Effect of molecular structure on liquid crystalline behaviour for chiral lactic acid derivatives

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Abstract

Liquid crystals are self-organizing materials that have great potential for practical applications. The relationship "molecular structure - mesomorphic properties" has not been fully established and understood despite numerous studies. We discuss a relatively broad subclass of calamitic chiral lactic acid derivatives and provide specific examples of effective tuning of their mesomorphic and electro-optical behaviour using various types of lateral substitution placed on the molecular core.

**Keywords**: Chiral liquid crystals; Lateral substitution; Ferroelectric smectic phase; Spontaneous polarization; Lactic acid.

Introduction

Thermotropic liquid crystals (LCs) belong to a fascinating class of self-assembled soft materials that have great potential for practical applications in the future. The field of liquid crystals is interdisciplinary, as it combines the main features of physics, chemistry, materials science, mathematics, medicine, biology, and engineering [1-5]. Since liquid crystals are fluid and ordered, and at the same time they have amazing optical, electro-optical and dielectric properties, they have value and practical utility.

Among self-organizing supramolecular smart systems, LCs can exhibit stable supramolecular helical organization if the mesogens are chiral. In 1975, the ferroelectric liquid crystal phase was discovered [6], and its unique physical properties opened the future for a wide variety of electro-optical applications in real-time optical processing, computing, control and measurement devices, etc., which stimulated great progress in the design and research of chiral smectic structures materials [7]. Due to these properties, we have high requirements for understanding the basic and additional physical properties of new chiral LC materials.

However, as it has been shown during several last decades of intense research, it is almost impossible to reach the desired specific mesomorphic and electro-optical properties in a single molecular structure. This can be solved by design of binary and multicomponent mixtures composed by the structurally similar [8-11] or structurally different [12-15] molecules mixed-up in a definite quantity. Incorporation of various reactive groups assures the induction of the supplementary functionality and may result in extraordinary mesomorphic and electro-optical behaviour. Design and synthesis of new chiral liquid crystalline materials with definite mesomorphic and electro-optical properties [11-12, 16-17] remains a main challenge for certain innovative applications, which require a deep information about the molecular structure – resulting property correlation and their impact on the mesomorphic behaviour [7]. The type of the chiral centre is very important while designing the chiral LC materials, and the chiral lactate group is one of the exceptional possibilities. There are several substantial advantages of the lactic acid derivatives [8, 17, 18-22], as a subclass of chiral self-assembling materials, that makes them very attractive [23].

The main goal of this work is to determine and discuss the effect of the lateral substitution on the molecular core on the mesomorphic behaviour for the specific class of chiral calamitic lactic acid derivatives. Some results presented in this work have been already published [1].

Experiment

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

Table 1: General chemical structure of the studied materials with indication of the used lateral substitution in ortho-position (X) to the non-chiral alkoxy chain and the references related to the specific material (or to the specific material series).

|  |  |  |
| --- | --- | --- |
|  | | |
| Compound name: | Substituent **X** | References |
| H 10/10 | Hydrogen atom | [17, 24, 25-27] |
| Cl 10/10 | Chlorine atom | [28-30] |
| Br 10/10 | Bromine atom | [31] |
| M 10/10 | Methyl group | [32, 24, 33, 25] |
| MO 10/10 | Methoxy group | [24, 25, 34] |

The sequence of mesophases was determined by the observation of the 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 (5×5 mm2)) were supplied by Military University of Technology (Warsaw, Poland). The cells were filled with the studied material in the 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 the temperature control, which allows temperature stabilisation within ±0.1 K.

The 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. The calorimetric measurements were performed on cooling/heating runs at a rate of 5 K min−1 for the precise evaluation of the phase transition temperatures. 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.

Values of the spontaneous polarisation *Ps*, 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 V/μm. 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 ±100 V. The Tektronix DPO4034 digital oscilloscope (Tektronix Co., Beaverton, Oregon, U.S.A.) provided information about the switching current profile versus time. The experiments are driven by the specific homemade software [12].

Thespontaneous tilt angle *θs*, values have been determined optically using well aligned samples at bookshelf-like surface stabilised structure, observing the difference between extinction positions at crossed polarisers under opposite DC electric fields ±40 kVcm-1. The tilt angle is the angle between the long molecular axis and the smectic layer normal.

## Results and discussion

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

Mesomorphic behaviour

The mesomorphic behaviour determined by POM and DSC is summarised in Table 2. The characteristic microphotographs of textures of different mesophases detected for individual compounds are presented in Figure 1. It has been found that for materials with such chemical structure, the melting point is quite high and a considerable range of the mesomorphic area is found to be of monotropic character (monotropic means that the whole phase or its part is observed on cooling only). All the studied compounds possess the tilted ferroelectric smectic C\* (SmC\*) phase over a broad temperature range before the onset of the crystal (Cr) phase.

