

CHAPTER 6

**Structural and mesomorphic
properties of a lactic acid derivative
with several ester linkages in the
molecular core**

6.1 Introduction

Self-assembling materials with desired functionality and physical properties currently represent a fascinating area of intense research and provides a highlighted approach for the design and study of new material structures. One of the most exciting but special classes of such smart organic materials that are able to self-assemble at nano- and meso-scopic length scales are those possessing the polar layered structure of nanometre dimensions, the so-called chiral smectic liquid crystals (LCs). The intermolecular interactions, responsible for the self-organization, can be precisely adjusted by appropriate molecular design, *i.e.* by building the molecule from various units [1-6]. The main objective of the present work is to contribute systematic data on molecular architecture – nano organization relationship for a specific type of nano-organized system, namely chiral ferroelectric liquid crystalline (FLC) materials [2,7]. This type of materials derived from lactic acid [6,8-14], can be considered to be of reasonably of high fundamental interest due to their marked advantages [10,15,16] and also as a starting point for mixture design [3,15-20] or for the preparation of functional macromolecular self-assembling materials [1,21-26] for future utilization in photonics and optoelectronics [1,3,27,28].

In chapter 5 the structural properties of a lactic-acid-based chiral liquid crystalline material, namely 4'-(1-(octyloxy)-1-oxopropan-2-yloxy) biphenyl-4-yl 4-(decyloxy) benzoate containing two ester linkages in the core have been discussed [29]. Incorporation of an ester linkage group between the aromatic core units [3,30-31] not only increases the molecular length and flexibility but also affects the longitudinal polarizability, planarity [32] and thereby enhances the spontaneous polarization in such ferroelectric liquid crystalline materials [26]. Hence, considerable interest in the design of new liquid crystalline molecules has emerged, which may self-assemble into mesophases with ferroelectric and antiferroelectric ordering [2,7,27]. However, the specific demands for certain applications might require a combination of definite material parameters like large spontaneous polarization, large tilt angle of molecules with respect to the smectic

layer normal, low viscosity and fast switching [3,8,16,26,33]. Since the shape of the molecules has a significant effect on self-assembling behaviour of ferroelectric liquid crystalline (FLC) materials, both the fundamental physics as well as the technology of FLCs have induced much interest. This work [34] yields a comprehensive study of self-assembling and structural properties of a certain lactic acid derivative, namely decyl-4-(4-(2-(hexyloxy)propanoyloxy)benzoyloxy)benzoate (denoted as **E 10/6**) with four ester linkages in the molecular core (Figure 6.1).

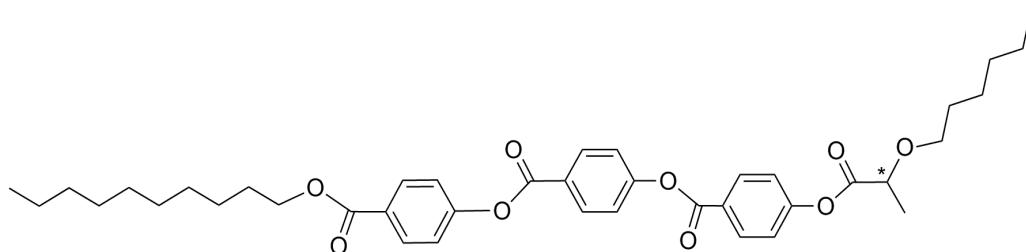


Figure 6.1 The chemical formula of decyl-4-(4-(2-(hexyloxy)propanoyloxy)benzoyloxy)benzoate.

6.2 Material

FLC compounds belonging to a series of the (s)-lactic acid derivatives possessing a flexible core with ester bridges connecting the benzene rings [35] exhibit quite stable chiral tilted smectic phase over a relatively broad temperature range. For these materials the presence of carboxyl group conjugated to the semi-rigid core leads to the appearance of the orthogonal smectic A* (SmA*) phase instead of the cholesteric phase [29].

The synthetic route of FLC **E 10/6** compound selected for the present study has been described in details by Pakhomov *et al.* [35]. The chemical formula of decyl-4-(4-(2-(hexyloxy)propanoyloxy)benzoyloxy)benzoate is presented in Figure 6.1. The compound has been obtained from the Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic and used without further purification.

6.3 Phase identification

The sequences of mesophases and phase transition temperatures determined from polarizing optical microscopy (POM), optical transmission (OT) measurement and differential scanning calorimetry (DSC) have been summarized in Table 6.1. The phase transitions temperatures obtained by these techniques (and also as presented in Ref. 35) slightly differ due to different calibrations and the values obtained from DSC have been taken as a standard. Figure 6.2 shows the DSC curves for **E 10/6** compound on heating and cooling runs. On heating, three endothermic peaks are detected at about 88°C, 93°C and 115°C which correspond to the Cr-SmC*, SmC*-SmA* and SmA*-Iso phase transitions respectively. On cooling, the Iso-SmA* and the SmA*-SmC* phase transitions are observed at about 113°C and 92.8°C respectively. A strong peak corresponding to the SmC*-Cr phase transition has been observed at 72.8°C. The characteristic textures for chiral smectic A (SmA*) and Smectic C (SmC*) phases have been observed using POM and the corresponding microphotographs of the textures are also presented in Figure 6.2. In Figure 6.2, the texture in right exhibit the fan-shaped texture of SmA* phase at T = 101°C and the other texture shows the broken fan-shaped texture of the SmC* phase at T = 90°C during cooling.

