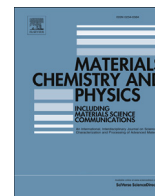




Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Effect of a bulky lateral substitution by chlorine atom and methoxy group on self-assembling properties of lactic acid derivatives

Maja Stojanović^{a,*}, Alexej Bubnov^b, Dušanka Ž. Obadović^a, Věra Hamplová^b,
Miroslav Cvetinović^a, Miroslav Kašpar^b

^a Department of Physics, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 4, 21000 Novi Sad, Serbia

^b Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague, Czech Republic

HIGHLIGHTS

- Chiral liquid crystalline materials derived from the lactic acid have been studied.
- Effect of bulky lateral substituents on self-assembling properties has been established.
- Bulky methoxy substitution suppresses spontaneous polarisation but increases the melting point.
- The compounds might have a strong potential for many advanced electro-optic applications.

ARTICLE INFO

Article history:

Received 5 June 2013

Received in revised form

14 February 2014

Accepted 23 February 2014

Keywords:

Liquid crystals

Differential scanning calorimetry (DSC)

Optical microscopy

Dielectric properties

X-ray scattering

ABSTRACT

Several chiral liquid crystalline materials derived from the lactic acid have been studied with the aim to establish the effect of bulky lateral substituents on their self-assembling properties. A chlorine atom and methoxy group have been used as lateral substituents in ortho position to ether group position on phenyl ring far from the chiral centre. All the studied materials possess tilted ferroelectric smectic C* phase in a broad temperature range. In dependence on the molecular structure namely type of lateral substituent and length of the chiral chain, the cholesteric mesophase, orthogonal paraelectric smectic A* and crystal mesophases have been detected. Lateral chlorine substitution results in decrease of both the clearing point and crystallisation temperature as well as in a distinct increase of spontaneous polarization. Bulky methoxy substitution slightly suppresses the spontaneous polarisation but strongly increases the melting point that results in monotropic peculiarity of the SmC* phase. Mesomorphic, spontaneous, structural and dielectric properties of the substituted compounds were established and compared to those of the non-substituted ones in order to contribute to better understanding of the structure–property relationship for such chiral self-assembling materials.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Materials that are able to self-assemble into supramolecular smart structures with desirable functionality and physical properties at nano- and meso-scopic length scales represent currently an exciting area of intense research, which provide a highlighted approach for design and synthesis of new functional materials [1,2]. One of the most fascinating classes of organic materials that are able to self-assemble are those possessing the liquid crystalline (LC) properties. The combination of fluidity and sensitivity to electric/

magnetic fields or illumination by UV-light makes polar fluids ideal for photonics, telecommunications, non-linear optics, etc [3–5]. From the fundamental point, chiral smectic liquid crystals i.e. those possessing self-assembling into the layered structure of nanometre dimensions, have attracted strong attention of the soft matter research community for the last three decades [6,7] while in our days the nematic LC materials are already extensively applied in mass production of various display devices. Possible applicability of smectic LCs put high demands on understanding their basic mesomorphic and physical properties and also on mixture formulation rules while reaching the properties responding definite demands [8–10].

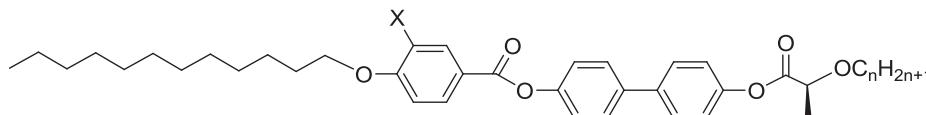
Lactate based chiral liquid crystalline materials (or the lactic acid derivatives) have been intensively studied for the last two decades

* Corresponding author.

E-mail address: maja.stojanovic@df.uns.ac.rs (M. Stojanović).

due to their attractive properties [2,11–21] but also due to a reasonably low production (synthetic) costs with respect to more commonly used LC materials with chiral part derived from (*S*)-2-octanol. Varying the molecular architecture [16,22–24], making the LC materials polymerisable by attaching various functional groups [23,25–29] and also mixing various LC materials [8,23,30,31] are the most commonly used tools to reach the desirable properties. However, design of LC monomers/polymers as well as mixing similar homologues or LC materials with quite different structure are out of scope of the present work. While designing chiral molecule special courtesy should be paid for the type and number of the attached chiral centres [23,32], structure of the molecular core and linkage groups [21,32,33], length and type of the end chains [19–21,34,35] and also for the place and type of the lateral substituents [17,36–38]. For chiral liquid crystalline materials bulky methyl [17,36,39,40] and methoxy [17,38] groups along with chlorine [17,41,42], bromine [37,43,44], fluorine [37,45–47] and even iodine atoms are the most commonly used lateral substituents that strongly affect the mesomorphic, spontaneous and structural properties of LC compounds with respect to that of the non-substituted related structures [16,17].

