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New ferroelectric and antiferroelectric liquid crystalline materials containing differing numbers of lactate units

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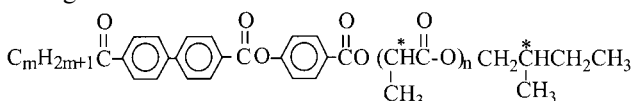
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A new series of chiral liquid crystalline materials having the same rigid core containing a keto group, and various numbers of (*S*)-lactate groups in the chiral segment, has been synthesized and studied. All the compounds contain a branched terminal alkyl chain derived from (*S*)-2-methylbutanol. The influence of the number of lactate units on mesogenic behaviour has been studied. All the compounds show the paraelectric SmA phase and the ferroelectric SmC* phase over rather wide temperature ranges. The antiferroelectric SmC_A* phase was observed for the compound possessing two lactate groups.

1. Introduction

The mesogenic behaviour of liquid crystal molecules is influenced not only by the structure of the rigid molecular core but also by the chiral part of the molecule. Using a lactate-based chiral segment has yielded many materials with rather broad ferroelectric phases [1–7]. Materials containing two lactate units have been described only in a few cases [8–11], even though some of these, showed antiferroelectric phase behaviour.

All the compounds presented here contain an (*S*)-2-methylbutyl chain in the chiral segment, the same rigid core containing a keto group and the same length of the alkyl chains. The aim of this work is to compare the mesomorphic behaviour and physical properties of new liquid crystalline materials with differing numbers of (*S*)-lactate groups in the chiral segment of the molecule. The general structure of the materials studied is:

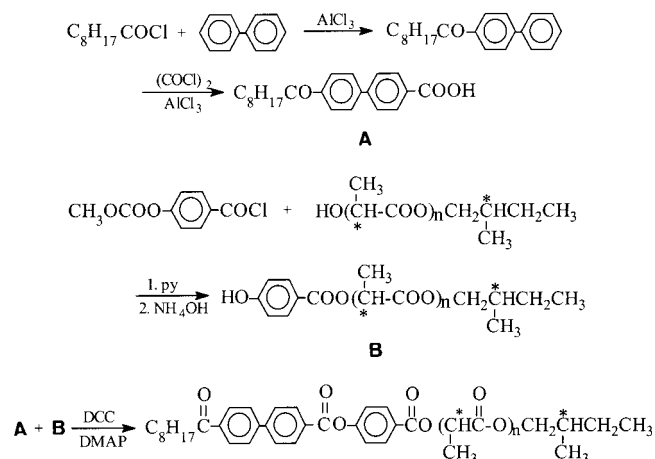


where $n = 1, 2, 3$ is the number of lactate groups in the molecule.

2. Synthesis

The general procedure for the preparation of the materials studied here, with differing numbers of lactate units, is summarized in the scheme.

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The synthesis of the rigid part of this structure was described recently elsewhere [7]. The chiral part of the molecule was prepared in a similar manner as reported in the literature [5, 9]. The structures of the final compounds were confirmed by NMR spectroscopy.

¹H NMR (200 MHz, CDCl₃) for compound $n = 1$ (denoted as **1**): 8.30 d (2H, *ortho* to $-\text{COOAr}$); 8.18 d (2H, *ortho* to $-\text{COOC}^*$); 8.08 d (2H, *ortho* to $-\text{CO}-$); 7.7–7.8 m (4H, *ortho* to Ar–Ar); 7.33 d (2H; *ortho* to $-\text{OCO}$); 5.35 q (1H, C*H); 4.0 m (2H, C*COOCH₂C*); 3.0 t (2H, CH₂CO); 1.2–1.8 m (15H, CH₂ + C*H); 1.65 d (3H, CH₃C*); 0.9 m (9H, 3 × CH₃).

