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1990 J. Phys.: Condens. Matter 2 SA271

(http://iopscience.iop.org/0953-8984/2/S/040)

J. Phys.: Condens. Matter **2** (1990) SA271–SA274. Printed in the UK

Phase transitions among paraelectric, ferroelectric, ferrielectric and antiferroelectric phases in a chiral smectic liquid crystal

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Received 9 July 1990

Abstract. Phase transitions among paraelectric, ferroelectric, ferrielectric and antiferroelectric phases in a chiral smectic liquid crystal, MHPOBC, have been investigated by means of circular dichroism (CD). It was found that the helix undergoes a complex variation through the transitions such as discontinuous jumps and handedness change. By considering the twisting power, the ferrielectric phase was found to be composed of ferroelectric and antiferroelectric structures in the ratio of 3:7. The finite induced CD signal in SmC^*_α and SmA in the vicinity of the transition point suggests the helical structure in these phases.

1. Introduction

Since tristable switching [1] was recognized as an electric-field-induced antiferroelectric–ferroelectric phase transition, [2, 3] a considerable number of chiral smectics showing the antiferroelectric phase have been synthesized. The phase sequences of these materials so far synthesized are classified into three: (i) SmA–SmC^*_α–SmC^*(SmC^*_β)–SmC^*_γ–SmC^*_A, (ii) SmA–SmC^*–SmC^*_A and (iii) SmA–SmC^*_A. The molecular orientational structures of these phases are summarized in figure 1, where overall helical structures can be imagined by twisting the figures according to their respective twisting power. The SmA and the SmC^* phases are well known paraelectric and ferroelectric phases, respectively. The antiferroelectric structure in the SmC^*_A phase was confirmed by the selective reflection in oblique incidence [2]. The SmC^*_γ phase was attributed to a ferrielectric phase by means of conoscope observation [4], dielectric measurements [5] and D–E hysteresis behaviour [6]. The SmC^*_α phase was tentatively assigned to a biaxial helical SmA (SmA^*_b) by the dielectric behaviour [5].

The purpose of this paper is to investigate the details of the molecular orientational structures of SmC^*_α and SmC^*_γ by observing circular dichroism (CD). The material used

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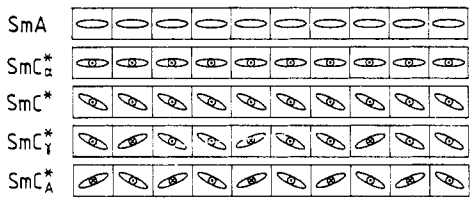

Figure 1. The proposed models of SmA, SmC$^*_\alpha$, SmC*, SmC$^*_\gamma$ and SmC$^*_A$.

in the present study, MHPOBC ($C_8H_{17}O$ COO COO*$CH(CH_3)C_6H_{13}$), [1, 2, 4–10] is so far the only one which shows the phase sequence (i).

2. Experimental details

Homeotropically aligned, 100 μm thick cells of MHPOBC were prepared by treating the substrate plates with a surfactant, AY43-21 (Toray-Dow Corning Silicon). The cell was placed in an oven, whose temperature was regulated within ± 0.02 °C. The CD spectra in the intrinsic absorption band due to the π–π^* transition of phenyl rings together with the absorption band of lightly doped methyl red were studied by an automatic recording spectrometer (JASCO J20).

3. Results and discussion

It is well known that a circular dichroism (CD) is induced at the absorption band, if the transition moment sits in a helical structure. For light propagating along the z direction, the magnitude of the induced CD is given by [11]

$$\varepsilon_L - \varepsilon_R = (n_x - n_y)(\varepsilon_x - \varepsilon_y)(\lambda_0/2\bar{n}\lambda_{ab}) \tag{1}$$

where ε_i values (i = L, R, x and y) are absorption coefficients for left (L) and right (R) circularly and x- and y-linearly polarized light, n_i ($i = x$ and y) are refractive indices for x- and y-polarized light, and $\bar{n}$ is their average. λ_0 and λ_{ab} are the wavelengths of a selective reflection band and an absorption band, respectively.

Figure 2 shows the CD spectra in (*a*) SmC*, (*b*) SmC$^*_\gamma$ and (*c*) SmC$^*_A$. The sharp increases at short wavelength are due to the induced CD at the tail of the intrinsic band. The increases at longer wavelength in figure 2(*a*) originate from the selective reflection band. As the selective reflection band approaches the absorption band, the CD peak due to the dye absorption is influenced. This is because the optical eigenmodes near the selective reflection band are no longer circularly polarized [12].

