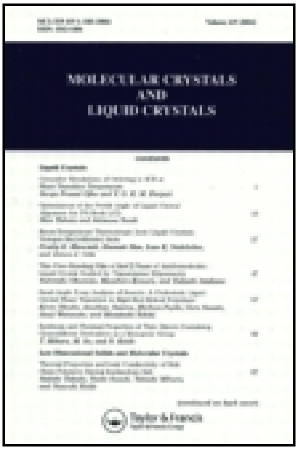

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Thin Free-Standing Film Of Smc$^*_\alpha$ Phase Of Antiferroelectric Liquid Crystal Studied by Transmission Ellipsometry

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THIN FREE-STANDING FILM OF SmC_{α}^{*} PHASE OF ANTIFERROELECTRIC LIQUID CRYSTAL STUDIED BY TRANSMISSION ELLIPSOMETRY

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A thin free-standing film of an antiferroelectric liquid crystal subphase was studied by means of the precise measurement of transmission ellipsometry. At a temperature in which the SmA phase is observed in the bulk sample, a small director tilt and helical structure was confirmed from the optical phase difference measurement, and an unwinding process under a high electric field was observed. The dependence of the threshold characteristics on layer numbers was also recognized. From the experimental results, it is estimated that the structure of SmC_{α}^{*} *is a tilted smectic structure with a small tilt angle and a fairly short pitch.*

Keywords: ellipsometry; free-standing film

INTRODUCTION

The compound 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC) was the first mesogen in which antiferroelectricity was confirmed [1]. It is well known that the bulk of MHPOBC has various subphases (viz. Cryst.-SmC_{A}^{*}-SmC_{γ}^{*}-SmC^{*}-SmC_{α}^{*}-SmA-Iso.). Previously, we reported the unique characteristics of free-standing films (FSFs) of the MHPOBC, where it is found that the layer structure of thin FSFs is different from that of bulk samples [2,3].

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Various kinds of investigations concerning the nature of these subphases have been performed. Among these subphases, the structure of the SmC_{α}^{*} phase had been regard as a mysterious subphase. Many remarkable papers have been published in which it was proposed that the SmC_{α}^{*} is a tilted smectic phase that appears just below the SmA phase, that the tilt angle is small [4], and that it is not easy to optically distinguish between SmC_{α}^{*} and SmA [5]. Bourny et al. reported the soft-mode behavior in the SmC_{α}^{*} phase studied by birefringence measurement [6]. The argument with regard to the helical pitch is divided. From a circular dichorism measurement, Yamada et al. concluded that the SmC_{α}^{*} phase has a dynamic helical structure with a very long average pitch [7]. On the other hand, Rastegar et al. reported that a light-scattering experiment suggested that the helical pitch of SmC_{α}^{*} is short of ~50 nm [8]. Hirst et al. and Fera et al. reported investigations of the layer by means of a resonant X-ray scattering technique applied to several materials, where they concluded that the helical pitch is very short [9] and depends on the compounds [10]. Cady et al. and Olson et al. reported the temperature dependence of the helical pitch of the SmC_{α}^{*} phase by means of a high-resolution differential optical reflectivity measurement or ellipsometry measurement, and reported that the obtained pitch also depends on the material [11,12]. Rovšek et al. demonstrated that the results of ellipsometric experiments for thick film are in quite remarkable agreement with the numerical predictions on the basis of the discrete model of antiferroelectric liquid crystals [13].

Especially in the SmC_{α}^{*} phase, the estimation of the helical pitch ofz MHPOBC, in which the SmC_{α}^{*} phase was found for the first time, was not fully examined. The phenomenon should be verified from two or more experiments. In this study, it is demonstrated by the precise measurement of the optical phase difference Δ that the SmC_{α}^{*} phase has a tilted structure with a short helical pitch.