The aim of this work is to study and discuss properties of the ferroelectric liquid crystalline materials derived from the lactic acid in relation to their molecular structure and type of lateral substituents [17] and, thus to contribute to better understanding of the molecular structure–mesomorphic property relationship for the self-assembling materials possessing polar mesophases. In order to study the effect of bulky lateral substitution placed far from the chiral centre in comparison to that for similar non-substituted materials [16] the methoxy group and chlorine atom have been chosen as a lateral substituents. General chemical formula of the materials under study is:



The materials without lateral substitution ($X = H$) are 4'-(2-(pentyloxy)propanoyloxy)biphenyl-4-yl 4-(dodecyloxy)benzoate denoted as **H 12/5** and 4'-(2-(heptyloxy)propanoyloxy)biphenyl-4-yl 4-(dodecyloxy)benzoate denoted as **H 12/7**; laterally substituted by chlorine atom 4'-(2-(pentyloxy)propanoyloxy)biphenyl-4-yl 3-chloro-4-(dodecyloxy)benzoate denoted as **Cl 12/5** ($X = Cl$) and four materials laterally substituted by a methoxy group **MO 12/n** ($X = OCH_3$, $n = 5, 7, 8, 10$), namely 4'-(2-(pentyloxy)propanoyloxy)biphenyl-4-yl 3-methoxy-4-(dodecyloxy)benzoate; 4'-(2-(heptyloxy)propanoyloxy)biphenyl-4-yl 3-methoxy-4-(dodecyloxy)benzoate; 4'-(2-(oktyloxy)propanoyloxy)biphenyl-4-yl 3-methoxy-4-(dodecyloxy)benzoate and 4'-(2-(decyloxy)propanoyloxy)biphenyl-4-yl 3-methoxy-4-(dodecyloxy)benzoate.

2. Synthetic procedure for the studied materials

Details on synthetic procedure of studied compounds have been presented earlier – for non-substituted compounds **H 12/5** and **H 12/7** in Ref. [15], for laterally substituted by chlorine atom **Cl 12/5** compound in Ref. [48] and for compounds **MO 12/5**, **MO 12/7**, **MO 12/8** and **MO 12/10** with methoxy group as a lateral substituent in Ref. [16]. The chemical purity of LC materials was checked by high pressure liquid chromatography (HPLC), which was carried out using a silica gel column (Biosphere Si 100-5 μm , 4×250 , Watrex) with a mixture of toluene and 0.2% of methanol used as eluent. The detection of the eluting products was done by UV–VIS detector ($\lambda = 290 \text{ nm}$). For all materials under the study, chemical

purity was found between 99.7% and 99.9% under these conditions. The structures of final compounds have been checked and confirmed by $^1\text{H NMR}$ (300 MHz, Varian) as it is shown below.

The optical rotations were measured using Polarimeter Optical Activity Ltd. For these compounds in spite of distinct differences in their molecular core structure very similar values of optical rotation $[\alpha]_D^{20}$ have been found: **H 12/5** – $[\alpha]_D^{20} = -25.0$ ($c = 0.10$, CHCl_3), **Cl 12/5** $[\alpha]_D^{20} = -22.5$ ($c = 0.10$, CHCl_3) and **MO 12/5** $[\alpha]_D^{20} = -23.0$ ($c = 0.10$, CHCl_3).

$^1\text{H NMR}$ of **H 12/5** (CDCl_3): 8.17 (d, 2H, ortho to $-\text{COO}-$); 7.60 (m, 4H, ortho to $-\text{Ar}$); 7.28 (d, 2H, ortho to ArCOO); 7.20 (d, 2H, ortho to $-\text{C}^*\text{COO}$); 6.98 (d, 2H, ortho to OCH_2); 4.22 (q, 1H, C^*H); 4.06 (t, 2H, CH_2OAr); 3.50 and 3.70 (m, 2H, CH_2OC^*); 1.83 (quint., 2H, $\text{CH}_2\text{CH}_2\text{OAr}$); 1.60 (d, 3H, CH_3C^*); 1.60–1.20 (m, 24H, CH_2); 0.90 (m, 6H, CH_3).

$^1\text{H NMR}$ of **H 12/7** (CDCl_3): 8.17 (d, 2H, ortho to $-\text{COO}-$); 7.60 (m, 4H, ortho to $-\text{Ar}$); 7.28 (d, 2H, ortho to ArCOO); 7.20 (d, 2H, ortho to $-\text{C}^*\text{COO}$); 6.98 (d, 2H, ortho to OCH_2); 4.22 (q, 1H, C^*H); 4.06 (t, 2H, CH_2OAr); 3.50 and 3.70 (m, 2H, CH_2OC^*); 1.83 (quint., 2H, $\text{CH}_2\text{CH}_2\text{OAr}$); 1.60 (d, 3H, CH_3C^*); 1.60–1.20 (m, 28H, CH_2); 0.90 (m, 6H, CH_3).