Substitution by the lateral methyl group (case of M 10/10) induces the Blue Phase (BP) and the cholesteric phase (N\*) in a very narrow temperature region on cooling from the isotropic (Iso) phase (see Figure 1ab). Unexpectedly, the bulkiest substituent used, namely the methoxy group (case of MO 10/10) likely returns the smectic ordering, and the ferroelectric SmC\* phase has been observed in a reasonable temperature range. For the materials with different lateral substitutions far from the chiral chain, the phase transition temperature to the SmC\* phase (determined on cooling) clearly decreases with increasing the size of the lateral substitution; this is probably related to the steric effects. Specifically (see Table 2), the temperature of the phase transition to the SmC\* was suppressed by more than 40 K while changing the lateral substituent size from the smallest (chlorine atom) to the bulkiest (methoxy group).

Table 2: The sequence of phases (PH) determined by POM; melting points, m.p. [°C] measured on heating; phase transition temperatures T [°C] measured on cooling (5 K min-1) determined by DSC for the laterally substituted lactic acid derivatives. Symbol “-” stands if the phase does not exist.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Comp | m.p. | PH | T | PH | T | PH | T | PH | T | PH |
| H 10/10 | 65 | Cr | 68 | SmC\* | 130 | - |  | - |  | Iso |
| Cl 10/10 | 94 | Cr | 54 | SmC\* | 108 | - |  | - |  | Iso |
| Br 10/10 | 87 | Cr | 21 | SmC\* | 102 | - |  | - |  | Iso |
| M 10/10 | 75 | Cr | 25 | SmC\* | 89 | N\* | 90 | BP | 91 | Iso |
| MO 10/10 | 78 | Cr | 45 | SmC\* | 89 | - |  | - |  | Iso |

The table is an alternation (in columns) of temperature and material phase. Results are presented during cooling with a differential scanning calorimeter (DSC). For example, material H10/10 is at temperatures above 130°C in the state of an isotropic liquid (Iso). And at 130°C it turns into a liquid crystal state in the smectic C\* phase. Up to a temperature of 68°C, it remains in the smectic C\* phase and then crystallizes at a temperature of 68°C. (Cr phase) For other materials, similarly, only the material M10/10 differs in a large number of phases, therefore the columns BP - blue phase and N\* - cholesteric phase and their corresponding temperatures are indicated. In other materials, these phases are absent and there are dashes. M.p. - the melting point for each material is measured when heated.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
| (a) | (b) | (c) | (d) |

Figure 1: Microphotographs of the characteristic textures obtained on cooling: (a) the platelet texture of the blue phase for M 10/10 at 90.7oC, (b); the oily streaks texture of the cholesteric phase for M 10/10 at 89.2oC; (c) the Iso-SmC\* phase transition (growth of bâttonnets with clearly visible dechiralisation lines from isotropic melt) for H 10/10 at 130.0oC, (d) the broken fan texture of the SmC\* for M 10/10 at 73.0oC. The width of all the microphotographs is about 250 μm.

The diagram presented in Figure 2 clearly shows the effect of the lateral substitution type on the width of the ferroelectric tilted SmC\* phase. It can be clearly observed that the lateral substitution clearly push down the values of the high temperature border of the SmC\* phase. The broadest SmC\* phase (over 80 K broad) was detected in case of lateral substitution by the bromine atom. However, the lowest melting point was detected for the bulkiest lateral substituents -the methyl and methoxy groups (see Table 2).



Figure 2: Columnar diagram comparing the temperature range of the ferroelectric SmC\* phase in dependence on the type of the lateral substituents.

Comparison of the spontaneous polarisation and tilt angle

The temperature dependence of the spontaneous polarisation, *Ps*, and tilt angle measured optically, *θs*, are presented in Figure 3. The value of the spontaneous polarisation increases on cooling without saturation [17]. The type of lateral substitution plays a distinct role on the *Ps* values. The highest values are detected for Br 10/10 compound reaching up to 260 nC/cm2 before the onset of the crystal phase.

The measured *θs* 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 only needs to be considered close to the phase transition to the ferroelectric SmC\* phase. In the vicinity of the phase transition to the SmC\* phase, the tilt angle increases by jump; this indicates the first order phase transition. For all the studied compounds the tilt angle values are quite high, reach the saturation about 10-15 K below the phase transition to the SmC\* phase on cooling and are in the range of 39-45°. The highest *θs* values were found for the methyl and methoxy substituted compounds (M 10/10andMO 10/10, respectively) reaching 45°and being almost temperature independent in a broad temperature range before the onset of the Cr phase.



