Lactic acid derivatives with terphenyl molecular core

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ABSTRACT
New lactic acid derivatives, based on terphenyl molecular core laterally substituted by chlorine atom, have been synthesised and their liquid crystalline properties studied. We varied the molecular structure by prolonging the non-chiral chain and analysed the mesogenic properties with respect to its length. We found that all new compounds reveal the SmA→SmC* phase sequence in an extremely broad temperature interval. The experimental techniques, namely the polarising optical microscopy, differential scanning calorimetry, x-ray diffraction and helical pitch measurements, have been applied to establish the physical properties. Studied compounds exhibit very high values of the spontaneous polarisation and the tilt angle grows continuously on cooling up to 42°. The pitch values drop down when prolonging the molecular non-chiral chain.

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1. Introduction
The requirements for any electro-optical application are differing. Nevertheless, the photochemical stability, low viscosity, high purity and wide thermal range of mesophases are the most important properties. The terphenyl core has a rod-like shape and can promote creation of calamitic mesophases.[1–6] Additionally, such a molecular core can be considered as a donor–π–acceptor structure, which is important from the point of view of photovoltaics. The terphenyl derivatives have been studied since the beginning of the liquid crystal research,[1–3] and it has been established that they have great potential. Unfortunately, generally they exhibit high transition temperatures, which can be overcome by a lateral substitution. Very often, fluorinated terphenyl derivatives were prepared and studied.[7–9]

On the other hand, the mesomorphic properties are influenced not only by the character of the molecular core, but also by the character of linking groups and/or
type of the chiral moiety. Lactic acid unit was often utilised in the chiral part for the synthesis of new liquid crystalline compounds.[10–15] Such derivatives exhibited good chemical and optical purity, and thermal stability, and their chirality is strong enough to promote the ferroelectricity. We have prepared and studied lactate derivatives with rather big four-phenyl-ring molecular core, consisted of one biphenyl and two phenyls connected by esters, with a lateral substitution of a halogen atom.[16–19] For one type of molecular structure, we have studied the role of halogen atom on the mesomorphic properties, started from nonsubstituted compounds and utilised chlorine, bromine and iodine atoms.[19] We have found practically linear decrease of the clearing and melting temperatures with respect to an increasing atomic weight of the substituent. For chlorine substitution, we have reached rather high spontaneous tilt angle and polarisation values [16,17] in comparison with nonsubstituted analogues. For bigger substituents, we have observed only small changes in the spontaneous polarisation and pitch values. Even higher tilt values were found for bromine compounds, so they were characterised as orthoconic-like.[18]

Last but not least, the influence of terminal alkyl chains on mesomorphic properties cannot be omitted. We studied lactic acid derivatives and varied the length of both terminal alkyl chains, chiral and non-chiral chains.[20] We established that the length of both chains had a strong effect on the SmC* phase presence and their roles were quite opposite. We found for studied series only short chiral chains and long non-chiral chains support the existence of the ferroelectric phase.

Herein, we synthesise and study new types of lactic acid derivatives based on four-phenyl-ring molecular core, created from a terphenyl and phenyl ring, terphenyl being laterally substituted by chlorine atom. We have prepared a series by varying the alkyl length in the non-chiral terminal chain and established its influence on the mesomorphic behaviour.

2. Synthesis

Synthetic route for preparation of the studied products, 4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl 3″-chloro-4″-(decyloxy)-[1,1′:4′,1″-terphenyl]-4-carboxylate designated as SOSn/6, is schematically depicted in Scheme 1. Terphenyl carboxylic acids have been prepared using condensation synthetic approach developed earlier.[21,22] The preparation of intermediates 1–4 and details of the synthesis are described in Supplemental online material.

The final product 4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl 3″-chloro-4″-(decyloxy)-[1,1′:4′,1″-terphenyl]-4-carboxylate was designated as SOSn/6 with n corresponding to the number of carbon atoms in the alkyl terminal chain (R=CnH2n+1). Final products were prepared by the standard method of esterification of 3-chloro-4-alkyl-p-terphenyl-1″-carboxylic acids 4 by 1-hexyloxy-1-oxopropan-2-yl 4-hydroxybenzoate with dicyclohexylcarbodiimide in the presence of dimethylaminopyridine in

![Scheme 1](image-url)