Table 6.1 Sequence of phases, phase transition temperatures (°C) and values of enthalpy [ΔH (J/g)] of the investigated compound obtained on cooling ($5\text{ }^{\circ}\text{Cmin}^{-1}$) from the isotropic phase; melting point (m.p.) obtained on heating ($5\text{ }^{\circ}\text{Cmin}^{-1}$) from polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). “•” the phase exists.

Expt.	m.p.	Cr	SmC*	SmA*	Iso
POM	89	•	76	•	93
DSC	88 [+45.0]	•	72.8 [-38.8]	•	92.8 [-0.3] 113 [-6.0] •

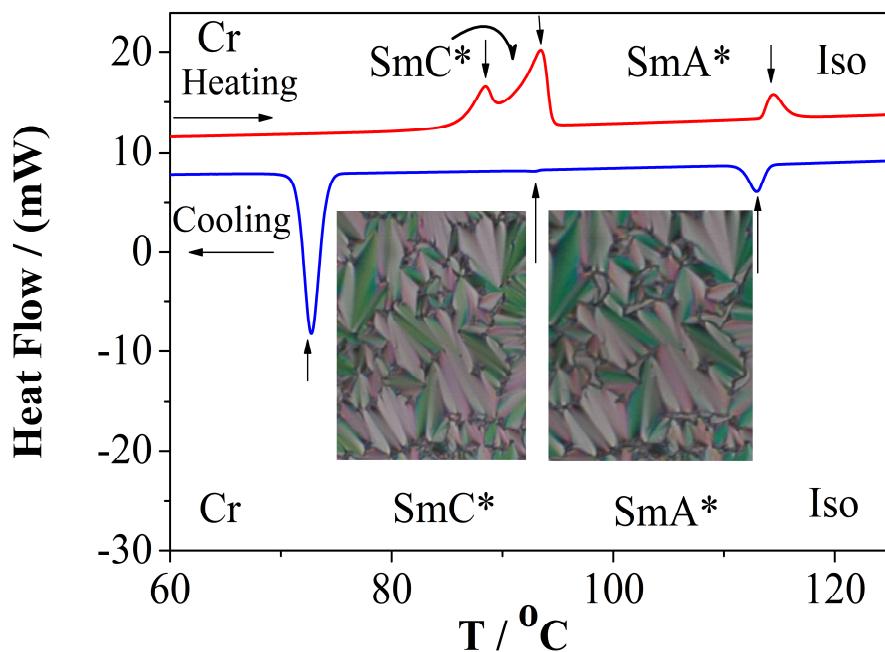


Figure 6.2 DSC thermogram for heating and cooling runs ($5^{\circ}\text{C}/\text{min}$) in nitrogen atmosphere. Vertical arrows indicate the peaks corresponding to phase transitions. Microphotographs of textures of SmA* and SmC* phase at 101°C and 90°C respectively during cooling, observed under the polarising optical microscope.

6.4 Optical transmission study

Figure 6.3 shows the temperature dependence of the transmitted light intensity measured on planar (HG) and homeotropically (HT) aligned cells of different thickness as indicated. Optical transmission (OT) method is not only an excellent system for the identification of phase transition temperatures, but it can also be used as a tool to identify the presence of tilted liquid crystalline phases [36-40]. The transition from the orthogonal SmA* phase to a tilted phase can be detected from Figure 6.3 (HT 8.9 μm) indicating the appearance of the tilted smectic C* phase at about 93°C .

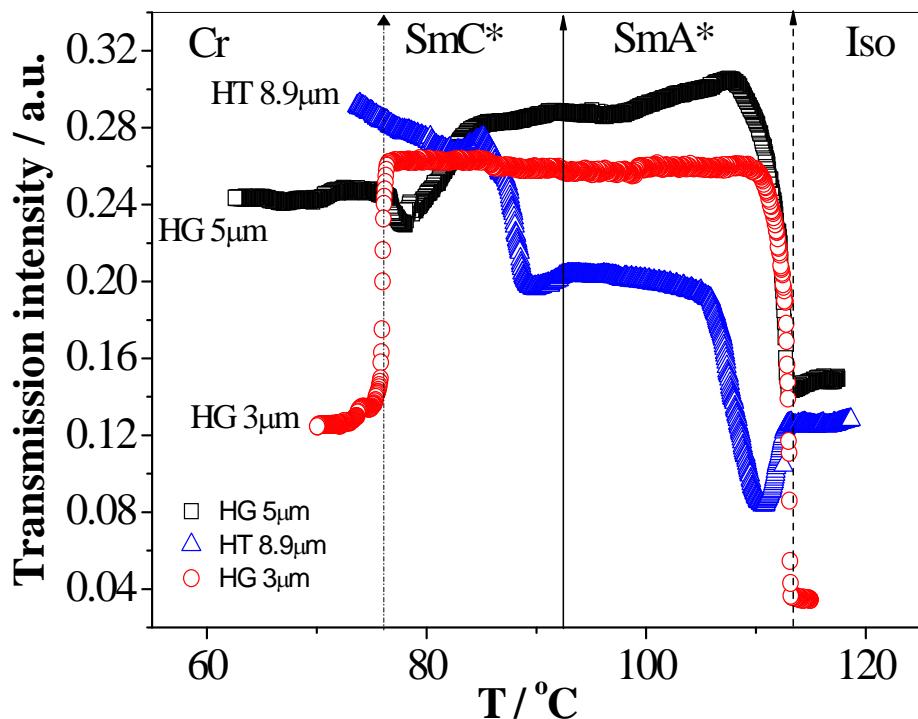


Figure 6.3 Transmitted intensity as a function of temperature measured on cooling. Dashed arrow represents the SmA*-Iso phase transition; solid arrow represents the SmC*-SmA* phase transition; dashed dot arrow represents the Cr-SmC* phase transition.

