

Anchoring of Liquid Crystals on Self-Organized Microwrinkles

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SUMMARY The self-organized microwrinkles can serve as a surface alignment layer to align nematic liquid crystals, which is primarily based on the groove mechanism. The azimuthal anchoring energy is discussed and estimated from the groove topography and the actual twist angle in the twisted nematic cell.

key words: liquid crystal, microwrinkles, self-organization, anchoring energy, microgrooves

1. Introduction

Nematic liquid-crystal (LC) molecules spontaneously align in a certain direction with a macroscopic coherent length [1], where the orientation is determined by the anisotropic external conditions. The examples are the electric and magnetic fields, which affect LC molecules directly, and the anisotropic boundary conditions, such as the surface microgrooves [2]–[6] and the molecular scale anisotropy (e.g., aligned polymer chains by rubbing or photoaligning [7]–[9]) of the surface, to which the LC contacts.

Exploiting such a variety of controllability of the LC orientation, the modern LC display technology and LC-based photonic devices have been developed. One of the basic devices is the optical shutter based on the twisted nematic (TN) cell, where the transmission of the light is switched by the electric field while the twisted state in the null electric field is held by two planar alignment surfaces. Thus, the mechanism and technology of the LC alignment on such anisotropic surfaces have been studied extensively. Such anisotropic surfaces are commonly obtained by mechanical rubbing of a polymer surface, microfabrication of grooves [4]–[6], and the photo-alignment method [7]–[9].

Recently, we have reported that the spontaneously-formed microwrinkles can align the nematic LCs [10]. When a thin and hard layer supported by a soft substrate is laterally compressed, the surface spontaneously undulates with the characteristic length, that is, the spatial wavelength λ [11]–[17]. The microwrinkle-based TN cell also shows a common opt-electric response. In contrast to the microgrooves fabricated through conventional lithography, such wrinkles can be categorized as one of the self-organized structures, which are promising for the low-cost

microfabrication technology. Since the microwrinkles generally form on the soft and flexible substrate, the system is likely to be applied to the flexible display technology, e.g., LC papers.

However, the understanding of the microwrinkle-induced LC alignment has not been matured yet. Especially, the azimuthal anchoring energy or strength remains unknown. Thus, in this study, we estimate it via (1) the measured topography of the microgrooves and (2) the actual twist angle in the twisted nematic cell (torque-balance method), and discuss the understanding of the results.

2. Experiment

2.1 Microwrinkles

The microwrinkles coated with various polymers were used as the LC alignment surfaces. To first fabricate anisotropic microwrinkles Au is deposited on a transparent sheet ($16 \times 16 \times 1 \text{ mm}^3$) of a silicone elastomer, polydimethylsiloxane (PDMS, sylgard 184, Dow-corning), under a uniaxial tensile strain of $\sim 10\%$ using an ion sputter, and then, strain is released (Fig. 1(a)). The Au thickness is $\sim 6 \text{ nm}$, with which the spatial wavelength of the microwrinkles, λ , is $1 \mu\text{m}$.

Four different polymers are used; poly (vinylalcohol) (PVA, Mw = 22k, MP Biomedicals), poly (vinyl-2-pyridine), (PVP, Mw = 122k, Sigma-Aldrich), poly (methylmethacrylate) (PMMA, Mw = 120k, Sigma-Aldrich) and AL1254 (JSR), which is a polyimide for LC alignment. Each 0.1–0.2 wt% solution of the *N*-methyl-2-pyrrolidone was spin-coated on the preformed anisotropic wrinkles. Then, the samples are heated at 80° in a vacuum ($\sim 2 \text{ Pa}$) for a half day. The polymer-coated microwrinkles are characterized by the atomic force microscope (AFM, Agilent). The result shows that $2A \sim 100 \pm 20 \text{ nm}$, where A is half the groove depth (Fig. 1(a)). Although it is difficult to determine the polymer thickness, the sinusoidal wavy shape remains after the polymer deposition (Fig. 1(b)). The room temperature nematic LC, 4'-pentyl-4-biphenylcarbonitrile (5CB), shows planar alignment on these polymers. Meanwhile, the 5CB on the microwrinkles without the polymers show the homeotropic alignment. The splay, twist, and bend elastic constants of 5CB, (K_1, K_2, K_3) $\approx (6, 3, 8 \text{ pN})$ at 25° [18]. The blue dichroic dye (LCD-118; Nippon Kayaku) is mixed with 5CB at $\sim 0.3 \text{ wt}\%$ to investigate the alignment, owing to the guest-host (GH) effect [19].

