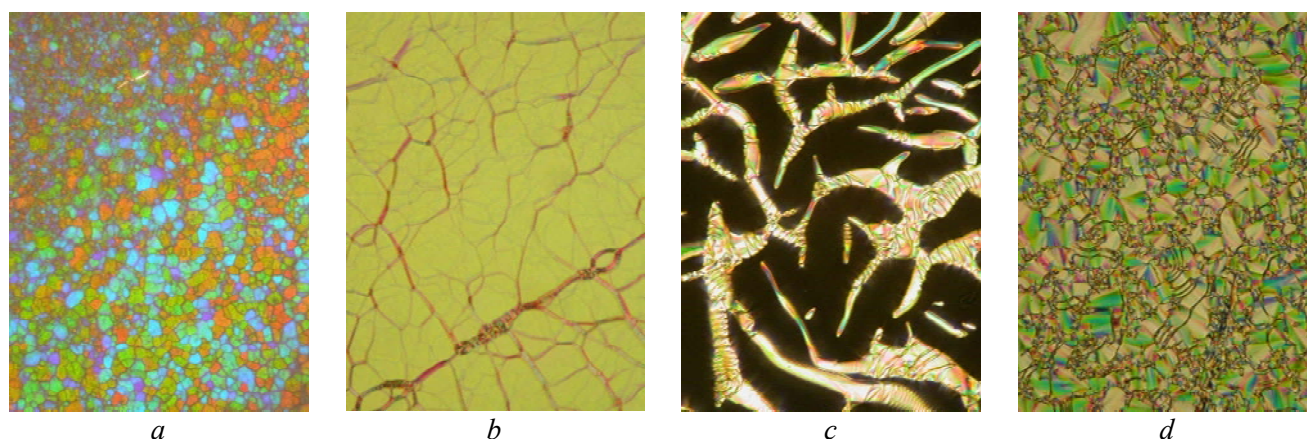


Fig. 1. Microphotographs of characteristic textures obtained on cooling of the laterally substituted lactic acid derivatives of **H-subseries**: *a* – platelet texture of blue phase (BP) of **M 10/10** at 90.5 °C, *b* – oily streaks texture of cholesteric N* phase of **M 10/10** at 89.5 °C, *c* – growth of bâtonnets of SmC* phase with clearly visible dechiralisation lines on cooling from isotropic melt of **H 10/10** at 130.0 °C, *d* – broken fan texture of SmC* phase of **M 10/10** at 75.0 °C. The width of all the microphotographs is about 250 µm

Lateral substitution by the methyl group (the case of compound **M 10/10**) induces Blue Phase (BP) and cholesteric phase (N*) in a very narrow temperature range on cooling from isotropic (Iso) phase (see Fig. 1, *a*, *b*). Lateral substitution by fluorine atom induces orthogonal non-polar hexagonally ordered smectic B (SmB) phase, which appears between SmC* and conventional crystal phase. Unexpectedly, in the case of compound **MO 10/10** of this specific subseries, the tuning the molecular structure by the bulkiest substituent (methoxy group) returns smectic ordering, and ferroelectric SmC* phase has been observed in a reasonable temperature range.

In the **H-subseries** with different lateral substitution far from the terminal chiral chain, the majority of compounds possess the ferroelectric SmC* phase. The phase transition temperatures to the SmC* phase (determined on cooling) clearly decrease with increasing the size of lateral substituent; this is probably due to sterical reasons. Specifically, the phase transition temperature to SmC* phase was suppressed by more than 40 K, when the lateral substituent size changed from the smallest fluorine atom to the bulkiest methoxy group. There is also a tendency of the decrease in melting point with the increase of lateral substituent size (see Table 3).

Table 3. Mesomorphism of the laterally substituted lactic acid derivatives of **H-subseries**

Compound	m.p.	Cr	SmB		SmC*		N*		BP		Iso	
H 10/10	65	●	68	—		●	130	—		—	●	
F 10/10	93	●	78	●	89	●	121	—		—	●	
Cl 10/10	94	●	54	—		●	108	—		—	●	
Br 10/10	87	●	21	—		●	102	—		—	●	
M 10/10	75	●	25	—		●	89	●	90	●	91	●
MO 10/10	78	●	45	—		●	89	—		—		●

Melting points (m.p., °C) were determined by POM, measured on heating. Phase transition temperatures [°C] were determined by DSC, measured on cooling (rate, 5 °C·min⁻¹). Symbol “–” stands if the phase does not exist

The mesomorphic behaviour of the compounds of the **ZL-subseries** determined by POM and DSC are summarised in Table 4. The characteristic texture microphotographs of different mesophases of individual compounds of this *subseries* are presented in Fig. 2. The mesomorphic behaviour of this *subseries* is much richer than that of the previously discussed **H-subseries**. The considerable preference in smectic phases formation has been observed that is probably related to different molecular core structure. The parent non-substituted compound **ZL 8/6** exhibits paraelectric orthogonal smectic A* (SmA*) and ferroelectric tilted