Figure 3: Temperature dependence of the spontaneous polarisation, *Ps*(T) and tilt angle, *θs*(T), determined optically for the compounds possessing different lateral substituents.

## Conclusions

Chiral liquid crystalline materials represent a very fascinating and promising sub-class of the self-organising materials that form the smectic phases with the polar ordering. In this work we make a comparison of substituents to specific series of the rod-like mesogens based on three-phenyl ring molecular core; the chirality was derived from the lactic unit.

The effect of the lateral substitution by several halogen atoms (chlorine, bromine) and by the bulky methyl and methoxy groups in the *ortho-* position to the non-chiral alkoxy chain has been established. We compared the mesomorphic properties and spontaneous quantities (values of the spontaneous polarisation and the tilt angle of molecules with respect to the 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. Lateral substitution by bromine atoms have been used very rarely in LC materials, due to the difficulties related to isolating of the very pure material with low content of conductive impurities, which makes it almost impossible to measure some of their specific physical characteristics. However, the most extraordinary mesophase sequences are shown by the bromine substituted compound [35, 36].

The mesomorphic properties and electro-optical behaviour of the laterally substituted materials was compared to that of the non-substituted ones. All the materials possess a broad temperature range of the tilted ferroelectric phase. The highest values of the spontaneous polarisation were reached for the bromine substituted compound (up to 250 nC/cm2); The compounds with methyl and methoxy lateral substitutions possess the highest values of the tilt angle (close to 45°). Such a high values of the tilt angle, being almost temperature independent for around 50 K, define the so-called orthoconic ferroelectric liquid crystalline materials [13, 37] which can assure the highest possible optical contrast.

Appropriate utilisation of the lateral substitution on the molecular core is an effective tool to tune and keep under control the resulting self-organising behaviour of the soft materials [38]. Compounds belonging to the lactic acid derivatives presented in this work can be potentially useful as chiral dopants in multicomponent mixtures targeted for electro-optic applications in photonics due to quite broad temperature range of the ferroelectric SmC\* phase down to room temperatures, very high values of the tilt angle close to 45°, very high chemical stability, and relatively high spontaneous polarisation.

