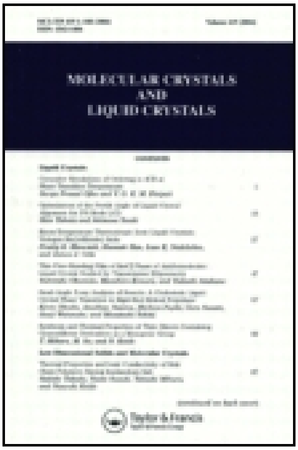

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Freedericksz Transition Occurring in the Surface Induced Ordered State of a Nematic Liquid Crystal at the Temperature Just Above the Clearing Temperature

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Besides the normal Freedericksz transition attributing to the variation of the molecular conformation in the bulk region of a homogeneously aligned nematic liquid crystal, 5CB, which appears at the critical voltage Vc_1, the second Freedericksz transition has been observed at the voltage Vc_2 which is about 83 times larger than Vc_1 at the temperature just above the clearing point. This phenomenon was observed exclusively only in samples prepared by using the orientation layers of the rubbed polyimide or the Y-type Langmuir-Blodgett films comprising 31 stacking layers, but not with the films of the obliquely evaporated SiO films.

1. INTRODUCTION

The evidence for the existence of the surface induced state in an ordinary nematic liquid crystal (NLC) even at an elevated temperature above the clearing point was given by several investigators.[1–3] They agreed with each other in obtaining a common conclusion claiming that the utilization of the orientation layers made of rubbed polymer films gave rise to the occurrence of the surface induced ordered state of an NLC even though the medium in the bulk region takes the isotropic state; however no such a state was observed in a sample prepared by using obliquely evaporated SiO films.

The present work has been done with the aim of knowing the effectiveness of the polyimide Langmuir-Blodgett (LB) films for aligning LC molecules in comparison with that of the rubbed polyimide films and of observing the Freedericksz transition occurring in the surface induced state.

Detailed mechanism of the surface anchoring of the LC is still not completely clear yet, however the alignment phenomena can be thought to consist of the following two effects; the one is the sticking (anchoring) and the other is the orientation. An appropriate quantity to characterize the latter may be the surface order parameter, S_s and that of the bulk, S_b. The anchoring energy for the polar deformation in the planar conformation of an NLC is proportional to the order parameter of the bulk medium S_b if we adopt a model of the steric interaction between the rod like NLC molecules and the smooth surfaces in a sandwich cell.[4] For these reasons the order parameter is one of the important parameters to characterize the surface anchoring phenomena. This paper reports the second Freedericksz transition occurring at a temperature of just above clearing point together with some data of the order parameters.

2. EXPERIMENTAL

In order to know the molecular order of the surface induced layer of an NLC, we made a measurement of the optical retardation. The measuring system used in this work was the same one that was reported in a previous paper.[5] The samples were prepared by using the following various orientation layers made of rubbed polyimide films, those of the Y-type polyimide Langmuir-Blodgett (PI-LB) films comprising 5 through 31 stacking layers, and obliquely evaporated (60 degrees) SiO films. The samples prepared using these films are designated as A, B, and C in this paper. The common thickness of the NLC layers were around 50 μm. It was necessary to subtract the background originated from the birefringence occurring in the orientation layers from the over all retardation; the background reached typically 3 degrees in the pair of the rubbed polyimide layers. The surface induced ordered state of the NLC was observed as a residual optical retardation occurring in a sample which was biased by applying an AC electric field that was far above the normal threshold voltage; however their values were typically below 0.5 degrees (Figure 1).

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

Figure 2 compares the temperature dependence of the residual retardation for the samples with various orientation films, under the application of the electric field of 2.0×10^4 (V/cm); the value of the residual retardation is thought to be expressed as

$$\Delta R = \frac{2\pi \Delta n d_2}{\lambda} \times 2$$

for two interfacial layers, where d_2 stand for the thickness that is equivalent to the coherence length of the surface induced state under the application of an electric field. The birefringence Δn is a function of the depth measured from the surface[1]; but it is approximated to be effectively flat in this work.

