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Establishment of phase diagram of a chiral smectic liquid crystal

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ABSTRACT

Chiral smectic liquid crystals are well known to exhibit the following sequence of phases as the temperature is increased: Sm-C^*_A, Sm-C^*_{Fi1}, Sm-C^*_{Fi2}, Sm-C^* and Sm-C^*_α. Surprisingly, some compounds appear in several publications to present other tilted phases, which not only do not belong to the previous series but change from one paper to the other although the studied compound is the same. Such is the chiral smectic liquid crystal (*R*) or (*S*)-12OF1M7 that we have re-synthesized and studied with various techniques: dielectric spectroscopy, optical rotatory power, conoscopic measurements and electro-optic properties. Our conclusion is that this compound presents the ordinary phase sequence at the exception of the Sm-C^*_α phase. In addition, the (*E*–*T*) phase diagram of this compound was established.

1. Introduction

In chiral smectic compounds, a variety of phases can arise as the temperature are varied. The phase sequence with decreasing temperature is generally presented as follows: Sm-*A*, Sm-C^*_α, Sm-C^*, Sm-C^*_{Fi2}, Sm-C^*_{Fi1}, Sm-C^*_A. The best known is the helielectric Sm-C^* phase, in which the molecules are tilted at an angle θ from the layer normal and develop a spontaneous helical structure. The other sub-phases have been characterized by resonant X-ray scattering: they present a periodicity corresponding to two layers (Sm-C^*_A), three layers (Sm-C^*_{Fi1}), four layers (Sm-C^*_{Fi2}) and incommensurate varying from three to eight layers (Sm-C^*_α) [1,2].

However, some unexpected results have been presented. For example the introduction of unusual phases FILC (Sm-C^*_{Fi3}) and Sm C^*_β in (*S*/*R*)-12OF1M7. In fact, several phase sequences (both enantiomers *S* and *R* are proved to possess the same) have been reported. On the basis of the differential scanning calorimetry and dielectric spectroscopy some authors have published the following phase sequence: Sm-*A*–(90.7 °C)–Sm-C^*–(82 °C)–Sm-C^*_{Fi1}–(78.3 °C)–Sm-C^*_A [3] and Sm-*A*–(92 °C)–Sm-C^*–(85 °C)–Sm-C^*_{Fi2}–(83 °C)–Sm-C^*_{Fi1}–(79.5 °C)–Sm-C^*_A [4,5]. Whereas using conoscopy and electro-optic measurements [3,6–8], the phase sequence becomes Sm-*A*–(93 °C)–Sm-C^*–(90 °C)–FILC–(85 °C)–Sm-C^*_{Fi2}–(83.5 °C)–Sm-C^*_{Fi1}–(78.3 °C)–Sm-C^*_A. One can see the appearance of ferrielectric sub-phase FILC in the temperature range (85–90 °C). However, according to the previous publication, the SmC^* phase exists in the temperature range (85–93 °C) and no other phase transition is observed in this temperature interval. In Ref. [9] is reported the ferrielectric Sm-C^*_β phase. Eventually another phase sequence with the Sm-C^*_α and Sm-C^*_{Fi2} phases is reported in Refs. [10–13].

This paper has one purpose. It is aimed at understanding the diversity of phase sequences reported for the (*R*)-12OF1M7 and try to obtain its correct one by combining several techniques.

2. Characterization

The (*R*)-12OF1M7 (99% purity) (Fig. 1) was synthesized in the Centre de Recherches Paul Pascal (CRPP). The phase transitions in bulk sample were obtained by the differential scanning calorimetry (DSC), the optical rotatory power (ORP), conoscopy and dielectric measurements.

2.1. Differential scanning calorimetry

DSC was performed in the cooling and heating runs at scanning rates of 1–3 °C/min. The bulk phase sequence obtained from Fig. 2 is the following: Sm-C^*_A–(80.2 °C)–Sm-C^*_{Fi1}–(81.8 °C)–Sm-C^*_{Fi2}–(84.7 °C)–Sm-C^*–(93.5 °C)–Sm-*A*.

Compared with that found in Ref. [3], one hardly notices the two distinct phases Sm-C^*_{Fi1} and Sm-C^*_{Fi2} and no evidence for the Sm-C^*_α phase.

2.2. Optical rotatory power

The ORP and conoscopy data of this compound were obtained with the 543.5 nm He–Ne green laser source for a 100 μm thick

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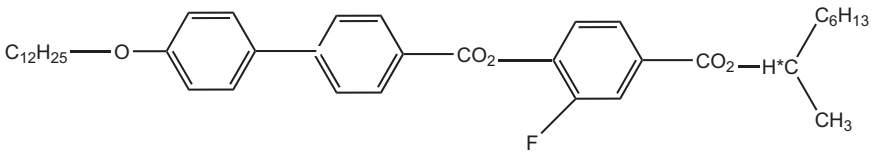

Fig. 1. The molecular structure of 12OF1M7 compound.

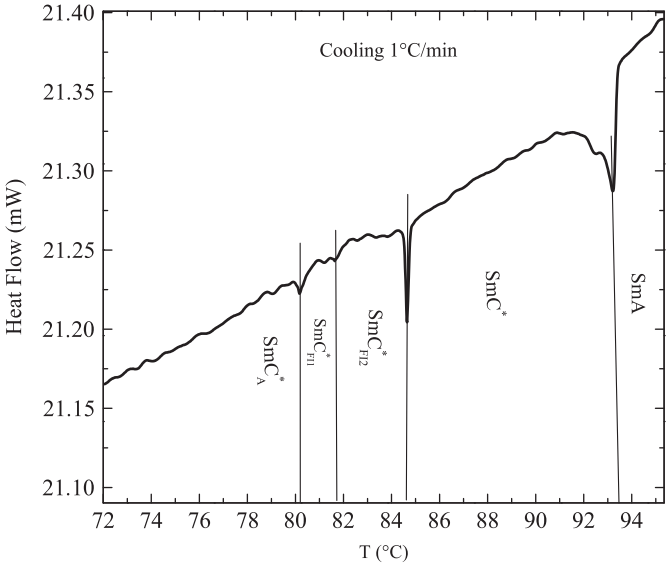

Fig. 2. DSC diagram of 12OF1M7 at a cooling rate of 1 °C/min.