Scheme 1. Scheme of synthetic route for preparation of product 4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl 3″-chloro-4″-(decyloxy)-[1,1′:4′,1″-terphenyl]-4-carboxylate, which was designated as SOSn/6. R corresponds to the alkyl CnH2n+1.
The optical rotations, \( \alpha^{20}_{D} \), for S05n/6 determined using a polarimeter in chloroform solution (\( c = 0.10 \)).

| S057/6  | -12.6 |
|---------|-------|
| S058/6  | -13.7 |
| S059/6  | -13.0 |
| S0510/6 | -13.6 |

dichloromethane. The procedure was described in detail recently,[23]

All raw products were purified by column chromatography on silica gel using a mixture of dichloromethane and acetone (99.5:0.5) as an eluent followed by crystallisations twice from ethanol. The molecular structure of the newly synthesised compounds and their purity were checked using standard analytical methods. \(^1\)H NMR spectra were acquired on a spectrometer Varian 300 MHz, deuterchloroform or DMSO-d6 serving as solvent and the signals of the solvent were used as internal standards. The chemical purity of the materials was checked by high-pressure liquid chromatography, which was carried out using a silica gel column (Biosphere Si 100-5 \( \mu \)m, 4 × 250, Watrex International, Clearwater, FL, USA) with a mixture of 99.9% of toluene and 0.1% of methanol as an eluent, and detection of the eluting products by a UV–VIS detector (\( \lambda = 290 \) nm). The chemical purity of all synthesised compounds was found within 99.5–99.9%. The optical rotation was measured using a polarimeter (Optical Activity Ltd., Ramsey, UK) in chloroform solution (\( c = 0.10 \)). The results are summarised in Table 1.

\(^1\)H NMR S010/6 (300 MHz, DMSO), \( \delta \): 0.88 (6H, m, CH\(_3\)), 1.20–1.70 (27H, m, CH\(_2\), CH\(_3\)), 2.72 (2H, t, CH\(_2\)Ar), 4.16 (2H, t, COOCH\(_2\)), 5.28 (1H, q, C'\(^\prime\)H), 7.40 (1H, d, meta to Cl), 7.48 (2H, d, ortho to OCOAr), 7.59 (1H, d, para to Cl), 7.71 (1H, s, ortho to Cl), 7.80 (6H, m, ortho to Ar), 7.93 (2H, d, meta to COOAr), 8.09 (2H, d, ortho to COOAr), 8.22 d (2H, d, ortho to COOC').

| Compound | Optical Rotation |
|----------|------------------|
| S057/6   | -12.6            |
| S058/6   | -13.7            |
| S059/6   | -13.0            |
| S0510/6  | -13.6            |

3. Experimental

The materials have been studied using differential scanning calorimetry (DSC, Pyris Diamond, Perkin Elmer, Shelton, CT, USA). The samples have been hermetically closed in aluminium pans and placed into the nitrogen medium. The masses of the samples were 2–4 mg and the cooling and heating rates of 5 K/min have been applied during the calorimetric measurements. The texture observation and dielectric study have been carried out in planar samples of 6 or 12 \( \mu \)m thickness, with 25 mm\(^2\) electrode area. The glass cell parts were coated with patterned transparent indium tin oxide (ITO) electrodes and polyimide layers providing strong planar anchoring. The cells have been filled in the isotropic phase. The temperatures of the samples are changed and stabilised with the accuracy ±0.1°C in the hot stage Linkam LTSE350 (Linkam, Tadworth, UK), placed on the table of the polarising microscope. Some texture studies have been carried out on samples with one free surface. In such samples, a homeotropic surface anchoring is preferred. The polarising microscope Nikon Eclipse (Nikon, Tokyo, Japan) has been used for texture observations.

The spontaneous polarisation, \( P_{s} \), was determined from the polarisation current peak at a triangular electric field switching at a frequency of 10 Hz and an electric field magnitude of 10 V/\( \mu \)m. The driving voltage from an Agilent 33210A function generator (Agilent, Santa Clara, CA, USA) was amplified by a linear amplifier providing the maximum amplitude of about ±120 V. The Tektronix DPO4034 digital oscilloscope (Tektronix, Beaverton, OR, USA) provided information about the switching current profile versus time. The spontaneous tilt angle, \( q_{s} \), was determined at the dc electric field ±10 V/\( \mu \)m, by measuring the angular difference between the extinction positions of the unwound structures under opposite fields.