It is clear from Figure 2 that the magnitude of the bulk order parameter S for the rubbed polyimide films (sample A) takes the best rank and the Y-type LB films (sample B) take the second best; further they are followed by the SiO films (sample C). Thus the data for the LB films add a new knowledge on the surface

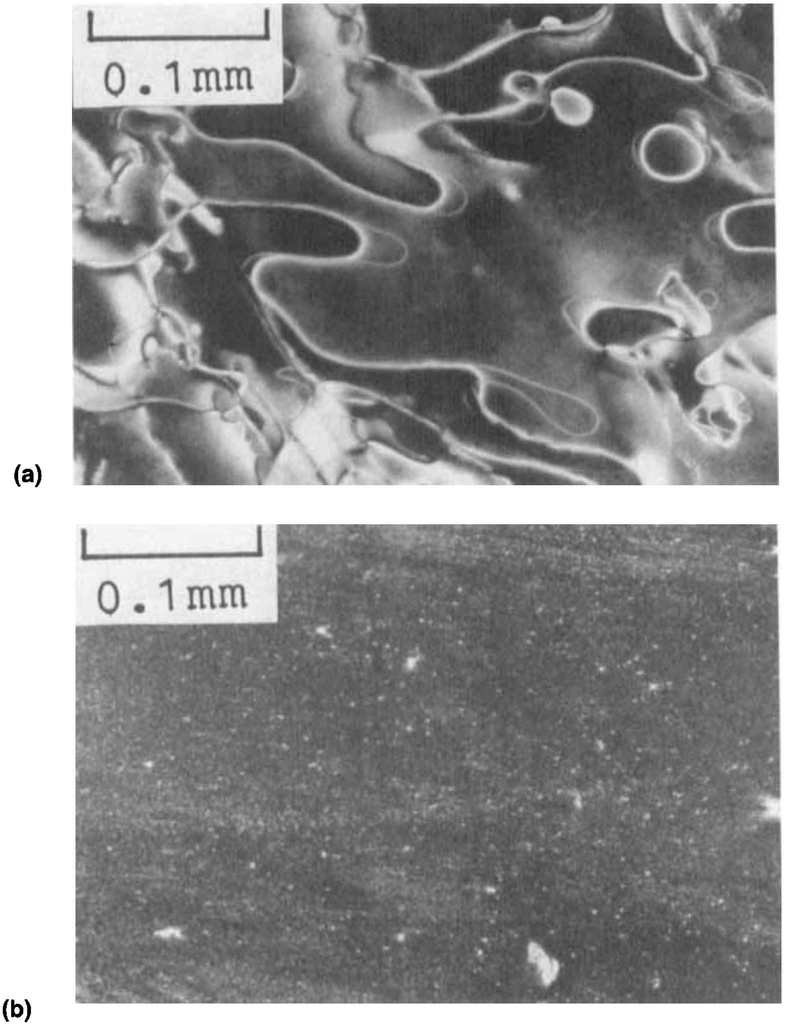

FIGURE 1 Microphotographs of textures of nematic liquid crystal, 5CB. (A) is for a cell with the Z-type PI-LB films; (B) is for that prepared with the Y-type PI-LB films. See Color Plate III.

anchoring of NLC. An evidence for the significant value of the residual surface order parameter at the elevated temperature far above the clearing point was not obtained in the above three cases.

By performing fitting the calculated values to those of observation, we obtained the surface anchoring strengths for the polar deformation in these samples as listed in Table I.

The magnitudes of anchoring strengths for the polar deformation takes the order, $A\ (A) > A\ (B) > A\ (C)$. According to Okano's formulation one obtains the order in the order parameters in the following way; $S\ (A) > S\ (B) > S\ (C)$. These trends support a validity of the Okano model.