Figure 6.4 shows the optical birefringence (Δn) of the investigated compound obtained from the transmitted intensity data for $3\mu\text{m}$ and $5\mu\text{m}$ thick cells. The experimental details have been discussed in details in the chapter 2. The experimental values of Δn in both the SmA* and SmC* phases increase with decrease in temperature. This behaviour is expected in the SmA* phase. However, in the SmC* phase this may be due to the fact that the molecular long axes in the SmC* phase of the surface aligned bulk sample are oriented parallel to the aligning surface and the layers are tilted with respect to the surface. The compound exhibits a moderate birefringence of around 0.10. The two data-sets show good overall agreement, though a relatively small mismatch is observed near the SmA*-Iso phase transition.

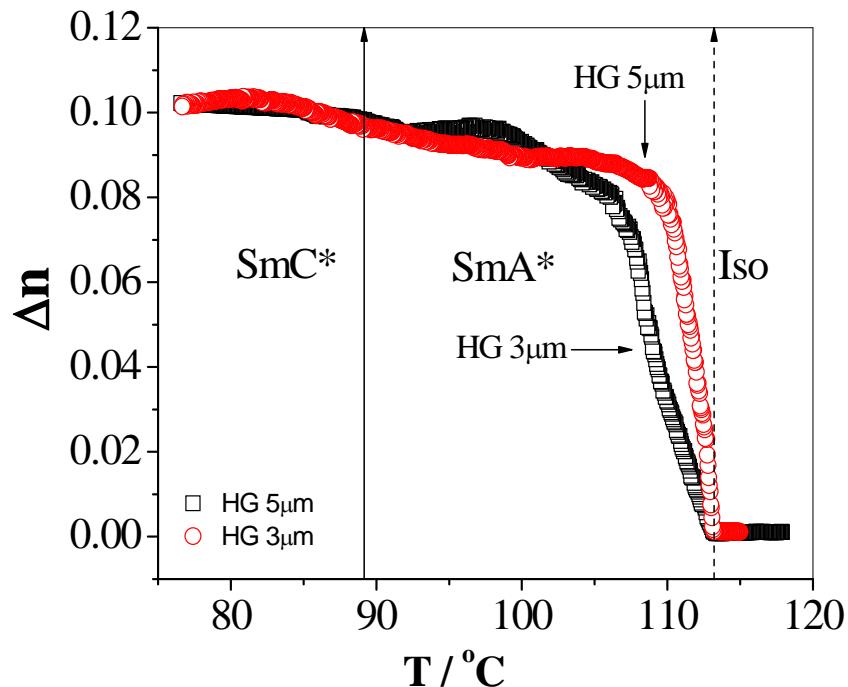


Figure 6.4 Birefringence (Δn) as a function of temperature obtained on $3\mu\text{m}$ and $5\mu\text{m}$ thick samples. Dashed arrow represents SmA*-Iso phase transition and solid arrow represents SmC*-SmA* phase transition.

The possible discrepancy may be due to the differences in the surface anchoring energy, surface effect and alignment of the liquid crystal layer in thick ($5\mu\text{m}$) and thin ($3\mu\text{m}$) cells. The surface anchoring in $3\mu\text{m}$ cell retain the monodomain alignment right up to the SmA*-Iso phase transition in comparison to that of the $5\mu\text{m}$ cell as observed in Figure 6.4. The transmitted intensities corresponding to four different orientations of analyser and polarizer in the temperature scanning technique [40] (as illustrated in chapter 2 of this thesis) have been presented in Figure 6.5.

The transmitted intensity data so obtained have been analyzed to determine the values of optical tilt angle following a procedure described by Saipa *et al.* [40]. The result is shown in Figure 6.6.