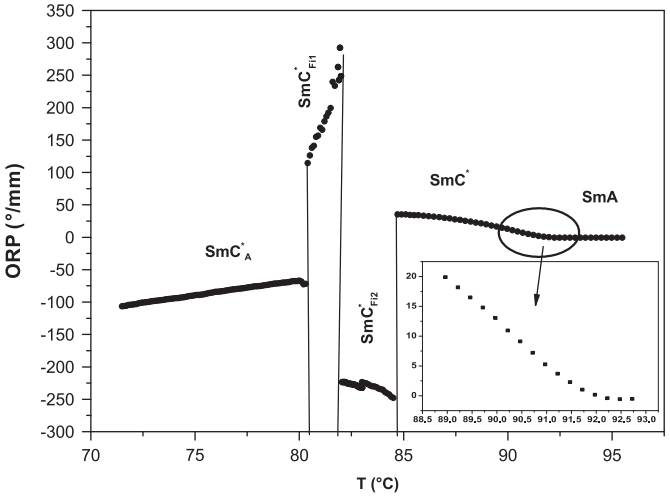

Fig. 3. The temperature variation of optical rotatory power for 100 μm thick sample of 12OF1M7.

sample aligned in the homeotropic geometry between two glass plates which have been treated with a polymer. In Figs. 3 and 4 we respectively present the experimental results of the ORP and conoscopy. All the measurements were carried out at milliKelvin stabilized temperatures.

The ORP results are similar to those found in other compounds [14–18] where the phase transitions are easily detectable by sign or amplitude changes. When cooling down from the Sm-*A*, the ORP appears smoothly about 92 °C. The SmC* phase shows a positive ORP which changes its sign at the Sm-*C**–Sm-C^*_{Fi2} phase transition due to the increase of the pitch. On cooling further the sample, entering the Sm-C^*_{Fi1} phase, the sign of the ORP changes

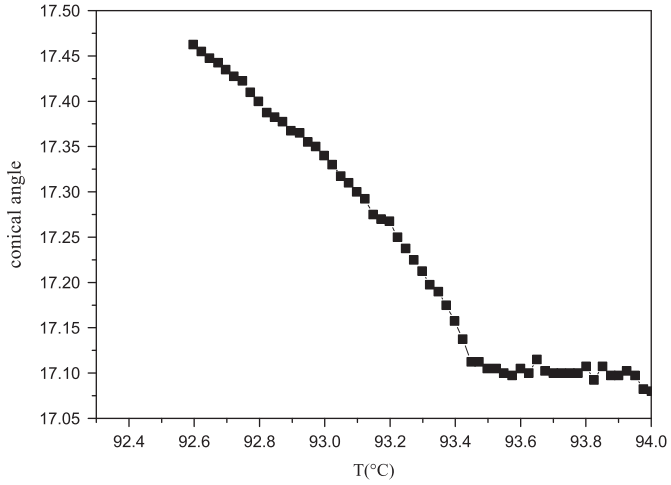

Fig. 4. Temperature dependence of conical angle for 100 μm thick sample of 12OF1M7.

reflecting an inversion of the sense of the helical twist. The Sm-C^*_{Fi1}–Sm-C^*_A phase transition is clearly observed at about 80.4 °C.

At this stage, DSC and ORP techniques give a phase sequence comprising all the classical sub-phases but the Sm-C^*_α. However, as other contradictory phase sequences have been published, we devised complementary experiments in order to check for the absence of the Sm-C^*_α phase at first.

2.3. Looking for a Sm-C^*_α phase

2.3.1. Conoscopy

In the ORP experiment, the Sm-*A*–Sm-*C** transition is not clearly detected because the rotation slowly grows from zero. This is due to the fact that in the regime of small pitches *p*, the ORP scales as $\sin^4(\theta)p^3$ where θ increases from zero. So there is a gap of about 1 K where the ORP is not measurable in the Sm-*C** phase. So we took advantage of our rotating cell setup [18] to measure the conical angle α corresponding to the first black circle in the uniaxial conoscopy figure. The retardation δ_1 is constant according to the formula [18]

$$\delta_1 = \lambda = \frac{(n_e - n_0)e\sin^2\alpha}{n_e\sqrt{n_e n_0 - \sin^2\alpha}} \quad (1)$$

Upon entering the first tilted phase the birefringence $(n_e - n_0)$ steeply decreases so that the conical angle α has to increase.

The temperature dependence of α is given in Fig. 4. We can see that the latter changes at 93.45 °C and increases gradually when the temperature decreases. This means that the extent of the region where the tilt has appeared but the ORP is not measurable is about 1.4 K which is reasonable for a Sm-*C** phase. Furthermore, if the first tilted phase was a Sm-C^*_α, the extent of tilt without ORP region would be larger than 1.4 K and there would be a discontinuity of ORP when entering the Sm-*C** [14].

Although we have now three experiments showing no evidence of a Sm-C^*_α phase, we also analyzed the evolution of the soft mode in the vicinity of the Sm-*A*–Sm-*C** phase transition.