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The essence of the anisotropic alignment of liquid crystal (LC) molecules at the substrate surface is derived from the distribution of the molecular direction of the LC, which is best described in terms of the order parameter. The order parameter of LC molecules at a polymer surface can be determined by measuring the contact angle of a nematic LC droplet at the nematic-isotropic phase transition temperature. In this study, we quantified the relationship between the surface order parameter and contact angle of the droplet for a homogeneous alignment LC cell. Based on the results, we propose a model for a droplet on a polymer surface. Its validity was confirmed by measuring the polarized infrared absorption. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2752100]

INTRODUCTION

The rapid development of the information society has produced a demand for high-quality display devices, such as high-quality liquid crystal displays (LCDs). A LCD cell consists of a liquid crystal (LC) layer sandwiched between two pieces of a substrate. Applying an external electric field changes the alignment of LC molecules in the cell. For precise control of the alignment, the alignment of the LC molecules at the substrate surface is important because the orientation of the LC molecules on the surface dominates elastically over the bulk LC alignment.[1] The directional alignment of the surface LC molecules is characterized using the order parameter, which denotes the uniformity of the LC molecular alignment.

Various ways to measure the surface order parameter of a LC have been proposed.[2–4] In this study, we measured the surface order parameter using the phase transition droplet method[5] because this technique is effective for measuring all LCs, from low to high order. However, the surface phenomenon of the phase transition droplet has remained unclear.[6] To resolve this issue, we investigated the effects of the surface layer in the phase transition droplet method. Furthermore, we discuss the anisotropic interaction between the LC molecules and polymer, which is thought to generate the absorbed LC surface layer on the polymer surface.

$$\gamma_{NS} = \gamma_{IS} + \gamma_{NI} \cos \theta, \tag{1}$$

where γ_{NS}, γ_{IS}, and γ_{NI} are the interfacial tensions between the nematic phase LC and polymer surface, between the isotropic phase LC and polymer surface, and between the nematic and isotropic phase LCs, respectively, and θ is the contact angle of the droplet. In addition, each interfacial tension can be subdivided into two surface tensions using Fowkes' equation:

$$\gamma_{NS} = \gamma_N + \gamma_S - 2\sqrt{\gamma_N \gamma_S}, \quad \gamma_{NI} = \gamma_I + \gamma_N - 2\sqrt{\gamma_I \gamma_N},$$

$$\gamma_{IS} = \gamma_I + \gamma_S - 2\sqrt{\gamma_I \gamma_S}. \tag{2}$$

From Eqs. (1) and (2), the following equation can be derived:

$$\cos \theta = \frac{\gamma_{NS} - \gamma_{IS}}{\gamma_{NI}} = \frac{\sqrt{\gamma_N} + \sqrt{\gamma_I} - 2\sqrt{\gamma_S}}{\sqrt{\gamma_N} - \sqrt{\gamma_I}}. \tag{3}$$

Both the nematic and isotropic phase LCs consist of the same LC molecules; the difference between the two phases is in their order parameters. Each surface tension can be written in terms of the second-order expansion of the order parameter using the Landau-de Gennes formalism[7] and higher terms are removed because the order parameter is much lower than 1 at T_{NI}. Generally, the order parameter is a one-directional parameter S, which is called a uniaxial order pa-

Phase transition droplet method

At the nematic-isotropic transition temperature (T_{NI}), a phase transition droplet forms on the polymer surface, as shown in Fig. 1. The contact angle of the droplet is determined by the balance of three interfacial tensions, which satisfies Young's equation, as shown in Fig. 1(b):
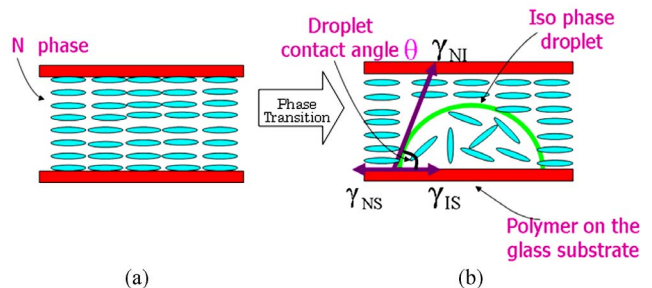

FIG. 1. (Color online) Phase transition droplet and contact angle (a) below the phase transition temperature and (b) at the phase transition temperature.

