Journal of Molecular Liquids 199 (2014) 162–166

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Review

Electric field induced transformations and dielectric properties of ferrielectric smectic phase

T. Soltani [a,*], M. Chemingui [a], N. Bouaziz [a], J.P. Marcerou [b], T. Othman [a]

[a] Laboratoire de Physique de la Matière Molle Faculté des Sciences de Tunis, Université de Tunis Elmanar, Tunisia
[b] Centre de Recherche Paul Pascal, Pessac, France

ARTICLE INFO

Article history:
Received 9 May 2014
Received in revised form 20 August 2014
Accepted 2 September 2014
Available online 7 September 2014

Keywords:
Liquid crystals
Dielectric properties
Optical properties
Phase transitions

ABSTRACT

Some of the antiferroelectric liquid crystal compounds (C12HH, C12F3 and MHPOBC) displaying ferrielectric phase are investigated. In a planar sample the ferrielectric (SmC^*_{FI1}) existing between the ferroelectric (SmC^*) and the anticlinic (SmC^*_A) phases is suppressed due to an anchoring surface. In this configuration, we report the first observation of this phase by heating. Therefore, its properties are studied by dielectric, electro-optic and microscopic techniques. The experiments, mentioned above, suggest that SmC^*_A–SmC^*_{FI1} transition is first order. The electric–temperature (E–T) phase diagram of the C12HH compound including the existence of induced intermediate phase is well established experimentally. At the same time, the electric–concentration (E–x) phase diagram is also determined in the intermediate phase of the mixtures formed from the enantiomers of the MHPOBC compound. This phase diagram shows a significant concentration dependence of induced phase stability and unwinding threshold.

Contents

1. Introduction . . . 162
2. Experimental . . . 163
3. Results and discussion . . . 163
4. Conclusion . . . 166
References . . . 166

1. Introduction

The response of smectic phases of chiral liquid crystals has drawn much research interest from fundamental and technological points of view. In these materials, various intermediate smectic phases are observed in the temperature range between the paraelectric phase SmA* at the top end and the anticlinic phase SmC^*_A at the bottom end [1–7]: the uniaxial subphase SmC*α with a short pitch emerges just below the non-tilted phase SmA*. The synclinic phase SmC* is locally ferroelectric ($P_S \neq 0$). The non-polar four-layer SmC^*_{FI2} phase. The polar three-layer SmC^*_{FI1} phase is referred to as ferrielectric. The recently discovered smectic-C*d6 has a six layer unit cell. The properties of these phases are investigated intensively for utilizing them in numerous applications such as display devices, memory devices, and optical signal processing. Usually these phases show a large electrooptic response and interesting behavior in an electric field, and sometimes new intermediate phases can be induced by the electric field [9–16]. However, the properties of some smectic phases have not been completely understood up to now. One reason for the limited understanding of these phases is the existence of many interactions, which results in a very complicated phase diagram. Indeed, the temperature, optical purity, external electric field, and surface anchoring strength are tunable parameters that can affect the behaviors of the sample. Among these phases, the ferrielectric (SmC^*_{FI1}) shows a strong sensitivity to these parameters. The AFLC compounds exhibiting the SmC^*_{FI1} are usually displayed in the following phase sequence: SmC^*–SmC^*_{FI2}–SmC^*_{FI1}–SmC^*_A. Therefore, the SmC^*_{FI1} has always a narrow temperature stability and is preceded by the SmC* phase. In the homeotropic sample all transitions between intermediate phases are detected and the phase diagram is similar to that in the bulk sample, while in the planar sample it has

* Corresponding author at: Université de Tunis Elmanar, Laboratoire de Physique de la Matière Molle Faculté des Sciences de Tunis, Tunisia.
E-mail address: tawfik_sol@yahoo.fr (T. Soltani).

http://dx.doi.org/10.1016/j.molliq.2014.09.007
0167-7322/© 2014 Published by Elsevier B.V.

been shown that on cooling, the SmC* still remains into the phases below it, such as SmC^*_{FI2}, SmC^*_{FI1} and high temperature range of SmC^*_A (supercooling phenomenon). The phase sequence mentioned above for the bulk sample becomes SmC*–coexistence–SmC^*_A [17,18] in planar cell. Song and Vij [19] and Manna et al. [20] suggest that the suppression of these intermediate phases and the direct phase transition from SmC* to SmC^*_A can occur. Hence, in thin planar sample the ferrielectric SmC^*_{FI1} phase has not been well studied. To solve this problem, Jaradat et al. [21] tried to expand the temperature range of the latter by mixing the liquid crystal with a chiral dopant and the measurements have been carried out at 8 °C below the SmC^*_{FI1}–SmC^*_{FI2} phase transition. Very recently Jogson et al. [22] show that introducing a chiral dopant to liquid crystal materials widens the stability of the intermediate phases, but this fact can also modify many parameters of the compound (polarization, tilt angle layer spacing and threshold depend on the chiral dopant concentration). In addition to this, the increase in electric energy EP_S with increasing chiral dopant concentration has been observed [23]. So the interest of our work is to investigate the ferrielectric phase in a pure compound without adding a chiral dopant. In the present work, we show the possibility of obtaining the pure state of the SmC^*_{FI1} phase by heating the sample from the pure state of SmC^*_A. This allows us to understand the characteristics of the latter and reduce the coexistence extent.

In this paper, we discuss the first order transition from anticlinic SmC^*_A to ferrielectric SmC^*_{FI1} phase on heating and the evolution of ferrielectric SmC^*_{FI1} phase under electric field, which shows its transition to the unwound SmC* via an intermediate phase. Our method including three experimental observations (electro-optic properties, dependence and optical purity dependence) confirms that this induced intermediate phase retains the ferrielectric character. Then, the (E–T) phase diagram of the studied compound C12HH is established.

