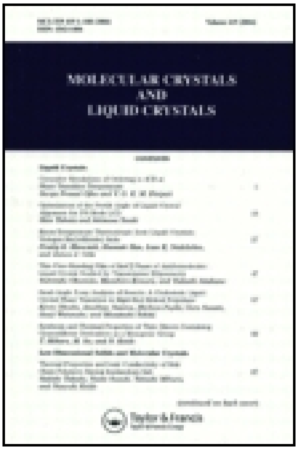

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Thin MHPOBC Free-Standing Film (FSF) was investigated by transmission ellipsometry. It was found that the temperature at which the remarkable change of Δ occurs increases with decreasing the layer number, and some of the subphase disappeared in case of thin FSF. The layer thickness of thin FSF was 2.5 nm which is shorter than the molecular length, and was not depend on the tilt angle.

Keywords: free standing Film; ellipsometry; antiferroelectric liquid crystal

Introduction

The compound, 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC), is the first mesogen in which antiferroelectricity was confirmed. As for MHPOBC, it is knows that it has complex phase sequence (Cryst.-SmC_A^*-SmC_γ^*-SmC^*-SmC_α^*-SmA^*-Iso.). Recently, we reported that the layer structure of thin FSF is different from bulk sample[1]. In this paper, we will report peculiar behavior of the layer structure of thin MHPOBC FSF.

Experimental System and Simulation Procedure

FSF was formed between the two stainless steel plate, which were placed inside the thermostatic oven. The stainless steel plates act as electrode to apply an electric field (~2.0V/mm) parallel to the smectic layer of FSF. Temperature of the FSF sample ranging from 90°C to 145°C was carefully controlled by the thermostatic oven. The rate of heating or cooling temperature was of $0.2 - 0.04°C/\text{min}$.

The phase difference Δ of the transmitted light, between the p-polarized and s-polarized light, was measured by means of transmission ellipsometry system which is composed of photoelastic modulator, He-Ne laser and a pair of Glan-Thompson prisms [2]. The incidence ray angle on the FSF was controlled by the rotating stage. The cartesian coordinate of FSF was set as such the z-axis parallel to the laser beam and the y-axis parallel to the electric field, thereby the incidence plane of light was of $x - z$ plane. The AFLC substance used in the study was 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC) [3], which exhibits several kind of phase and subphases such as SmA, SmC^*_α, SmC^*, SmC^*_γ and SmC^*_A in the bulk state.

In order to estimate the experimental results from the theoretical viewpoint, structural analysis supported by 4×4 matrix method was considered. The FSF was regarded to be composed of constituent thin smectic layer, where the molecular director inside the layer is supposed to align uniformly and make an polar angle θ with the layer normal.

On a basis of this FSF model, simulation on Δ was carried out by 4×4 matrix method. The parameters used in the simulations were $n_{\parallel} = 1.64, n_{\perp} = 1.50$.

Result and Discussion

The temperature dependence of Δ for several layer numbers of FSFs was shown in Fig. 1. In the case of the layer number N=2, monotonouous change of Δ against the temperature was found in Fig. 1. It is supposed that Δ simply depends on the tilt angle θ rather than the temperature dependence of $\Delta n (= n_e - n_o)$, and structural change may not be induced. In the case of the layer number N=3, additionally, remarkable change of Δ which implies the structural change was found. It has been proposed that the phase transition behavior of the bulk LC substance is quite different from that of FSF [4], *e.g.* some of the subphase disappeared in case of thin FSF. *i.e.*, the *shape* of the substance such as the container and/or the thickness of the LC layer may affect the phase behavior, because the layer-layer (neighbor molecules) interaction and layer-boundary surface interaction may influence the phase behavior. Furthermore, it is also reported that the phase transition temperature depends on the layer number. In Fig. 1, it is recognized that the temperature at which the remarkable change of Δ occurs increases with decreasing the layer number. In case of N=8, the remarkable change occurs around the temperature of 120°C, which corresponds to the SmA - SmC_A^* phase transition of bulk MHPOBC.