The frequency dispersion of permittivity was measured in cooled using a Schlumberger 1260 impedance analyser (Schlumberger, Houston, TX, USA) in the frequency range of 10 Hz–1 MHz, keeping the temperature of the sample stable during frequency sweeps within ±0.1 K. The frequency dispersion data were analysed using the Cole–Cole formula (1) for the frequency-dependent complex permittivity, which was complemented by the second and third terms to eliminate the low frequency contribution from dc conductivity \( \sigma \) and the high frequency contribution due to resistance of the ITO electrodes, respectively:

\[
\varepsilon' - \varepsilon_\infty = \frac{\Delta \varepsilon}{1 + (i f / f_0)^{(1 - 0)}} - i \left( \frac{\sigma}{2 \pi \varepsilon_0 f_0} + A f^m \right) \tag{1}
\]

where \( f_0 \) is the relaxation frequency, \( \Delta \varepsilon \) the dielectric strength, \( \alpha \) the distribution parameter of relaxation, \( \varepsilon_0 \) the permittivity of vacuum, \( \varepsilon_\infty \) the high frequency permittivity and \( n, m, A \) are parameters of fitting. The measured real, \( \varepsilon' \), and imaginary, \( \varepsilon'' \), parts of the dielectric permittivity \( \varepsilon'(f) = \varepsilon' - i \varepsilon'' \) were simultaneously fitted to formula (1). For dielectric measurements, we utilised commercial 7 \( \mu \)m cells.

Small-angle X-ray scattering measurements have been performed to determine the structural properties of the identified mesophases. We have used a Bruker D8 DISCOVER Super Speed device (Bruker, Santa Barbara, CA, USA) with a rotating Cu anode.
(wavelength, $\lambda = 1.5418$ Å), working with 12 kW power and equipped with the following elements: a parabolic Göbel mirror conditioning the incident beam, a LiF monochromator and a scintillation detector on the side of the diffracted beam. An Anton Paar DCS 350 chamber (Anton Paar, Graz, Austria) has been used for the temperature control (accuracy in temperature stabilisation is 0.1 K). The positions of the peaks and the intensity have been determined by a computational simulation using Bruker EVA 13 software. The layer thickness, $d$, has been determined using Bragg’s law ($n\lambda = 2d \sin \phi$), from the position of the scattering angle peak.

The helical pitch, $p$, has been established from a diffraction of the He–Ne laser light on the dechirisation lines, which are present in the planar sample due to the strong polar anchoring at the glass surfaces. This method is applicable when the value of $p$ is within the interval, approximately $0.8\mu m < p < 4\mu m$. For such measurements of pitch, thick planar samples (50 μm) have been used.

4. Results

We have studied the mesomorphic properties of a new series of lactic acid derivatives with four-phenyl-ring molecular core, varying the length of the non-chiral terminal chain (see Scheme 1). For all studied compounds designated as SOS$n/6$, the calorimetric measurements have been performed and the phase transition temperatures and associated enthalpy changes have been determined. The results are summarised in Table 2. DSC thermographs taken on the second cooling runs are demonstrated in Figure 1 for two compounds. The upper curves show the second heating run and the lower curves the subsequent cooling run. Mesophases were identified according to their typical textures observed under the polarising microscope. All studied materials exhibit the paraelectric SmA* – ferroelectric SmC* phase sequence on cooling from the isotropic phase. Planar fan-shaped textures observed in the SmA* phase changed into broken-fan-shaped ones in the SmC* phase and array of dechirisation lines appeared just below the SmA*–SmC* phase transition. It is necessary to point out that when leaving the sample for electro-optical studies at the room temperature for several hours, partially, the crystallisation started in a form of areas (islands), which do not respond to the applied electric field.