$^1\text{H NMR}$ of **Cl 12/5** (CDCl_3): 8.24 (d, 1H, ortho to $-\text{Cl}$); 8.09 (dd, 1H, para to Cl); 7.60 (m, 4H, ortho to $-\text{Ar}$); 7.28 (d, 2H, ortho to ArCOO); 7.20 (d, 2H, ortho to $-\text{C}^*\text{COO}$); 7.01 (d, 1H, meta to Cl); 4.22 (q, 1H, C^*H); 4.14 (t, 2H, CH_2OAr); 3.50 and 3.70 (m, 2H, CH_2OC^*); 1.90 (quint., 2H, $\text{CH}_2\text{CH}_2\text{OAr}$); 1.60 (d, 3H, CH_3C^*); 1.60–1.20 (m, 24H, CH_2); 0.90 (m, 6H, CH_3).

$^1\text{H NMR}$ of **MO 12/5** (CDCl_3): 7.86 (dd, 1H, para to $-\text{CH}_3\text{O}$); 7.69 (d, 1H, ortho to $-\text{CH}_3\text{O}$); 7.61 (m, 4H, ortho to $-\text{Ar}$); 7.28 (d, 2H, ortho to ArCOO); 7.19 (d, 2H, ortho to $-\text{C}^*\text{COO}$); 6.96 (d, 1H, meta to $-\text{CH}_3\text{O}$); 4.22 (q, 1H, C^*H); 4.12 (t, 2H, CH_2OAr); 3.96 (s, 3H, CH_3OAr); 3.50 and 3.70 (m, 2H, CH_2OC^*); 1.90 (quint., 2H, $\text{CH}_2\text{CH}_2\text{OAr}$); 1.59 (d, 3H, CH_3C^*); 1.50–1.20 (m, 24H, CH_2); 0.90 (m, 6H, CH_3).

$^1\text{H NMR}$ of **MO 12/7** (CDCl_3): 7.86 (dd, 1H, para to $-\text{CH}_3\text{O}$); 7.69 (d, 1H, ortho to $-\text{CH}_3\text{O}$); 7.61 (m, 4H, ortho to $-\text{Ar}$); 7.28 (d, 2H, ortho to ArCOO); 7.19 (d, 2H, ortho to $-\text{C}^*\text{COO}$); 6.96 (d, 1H, meta to $-\text{CH}_3\text{O}$); 4.22 (q, 1H, C^*H); 4.12 (t, 2H, CH_2OAr); 3.96 (s, 3H, CH_3OAr); 3.50 and 3.70 (m, 2H, CH_2OC^*); 1.90 (quint., 2H, $\text{CH}_2\text{CH}_2\text{OAr}$); 1.59 (d, 3H, CH_3C^*); 1.50–1.20 (m, 28H, CH_2); 0.90 (m, 6H, CH_3).

$^1\text{H NMR}$ of **MO 12/8** (CDCl_3): 7.86 (dd, 1H, para to $-\text{CH}_3\text{O}$); 7.69 (d, 1H, ortho to $-\text{CH}_3\text{O}$); 7.61 (m, 4H, ortho to $-\text{Ar}$); 7.28 (d, 2H, ortho to ArCOO); 7.19 (d, 2H, ortho to $-\text{C}^*\text{COO}$); 6.96 (d, 1H, meta to $-\text{CH}_3\text{O}$); 4.22 (q, 1H, C^*H); 4.12 (t, 2H, CH_2OAr); 3.96 (s, 3H, CH_3OAr); 3.50 and 3.70 (m, 2H, CH_2OC^*); 1.90 (quint., 2H, $\text{CH}_2\text{CH}_2\text{OAr}$); 1.59 (d, 3H, CH_3C^*); 1.50–1.20 (m, 30H, CH_2); 0.90 (m, 6H, CH_3).

$^1\text{H NMR}$ of **MO 12/10** (CDCl_3): 7.86 (dd, 1H, para to $-\text{CH}_3\text{O}$); 7.69 (d, 1H, ortho to $-\text{CH}_3\text{O}$); 7.61 (m, 4H, ortho to $-\text{Ar}$); 7.28 (d, 2H, ortho to ArCOO); 7.19 (d, 2H, ortho to $-\text{C}^*\text{COO}$); 6.96 (d, 1H, meta to $-\text{CH}_3\text{O}$); 4.22 (q, 1H, C^*H); 4.12 (t, 2H, CH_2OAr); 3.96 (s, 3H, CH_3OAr); 3.50 and 3.70 (m, 2H, CH_2OC^*); 1.90 (quint., 2H, $\text{CH}_2\text{CH}_2\text{OAr}$); 1.59 (d, 3H, CH_3C^*); 1.50–1.20 (m, 34H, CH_2); 0.90 (m, 6H, CH_3).

3. Experimental

Sequence of phases and phase transition temperatures were determined on cooling from the isotropic phase from characteristic

Download English Version:

<https://daneshyari.com/en/article/1521776>

Download Persian Version:

<https://daneshyari.com/article/1521776>

[Daneshyari.com](https://daneshyari.com)