¹H NMR (200 MHz, CDCl₃) for compound $n = 2$ (denoted as **2**): 8.30 d (2H, *ortho* to $-\text{COOAr}$); 8.18 d (2H, *ortho* to $-\text{COOC}^*$); 8.08 d (2H, *ortho* to $-\text{CO}-$);

7.7–7.8 m (4H, *ortho* to Ar–Ar); 7.33 d (2H; *ortho* to –OCO); 5.40 q (1H, ArCOOC*H); 5.20 q (1H, C*H); 4.0 m (2H, C*COOCH₂C*); 3.0 t (2H, CH₂CO); 1.2–1.8 m (15H, CH₂+C*H); 1.75 d (3H, CH₃C*OCOAr); 1.54 d (3H, CH₃C*); 0.9 m (9H, 3 × CH₃).

¹H NMR (200 MHz, CDCl₃) for compound *n*=3 (denoted as **3**): 8.30 d (2H, *ortho* to –COOAr); 8.18 d (2H, *ortho* to –COOC*); 8.08 d (2H, *ortho* to –CO–); 7.7–7.8 m (4H, *ortho* to Ar–Ar); 7.33 d (2H; *ortho* to –OCO); 5.40 q (1H, ArCOOC*H); 5.25 m (2H, 2 × C*H); 4.0 m (2H, C*COOCH₂C*); 3.0 t (2H, CH₂CO); 1.2–1.8 m (15H, CH₂+C*H); 1.75 d (3H, CH₃C*OCOAr); 1.60 d (3H, CH₃C*); 1.54 d (3H, CH₃C*); 0.9 m (9H, 3 × CH₃).

3. Experimental

Glass cells consisting of ITO transparent electrodes with unidirectionally rubbed polyimide layers, to ensure the adoption of a planar (bookshelf) geometry, were filled with the new compounds. The sample thickness was defined by mylar sheets as 25 μm. Sample alignment was improved using an electric field (10–20 Hz, 40 kV cm⁻¹) applied for 5–20 min.

Values of the spontaneous polarization, P_s , were evaluated from the $P(E)$ hysteresis loop measured during P_s switching by an a.c. electric field, E , of frequency 60 Hz.

The values of the spontaneous tilt angle, θ_s , were determined optically from the difference between the extinction positions at crossed polarizers under opposite d.c. electric fields ± 40 kV cm⁻¹.

In the SmC* phase, the values of helix pitch length, p , were established by the diffraction of He-Ne laser light (630 nm) on disclination lines; the line spacing equals p . p could not be measured for compound **3**, as the helix was spontaneously unwound.

X-ray studies were performed with a modified DRON system equipped with a Gemonochromator, working in reflection mode. Samples were prepared on glass with one surface left free, ensuring homeotropic alignment. The temperature was controlled to within 0.1 K.

The frequency dispersion of the complex permittivity was measured using a Schlumberger 1260 impedance

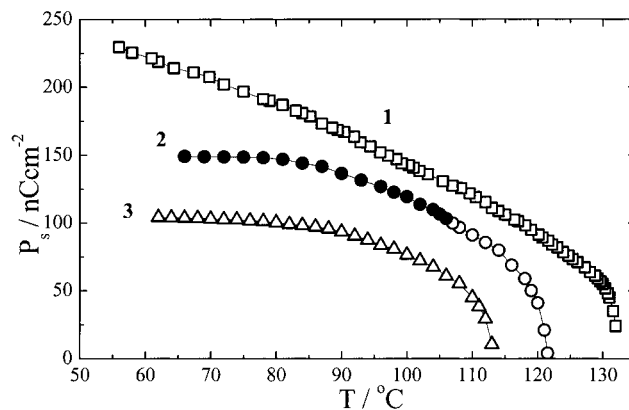


Figure 1. Temperature dependences of the spontaneous polarization, P_s , for indicated materials. Solid points indicate P_s values in the antiferroelectric phase.

analyser in the frequency range 1 Hz–1 MHz, keeping the temperature of the sample stable to within ± 0.1 K.