It should be noted that the polymers on the microwrin-

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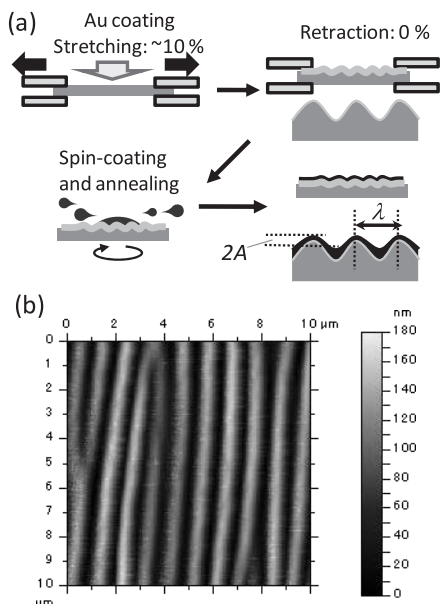


Fig. 1 (a) Preparation and (b) AFM image of the microwrinkles coated with a polymer.

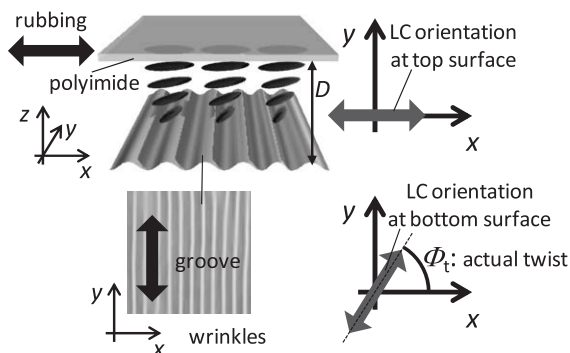


Fig. 2 Schematics of the 90° TN cell with the coordinates. The definition of the actual twist angle is shown for one of the twist chiralities.

kles have neither experienced strain and nor been stretched during the experiments. Thus, here we can evaluate the pure groove-induced alignment rather than the stretching-induced alignment [20].

2.2 TN Cell

The TN cells are also fabricated to investigate the anchoring property under the torque transmitted from the TN. Using a rubbed polyimide as the counter alignment surface (top surface in Fig. 2) and polyimide spacers, the 90° TN cells are fabricated. The cell gap, D , is measured by the UV spectrometer to be in the range of $10\text{--}15\ \mu\text{m}$. The LC with the dichroic dye is injected at temperature beyond the clearing point and cooled down to 25° . The polarized light is illuminated from the bottom and the transmitted light is observed from the top of the TN cell. Here, the blue color becomes clear when the angle of the polarizer is close to that of the LC orientation owing to the GH effect. To quantify the ac-

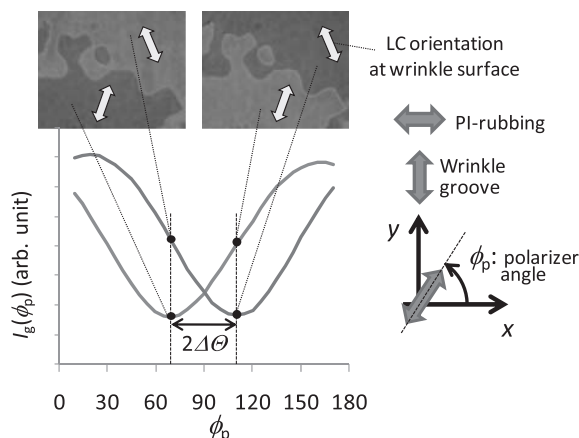


Fig. 3 Example of the plots of the green color intensities I_g with respect to the polarizer angle ϕ_p at the different domains with opposite TN chiralities. The optical microscopy images ($100 \times 80\ \mu\text{m}^2$) with only a polarizer at two minima are also shown (top).

tual twist angle Φ_t , we analyze the average intensity of the green color, $I_g(\phi_p)$, which is in the absorption band of the present dye, in the area of interest, and where ϕ_p is the polarizer angle. At the minimum of $I_g(\phi_p)$, $\phi_p = \Phi_t$, showing the maximum degree of the blue color. Here, using two plots of $I_g(\phi_p)$ at two domains with opposite chiralities (Fig. 3), the angle difference between the two minima, $2\Delta\Theta$, is read, and then, the actual twist angle is calculated via the equation, $\Phi_t = (\pi - 2\Delta\Theta)/2$, where $\Delta\Theta$ is the misfit angle described later.

3. Results and Discussions

LC aligns on wrinkles as reported previously [10]. Here, we estimate the effect of the microgrooves on the Frank elastic energy with employment of the theory derived by Berreman and Fukuda et al. [2], [3]. If the LC is forced to align perpendicular to the microgrooves, the Frank elastic energy increases by Δf_{calc} owing to the undulation of the nematic director at the interface. Thus, we can calculate the increased energy that relates to the anchoring strength using the relationship, $\Delta f_{calc} = 1/4 (K_1 K_3)^{1/2} A^2 (2\pi/\lambda)^3$ [2], [3], resulting in $\Delta f_{calc} \sim 1.2 \times 10^{-6}\ \text{Jm}^{-2}$ (error: $\pm 30\%$) for 5CB on the present microwrinkles.