## References

1. V. Hamplová, et al. Lateral substitution as effective tool for tuning self-organising behaviour of chiral mesogens. *Liq Cryst Appl* **21**(4): 23–36, 2021.
2. Kato T., et al. Functional liquid‐crystalline assemblies: self‐organized soft materials. *Angew Chem Int Ed* **45**: 38-68, 2006.
3. Lagerwall J.P.F., Scalia G. A new era for liquid crystal research: Applications of liquid crystals in soft matter nano-, bio- and microtechnology. *Curr Appl Phys* **12**: 1387-1412, 2012.
4. Uchida J., et al. Advanced Functional Liquid Crystals. *Adv Mater* **34**, 2109063, 2022.
5. Galeeva A.I., et al. Rheological properties of chitosan – lactic acid lyotropic liquid crystal systems. *Liq Cryst Appl* **21**(1): 23-33, 2021.
6. Meyer R.B., et al. Ferroelectric liquid crystals. *J Physique Lett* **36**(3): 69-71, 1975.
7. Lagerwall J.P.F., Giesselmann F. Current topics in smectic liquid crystal research. *Chem Phys Chem* **7**: 20-45, 2006.
8. Bubnov A., et al. Effect of multilactate chiral part of liquid crystalline molecule on mesomorphic behaviour. *J Mol Struct* **892**(1-3): 151-157, 2008.
9. Kurp K., et al. Ferroelectric compounds with chiral (S)-1-methylheptyloxycarbonyl terminal chain – their miscibility and a helical pitch. *Liq Cryst* **42**(2): 248-254, 2015.
10. Obadović D.Ž., et al. Thermal analysis and X-ray studies of chiral ferroelectric liquid crystalline materials and their binary mixtures. *J Therm Anal Calorim* **82**(2): 519-523, 2005.
11. Fitas J., et al. Electro-optic and dielectric properties of new binary ferroelectric and antiferroelectric liquid crystalline mixtures. *Liq Cryst* **44**(9): 1468–1476, 2017.
12. Kurp K., et al. Design of functional multicomponent liquid crystalline mixtures with nano-scale pitch fulfilling deformed helix ferroelectric mode demands. *J Mol Liq* **290:** 111329, 2019.
13. Piecek W., et al. An effect of structurally non compatible additive on the properties of a long pitch antiferroelectric orthoconic mixture. *Ph Transit* **83**(8): 551-563, 2010.
14. Bubnov A., et al. Tuning the phase diagrams: the miscibility studies of multilactate liquid crystalline compounds. *Ph Transit* **89**(9): 885-893, 2016.
15. Czerwiński M., et al. Pyrimidine-based ferroelectric mixtures–The influence of oligophenyl based chiral doping system. *J Mol Liq* **303**, 2020.
16. Lagerwall S.T. *Ferroelectric and Antiferroelectric Liquid Crystals.* Wiley-VCH: Weinheim, Germany, 1999.
17. Bubnov A., et al. Design of polar self-assembling lactic acid derivatives possessing submicrometre helical pitch. *Beilstein J Nanotechnol* **9**(1): 333-341, 2018.
18. Tsai W.-L., Kuo H.-L. Ferroelectric liquid crystals containing a 2(S)-[2(S)-methylbutoxy]propionyloxy unit. *Liq Cryst* **13**(6): 765-773, 1993.
19. Tschierske C., et al. Liquid crystalline thiadiazole derivatives V: New ferroelectric thiaoiazole derivatives. *Mol cryst liq cryst inc nonlinear opt* **191**(1): 231-235, 1990.
20. Navailles L., et al. Smectic A twist grain boundary phase in three new series with chiral (L) lactic acid derivatives. *Liq Cryst* **15**(4): 479-495, 1993.
21. Brombach F., et al. The chiral pool as valuable natural source: new chiral mesogens made from lactic acid. *Mol Cryst Liq Cryst* **542**(1): 62/[584]-74/[596], 2011.
22. Wu S.L., Lin C.Y. Synthesis and mesomorphic properties of chiral liquid crystals derived from (S)-lactic acid with 3-pentanol. *Liq Cryst* **29**(12): 1575-1580, 2002.
23. Bubnov A., et al. Effect of alkyl chains length on properties of ferroelectric liquid crystals with the keto group attached to the molecule core. *Ph Transit* **85**(10): 849-860, 2012.
24. Kaspar M., et al. The effect of a lateral substituent on the mesomorphic properties in a series of ferroelectric liquid crystals with a 2-alkoxypropionate unit. *Liq Cryst* **22**: 557-561, 1997.
25. Vajda A., et al. Structure-property relationship studies on chiral lactic acid derivatives. *Res J Phys* **29**(2):107-113, 2003.
26. Kašpar M., et al. Synthesis and mesomorphic properties of a new ferroelectric liquid crystal with 2-alkoxypropionate chiral groups. *Ferroelectrics* **148**: 103-110, 1993.
27. Stojanovič et al. Effect of the chiral chain length on structural and phase properties of ferroelectric liquid crystals. *Ph Transit* **84**: 380-390, 2011.
28. Glogarová M., et al. Low frequency modes in ferroelectric liquid crystals. *Proc SPIE* **3318**: 39-48, 1998.
29. Stojanović M., et al. Effect of a bulky lateral substitution by chlorine atom and methoxy group on self-assembling properties of lactic acid derivatives. *Mater Chem Phys* **146**(1-2): 18 – 025, 2014.
30. Garić M., et al. Study of ferroelectric liquid crystals with 2-alkoxypropionate chiral group by X-ray measurements. *Mol Cryst Liq Cryst* **412**(1): 19-28, 2004.
31. Kašpar M., et al. Effect of lateral substitution by fluorine and bromine atoms in ferroelectric liquid crystalline materials containing a 2‐alkoxypropanoate unit. *Liq Cryst* **34**(10): 1185-1192, 2007.
32. Bubnov A., et al. Orientational and structural properties of ferroelectric liquid crystal with a broad temperature range in the SmC\* phase by 13CNMR, x-ray scattering and dielectric spectroscopy. *J Phys Condens Matter* **21**(3): 035102, 2009.
33. Malik P., et al. Electro-optic switching and dielectric spectroscopy studies of ferroelectric liquid crystals with low and high spontaneous polarization. *Thin Solid Films* **519**(3): 1052‑1055, 2010.
34. Kašpar M., et al. The effect of a lateral methoxy group on the mesomorphic properties of ferroelectric liquid crystals. *Liq Cryst* **19**(6): 775-778, 1995.
35. Glogarová M., Novotná V. Frustrated smectic liquid crystalline phases in lactic acid derivatives. *Ph Transit* **89**(7-8): 829-839.
36. Podoliak N., et al. Anomalous phase sequence in new chiral liquid crystalline materials. *Liq Cryst* **41**(2): 176-183, 2014.
37. Czerwiński M., T et al. The influence of structure and concentration of cyanoterminated and terphenyl dopants on helical pitch and helical twist sense in orthoconic antiferroelectric mixtures. *Liq Cryst* **39**(12): 1498–1502, 2012.
38. Dierking I. Chiral liquid crystals: structures, phases, effects. *Symmetry* **6**: 444-472, 2014.

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