EXPERIMENTAL

Figure 1 shows the experimental system for measuring the phase difference Δ between the parallel polarization (p-polarization) and the perpendicular polarization (s-polarization) by transmission ellipsometry [14] using a PEM (PEM-90, Hinds Instruments Co., USA), an He-Ne laser ($\lambda =$ 632.8 nm), and a pair of Glan-Thompson prisms [15]. The resolutions of Δ in our system is 0.01°. The light beam modulated by PEM passes through FSF and is detected by a photodetector after passing through an analyzer. The detected signal was put into a lock-in amplifier (5610B, NF Electric Instruments Co., Japan) and the value of Δ was obtained from the fundamental wave component and the second harmonic component of the intensities of the transmitted light with respect to the modulation frequency of

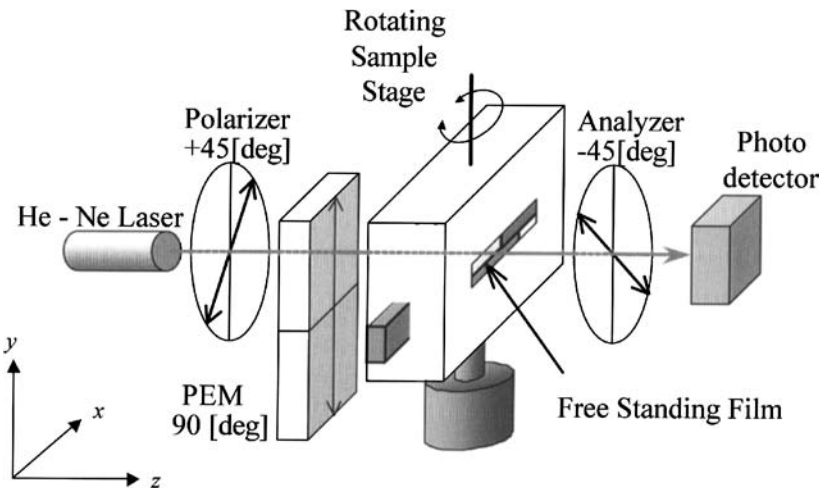

FIGURE 1 Schematic diagram of the experimental system for measuring Δ by transmission ellipsometry.

the PEM. The incidence plane of the laser beam was the x–z plane (the z axis along the layer normal, the y-axis along the electric field) [2]. We measured the incidence angle dependence of Δ. FSF was formed inside a frame made by stainless steel plates, which was placed inside a thermostatic oven in order to control the temperature. The stainless steel plates also act as electrodes to apply an electric field (~9.0 V/mm) parallel to the smectic layer of FSF. The substance used in this study was (R)-MHPOBC [1]. By fitting the incidence angle (θ_i) dependence of Δ with the simulation based on the 4×4 matrix method, the layer structure of the FSF was estimated.

RESULTS AND DISCUSSION

Figure 2 shows the experimental results of the temperature dependence of Δ, where the measurements were carried out at the incidence angle $\theta_i = 45°$. From the numerical fitting procedure, the number of layers (N) can be determined to be 14. In Figure 2, the dashed lines represent the phase transition point between the SmA, SmC^*_α, SmC^*, SmC^*_γ, and SmC^*_A phases of the bulk samples. From Figure 2, it is found that a remarkable change of Δ was exhibited around the temperature of 120°C, which corresponds to the SmA ~SmC^*_A subphase transition region of the bulk samples. The nature around this temperature region seems to be a kind of antiferroelectric subphase, which will be discussed elsewhere. It was also found that Δ changes, corresponding to the polarity of the electric field within a temperature range where the SmA is exhibited in the bulk samples. Here