Next, we estimate the Rapini-Papoular (RP) azimuthal anchoring strength [21] using the measured actual twist angle via the torque-balance method [22]. The RP-type anchoring energy is written as $f_{RP}(\Delta\Theta) = 1/2 W_{RP} \sin^2(\Delta\Theta) [=1/2 W_{RP} \cos^2(\Phi_t)]$, where W_{RP} is the RP anchoring strength and $\Delta\Theta$ is the misfit angle with respect to the easy axis. This RP-type of the energy function is one of the simplest forms that fulfill the symmetrical requirement from the indistinguishable nematic directors \mathbf{n} and $-\mathbf{n}$. In the present case, the anchoring strength of the rubbed polyimide surface is assumed to be much larger than that of the wrinkles. Since the torques transmitted from the bulk twisted nematic $[d(K_2 \Phi_t^2/2D)/d\Phi_t = K_2 \Phi_t/D]$ and the azimuthal anchoring $[d(f_{RP})/d\Phi_t = -1/2 W_{RP} \sin(2\Phi_t)]$ at the microwrinkle sur-

face cancel out at the equilibrium state, W_{RP} can be calculated from $W_{RP} = 2K_2\Phi_t/[D \sin 2\Phi_t]$ [22] (the detailed derivation is omitted here). The energy difference between two configurations, $f_{RP}(0)$ (easy axis) and $f_{RP}(\pm\pi/2)$ (perpendicular to the easy axis), $\Delta f_{RP} = 1/2W_{RP}$, which can be compared with Δf_{calc} calculated from the topographic parameters determined by the atomic force microscopy.

The actual twist angles Φ_t for microwrinkles coated with different polymers result in $70^\circ \pm 4^\circ$. We use this value to calculate the anchoring energy, resulting in $\Delta f_{RP} = 0.94 \times 10^{-6} \text{ Jm}^{-2}$ (error: $\pm 20\%$). Thus, $\Delta f_{calc} \approx \Delta f_{RP}$ within the error range, suggesting that the TN configuration is mainly supported by the microgroove-induced anchoring.

Meanwhile, if we assume the surface memory effect (SME), it is questionable that the obtained anchoring energy is the final value after a period of time (e.g. several minutes). The SME means that the orientation of the LC alignment is memorized on to the surface [23]–[26]. It is believed that the nematic orientation is imprinted to the surface, to which the LC contacts. Although the mechanism remains unclear, it is assumed that some flexible parts at the interface yield to be aligned by the bulk LC order [24], [25] or that the LC molecules with a certain anisotropic order strongly absorb on the surface [23]. In either case, the memorization should be time-dependent. Thus, the azimuthal anchoring energy should vary (increase) with time in addition to the pure microgroove-induced anchoring energy. In future study, the contribution from the SME to the time-dependent anchoring energy will be investigated to clarify the anchoring mechanism and for the design as a LC-alignment surface.

4. Conclusions

The self-organized microwrinkles can serve as an easily-generated surface to align nematic LCs. The anchoring energy has been estimated using (1) the theoretical equation for the microgroove-induced alignment with the measured topographic parameters and (2) the torque-balance method, showing a good correspondence between their values, $\sim 10^{-6} \text{ Jm}^{-2}$. However, the final anchoring energy still remains elusive and is likely to be much larger than the present value, because the SME may have significant contribution to the anchoring strength as time advances.