The sign change of the CD signal in figure 2(*a*), (*b*) and (*c*), certifies that the helix handedness changes at the transition point between SmC* and SmC$^*_\gamma$, as observed by the optical rotatory power measurement [2]. By comparison the CD signals in SmC$^*_\gamma$ and SmC$^*_A$, and using λ_0 in SmC$^*_A$, [2] λ_0 in SmC$^*_\gamma$ can be estimated to be about 3.3 μm. The model structure of the ferrielectric phase composed of the ferroelectric and the antiferroelectric region [4, 6] requires the conservation of the twisting power including the handedness:

$$1/\lambda_0(\text{SmC}^*_\gamma) = -[F/\lambda_0(\text{SmC}^*)] + [(1 - F)/\lambda_0(\text{SmC}^*_A)] \tag{2}$$

where F is the fraction of SmC*. Using λ_0(SmC*) = 0.71 μm and λ_0 (SmC$^*_A$) = 1.0 μm

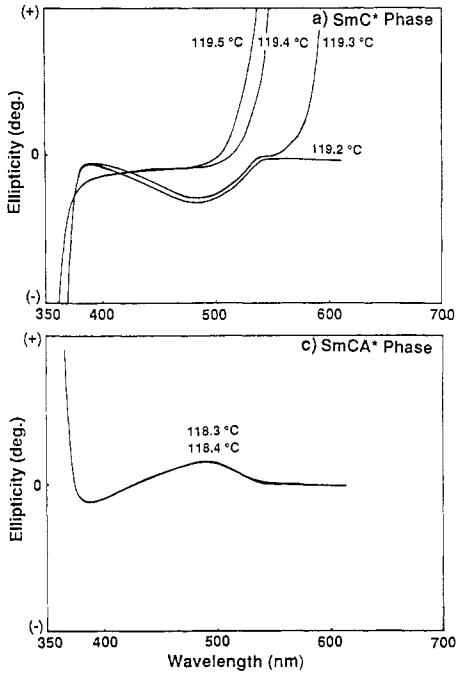

Figure 2. The CD spectra in (*a*) SmC*, (*b*) SmC$_\gamma^*$ and (*c*) SmC$_A^*$ of (S)-MHPOBC.

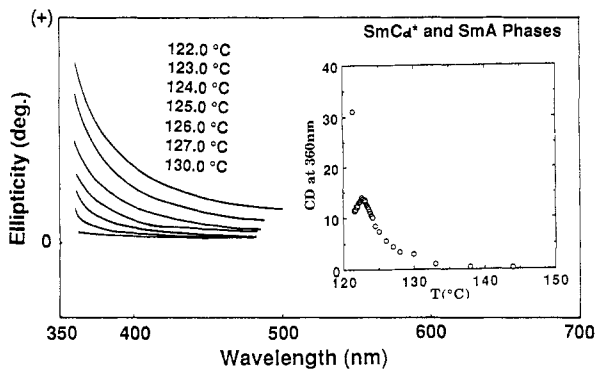

Figure 3. The CD spectra in SmA and SmC$_\alpha^*$ at the intrinsic absorption tail of (R)-MHPOBC. In the inset, the temperature dependence of the CD signal of (S)-MHPOBC at 360 nm is also shown.

previously measured [2], F is determined to be about 0.3. Therefore, it is concluded that the ferrielectric phase is a structure composed of the ferroelectric and the antiferroelectric regions in the ratio of about 3 : 7.

Though no CD signal was detected at the dye absorption band in SmC$_\alpha^*$ and SmA, we could observe the CD tail due to the intrinsic absorption as shown in figure 3. This fact means that there is a helical structure in SmC$_\alpha^*$ and even in SmA. The CD signal intensity at 360 nm is plotted as a function of temperature in the inset of figure 3. The CD signal intensity increases with decreasing temperature in SmA. There is a narrow but

distinct temperature region between SmA and SmC*, suggesting the SmC^*_α range. The same behaviour was also observed in an optical rotatory power measurement.

Thus, it is concluded that the SmC^*_α phase is a helical biaxial SmA (SmA^*_b) as illustrated in figure 1. It was also found that the helical structure of the biaxial molecules is also formed even in SmA as a pretransitional effect. It is worth noting that no induced CD signal was observed in SmA of a non-chiral compound,

$$C_6H_{13}O \qquad C_8H_{17}.$$

Further experiments are now going on in our laboratory.

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