4. Mesomorphic properties

For the materials studied, the sequences of phases and phase transition temperatures were determined by observing characteristic textures and their changes using a polarizing microscope and from DSC measurements. All the compounds show the paraelectric SmA phase and the ferroelectric SmC* phase over a broad temperature range. The antiferroelectric SmC_A* phase was detected for the compound possessing two lactate groups (see the table).

5. Physical properties

In the polar SmC* and SmC_A* phases, P_s values decrease as the number of lactate units increase: for compound **1** with one lactate group P_s reaches about 200 nC cm⁻² (see figure 1).

For all the compounds, the values of θ_s are about 28–32° at saturation. No difference in θ_s was detected on changing the number of lactate groups (see figure 2).

In the SmC* phase, the helix pitch was found to be temperature independent for compounds **1** and **2** except for over a few degrees just below the SmA–SmC* phase transition (see figure 3). It can be seen that p increases as the number of lactate groups increases. For

Table 1. Sequence of phases, phase transition temperatures (°C), melting points m.p. (°C), transition enthalpies ΔH (J g⁻¹) (in parentheses) from DSC, and values of the spontaneous polarisation P_s (nC cm⁻²) at 45 K below the transition from the SmA phase.

Compound	M.p.	Cr	SmC _A *	SmC*	SmA	I	P_s
1	53 (8.8)	• 52 (-27.5)	—	• 130 (-0.2)	• 153 (-7.1)	•	183
2	76 (43.3)	• 63 (-35.6)	• 105 (-0.1)	• 119 (-0.3)	• 131 (-6.0)	•	149
3	84 (28.2)	• 61 (-25.4)	—	• 113 (-0.3)	• 127 (-4.5)	•	104

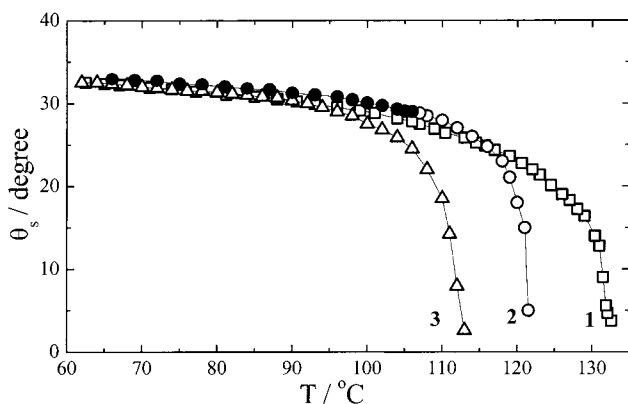


Figure 2. Temperature dependences of the spontaneous tilt angle, θ_s , for indicated materials. Solid points indicate θ_s values in the antiferroelectric phase.

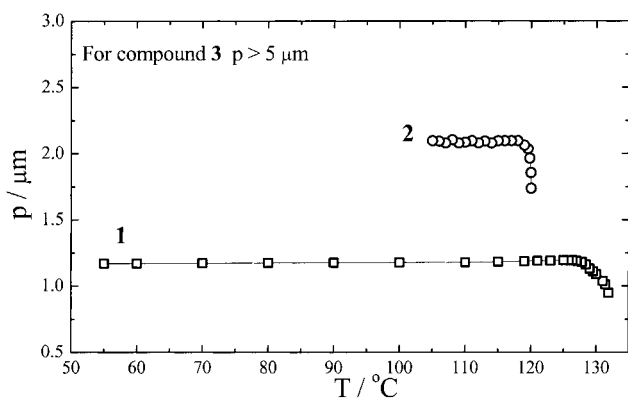


Figure 3. Temperature dependences of the helix pitch length, p , for indicated materials in the SmC^* phase. For compound **3** the helix pitch was unwound.

compound **3**, the helical pitch was found to be greater than $5\ \mu\text{m}$. For compound **2**, the helix pitch length in the antiferroelectric SmC_A^* phase is too short (smaller than $1\ \mu\text{m}$) to be detected using the diffraction method.

The temperature dependences of the layer spacing, d , for all the compounds studied are shown in figure 4.