SmC* phases over a broad (over 100 K) temperature range. Moreover, on cooling at the temperatures below SmC* phase range, a non-polar smectic phase denoted here as SmX was detected, which might be identified as highly ordered smectic phase. The characteristic fan-shaped textures of orthogonal SmA* phase and the specific fan-shaped texture of SmC* phase with the change of colours through the fans (it indicates the presence of dechiralisation lines, and, hence the helical pitch is less than 1 μm) are shown in Fig. 2, *a*, *b*; the type of mesophases was determined in analogy with Ref. [89].

Table 4. Mesomorphism of the laterally substituted lactic acid derivatives of **ZL-subseries**

Compound	m.p.	Phase		Phase		Phase		Phase		Phase	
ZL 8/6	56	Cr	< 0	SmX	48	SmC*	82	SmA*	148	–	Iso
BCl 8/6	41	Cr	20	–		SmC*	47	SmA*	84	N*	90 Iso
BBr 8/6	52	Cr	-10	TGBC*	36	TGBA*_{re}	46	SmA*	79	TGBA*	81 Iso
BI 8/6	56	Cr	-19	SmX	27	SmC*	42	–		–	Iso

Melting points (m.p., °C) were determined by POM, measured on heating. Phase transition temperatures [°C] were determined by DSC, measured on cooling (rate, 5 °C·min⁻¹). Symbol “–” stands if the phase does not exist

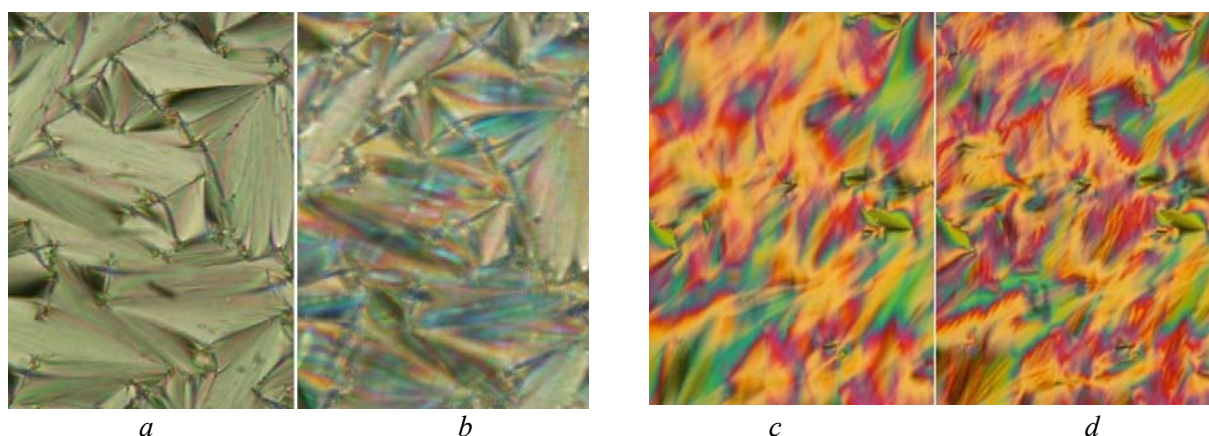


Fig. 2. Microphotographs of the characteristic textures obtained on cooling for the compounds of **ZL-subseries**: *a* – fan-shaped texture of SmA* phase of **ZL 8/6** at 120.0 °C, *b* – fan-shaped texture of the SmC* phase for **ZL 8/6** at 80.0 °C (the colour change through the fans indicates the presence of dechiralisation lines), *c* – the texture of re-entrant TGBA*_{re} phase of **BBr 8/6** at 45.0 °C, *d* – the texture of TGBC* phase of **BBr 8/6** at 35.0 °C (it is the sample same area as in (*c*)).

The width of all the microphotographs is about 250 μm

The lateral substitution by chlorine atom placed far from the chiral centre (**BCl 8/6** compound) considerably suppress mesophase temperatures and simultaneously induced the cholesteric phase, which is a few degrees broad and exists above the paraelectric SmA*

phase. The orthogonal paraelectric SmA* phase is absent in the case of substitution by iodine atom (**BI 8/6** compound) but the temperature range of ferroelectric SmC* phase was further narrowed and shifted to lower temperatures. The undetermined non-polar smectic

phase (like the SmX described above) was detected on cooling below the temperature range of ferroelectric SmC* phase.