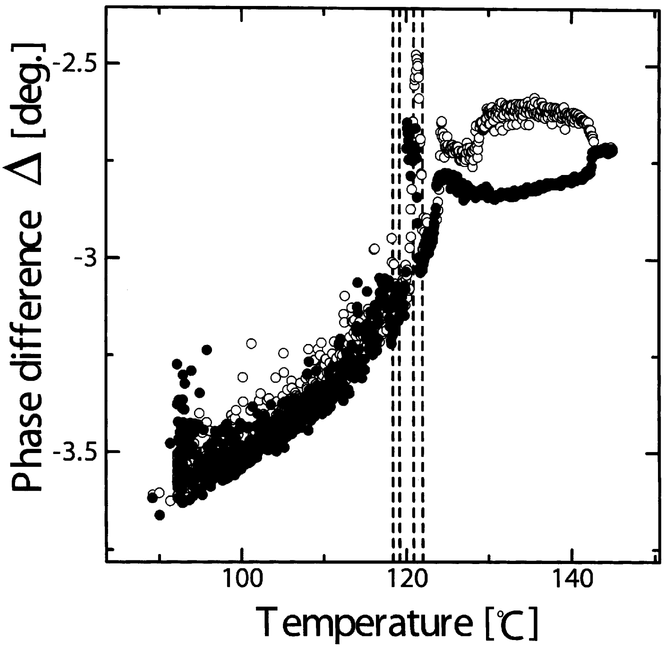

FIGURE 2 The temperature dependence of Δ for 14 layer numbers of FSF. The open circles represent the results in a positive electric field and the closed circles represent those in a negative electric field.

we would like to focus on this temperature region. This result shows that the layer structure is asymmetric rather than symmetric, such as the SmA structure, that the director inside the layer can be tilted, and that its tilt direction is perpendicular to the electric field. However, the layer structure seems not to be an antiferroelectric structure such as SmC_A^*, because, in the case of the even-number–layered FSF, the tilt direction should be parallel to the electric field, provided that the layer structure is antiferroelectric [3,16]. From the supporting evidence mentioned below, we conclude that the SmC_α^* phase appeared in the temperature region.

Figure 3 shows an electric field dependence of the phase difference Δ for FSF of N = 14, where the measurement was carried out at the temperature of 135°C. When the changing rate of the electric field strength is small enough, the electric field dependence of Δ does not exhibit hysteresis. As shown in magnification in Figure 3, around the electric field E = 0.8 ~1.2 V/mm, a remarkable change of Δ was found. It seems to be a threshold characteristic, where structural reformation such as unwinding of the helical structure is induced.

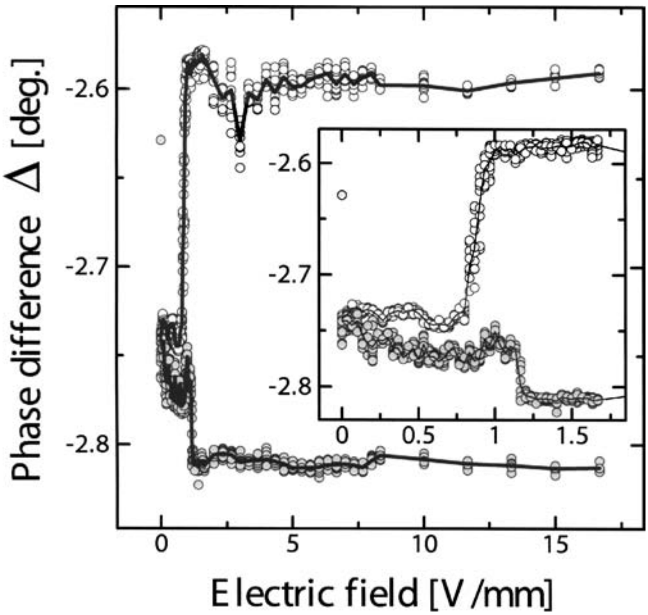

FIGURE 3 The electric field dependence of the phase difference Δ for 14 layer numbers of FSF. The open circles represent those in a negative electric field. The temperature was 135°C.