The lengths of the most extended conformers of the molecules, L , were estimated using HyperChem software. After the optimization of the structures, we obtained values for L of 32.6 , 37.8 and $41.1\ \text{\AA}$ for **1**, **2** and **3**, respectively. The effective layer spacing, d/L , decreases on increasing the number of lactate units (in the SmA phase $d/L = 0.96$, 0.94 , 0.92 for $n = 1, 2, 3$, respectively). This seems to be reasonable given that lengthening the non-rigid part of the molecule may result in a reduced molecular ordering due to statistical averaging of a greater number of conformers.

The frequency dispersion data were analysed over the whole temperature range of the SmA , SmC^* and SmC_A^*

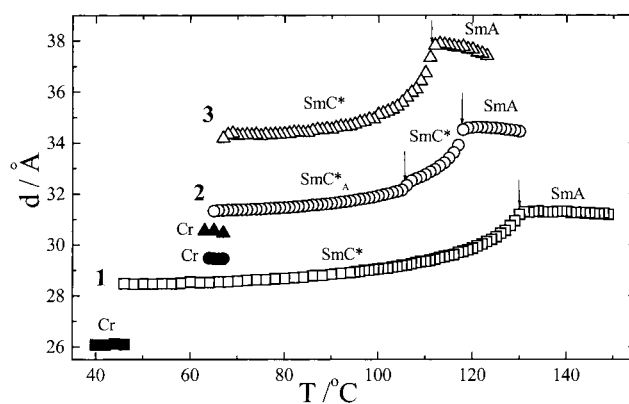


Figure 4. Temperature dependences of the layer spacing, d , for indicated materials. Molecular lengths were estimated for the most extended conformers.

phases using the Cole–Cole formula:

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (if/f_T)^{1-\alpha}} - i \frac{\sigma}{2\pi\varepsilon_0 f^n} + Af^m$$

where f_T is the relaxation frequency, $\Delta\varepsilon$ is the dielectric strength, α is the distribution parameter of the mode and n, m, A are fitting parameters. The second and third terms in the equation are used to eliminate a low frequency contribution to ε'' from d.c. conductivity, σ , and a high frequency contribution to ε'' , respectively. In figures 5 and 6, the results of these fittings are shown, and specifically, these figures show that the temperature dependences of the relaxation frequency and dielectric strength, respectively, in the whole range of the SmA , SmC^* and SmC_A^* phases. In the *paraelectric* SmA phase, the relaxation frequency of the soft mode linearly decreases while the dielectric strength increases steeply, when approaching the transition temperature to the ferroelectric SmC^* phase. There is a great

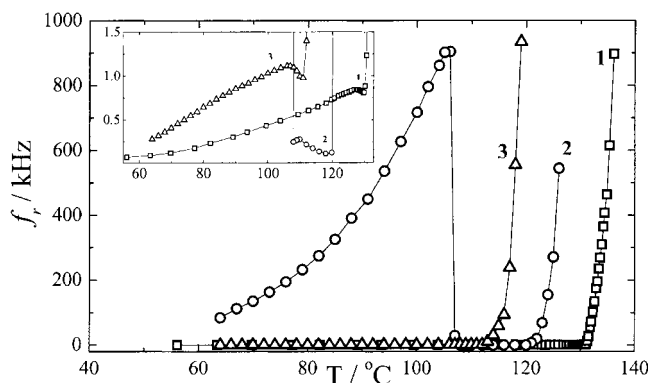


Figure 5. Temperature dependences of relaxation frequency, f_r , for compounds **1**, **2** and **3** in the whole temperature range of the *paraelectric*, *ferroelectric* and *antiferroelectric* phases.