The substitution by bromine atom (**BBr 8/6** compound) resulted in quite unconventional and reach mesomorphic behaviour, which is observed quite rarely for chiral calamitic liquid crystalline materials. Several frustrated smectic phases with twist grain boundary structure were detected. On cooling from isotropic phase, the twist grain boundary smectic A* (TGBA*) phase appears. On further cooling, the conventional orthogonal paraelectric SmA* phase exists within more than 35 K temperature range. Then, the TGBA* phase structure is started to be favourable again and the quite rare re-entrant TGBA*_{re} phase exists in about 10 K broad temperature region. Below the TGBA*_{re} phase, the tilted smectic phase with twist grain boundary structure (TGBC*) is present until the transition to crystal phase occurs. This extraordinary mesophase sequence and the structures of the uncommon mesophases were clearly confirmed by X-ray scattering and other techniques [53, 87]. The characteristic texture microphotographs of the unconventional frustrated TGBA*_{re} and TGBC* phases are shown in Fig. 2, *c*, *d*; the type of mesophases was determined in analogy with Ref. [89].

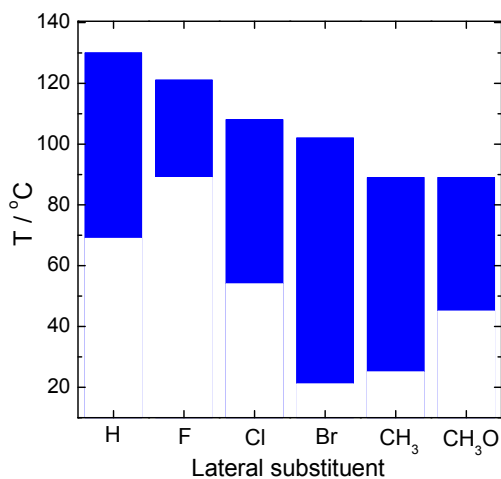


Fig. 3. The dependence of the ferroelectric SmC* phase temperature range on the type of lateral substituents of the *H*-subseries

The diagram presented in Fig. 3 clearly shows the effect of lateral substitution type on the temperature range of ferroelectric tilted SmC* phase for compounds of the *H*-subseries. It is clearly seen that lateral substitution considerably suppresses the values of the upper temperature boarder of SmC* phase. The broadest SmC* range (over 80 K) was detected in the case of lateral substitution by bromine atom. However, the lowest melting points were detected for the bulkiest lateral substituents, such as methyl and methoxy groups (see Table 3).

Comparison of spontaneous polarisation and tilt angle

The temperature dependences of the spontaneous polarisation (P_s) and the optically measured tilt angle (θ_s) for the compounds with different lateral substituents of the *H*-subseries are presented in Fig. 4, *a*, *b*, respectively. The temperatures were normalised with respect to the phase transition temperature (T_c), which is the phase transition temperature to SmC* phase. The spontaneous polarisation values increase on cooling without saturation [41]. The type of lateral substitution plays a distinct role on the P_s values. The highest value was detected for compound **Br 10/10**, it reaches 260 nC/cm² before the onset of crystal phase.

The measured θ_s values consist of the spontaneous tilt angle (without electric field) and the field induced tilt angle (due to the electroclinic effect). In principle, the field-induced tilt angle needs to be considered only close to the phase transition to ferroelectric SmC* phase. In the vicinity of the phase transition to SmC* phase, the tilt angle increases jump-like indicating the first order phase transition. For all studied compounds of the *H*-subseries, the tilt angle values are in the range of 39–45 degrees and reach the saturation at about 10–15 K below the phase transition to SmC* phase on cooling. The highest θ_s values reaching 45 degrees were found for the methyl and methoxy substituted compounds (**M 10/10** and **MO 10/10**). These tilt angles are almost temperature independent in a broad temperature range before the crystallisation onset.