Figure 4 shows the dependence of Δ of the FSF of N = 14 on the incidence angle θ_i at the temperature of 135°C, where the measurement were carried out under an electric field of 0.6 V/mm (Figure 4(a)) and 9.0 V/mm (Figure 4(b)). The symbols in Figure 4 correspond to the positive (+) or negative (×) electric field, respectively. In the case of E = 0.6 V /mm, it was found that the curve of Δ versus θ_i is symmetric with respect to $\theta_i = 0$, and the measured results were almost the same, even when the polarity of the electric field was reversed. On the other hand, in the case of E = 9.0 V/mm, it was recognized that the curves of Δ versus θ_i are not symmetric with respect to $\theta_i = 0$. However, these asymmetric curves exhibit a mirror symmetry with respect $\theta_i = 0$ against the polarity of the electric field. Therefore, the layer structure seems to be SmC*. These experimental results can be interpreted as follows: when the electric field strength was below the threshold, the layer structure was not SmA but a helical structure with a short pitch. The helices seem to be wound several times inside the FSF. On the other hand, when the electric field strength was higher than the threshold, the helical structure was unwound and a homogeneously tilted structure like SmC was induced. Following these assumptions, numerical simulation was carried out and also plotted in Figure 4

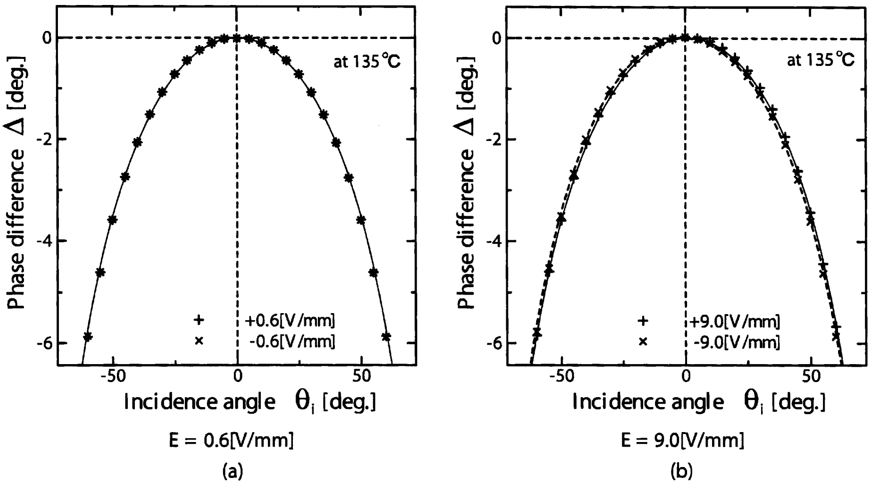

FIGURE 4 The incidence angle dependence of Δ for 14 layer numbers of FSF. The temperature was 135°C. The symbol (+) represents the results when a positive electric field was applied and the symbol (×) represents those when a negative electric field was applied. (a) The solid curves represent simulated results for the SmC* structure, where the helical structure with a 3° tilted director was assumed. (b) The solid and dashed curves represent simulated results, where the SmC structure with a synclinic arrangement (unwound) was assumed. The solid line and dashed line correspond to the polarity of the electric field.

by the solid and dashed lines. From these simulations, the tilt angle was estimated to be 3°. In these simulations corresponding to Figure 4, a helical structure was assumed, i.e., the *c*-directors were not localized. On the other hand, in the case of the simulation for the SmC structure, the *c*-directors were assumed, to have a synclinic arrangement with one stable state (solid line) or another stable state (dashed line), respectively.

Figure 5 shows the electric field dependence of Δ for several layer numbers of FSFs (N = 4,5,7). These results, shown in Figure 5, are typical and reproducible. Even in the case of 5 layer numbers of FSF, it is recognized by the Δ versus θ_i experiment that the macroscopic anisotropy disappeared under the electric field below the threshold, which implies the existence of a helical structure. In the case of N = 5 and 7, the threshold electric field was almost the same and was higher than that in the case of N = 14, as shown in Figures 3 and 5. However, in the case of N = 4, a thresholdless characteristic was observed. This result implies that the thickness of the FSF is less than the helical pitch. Therefore, the helical structure disappeared even at a low electric field strength, because the twisted power in N = 4 is weaker than that of the other layer numbers of FSFs. From these