Figure 2 shows the dependence of Δ on the incidence angle θ_i under the DC applied electric field, where the measurements were carried out at the temperature of 145°C (N = 2 - 6) or 140°C (N = 8). The symbols (+, ×) correspond to the positive or negative electric field, respectively. The fitting curves, which were lead by numerical simulation and will be mentioned below, were also depicted. In cases of N = 3 - 8, as shown Fig. 2, it is 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 the polarity of the field was reversed. These results insist that these structure of FSF are SmA like structure. In case of N = 2, however, the curve of Δ does not exhibit such symmetry. This result was interpreted that the FSF was not SmA-like structure since the temperature was not high enough to exhibit a SmA-like structure.

By fitting these results with numerical simulation, these film thickness were determined to be 5.0nm(N=2), 7.5nm(N=3), 10.0nm(N=4) 12.5nm(N=5), 15.0nm(N=6), 20.0nm(N=8) respectively. From the discrete FSF thickness, it was found that the smectic layer thickness is assumed to be 2.5nm, which is much smaller than the molecular length [5].

Figure 3 shows the dependence of Δ on the incidence angle θ_i under the DC applied electric field, where the measurements were carried out at the temperature of 90°C (N = 2 - 6) or 95°C (N = 8), because the phase of FSF seems not to be SmA. In case of N=2, 4, 6, 8, *i.e.* even number of layers, it is recognized that the curve of Δ versus θ_i is symmetric with respect to $\theta_i = 0$, and further, Δ was measured to be a negative values. On the other hand, however, such symmetric curve were not found in case of N=3, 5. These asymmetric curves, however, exhibit a mirror symmetry against the polarity of electric field. And further, Δ was measured to be positive values, when $\theta_i = 0$. These odd-even characteristics were interpreted as follows; from the experimental results of Fig. 1, the layer structures were not symmetric such as SmA phase at that temperature. In other word, the director may exhibit a kind of tilted structure, and the related spontaneous polarization perpendicular to the director may be revealed. Under an electric field applied parallel to the FSF, spontaneous polarization may have an interaction with the electric field. If the layer structure was synclinic, such a odd-even number characteristics should not be found, therefore the layer structure was considered to be a kind of anticlinic structure. In case of the odd number layered FSF, the transverse spontaneous polarization can not be canceled, as a result, the director seems to be switched by the corresponding polarization of the electric field because of the residual polarization. On the other hand, in case of the even number layered FSF, the transverse spontaneous polarization may be canceled. Under these circumstances, director does not exhibit such switching characteristics. Previously, Link *et al.* proposed that the directors may be aligned in an anticlinic manner and tilted toward the electric field direction, because the net longitudinal spontaneous polarization parallel to the director has an interaction with the applied field. These interpretation can explain our experimental result as well. Following these anticlinic model, numerical simulation was carried out and also plotted in fig. 3. Here the layer thickness was assumed to be 2.5nm which coincides with the simulation for the higher temperature region mentioned above. As shown in Fig. 3, this simulation where d was provided $d = 2.5$nm gave a best fit to our experimental result. Previously, the layer thickness d was assumed to be equal to the molecular length in SmA phase, and the relationship between d and l was assumed as $d = l \times \cos\theta$ at the tilted phase[1], that is, the layer thickness should be reduced at the tilted phase. However, it is suggested that the layer thickness even in the SmA phase obtained from out experiment is quite thin compared to the molecular length (3.5nm) measured by the X-ray experiment for the bulk sample [5]. Furthermore the reduction of the layer thickness did not be recognized from the numerical fittings.