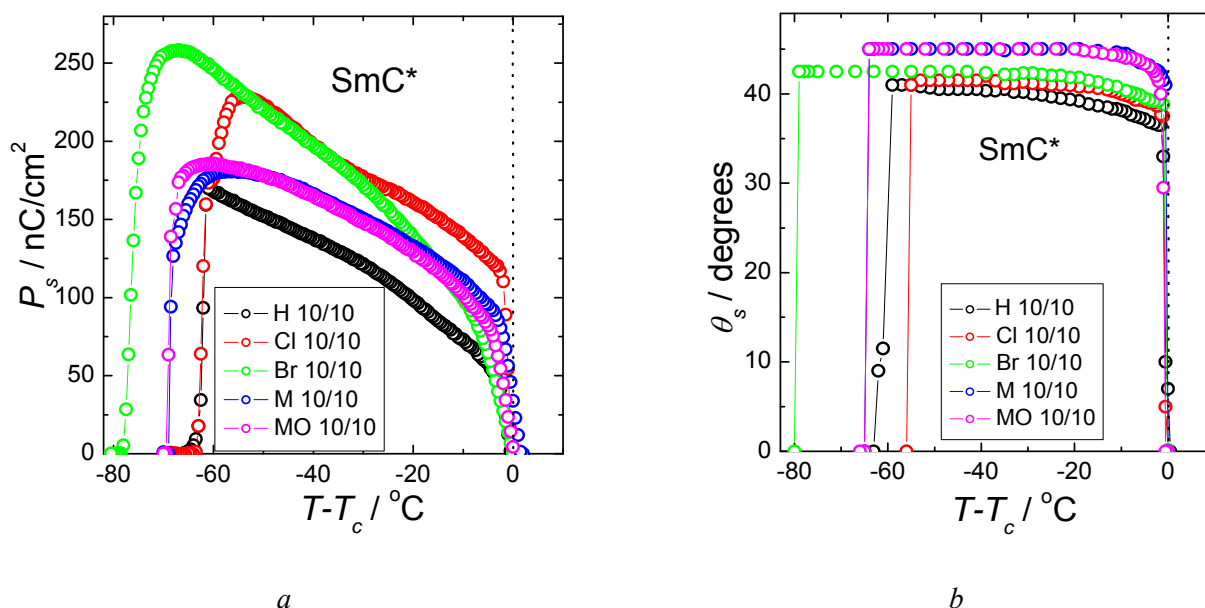


Fig. 4. Temperature dependences of: *a* – spontaneous polarisation (P_s) and *b* – tilt angle determined optically (θ_s) of the compounds of the *H-subseries* possessing different lateral substituents in molecular core. The dashed vertical lines stand for the temperature T_c , which is the phase transition temperature to ferroelectric SmC^* phase on cooling

Conclusions

Chiral liquid crystalline materials represent a very exciting and promising sub-class of the self-organising materials that form the smectic phases with polar ordering. In this mini-review we have made a comparison of two specific subseries of rod-like mesogens based on three phenyl ring molecular core with the chiral lactic unit. Specifically, the chiral group of *H-subseries* is derived from the commercially available (*S*)-ethyl lactate, while for *ZL-subseries* the starting material is the lactic acid, which is also chemically and thermally stable and commercially available at reasonable optical purity. The main differences in the molecular structure between the two subseries are the sequence of the phenyl and biphenyl nuclei in the molecular core and the length of the polarised part of molecular core, being considerably longer for *ZL-subseries*.

The effect of the lateral substitution by several halogen atoms (fluorine, chlorine, bromine and iodine) and by the bulky methyl and methoxy groups in the *ortho*-position to the non-chiral alkoxy chain has been checked and established. We compared the mesomorphic properties and spontaneous quantities (values of

the spontaneous polarisation and the tilt angle of molecules with respect to smectic layer normal) of non-substituted LC-materials with those of halogen-substituted materials with increasing atomic weight or other substituents with increasing van der Waals radius. Specifically, the substitution by fluorine, chlorine, bromine atoms and methyl/methoxy groups was used for *H-subseries*. For the *ZL-subseries*, the substitution by chlorine, bromine and iodine atoms was checked and studied. The fluorine atom combines large electronegativity and small atom size. The lateral substitution by bromine or iodine atoms have been used very rarely in LC-materials. It is due to the purification difficulties of conductive impurities, which makes almost impossible to measure some specific physical characteristics. However, the most extraordinary mesophase sequence was shown exactly by the bromine substituted compound: on cooling from isotropic phase the frustrated orthogonal twist grain boundary A^* phase was followed by the ordinary orthogonal SmA^* , which comes back as the re-entrant TGBA^* phase and followed by the frustrated tilted TGBC^* phase down to quite low temperatures [53, 87]. This is truly unique mesophase sequence.

The mesomorphic properties and electro-optical behaviour of the laterally substituted materials was compared to that of the non-substituted ones. All compounds of both subseries possess a broad temperature range of the tilted ferroelectric phase. The highest values of the spontaneous polarisation were reached for the bromine substituted compound of H-subseries (up to 250 nC/cm²); The compounds with methyl and methoxy lateral substitution possess the highest values of the tilt angle being close to 45 degrees. Such high values of the tilt angle, being almost temperature independent within about 50 K, are typical of so-called orthoconic ferroelectric liquid crystalline materials [12, 65], which can assure the highest possible optical contrast.

Appropriate utilisation of the lateral substitution on molecular core is an effective tool to tune and keep under control the self-organising behaviour of soft materials [90]. The compounds of two subseries presented in this mini-review can be potentially useful as chiral dopants in multicomponent mixtures targeted for electro-optical applications in photonics due to such remarkable properties as: quite broad temperature range of ferroelectric SmC* phase existing up to room temperatures, very high values of tilt angle close to 45 degrees, very high chemical stability and relatively high spontaneous polarisation.

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