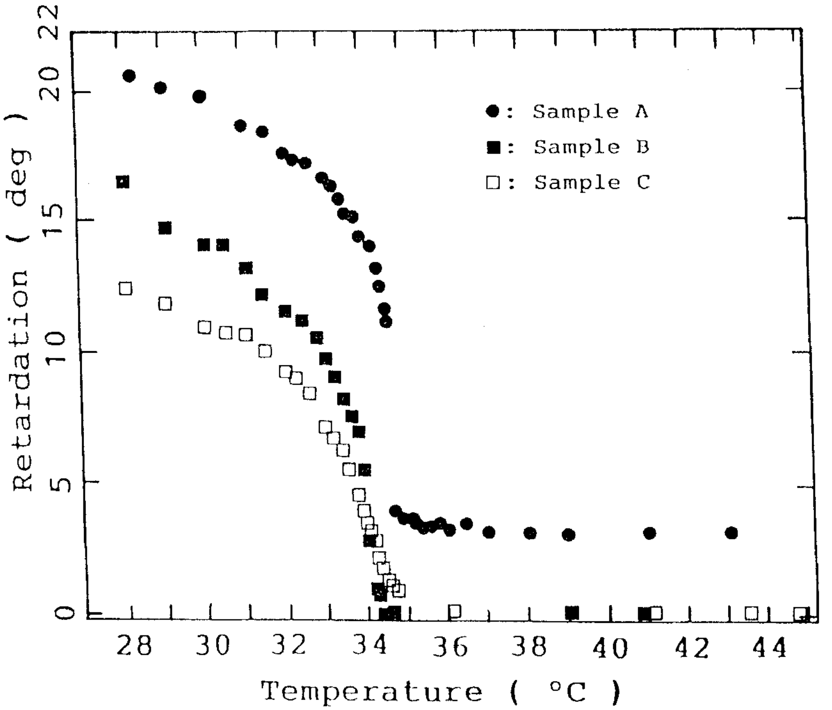

FIGURE 2 Observed retardation for sample A, B, and C versus temperature. The samples are biased at the field intensity of $E = 2.0 \times 10^4$ (V rms/cm).

TABLE I

Anchoring strength for the polar deformation

Sample	Orientation films	A_0 ($\times 10^{-3}(J/m^2)$) $T = 30°C$
A	rubbed PI	1.0
B	PI-LB(31 layers)	0.4
C	SiO60°	0.2

As shown in Figures 3 and 4, besides the normal Freedericksz transition which takes place in the bulk region of a NLC medium, another Freedericksz transition, which may be called that of the second kind occurring in the surface induced phase, was observed, for the first time, as far as the authors know, at a temperature just above clearing point ($T - T_c^* = 0.08$ deg).

This phenomenon was observed as an abrupt change in the optical retardation occurring at the field intensity of $Vc_2 = 49.5$ volts for the sample of 5CB with 50 μm thick aligned by the rubbed polyimide films, while the normal Freedericksz transition occurred at $Vc_1 = 0.6$ volts.

It is worth pointing out that the second Freedericksz transition takes place remarkably only during the course of decreasing the field; there is a hysteresis. The same phenomenon was also observed in a sample with the LB film with a slight difference in the Ec_2 (Figure 4). The observed ratio for Vc_2/Vc_1 is equal to 83 in