We have measured the spontaneous polarisation, $P_s$, and the spontaneous tilt angle, $\Theta_s$, in a broad temperature interval of the ferroelectric SmC* phase, down to room temperature on cooling. Temperature dependences of $P_s$ and $\Theta_s$ are presented in Figure 2. One can see that the spontaneous polarisation does not reveal any saturation tendency on cooling and $P_s$ values grow in a linear way with similar slope not changing with the length of the non-chiral chain. Both spontaneous values are growing in a continuous way at the SmA*–SmC* phase transition, evidencing its second-order character of this phase transition.

| SOS$n/6$ | m.p. [$\Delta H$] | $T_{cr}$ [$\Delta H$] | SmC* | $T_c$ [$\Delta H$] | SmA* | $T_i$ [$\Delta H$] | Iso |
|----------|-----------------|-----------------|------|-----------------|------|-----------------|-----|
| SOS7/6   | 9 [+2.42]       | 3 [-1.86]       |      | 110 [-0.09]    |      | 185 [-4.08]    |     |
| SOS8/6   | 1 [-1.25]       | 3 [-1.82]       |      | 119 [-0.17]    |      | 180 [-2.44]    |     |
| SOS9/6   | 3 [+5.55]       | 3 [-5.27]       |      | 126 [-0.24]    |      | 181 [-4.27]    |     |

Melting points (m.p.) have been indicated on the second heating. All thermographs have been taken at a rate of 5 K/min.
neous tilt angle values are increasing on cooling within the SmC* phase continuously and similarly to \( P_s \) values, \( \Theta_s \) values do not show any significant difference with \( n \) value. Getting to the room temperature, \( \Theta_s \) values are approaching 42°.

We confirmed the phase identification utilising x-ray scattering technique in the small angle region. One sharp peak with corresponding commensurate satellites has been observed in the temperature interval of liquid crystalline mesophases, which is consistent with smectic packing of molecules. Fitting the x-ray data allowed us to establish the layer spacing value, \( d \). Temperature dependences \( d(T) \) for all studied compounds are shown in Figure 3. Within the SmA* phase, the layer spacing slightly grows on cooling, which is often observed in the SmA* phase and usually explained by the stretching of alkyl chains on cooling. Below the SmA*–SmC* phase transition on cooling, \( d(T) \) decreases on cooling, which reflects tilting of molecules in the ferroelectric SmC* phase. We have calculated the length of an isolated molecule, \( l \), using a standard computing programme and found \( l = 31 \) Å for SOS7/6 and \( l = 34 \) Å for SOS10/6. It should be pointed out that the measured layer spacing is higher than the length of fully extended molecule. Probably, the molecules are mutually shifted when packing in smectic layers due to the presence of the big lateral substituent. Additionally, the molecular core created by terphenyl is rather rigid and may support such shifting of molecules in layers as well.

We have established the pitch length in the ferroelectric SmC* phase for all studied compounds. From Figure 4, where the data are summarised, it follows that the increase of the non-chiral chain leads to the decrease of the pitch. Additionally, below the SmA*–SmC* phase transition on cooling, we have observed an abrupt increase, then a gradual decrease and then stabilisation with temperature. Nevertheless, such behaviour of the pitch is usual and was often described in the literature.\(^{24}\)
We have studied the dielectric spectroscopy data, which exhibit one distinct mode in the SmC'/C3 phase and one weak mode in the SmA'/C3 phase above the SmA'/C3–SmC'/C3 phase transition. In Figure 5, three-dimensional plots of permittivity in a broad temperature and frequency interval are shown for compound SOS7/6 in a commercial planar cell, 7 μm thick. We have fitted all data by the Cole–Cole formula (1) and obtained information about values of the fitting parameters. The relaxation frequency, $f_r$, and the dielectric strength, $\Delta \varepsilon$, were analysed (see Figure 6 with these parameters for SOS7/6). In the SmA' phase, $f_r$ of the mode decreased linearly on cooling, and $\Delta \varepsilon$ is growing when approaching the SmA'–SmC' phase transition, which is a typical behaviour for the soft mode (fluctuation of the molecular tilt). In the SmC' phase, the Goldstone mode connected with fluctuation of the azimuthal orientation is observed, with characteristic high $\Delta \varepsilon$ and low $f_r$ values. For all SOSn/6 compounds, high values of $\Delta \varepsilon$ and low values of $f_r$ have been detected. The relaxation frequency decreased on cooling within the SmC' phase, and when $f_r$ fell below 50 Hz, we were not able to fit properly the data (see, e.g., Figure 5).

5. Discussion and conclusions

We have prepared and studied new types of lactic acid derivatives, with a molecular core based on terphenyl laterally substituted by a chlorine atom. We established the SmA'/C3–SmC'/C3 phase sequence on cooling from the isotropic phase in a very broad temperature interval. The mesomorphic properties are not basically influenced by the non-chiral alkyl chain length. The Iso-SmA' phase transition temperature decreases with prolonging the molecule. On contrary, the SmA'/SmC' phase transition increases with increasing $n$ ($n$ is the number of carbon atoms in the terminal alkyl chain).