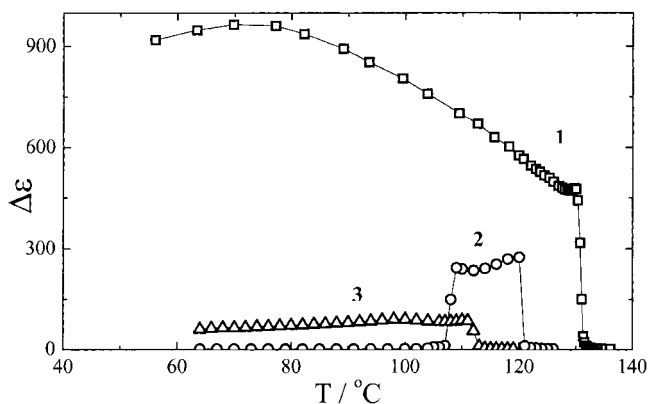


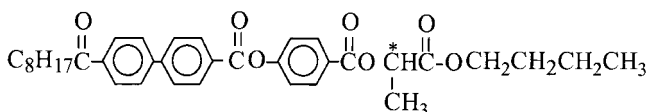
Figure 6. Temperature dependences of dielectric strength, $\Delta\epsilon$, for compounds **1**, **2** and **3** in the whole temperature range of the *paraelectric*, *ferroelectric* and *antiferroelectric* phases.

increase in the permittivity on cooling from the SmA phase to the *ferroelectric* SmC* phase due to the strong contribution of the Goldstone mode in the SmC* phase. Moreover, the dielectric strength of this mode strongly decreases with increasing number of lactate groups in the molecule. For compound **2**, the high frequency mode was detected in the *antiferroelectric* SmC_A* phase. The relaxation frequency of this mode softens from about 900 kHz to about 90 kHz, probably due to the decrease of the viscosity.

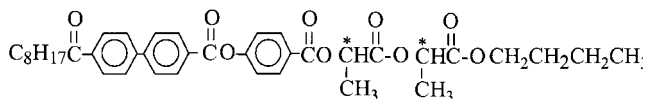
6. Discussion and conclusions

A new series of chiral liquid crystals differing in the number of (*S*)-lactate groups in the chiral part of the molecule has been synthesized and characterized. All the compounds show the *paraelectric* SmA and *ferroelectric* SmC* phases over rather broad temperature ranges; the phase transition temperatures decrease when the the number of lactate groups, n , increases from 1 to 3; by contrast, the melting points increase for the same structure changes. The *antiferroelectric* SmC_A* phase was detected only for the compound possessing two lactate groups. The same changes in phase transition temperatures on increasing the number of lactate units in the chiral chain were observed for similar compounds having an *n*-butyl chain [7, 10] instead of the (*S*)-2-methylbutyl moiety in the chiral segment.

For the series studied, the values of spontaneous polarization decrease with increasing n . We should compare this behaviour with that of similar compounds having an *n*-butyl chain instead of the 2-methylbutyl,



denoted as K 8/4 in [7] and



denoted as KLL 8/4 in [10].

The value of spontaneous polarisation \mathbf{P}_s for compound K 8/4 is only 120 nC cm^{-2} at $T = T_c - 50 \text{ K}$ [7], while for compound KLL 8/4 \mathbf{P}_s reaches a value of 170 nC cm^{-2} at $T = T_c - 50 \text{ K}$ [10], which means that the effect of increasing the number of lactate groups is opposite in sense to that observed for the compounds studied here. This may be connected to the different proportions of individual conformers arising through the rotation around C–C bonds in both types of compound, which affects the resulting transverse dipole moment in the chiral part of the molecule. The possible number of conformers increases with increasing number of flexible C–C bonds in the chain and, thus, a partial compensation of the dipole moments of lactate groups in a molecule may be expected.

In the ferroelectric SmC* phase, the helix pitch length increases on increasing the number of lactate units.

As for the temperature dependence of the layer spacing, the phase transition from the orthogonal SmA to the tilted SmC* phase was observed as a gradual decrease in the layer thickness, associated with the molecules tilting. In compound **2**, at the SmC* → SmC_A* phase transition, there is a decrease in the layer thickness, similar to that described elsewhere [12], which is presumably connected to an increase in the smectic order.

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