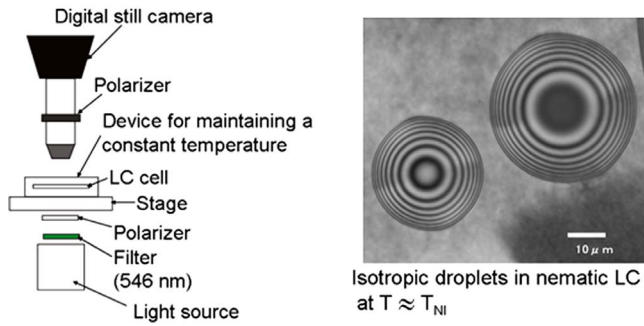[a] Electronic mail: oh.sejoon@ec.ecei.tohoku.ac.jp

FIG. 2. (Color online) Apparatus for measuring the contact angle of a droplet on the polymer surface. (b) Measured birefringence rings of isotropic droplets.

FIG. 3. (Color online) Rubbing-strength dependence of the contact angle of the droplet.

rameter in this paper. In contrast, the two-parameter descriptions S and D are adequate for biaxial media, such as a nematic LC near the surface. D stands for the biaxiality of the media, which is called the biaxial order parameter in this paper. Since the contact angle of the droplet is strongly affected by the order parameter difference between the nematic and isotropic phases, only the uniaxial order parameter S contributes to the contact angle of the droplets and is used in the expansion. This expansion can also be applied to the surface tension of the polymer, γ_S. Then,

$$\gamma_N = \gamma_0 - \alpha S_N + \beta S_N^2, \quad \gamma_I = \gamma_0, \quad \text{and}$$

$$\gamma_S = \gamma_{0S} - \alpha_S S_S + \beta_S S_S^2 \tag{4}$$

are obtained, where γ_N, $\gamma_I(=\gamma_0)$, γ_S, and γ_{0S} represent the surface tensions of the nematic phase LC, isotropic phase LC, polymer, and unrubbed polymer, respectively; S_N is the order parameter of the nematic phase; S_S is the order parameter of the polymer surface, which is assumed to be the same as the surface order parameter of the LC; and α, β, α_S, and β_S are coefficients. Substituting Eq. (4) into Eq. (3) gives

$$\cos\theta \approx 1 - \frac{2\alpha_S\sqrt{\gamma_0}}{\alpha\sqrt{\gamma_{0S}}}\left(\frac{S_S}{S_N}\right) + (\sqrt{\gamma_0} - \sqrt{\gamma_{0S}})$$

$$\times\left[\frac{1}{\sqrt{\gamma_0}} + \frac{4\sqrt{\gamma_0}}{\alpha}\left(\frac{\beta}{\alpha} - \frac{1}{S_N}\right)\right]. \tag{5}$$

As shown in Eq. (5), the contact angle of the droplet is a function of the surface order parameter S_S.

However, the relationship between the order parameter of the polymer and that of the LC on the polymer surface is still not known. To clarify this point, the contact angle of the phase transition droplet and the behavior of the liquid crystal on the polymer surface must be measured.

Measuring the contact angle of droplets

The contact angle of a droplet at the surface can be calculated by measuring its diameter and height. This is achieved by placing the cell in a constant-temperature container and controlling the temperature accurately so that the shape of the droplet does not change during the measurement. A microscope with crossed polarizers is used to analyze the shape of the phase transition droplet, as shown in
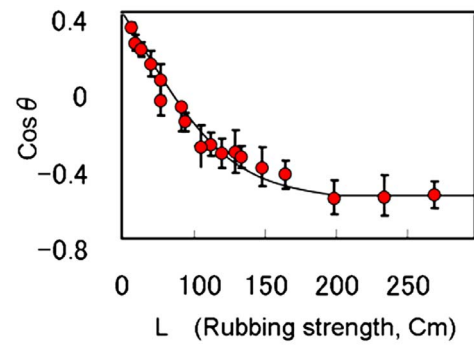
Fig. 2(a). Light from a source is passed through a narrow band filter to obtain a clear birefringence image using a digital camera. The observed image of the droplet on the rubbed polyimides is shown in Fig. 2(b). The height of the droplet, which is about 45 μm, can be measured by counting the number of birefringence rings corresponding to equal retardation contours. The diameter was measured by processing the image of a droplet.

The rubbing-strength dependence of the contact angle of the droplet was measured, as shown in Fig. 3. This confirmed that the contact angle of the droplet is strongly related to the rubbing strength, i.e., the greater the rubbing strength is, the greater the contact angle of the droplet.