To examine this inconsistency concerning the layer thickness, Fig. 4 represents the experimental and simulated results of Δ vs θ_i curves under the positive electric field. The layer thickness d was assumed to $d = d_{SmA}$ (solid line), $d = d_{SmA} \cos\theta$ and $\theta = 30°$ (dashed line), $d = l \cos\theta$ and $\theta = 24°$ (dotted line), respectively. The tilt angle θ was fixed so that the Δ vs θ_i curves may give a best fitting to the even number case (N = 4) as well as the odd number case (N = 5). As shown in Fig. 4, the simulated result in which the layer thickness was assumed not be reduced (*i.e.* $d = d_{SmA}$) provided the best fitting among these three simulation curves. This numerical results suggest that this hypothesis such that the layer thickness reduced in the tilted phase does not give a reasonable explanation of the relationship between the tilt angle and the layer thickness, though, it is offten assumed that this hypothesis may give a good explanation concerning the appearance of chevron structure of SmC* phase in the sandwich cell. These results can be understood if we assumed that the molecules in thin FSFs were superposed each other and formed interdigitated structure between the layer. The thickness of such a smectic layer consisted of interdigitated structure may be smaller than the molecular length. And further it is probable that the layer thickness does not depend on the tilt angle θ, as illustrated in Fig. 5. In fact, the dimerization between the molecules was observed sometimes, and in such a case it is quite difficult to evaluate the size of the constituent molecule.

It is concluded that the layer structure of FSF is considered to be anticlinic structure around this temperature at which the bulk sample shows SmC_A^* phase.

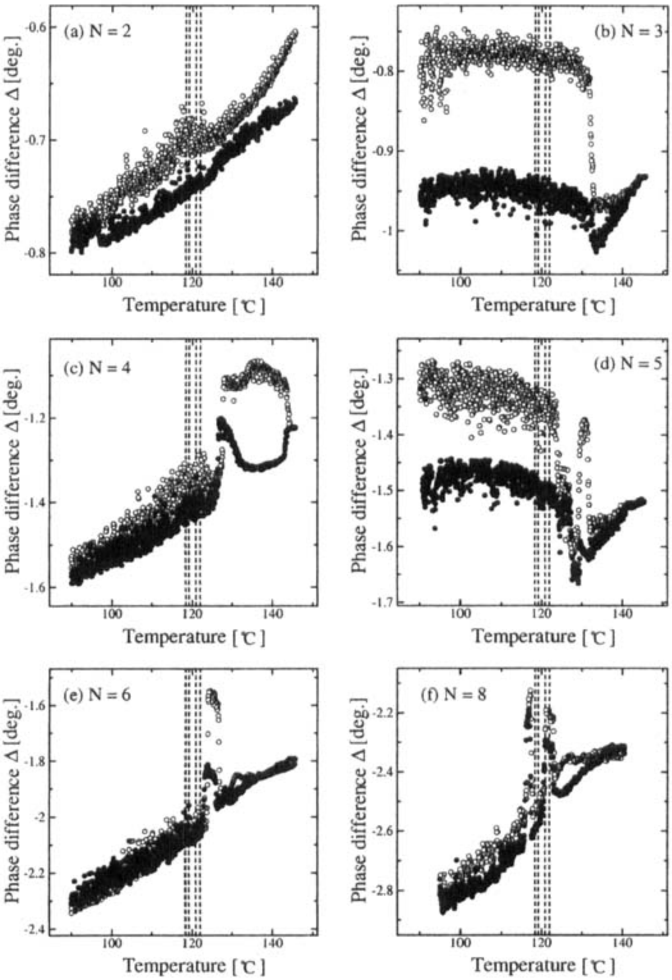

Figure 1: The temperature dependence of Δ for several layer numbers of FSFs. The temperature scan rate was 0.2 ℃/min. The open circle represent the results at positive electric field and the closed circle represent those at negative electric field. (a) for two layers, (b) for three layers, (c) for four layers, (d) for five layers, (e) for six layers, (f) for eight layers.