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References

[1] P.G. de Gennes and J. Prost, The physics of liquid crystals, Oxford

- Univ. Press, New York, 1993.
- [2] D.W. Berreman, "Solid surface shape and the alignment of an adjacent nematic liquid crystal," *Phys. Rev. Lett.*, vol.28, pp.1683–1686, 1972.
 - [3] J. Fukuda, M. Yoneya, and H. Yokoyama, "Surface-groove-induced azimuthal anchoring of a nematic liquid crystal: Berreman's model re-examined," *Phys. Rev. Lett.*, vol.98, 187803, 2007; vol.99, 039902, 2007.
 - [4] D.C. Flanders, D.C. Shaver, and H.I. Smith, "Alignment of liquid crystals using submicrometer periodicity gratings," *Appl. Phys. Lett.*, vol.32, pp.597–598, 1978.
 - [5] H. Yokoyama, S. Kobayashi, and H. Kamei, "Effect of substrate surface on the formation of nematic phase at the isotropic-nematic transition," *Appl. Phys. Lett.*, vol.41, pp.438–440, 1982.
 - [6] J.A. Castellano, "Surface anchoring of liquid crystal molecules on various substrates," *Mol. Cryst. Liq. Cryst.*, vol.94, pp.33–41, 1983.
 - [7] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, and K. Aoki, "Reversible change in alignment mode of nematic liquid crystals regulated photochemically by "command surfaces" modified with an azobenzene monolayer," *Langmuir*, vol.4, pp.1214–1216, 1988.
 - [8] W.M. Gibbons, P.J. Shannon, S.-T. Sun, and B.J. Swetlin, "Surface-mediated alignment of nematic liquid crystals with polarized laser light," *Nature*, vol.351, pp.49–50, 1991.
 - [9] M. Schadt, H. Seiberle, and A. Schuster, "Optical patterning of multi-domain liquid-crystal displays with wide viewing angles," *Nature*, vol.381, pp.212–215, 1996.
 - [10] T. Ohzono, H. Monobe, and Y. Shimizu, "Liquid crystal alignment on self-organized microwrinkles," *Appl. Phys. Exp.*, vol.1, 065001, 2008.
 - [11] N. Bowden, S. Brittain, A.G. Evans, J.W. Hutchinson, and G.M. Whitesides, "Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer," *Nature*, vol.393, pp.146–149, 1998.
 - [12] D. Moldovan and L. Golubovic, "Buckling dynamics of compressed thin sheets (membranes)," *Phys. Rev. Lett.*, vol.82, pp.2884–2887, 1999.
 - [13] N. Uchida, "Orientational order in buckling elastic membranes," *Physica D*, vol.205, pp.267–274, 2005.
 - [14] D.Y. Khang, H. Jiang, Y. Huang, and J.A. Rogers, "A stretchable form of single-crystal silicon for high-performance electronics on rubber substrates," *Science*, vol.311, pp.208–212, 2006.
 - [15] J. Genzer and J. Groenewold, "Soft matter with hard skin: From skin wrinkles to templating and material characterization," *Soft Matter*, vol.2, pp.310–323, 2006.
 - [16] T. Ohzono and M. Shimomura, "Ordering of microwrinkles by compressive strain," *Phys. Rev. B*, vol.69, 132202(4), 2004.
 - [17] T. Ohzono and M. Shimomura, "Geometry-dependent stripe rearrangement processes induced by strain on preordered microwrinkle patterns," *Langmuir*, vol.21, pp.7230–7237, 2005.
 - [18] J.D. Bunning, T.E. Faber, and P.L. Sherrel, "The Frank constants of nematic 5CB at atmospheric-pressure," *J. Phys. (Paris)*, vol.42, pp.1175–1182, 1981.
 - [19] G.H. Heilmeyer and L.A. Zanoni, "Guest-host interactions in nematic liquid crystals. a new electro-optic effect," *Appl. Phys. Lett.*, vol.13, pp.91–92, 1968.
 - [20] H. Aoyama, Y. Yamazaki, M. Matsuura, H. Mada, and S. Kobayashi, "Alignment of liquid crystals on the stretched polymer films," *Mol. Cryst. Liq. Cryst.*, vol.72, pp.127–132, 1981.
 - [21] A. Rapini and M. Papoular, "Distorsion d'une lamelle nématique sous champ magnétique conditions d'ancrage aux parois," *J. Phys. (Paris)*, Colloq., vol.30, pp.C4-54, 1969.
 - [22] T. Akahane, H. Kaneko, and M. Kimura, "Novel method of measuring surface torsional anchoring strength of nematic liquid crystals," *Jpn. J. Appl. Phys.*, vol.35, pp.4434–4437, 1996.
 - [23] H. Yokoyama, S. Kobayashi, and H. Kamei, "Role of surface adsorption in the surface-induced alignment of nematic liquid crystals on evaporated SiO films," *J. Appl. Phys.*, vol.56, pp.2645–2654, 1984.

- [24] N.L. Clark, "Surface memory effect in liquid crystals: Influence of surface composition," *Phys. Rev. Lett.*, vol.55, pp.292–295, 1985.
- [25] Y. Ouchi, M.B. Feller, T. Moses, and Y.R. Shen, "Surface memory effect at the liquid-crystal-polymer interface," *Phys. Rev. Lett.*, vol.68, pp.3040–3043, 1992.
- [26] R. Berberi, I. Dozov, M. Giocondo, M. Ivane, P. Martinot-Lagarde, D. Stoenescu, S. Tonchev, and L.V. Tsonev, "Azimuthal anchoring of nematic on undulated substrate: Elasticity versus memory," *Eur. Phys. J. B*, vol.6, pp.83–91, 1998.



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