In the studied compounds of SOSn/6, we have observed rather high polarisation values as well as high tilt angles approaching to 42°. Both factors are important for the perspective of applications. We can compare the compounds under scope with previously studied lactic acid derivatives with four-ring-phenyl core laterally substituted by chlorine. The former mesogens (see Figure 7 with chemical formula to be compared with the studied compounds) exhibited higher transition temperatures, at least by 20°C. [16,17] Additionally, for the previously reported compounds, rather high melting points and crystallisation
temperatures were observed; the clearing points were 200–220°C. Surprisingly, polarisation, tilt angle and pitch values are very similar for both types of molecular cores. From this point of view, the drop down of transition temperatures is the most important advantage of the new compounds presented herein.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Gray GW, McDonnell DG. Synthesis and liquid-crystal properties of chiral alkyl-cyano-biphenyl (and alkyl-cyano-p-terphenyls) and of some related chiral compounds derived from biphenyl. Mol Cryst Liq Cryst. 1976;37:189–211. doi:10.1080/15421407608084356.

[2] Goulding MJ, Greenfield S. Mesomorphic properties of some laterally fluorinated 4-alkyl,4′-oxoalkyl 1,1′,4′,1″-terphenyls. Liq Cryst. 1993;13:345–351. doi:10.1080/0267899308026308.

[3] Gray GW, Hird M, Lacey D, et al. The synthesis and transition temperatures of some 4,4″-dialkyl- and 4,4″-alkoxyalkyl-1,1′,4″-terphenyls with 2,3- or 2,3″-difluoro substituents and of their biphenyl analogs. J Chem Soc, Perkin Trans. 1989;12:2041–2053. doi:10.1039/P29890002041.

[4] Bezborodov VS, Kondratenkov VM, Lapanik VI, et al. Synthesis and mesomorphic properties of 4-alkyl-3,4″-disubstituted biphenyls and terphenyls. Liq Cryst. 1991;10:799–802. doi:10.1080/02678299108036454.

[5] Hird M, Gray GW, Toyne KJ. The synthesis and transition temperatures of some laterally cyano-substituted 1,1′:4″,1″-terphenyls. Mol Cryst Liq Cryst. 1991;206:205–221. doi:10.1080/0268949108037731.

[6] Glendenning ME, Goodby JW, Hird M, et al. The synthesis and mesomorphic properties of 2,2′,3,3′-triaromatic rings in the mesogenic core. Liq Cryst. 2002;29:1435–1439. doi:10.1080/0267829020000031234.

[7] Glendenning ME, Goodby JW, Hird M, et al. The synthesis and mesomorphic properties of biphenyl bismesogen with four aromatic rings in the mesogenic core. Liq Cryst. 2002;27:2645–2654. doi:10.1080/0267829021000031234.

[8] Hamplová V, Kaspar M, et al. Highly tilted smectogens with four-phenyl-ring molecular core, laterally substituted by iodine atom. Liq Cryst. 2015;42:404–411. doi:10.1080/02678292.2014.996791.
[20] Kašpar M, Hamplová V, Novotná V, et al. The effect of the alkyl chain length on the mesomorphic properties of new lactic acid derivatives. Liq Cryst. 2014;41(8):1179–1187. doi:10.1080/02678292.2014.910315.

[21] Bezborodov V, Sasnouski G, Lapanik V. New liquid crystalline cyclohexene and cyclohexane derivatives and compositions based upon them. Liq Cryst. 2002;29:521–528. doi:10.1080/02678290110118581.

[22] Sasnouski G, Lapanik V, Dabrowski R, et al. Synthesis of new LC compounds with high optical anisotropy: pentaphenyl derivatives lateral substituted. Phase Trans. 2012;85:309–313. doi:10.1080/01411594.2011.646267.

[23] Podoliak N, Novotná V, Kašpar M, et al. Anomalous phase sequence in new chiral liquid crystalline materials. Liq Cryst. 2014;41:176–183. doi:10.1080/02678292.2013.846424.

[24] Goodby JW, Blinc R, Clark NA, et al. Ferroelectric liquid crystals: Principles, properties and applications. Philadelphia (PA): Gordon and Breach Science Publishers; 1991.