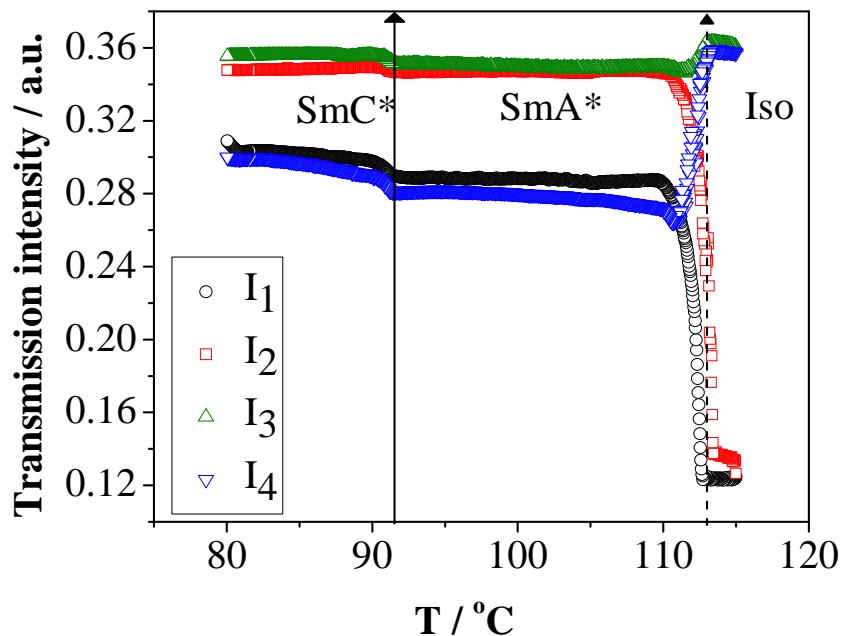


Figure 6.5 Transmitted light intensity obtained in repeated temperature scans at four different orientations of polarizer and analyzer (I_1 - I_4) of the present LC sample of thickness $3\mu\text{m}$. Dashed arrow represents the SmA^* -Iso phase transition and solid arrow represents the SmC^* - SmA^* phase transition

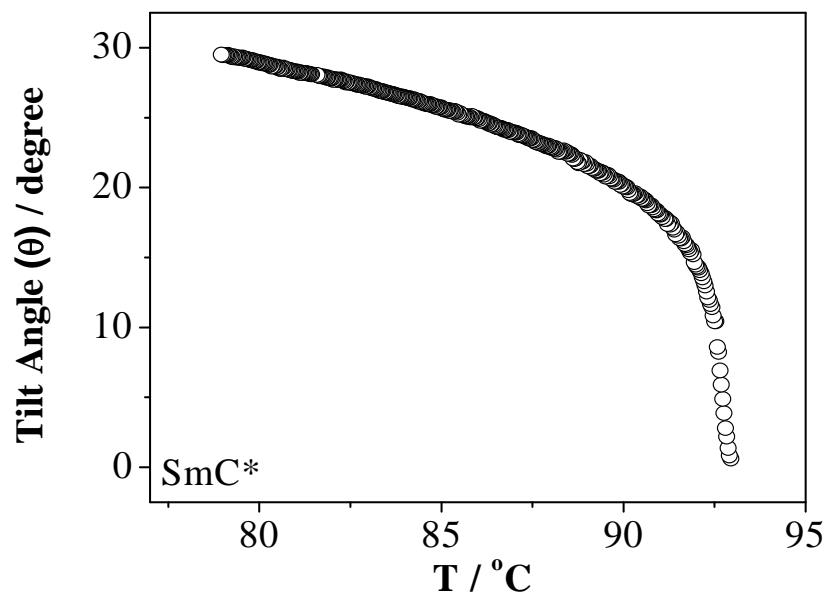


Figure 6.6 Optical tilt angle at wavelength $\lambda = 632.8\text{nm}$ in the SmC^* phase.

The optical tilt value increases continuously from zero and attains a saturation value 29.4° in the SmC* phase. The fact clearly indicates that the nature of SmA*-SmC* transition is of second order. A similar phenomenon is observed in case of spontaneous polarization.

6.5 Spontaneous polarization measurement

Figure 6.7 displays the temperature dependence of spontaneous polarization (P_s) measured within the SmC* phase. Spontaneous polarisation has been measured on $25\mu\text{m}$ thick cell to avoid the influence of surface anchoring effect [41-43]. The saturated value of P_s attained in the SmC* phase is slightly below 97nCcm^{-2} at 70°C . The increasing trend of spontaneous polarization values with decreasing temperature may be explained in terms of the reorientation of the dipolar and electrostatic interactions between the neighbouring molecules. The molecular structure of this compound is expected to have a pronounced effect on the P_s values. The hexyl terminal chain attached to the chiral centre and the additional methylene group also restricts the motion of the chiral lactate unit. The investigated compound is composed of four ester linkage in the core. The resulting zigzag structure and transverse dipole moment of the ester linkage hinders the motion and is perhaps responsible for the relatively large values of the spontaneous polarization.

The P_s data shown in Figure 6.7 have been fitted using the Equation 6.1 [44].

$$P_s = P_0(T_C - T)^\beta \quad \text{for } T < T_C \quad (6.1)$$

Where, T_C is the SmC*-SmA* transition temperature, β and P_0 are the fitting parameters. The agreement between the experimental data and the theoretically fitted curve (Equation 6.1) is quite good. The corresponding fitting parameters determined are $P_0 = 33.1 \text{ nC cm}^{-2}$, $T_C = 364 \text{ K}$ (or 91°C) and $\beta = 0.32$. The critical exponent β is close to the value $0.3125 (= 5/16)$ predicted by the three-dimensional

(3D) Ising model [45], and is in good agreement with those reported by others [46].