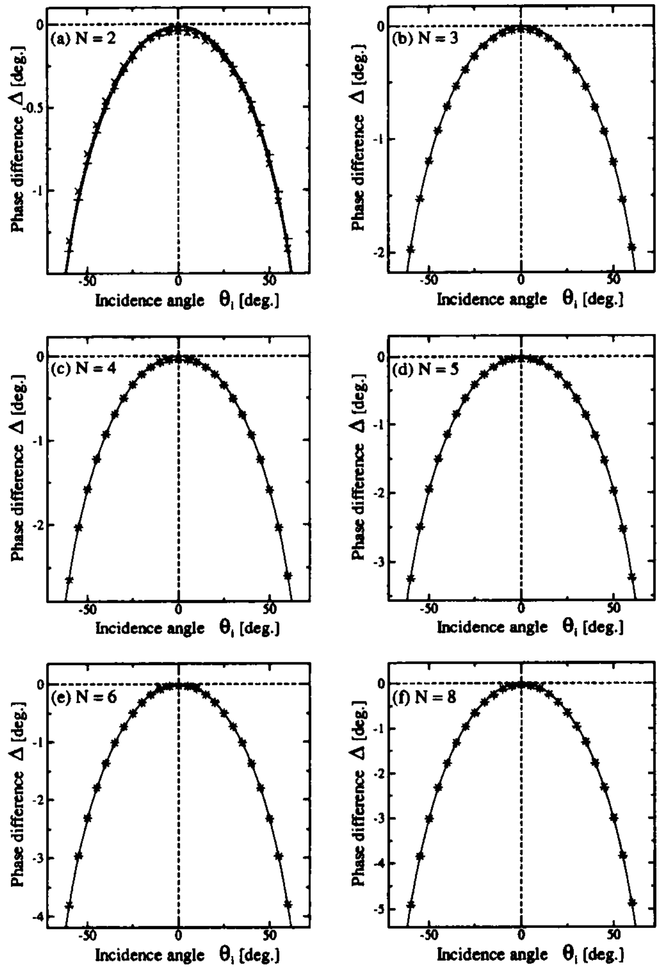

Figure 2: The dependence of Δ on the incidence angle θ_i under the DC applied electric field ($\pm$2.0 V/mm), where the measurements were carried out at the temperature of 145°C (N = 2 - 6) or 140°C (N = 8). In case of N=2, $\theta = 10°$, $\phi = 110, 250°$(solid curve) and $\theta = 10°$, $\phi = 70, 290°$(dash curve). In case of 3-8, solid curves represent simulated results for the SmA structure. The layer thickness is 2.5nm.