2. Experimental

The dielectric and electro-optic measurements were performed using commercial cells (EHC, Japan) coated with indium tin oxide (ITO). The thickness of the cells is 6 μm. The active area is 25 mm^2. The cells were filled with liquid crystals by capillary action from the isotropic phase. A good planar alignment was obtained by slowly cooling the sample from isotropic to SmA phase. The complex dielectric constant $\varepsilon^* = \varepsilon' - j\varepsilon''$ was measured with an impedance meter having the frequency range of 10 Hz–200 kHz. At the same time a sinusoidal voltage modulation of 500 mVpp was applied. The dielectric dispersion data were analyzed by the generalized Cole–Cole equation:

$$\varepsilon^*(f) = \varepsilon_\infty + \sum_i^n \frac{\Delta\varepsilon_i}{1+\left(j\frac{f}{f_{ri}}\right)^{\alpha_i}} \quad (1)$$

where the ε_∞ is the dielectric constant at the high frequency limit, and $\Delta\varepsilon_i$, f_{ri}, and α_i, are the dielectric strength, the relaxation frequency, and the distribution parameter of mode (i) respectively. Spontaneous polarization was measured by integrating the switching current recorded during polarization reversal under applied triangular voltage with frequency of 25 Hz. The voltage was increased from 0 to 8 V. The structures of the investigated compounds are given in Fig. 1.

The C12HH compound has been studied before [15]; the phase sequence of this compound given by differential scanning calorimetry (DSC), optical birefringence and optical rotator is K–(78 °C)–SmC^*_A–(96.5 °C)–SmC^*_{FI1}–(98 °C)–SmC^*_{FI2}–(100 °C)–SmC*–(119 °C)–SmA. In the planar sample, it was found that both intermediate phases SmC^*_{FI1} and SmC^*_{FI2} are suppressed. For such cell thickness, in our previous publication [18] it was found that the supercooling persists up to the temperature of 84 °C, so the pure SmC^*_A exists in the temperature range of 84–78 °C. In the present study we show that it is possible to obtain the pure state of SmC^*_{FI1} by heating the sample from low temperature in SmC^*_A (78 < T < 84 °C). The C12F3 exhibits the following phase sequence: SmC^*_A–(117.2 °C)–SmC^*_{FI1}–(118.2 °C) SmC^*_{FI2}–(119.2 °C)–SmC*–(120.8 °C)–SmCα*–(122 °C)–SmA [24]. For the MHPOBC (Fig. 1(b)), the phase sequence is described as SmC^*_A–(117.2 °C)–SmC^*_{FI1}–(118.2 °C)–SmC^*_{FI2}–(119.2 °C)–SmC*–(120.8 °C)–SmCα*–(122 °C)–SmA [25].

3. Results and discussion

The experimental study was carried out during heating from low temperature of pure SmC^*_A (T = 82 °C); the transition from the SmC^*_A phase to SmC^*_{FI1} phase is manifested by a qualitative and quantitative change of the dielectric spectrum. In the antiferroelectric SmC^*_A phase (T < 96.5 °C), the only soft mode contribution on the dielectric response is observed, as presented in Fig. 2(a). While, in the SmC^*_{FI1}

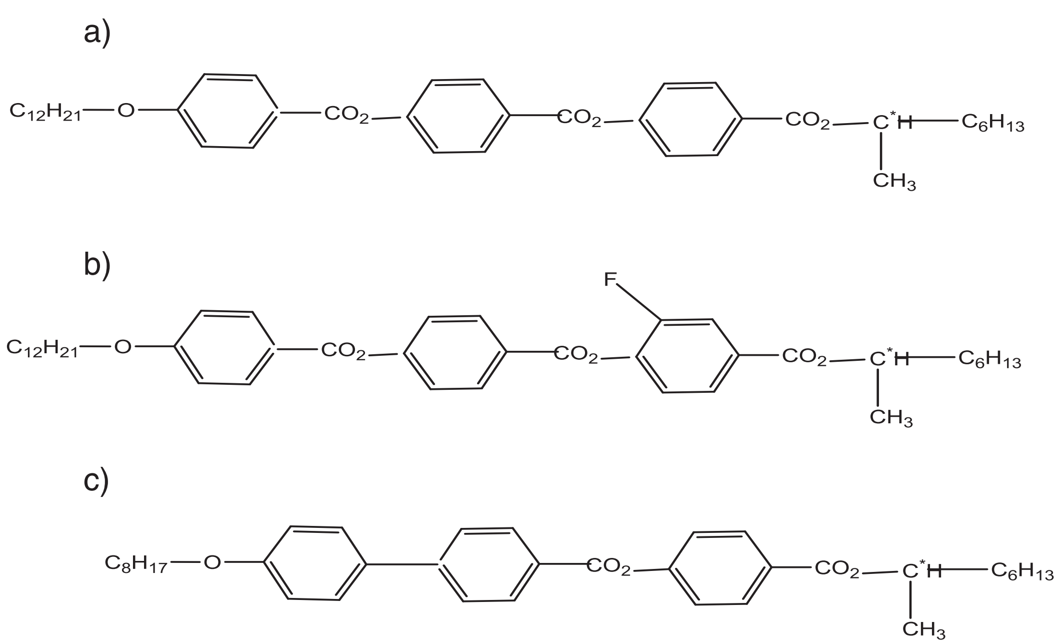

Fig. 1. Chemical structures of C12HH (a), C12F3 (b) and MHPOBC (c) materials.