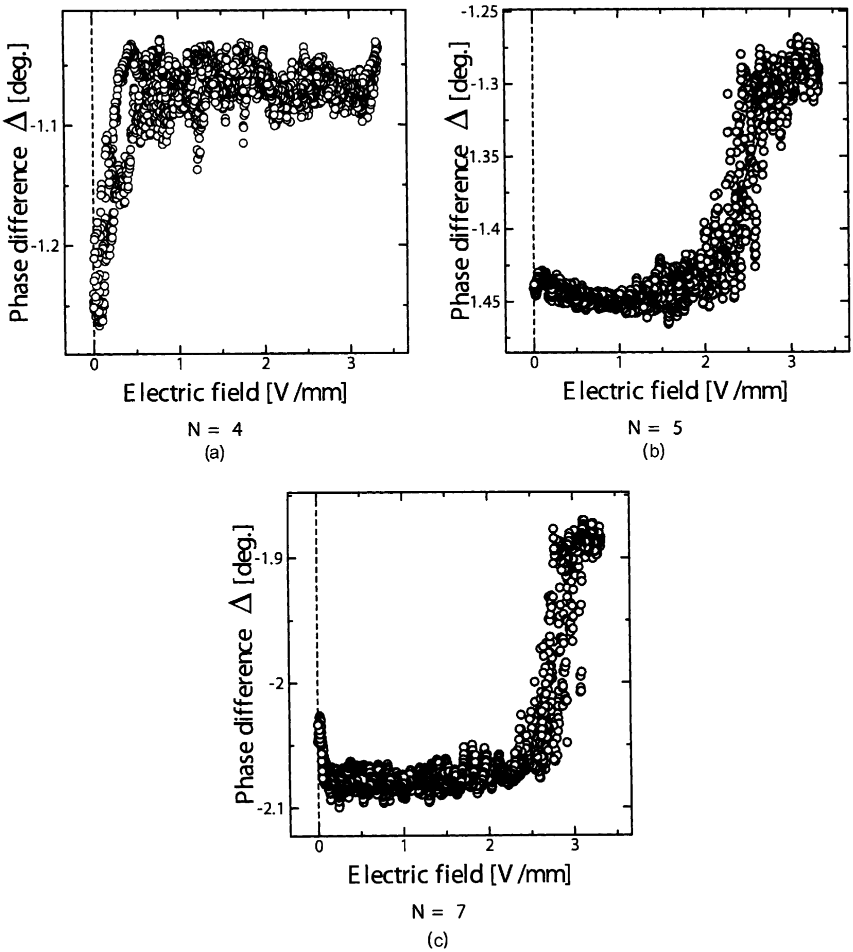

FIGURE 5 The electric field dependence of the phase difference Δ for several layer numbers of FSFs: (a) N = 4, (b) N = 5, and (c) N = 7.

results, we conclude that the helical pitch is fairly short, at least below 5 layers.

From this study described above, the layer structure assumed to be SmC^*_α is understood as follows:

1. The layer structure seems to be a tilted smectic phase having a small tilt angle of 3°.
2. Under an electric field below the threshold, the layer structure is a helical structure and the pitch is between 4 and 5 layers thick.

3. The layer structure is not easy to optically distinguish from SmA.
4. Under an electric field strength above the threshold, the director is realigned homogeneously from the layer normal and forming SmC.

CONCLUSION

A thin FSF of MHPOBC was studied by means of the precise measurement of transmission ellipsometry. At a temperature in which the SmA phase was observed in the bulk samples, a small director tilt and helical structures was recognized from the optical phase difference measurement, and an unwinding process under a high electric field was observed. The dependence of the threshold characteristic on layer numbers was also recognized. From the experimental results, it is estimated that the structure of SmC_{α}^{*} is a tilted smectic structure with a small tilt of 3° and a fairly short pitch, at least below 5 layers. These conclusions are in agreement with predecessors' results [8–12].

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