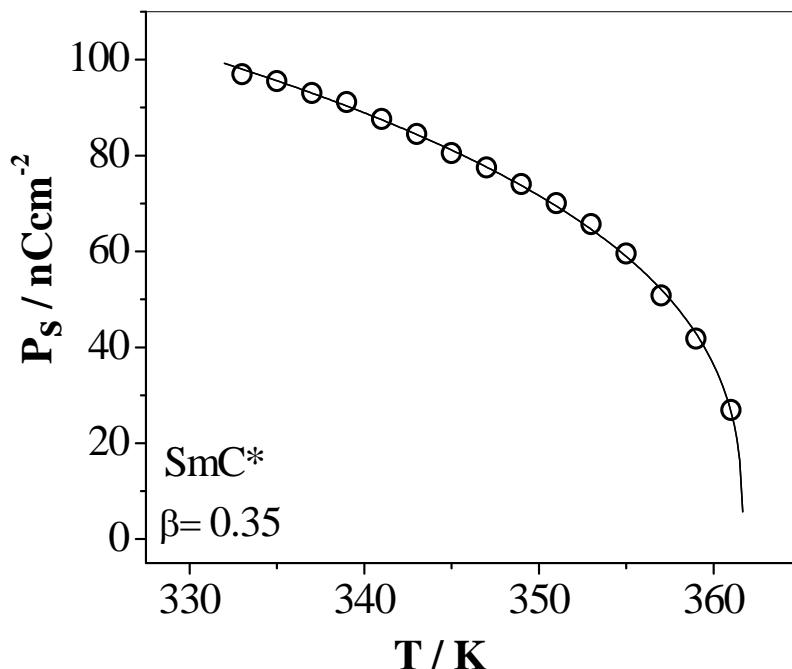


Figure 6.7 Temperature dependence of spontaneous polarization in the SmC* phase. Solid line corresponds to the fit according to Equation 6.1.

6.6 Static dielectric permittivity measurements

The temperature dependence of the parallel and perpendicular dielectric parameters (ε_{\parallel} and ε_{\perp}) is shown in Figure 6.8. The investigated LC compound exhibits negative dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$). In the vicinity of the SmC*-SmA* phase transition, the increment of ε_{\perp} is more pronounced than that of ε_{\parallel} which is consistent with the observations of others [47].

The dielectric anisotropy ($\Delta\varepsilon$) exhibits an abrupt increase in the SmC* phase as shown in Figure 6.8. This is a typical behaviour of ferroelectric liquid crystalline materials as the dielectric constant for such materials is inversely

proportional to the absolute temperature, obeying the Curie-Weiss' law:

$$\varepsilon = \frac{C}{(T_c - T)} \quad (6.2)$$

where C is the Curie constant and T_c is a Curie temperature respectively.

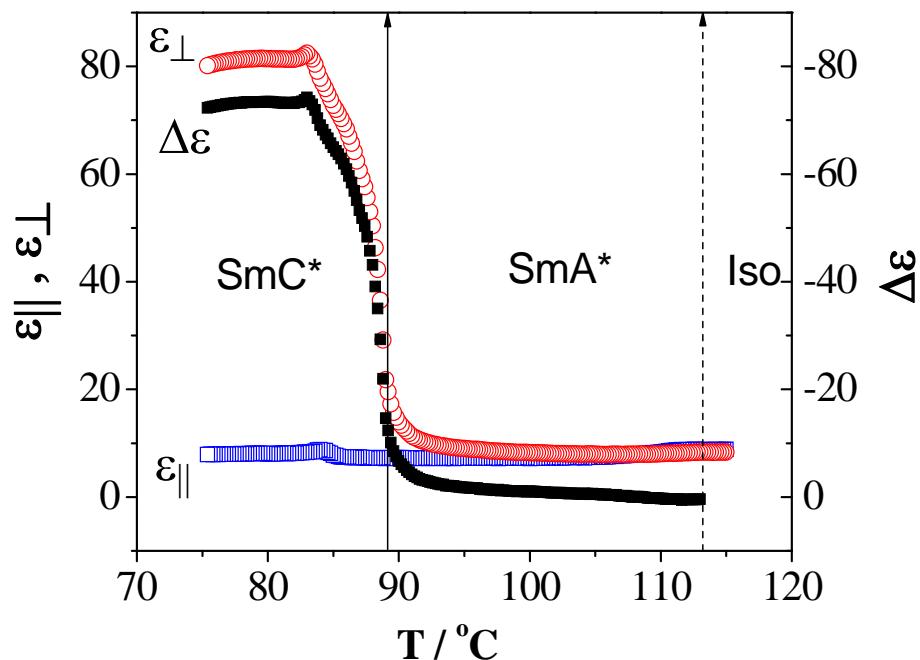


Figure 6.8 Temperature dependence of parallel (ε_{\parallel}), perpendicular (ε_{\perp}) components of dielectric permittivity and the resulting dielectric anisotropy ($\Delta\varepsilon$). Dashed arrow indicates the SmA*-Iso phase transition and solid arrow indicates the SmC*-SmA* phase transition.

A small hump has been observed in the temperature variation of both the parallel (ε_{\parallel}) and perpendicular (ε_{\perp}) permittivity near 83°C which may be due to the appearance of a SmC* sub-phase in the mesomorphic phase sequence. The existence of sub-phases can be attributed by many factors such as the content of chemical impurities, interactions with surfaces and the sample history.