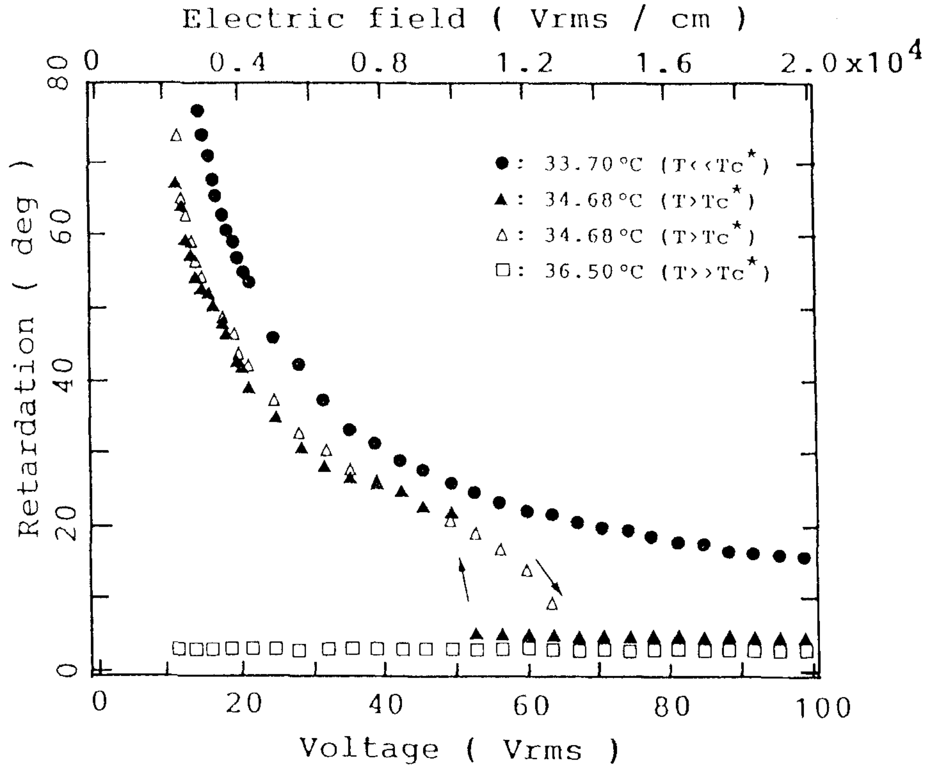

FIGURE 3 The dependence of the optical retardation versus applied voltage (V rms). The LC was oriented with rubbed PI film. The full dots represent the data for the sample at the temperature T = 33.70°C, which is far below T_c^* (34.60°C); open squares represent those for the sample kept at T = 36.50°C (far above T_c^*); and the triangles represent for T = 34.68°C which is just above T_c^*, where the full triangles correspond to the process of decreasing fields whereas open triangles correspond to the increasing process of the field. An abrupt rise in the former is observed. There occurs a hysteresis.

the case of the rubbed polyimide (Figure 3); this value may be explained by assuming that the critical field is given by

$$Ec = (\pi/d)\sqrt{K/\Delta\varepsilon} \tag{1}$$

both for the bulk and the interface regions, where K and $\Delta\varepsilon$ stand for the elastic constant and the dielectric anisotropy, respectively. The ratio Vc_2/Vc_1 may ge given as

$$Vc_2/Vc_1 = 2\left(\frac{K_2}{\Delta\varepsilon_2}\Big/\frac{K_1}{\Delta\varepsilon_1}\right)^{1/2} \cdot \frac{\varepsilon_2 \cdot d_1}{\varepsilon_1 \cdot d_2} \tag{2}$$

where the suffixes 1 and 2 characterize the quantities of bulk and surface regions, respectively.

Furthermore it may be assumed that $K \propto S^2$ and $\Delta\varepsilon \propto S$, then the Ec is proportional to $\sqrt{S}$.[6]