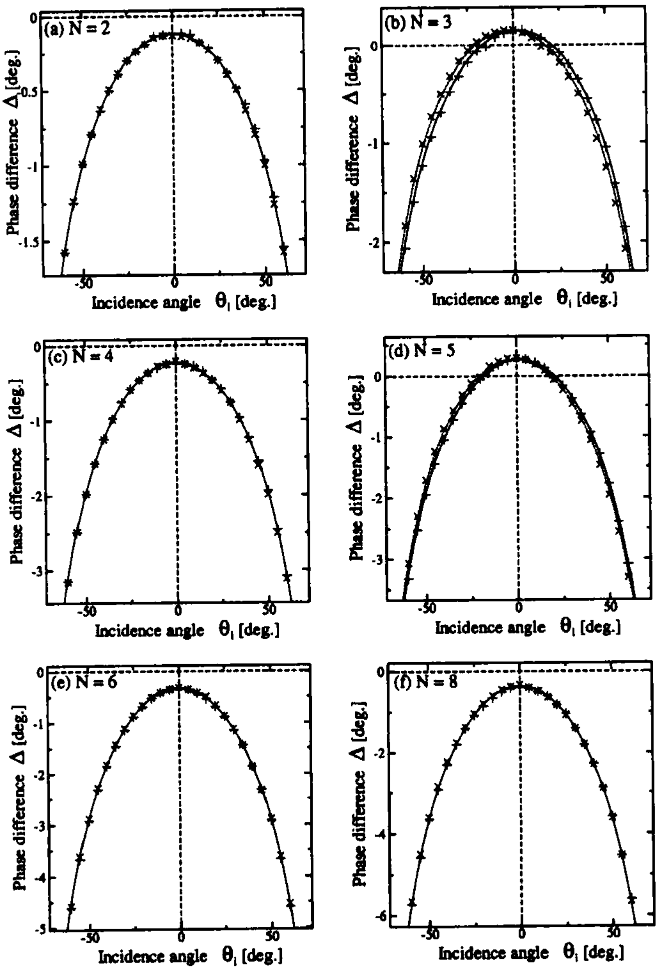

Figure 3: The dependence of Δ on the incidence angle θ_i under the DC applied electric field (±2.0 V/mm), where the measurements were carried out at the temperature of 90°C (N = 2-6) or 95°C (N = 8). The curves represent simulated results for SmC_A^* structure. For even number of layers, the director tilted in $y - z$ plane. For odd number of layers, the director tilted in $x - z$ plane.

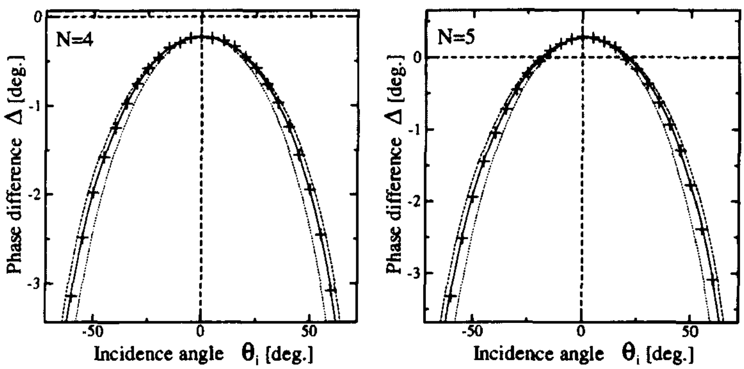

Figure 4: The incidence angle dependence of Δ for thin FSFs. the measurements were carried out at the temperature of 90°C. Curves represent simulated results. $d = d_{\mathrm{SmA}}$, $d = d_{\mathrm{SmA}} \times \cos\theta$ (dash line) and $d = l \times \cos\theta$ (dot line) (d : layer thickness, d_{SmA} : layer thickness in SmA, l : molecule length, θ : tilt angle).

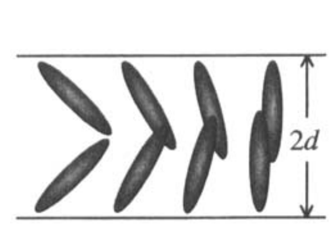

Figure 5: The relations between the tilt angle and the layer thickness in a thin FSFs

References

[1] H. Kobayashi, N. Matsuhashi, Y. Okumoto and T. Akahane: Jpn. J. Appl. Phys., **38**, 6428, (1999).

[2] S, Kuniyasu, H. Fukuro, S. Maeda, K. Nakaya, M. Nitta, M. Ozaki and S. Kobayashi: Jpn. J. Appl. Phys. **27** (1988) 827.

[3] A. D. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe and A. Fukuda: Jpn. J. Appl. Phys. **28** (1989) L1265.

[4] Ch. Bahr and D. Fliegner: Physical Review A **46** (1992) 7657.

[5] Yuichi Takanishi, Kazuyuki Hiraoka, Vijay K. Agrawal, Hideo Takezoe, Atsuo Fukuda, Mitsugu Matsushita: Jpn. J. Appl. Phys., **30**, 2023, (1991).
[6] D.R. Link, J.E. Maclennan and N.A. Clark: Phys. Rev. Lett., **77**, 2337, (1996).