Birefringence of the surface LC layer

At the interface between the polymer surface and the bulk LC at T_{NI}, it was reported that the ordered layer undergoes continuous phase transition at the surface[8] and that alignment treatment on the surface induces an aligned LC layer, even when the bulk LC is in the isotropic phase.[9] Based on these reports, an ordered LC layer should exist on the polymer above T_{NI}. To verify the presence of this LC layer on the polymer above T_{NI}, we measured the birefringence of LC molecules on a polymer surface, excluding the bulk LC, using spectroscopic ellipsometry. The temperature of the cell was maintained constantly near T_{NI}, as shown in Fig. 4. Two kinds of polyimide were coated on a glass substrate using spin coating: AL1254 and PI-3 (JSR). A homogeneous alignment LC cell is made by stacking the two substrates in an antiparallel rubbing direction. Nematic liquid crystal 5CB (Chisso) was used. The results of the birefrin-
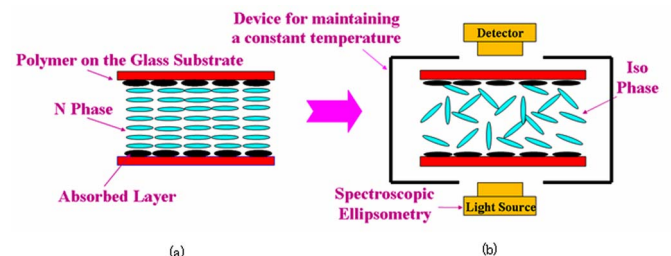

FIG. 4. (Color online) Measuring the birefringence of LC molecules on the polymer surface using spectroscopic ellipsometry and a device to maintain a constant temperature.
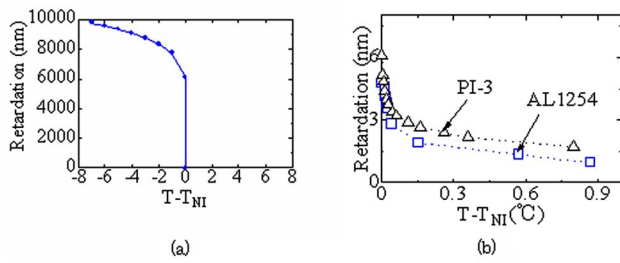
FIG. 5. (Color online) Measured retardation of the LC on the polymer surface. (a) Retardation near the phase transition temperature. (b) Enlargement of (a) showing the values of temperature between 0 and 0.9 °C.

FIG. 7. (Color online) Detailed model of a phase transition droplet.

gence measurement are shown in Fig. 5, in which the birefringence of the glass and polymer was subtracted. Both surfaces on the AL1254 and PI-3 produced slight birefringence at temperatures over T_{NI}. This birefringence is thought to have originated in the surface layer of the nematic LC absorbed on the polymer surface. The depth of the layer, which was about 45 nm, was calculated from the results of the birefringence measurement. The surface order parameter may shift from the surface value S_S toward the bulk value in the layer based on the short-range order. In that case, the order parameter is suggested to change from S_S to the bulk value in the nematic phase and from S_S to zero in the isotropic phase at the phase transition temperature. If this order-varying interfacial layer between the surface and the droplet is considered, the interface layer between the nematic and isotropic phases must also be considered. In this method, this layer was simplified so that we also regarded the order parameter measured from the contact angle as the surface order parameter S_S, as shown in Fig. 6. However, the details cannot be discussed here due to lack of supporting data.

Based on this result, we proposed a droplet model, which is shown in Fig. 7. A phase transition droplet did not form on the polymer surface but on the surface LC layer on the polymer in our model. Based on this model, the surface tension of the polymer surface can be replaced with the surface tension of the nematic phase LC in Eq. (5). Consequently, Eq. (5), which represents the relationship between S_S and $\cos \theta$, can be simplified to a linear relationship by substituting γ_0 and α instead of γ_{0S} and α_S, respectively:

$$\cos \theta \approx 1 - 2 \frac{S_S}{S_N}. \tag{6}$$

Measuring the surface order parameter

To verify Eq. (6), the relationship between the contact angle θ of the droplet and the surface order parameter S_S was

determined independently using the following procedure. First, the rubbing-strength dependence of the polarized infrared (IR) light absorption of the cell was measured. Then, the rubbing-strength dependence of the contact angle θ of the droplet was also obtained. Based on these results, the contact angle θ was related to the surface order parameter S_S using the same rubbing condition.

Two surface order parameters [the uniaxial order $S(d)$ and biaxial order $D(d)$] were measured, as shown in Fig. 8. These order parameters can be derived as follows:[10]

$$S(d) = \frac{1}{2} \frac{2\alpha_{\|} - (\alpha_{\perp 1} + \alpha_{\perp 2})}{\alpha_{\|} + \alpha_{\perp 1} + \alpha_{\perp 2}}, \quad D(d) = \frac{1}{2} \frac{\alpha_{\perp 1} - \alpha_{\perp 2}}{\alpha_{\|} + \alpha_{\perp 1} + \alpha_{\perp 2}}. \tag{7}$$