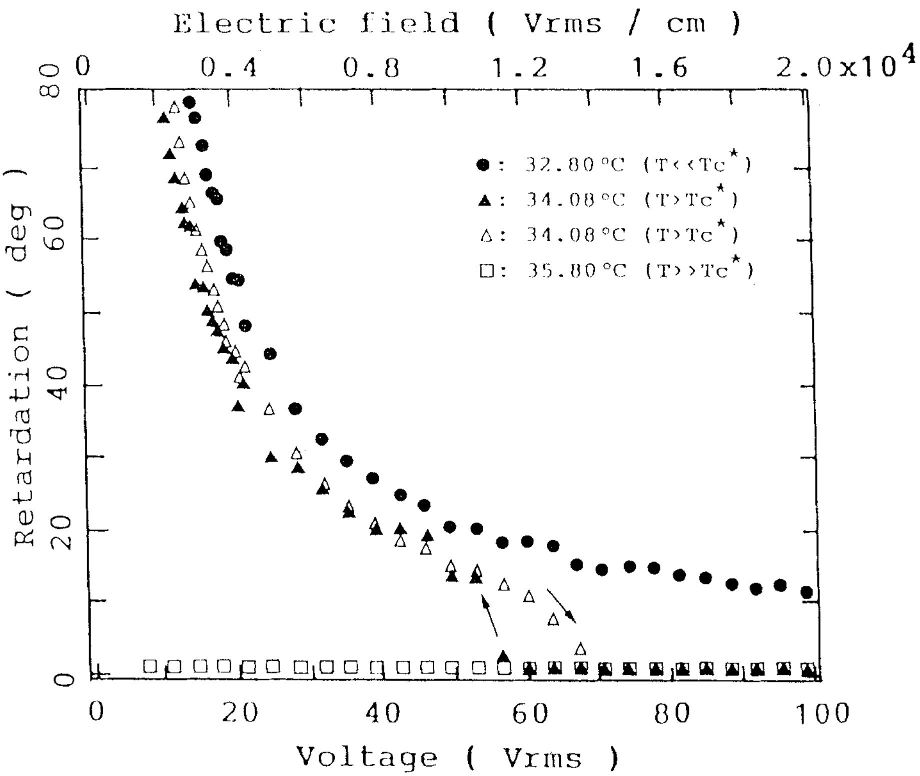

FIGURE 4 The dependence of the optical retardations versus applied voltage (V rms). The LC was oriented with the Y-type PI-LB films. The full dots represent the data for the sample at the temperature $T = 32.80°C$, which is far below T_c^* (34.00°C); open squares represent those for the sample kept at $T = 35.80°C$ (far above T_c^*); and the triangles represent for $T = 34.08°C$ which is just above T_c^*, where the full triangles correspond to the process of decreasing fields whereas open triangles correspond to the increasing process of the field. An abrupt rise is also seen in the former. There occurs a hysteresis.

Thus the ratio leads to

$$Vc_2/Vc_1 = 2\,(\varepsilon_2 \cdot d_1/\varepsilon_1 \cdot d_2)\,\sqrt{S_s/S_b} \tag{3}$$

By substituting the following values into Equation (3) as $d_1 = 50\ \mu\text{m}$, $d_2 = 300$ nm that was determined from the data of the retardation, $\varepsilon_1 = \bar{\varepsilon} = 10$ and $\varepsilon_2 = \varepsilon_\perp = 8$, therefore $\varepsilon_1/\varepsilon_2 = 1.25$; furthermore $S_s = 0.17$ and $S_b = 0.44$; one obtains the ratio is 83. This value is qualitatively in agreement with that of the direct measurement.

From this approximate analysis we succeeded in giving a qualitative explanation for the Freedericksz transition of the second kind.

As a reference, we made a plot of the retardation as functions of applied field intensities. The results showed almost parallel lines. This suggests that no significant evidence for the Kerr effect is obtained in the samples used in this work. This negligible smallness of the Kerr effect is thought to be attributable to the very thinness of the sample media compared to those reported in the past literature.[7–9]

Finally, we will discuss the relationship between the coherence length d_2 and the anchoring strengths. For the bulk region the equation of the spatial variation of the tilt angle is

$$\frac{d\theta}{dz} = \left\{\frac{\Delta\varepsilon\varepsilon_0 E^2}{K_{11}}\left(\sin^2\theta_m - \sin^2\theta\right)\right\}^{1/2} \tag{4}$$

and the equation of the surface torque is

$$K_{11}\frac{d\theta}{dz} = \frac{\partial}{\partial\theta}Fs = \sum_{n=1}^{\infty} A_{2n}\sin^{2n-1}\theta \cdot \cos\theta \tag{5}$$

where we assume $K_{11} = K_{33}$ and θ_m stands for the tilt angle at the midplane; furthermore surface energy Fs is assumed to be

$$Fs = \sum_{n=1}^{\infty}\frac{1}{2n}A_{2n}\sin^{2n}\theta \tag{6}$$

For a very strong field, θ at the surface tends to 90 degrees, then the as above equations reduce to

$$\frac{d\theta}{dz} = \frac{\pi}{d_2}\cos\theta \quad \text{and} \tag{7}$$

$$K_{11}\frac{d\theta}{dz} = \sum_{n=1}^{\infty} A_{2n}\sin^{2n-1}\theta \cdot \cos\theta \tag{8}$$

Then one obtains the relationship between the coherence length d_2 (for $An = \infty$) and the couplins strengths An as follows:

$$\frac{1}{K_{11}}\sum_{n=1}^{\infty} A_{2n} = \frac{\pi}{d_2} \tag{9}$$

therefore

$$d_2 = \frac{\pi K_{11}}{\sum_{n=1}^{\infty} A_{2n}} \tag{10}$$

4. CONCLUDING REMARKS

The second Freedericksz transition phenomena were observed in 5CB at the temperature just above the clearing point for samples prepared by using rubbed polyimide and the Y-type polyimide Langmuir-Blodgett orientation films. The observed voltage for the second Freedericksz transition was shown to be 83 times larger than that for the normal Freedericksz transition. This ratio was interpreted qualitatively by taking account of the temperature variations of the order parameters and the coherence length for surface ordered state.

Detailed experimental and analytical research works are now being underway and the results will be published elsewhere.

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