6.7 Structural properties

The temperature dependence of the smectic layer thickness measured by small angle x-ray diffraction is shown in Figure 6.9. The layer spacing (d), determined from x-ray diffraction measurement is almost temperature independent in the orthogonal SmA* phase. The d values decreases from 41.5 Å at the SmC*-SmA* transition to 37.5 Å near the transition to crystal (Cr) phase occurs. This is a consequence of the molecular tilt angle in the SmC* phase. The slight increase in the layer spacing in SmA* phase is related to the stretching of the aliphatic molecular chains and increased orientational order of the molecular long axes [21,31].

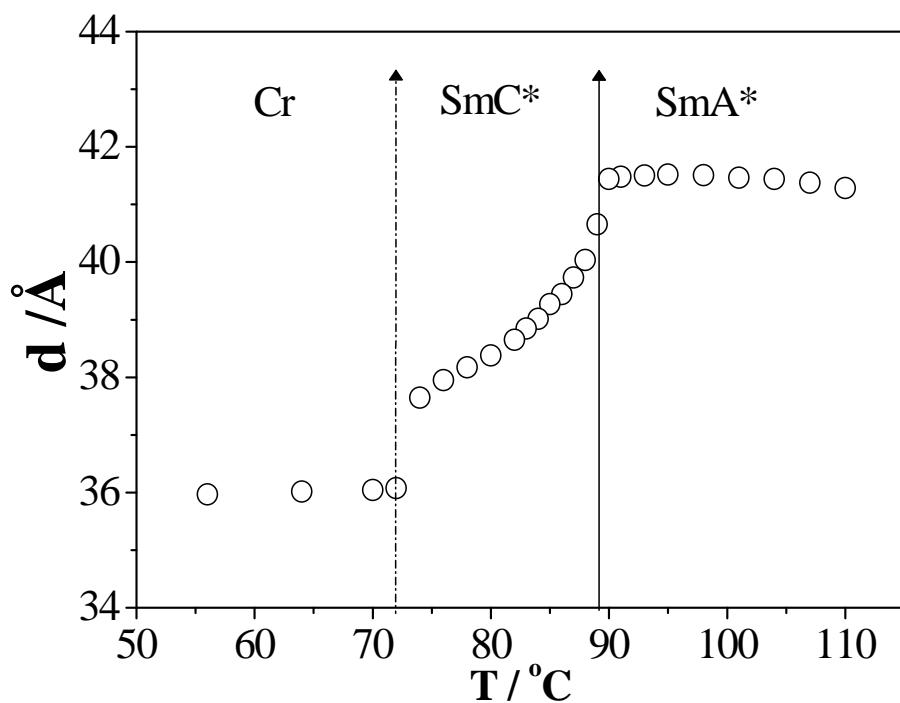


Figure 6.9 Temperature dependence of the layer spacing (d). Solid arrow represents the SmC*-SmA* phase transition and dashed dot arrow represents the Cr-SmC* phase transition.

The length of the most extended conformers of the molecules, L , has been estimated using the semi-empirical molecular orbital package MOPAC model. In

Figure 6.10, a model of this molecule with the axis corresponding to the smallest principal moment of inertia has been presented. After the optimization of the structure, an approximate value for L has been found to be around 42.0 Å. The layer spacing determined by small angle x-ray diffraction is about 41.5 Å. It is noteworthy to mention that the SmA* layer spacing data are remarkably close to the values of the molecular length obtained from the molecular modelling [31].

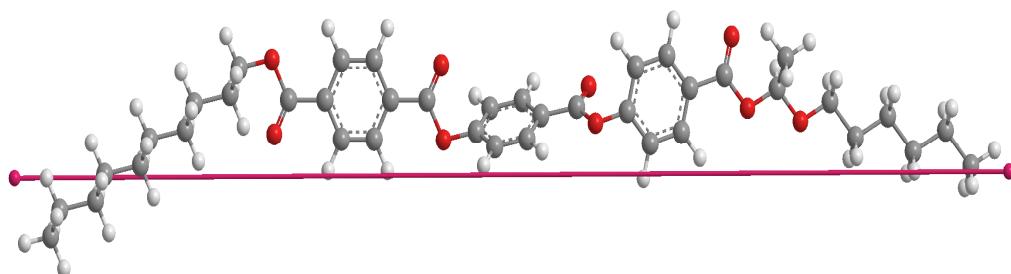


Figure 6.10 Model of the molecular structure after energy minimization using MOPAC. Length of the most extended conformer (L) is calculated to be around 42.0 Å (red line).

In chiral smectic liquid crystal, the tilt angle of the director induces polarization in the medium, therefore the tilt angle is considered to be the primary order-parameter. The tilt angles have been determined using the values of the layer thickness in the SmA* and SmC* phases. The calculated tilt angles (θ) values [48] are shown in Figure 6.11. The θ values increase continuously from zero and attain a maximum value of 25° in the SmC* phase. This clearly suggests that the nature of the SmA*-SmC* transition is of second order. Similar trend has also been observed in case of temperature dependence of spontaneous polarization.

The tilt angle values in the SmC* phase measured from x-ray diffraction method is somewhat lower than those obtained from temperature scanning technique except close to the clearing temperature, as shown in Figure 6.12. The ratio of the tilt angle determined from x-ray measurement to optical tilt angle is around 0.85 [49,50]. This discrepancy is due to the fact that the two methods probe different parts of the molecular structure [39]. The optical method determines the averaged orientation of the molecular core, which mainly defines

the optical axis, whereas the x-ray measurement probes the whole molecule by comparing the layer spacing of the SmA* phase with the d values of the SmC* phase. This observation also indicates that the molecular cores are always considerably more tilted than the terminal alkyl chains.