$a_{\|}$, $a_{\perp 1}$, and $a_{\perp 2}$ are the IR-absorbance coefficients defined as

$$A_{\|}(d) = \int_0^d \alpha_{\|}(x)dx, \quad A_{\perp 1}(d) = \int_0^d \alpha_{\perp 1}(x)dx,$$

$$A_{\perp 2}(d) = \int_0^d \alpha_{\perp 2}(x)dx, \tag{8}$$

where $A_{\|}$, $A_{\perp 1}$, and $A_{\perp 2}$ are the integrated IR absorption throughout the cell and can be obtained experimentally. However, it is difficult to measure the order parameter of the LC absorbed on a polymer ($d \approx 0$) using this method. To determine the uniaxial and biaxial surface order parameters $S(0)$ and $D(0)$, respectively, the relationship between the IR-absorbance coefficient and the gap of a wedge cell was used, from which $S(0)$ and $D(0)$ were obtained by extrapolation.
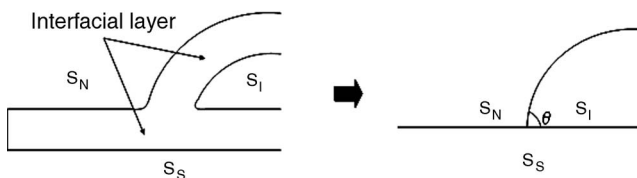

FIG. 6. Interfacial layers of the droplet. S_N, S_I, and S_S indicate the order parameter of the nematic phase, isotropic phase, and surface, respectively.
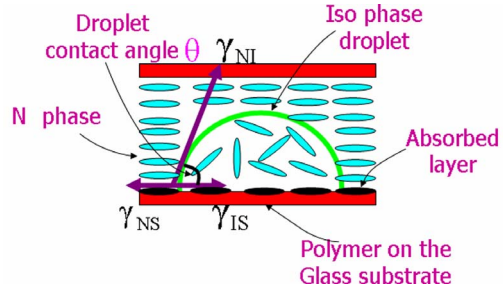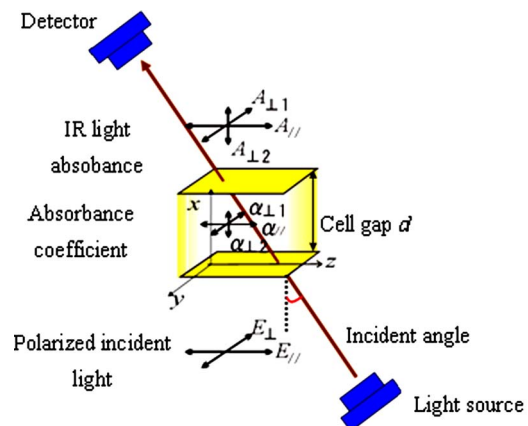

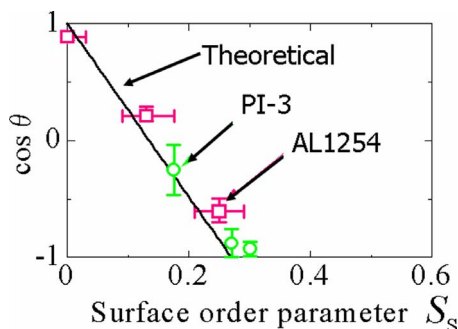FIG. 8. (Color online) Measuring the polarized infrared light absorbance.

FIG. 9. (Color online) Relationship between the surface order parameter and contact angle.

The wedge cell adopted a sandwich structure consisting of two CaF_2 substrates that transmit IR light. Consequently, only the absorption of the C-N radical at wave number of 2227 cm^{-1} of the LC molecules was detected.

RESULTS AND DISCUSSION

The experimental relationship between the surface order parameter of a LC cell measured using polarized IR light absorption and the contact angle of a droplet is shown in Fig. 9. The experimental results were compared with the theoretical line of Eq. (6) in Fig. 9, where $S_N = 0.27$ was obtained from the relationship between the refraction index and order parameter of nematic LC molecules in the bulk layer near T_{NI}.[11] The graph shows good agreement between the experimental and theoretical results, confirming the validity of our model. Based on this graph, the linear relationship between S_S and $\cos\theta$ given by Eq. (6) was verified. As Eq. (6) dem-

onstrates, the contact angle of a phase transition droplet is determined by the ratio of the surface order parameter to the bulk order parameter S_S/S_N.

CONCLUSION

This study demonstrates that the contact angle of a phase transition droplet is determined by the order parameter of the LC absorbed on the polymer surface when an absorbed LC layer is present on the polymer surface. On measuring the polarized IR absorption of a LC cell and the contact angle of the phase transition droplet, we found the relationship between the contact angle $\cos\theta$ and the surface order parameter S_S to be linear. Furthermore, the contact angle $\cos\theta$ was determined from the ratio of the surface order parameter to the bulk order parameter S_S/S_N. In conclusion, the contact angle of a phase transition droplet gives the order parameter of the LC absorbed on the polymer surface.

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