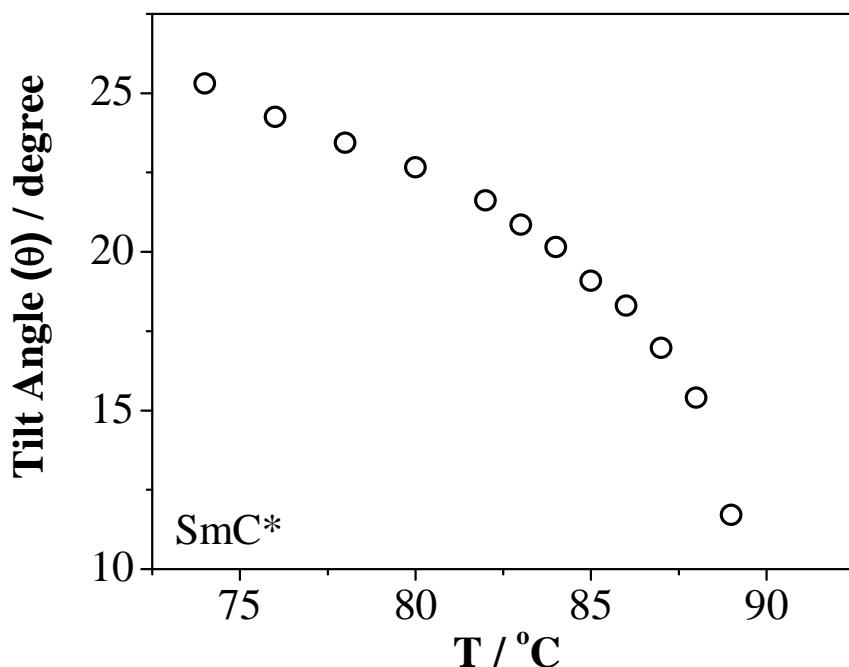


Figure 6.11 Temperature dependence of the tilt angle θ determined from the x-ray diffraction measurement in the SmC* phase.

In the SmC* phase, the tilt angle obeys the power law Equation 6.3 [40]:

$$\theta \propto (T_c - T)^\beta \quad (6.3)$$

with $T < T_c$, where the T_c is the SmC*-SmA* phase transition temperature and β is the critical exponent corresponding to the SmC*-SmA* phase transition. From the Arrhenius plot (Figure 6.13(a-b)) of the experimentally obtained tilt angle determined from x-ray measurement and optical transmission, as a function of $\ln(T_c - T)$, β has been determined to be around 0.28 and 0.30 respectively. This result is in a good agreement with those obtained previously by other workers [51].

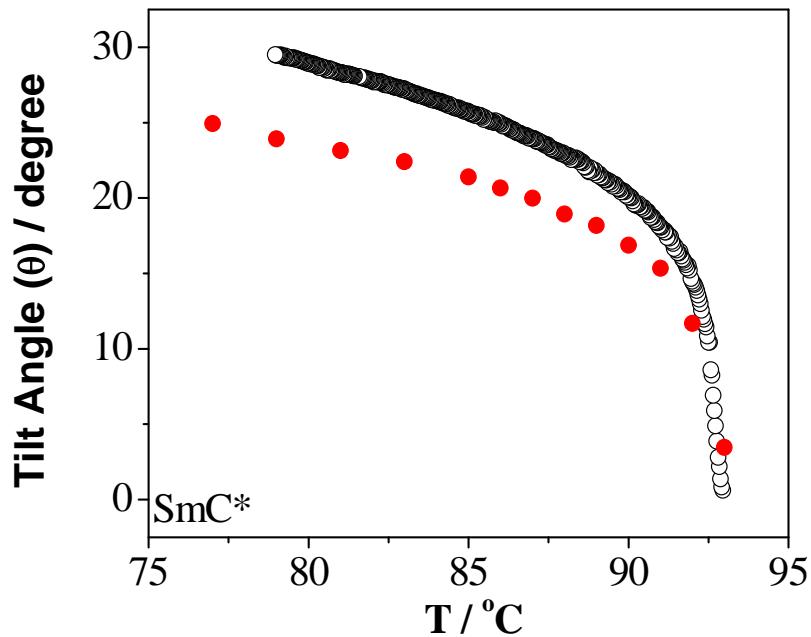


Figure 6.12 Temperature dependent tilt angle from x-ray measurement (closed symbol) and optical transmission study (open symbol) respectively in the SmC* phase.

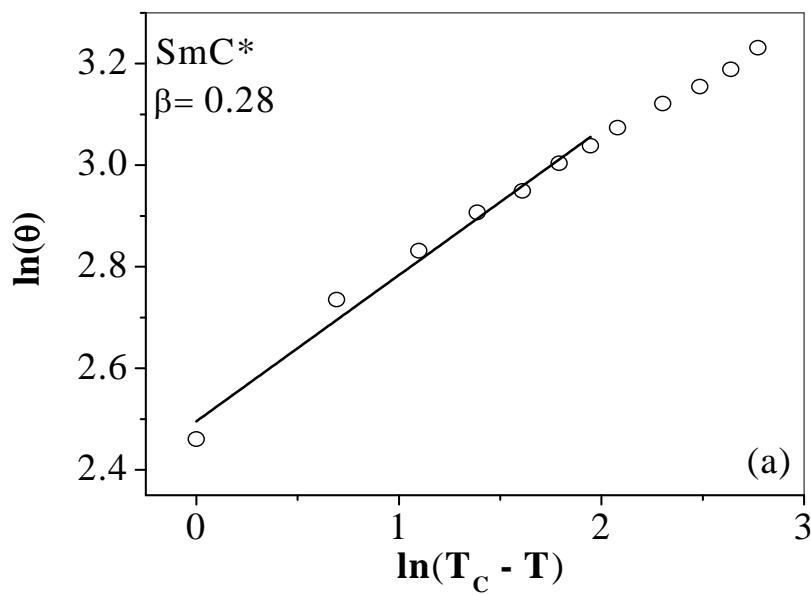


Figure 6.13(a) Arrhenius plot of the tilt angle from x-ray measurement as a function of $\ln(T_c - T)$ in the SmC* phase. Solid line represents the fit to Equation 6.3.

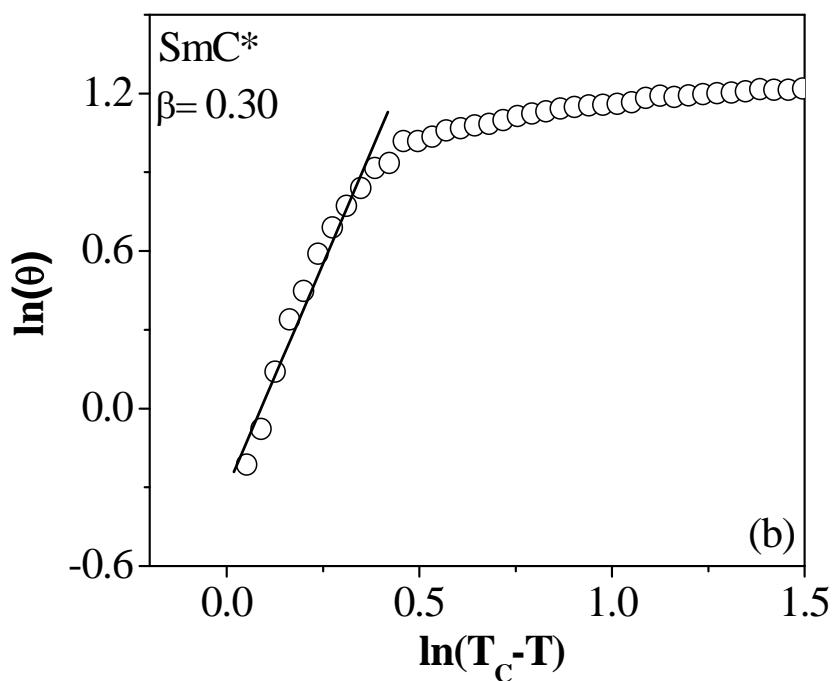


Figure 6.13(b) Arrhenius plot of the optical tilt angle as a function of $\ln(T_c - T)$ in the SmC^* phase. Solid line represents the fit to Equation 6.3.

6.8 Conclusion

A comprehensive study of a lactic acid derivative with four ester linkage groups in the molecular core has been reported. The compound exhibits thermally stable paraelectric SmA^* and ferroelectric SmC^* phases over a relatively broad temperature range. The temperature variation of both the order parameters *i.e.* the tilt angle and spontaneous polarization confirms the second-order nature of the $\text{SmC}^*\text{-}\text{SmA}^*$ phase transition. The values of the critical exponent $\beta = 0.32$ and 0.28 determined independently from spontaneous polarization and tilt angle measurements respectively, are quite close to the value of 0.31 as predicted by the 3D Ising model [45]. The values of the spontaneous polarization is relatively high reaching about 100 nCcm^{-2} (at 70°C) due to the zigzag molecular structure arising out of the presence of several ester linkage groups in the molecular core and an additional methylene group, which hinders the motion of the chiral centre. The layer spacing in the orthogonal SmA^* phase is more or less constant but due to the

molecular tilt in the SmC* phase it decreases with decrease in temperature. The calculated length (42.0 \AA) of the most extended conformer is in good agreement with the experimental value of layer spacing (41.5 \AA) in the orthogonal SmA* phase [31].

Generally, lactic acid derivatives with four ester groups in the molecular core possessing the self-assembling properties are quite fascinating materials. The existence of four ester groups usually results in formation of the nano-size structure *i.e.* the smectic phases which are quite stable and cover a reasonably broad temperature range [3,4,30,31,35]. These compounds with fairly high spontaneous polarization may be utilized in mixture design for photonic and optoelectronic devices, operated at low voltages. However, the hindrance of the chiral centre of the molecule increases the viscosity and therefore may negatively affects its utilization in devices. This effect strongly depends on the exact molecular structure, namely the length of the alkyl chains [5,21,35], type of the molecular core [5,6,10,21] and presence of lateral substituent [3,21,31]. Thus, further structural modifications into such compounds and study of their physical properties are required to tune their properties for utilization in industrial applications [27-28].

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