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Anchoring transitions of transversely polar liquid-crystal molecules on perfluoropolymer surfaces

Surajit Dhara,[*] Jin Ki Kim, Soon Moon Jeong,[†] Reiri Kogo, Fumito Araoka,
Ken Ishikawa, and Hideo Takezoe[‡]
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-S8-42 O-okayama,
Meguro-ku, Tokyo 152-8552, Japan

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We report a strong discontinuous orientational transition (anchoring transition) of liquid-crystal molecules with a large transverse dipole moment. A perfluoropolymer was used as an alignment layer and the transition was observed from planar to homeotropic with decreasing temperature in the nematic phase. Conversely a gradual variation in tilt angle from homeotropic to conical was observed in a liquid crystal with a comparatively smaller transverse dipole moment on the same alignment layer. The experimental results clearly demonstrate the competition between a short-range dipolar force and long-range van der Waals force at the interfacial region. Using discontinuous anchoring transition in the sample, we demonstrate a possible bistable device for memory and light-driven display.

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Aligning liquid-crystal molecules to particular directions at solid substrate surfaces is very important from technological as well as fundamental points of view [1]. Generally, two different categories of alignment layers are used in liquid-crystal display devices (LCDs), i.e., parallel (homogeneous or planar) and vertical (homeotropic) alignment of the director (the average molecular direction). Apart from LCDs, depending on the strength of the anchoring energy, liquid crystals can also exhibit a rich variety of behaviors such as memory effects [2], surface melting [3], orientational wetting [4,5], etc. In appropriate surface conditions and interaction energies with liquid-crystal molecules on the surfaces, anchoring transitions, i.e., spontaneous change in the preferred director orientation, may occur. There are some theoretical and experimental reports on various anchoring transitions [6–21]. Among these few reports about the continuous anchoring transition on various alignment layers with longitudinal dipole moment as a function of temperature are known [6,10,15,16]. Recently Faget *et al.* [7] demonstrated conical-planar-anticonical transitions on grafted polystere surface and also theoretically explained including the non-Rapini-Papoular terms in the anchoring energy. A brief and qualitative report on discontinuous anchoring transition in the mixture of liquid crystals with a longitudinal dipole moment [4-cyano-4′-*n*-octylbiphenyl (8CB) and 4-cyano-4′-*n*-octyloxycyanobiphenyl (8OCB)] as a function of temperature was made by Birecki [8]. However no quantitative measurements were reported to reveal the role of permanent dipole moment and different surface forces.

Here we report two important experimental observations. (1) A strong discontinuous anchoring transition of liquid-crystal director from planar to homeotropic with decreasing temperature in a nematic liquid crystal with a large transverse dipole moment on an unrubbed as well as rubbed alignment layer with perfluoropolymers. (2) The same perfluoropolymer surface also gives gradual variation in tilt angle from homeotropic to conical in a liquid crystal with a comparatively smaller transverse dipole moment. Finally we show that the discontinuous anchoring transition can be exploited to fabricate light-driven bistable memory devices.

We used spin-cast perfluoropolymer, poly[perfluoro(4-vinyloxy-1-butene)], known as CYTOP (Asahi Glass Co., Ltd.) as an alignment layer, and two liquid crystals, 4′-butyl-4-heptyl-bicyclohexyl-4-carbonitrile (CCN-47) and methoxybenzilidene butylanline (MBBA). CCN-47 exhibits the following phase transitions: cry 28 °C Sm-A 30.6 °C N 54.4 °C I, and has a large negative dielectric anisotropy ($\Delta\epsilon = -10.0$ at 20 °C). MBBA exhibits the following phase transitions: cry 25 °C N 38 °C I, and has a small negative dielectric anisotropy ($\Delta\epsilon = -0.6$ at 30 °C). The materials were sandwiched by two glass substrates coated with perfluoropolymer (upper right in Fig. 1).

Let us first show that texture changes with decreasing temperature. CCN-47 showed a planar texture at 50 °C as shown in Fig. 1(a). Interestingly the system mostly exhibits $\pm 1/2$ strength wedge disclinations. The scarcity of ± 1 disclinations is sometimes regarded as an evidence of biaxial system [22], but the present medium is definitely uniaxial, as is clear by a complete dark view in the homeotropically aligned state [Fig. 1(c)]. A similar texture was also observed in the nematic phase of a lyotropic liquid crystal [23]. The physical implication is that the director is in the plane as any tilting in such case is not allowed topologically, so that ± 1 disclinations, if they exist, cannot escape from the line defects to point defects. The details of defect dynamics and the correlations will be reported elsewhere. On further cooling the sample temperature below 45 °C the dark region grows abruptly and randomly [Fig. 1(b)] and the whole area becomes dark within a temperature range of ~1° [Fig. 1(c)]. It indicates that the director orientation spontaneously changes from planar to vertical direction (homeotropic alignment).

We measured the transmitted intensity of 545 nm light

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[*] Corresponding author. On leave of absence from School of Physics, University of Hyderabad, Hyderabad–500046, India. sdsp@uohyd.ernet.in.

[†] Present address: Central Technical Research Laboratory, Nippon Oil Corporation, 8 Chidori-cho, Naka-ku, Yokohama 231–0815, Japan.

[‡] Corresponding author: takezoe.h.aa@m.titech.ac.jp.

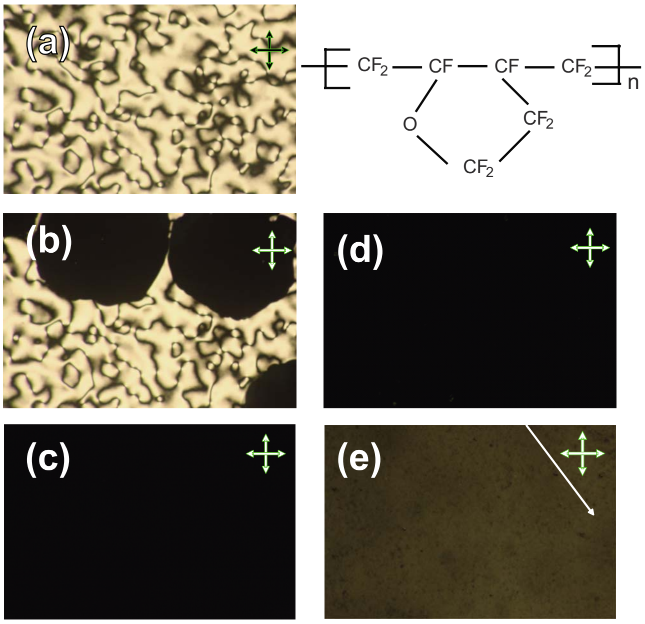

FIG. 1. (Color online) Photomicrographs of the textures showing anchoring transitions in CNN-47 and MBBA under crossed polarizers (white crossed arrows): (a) CCN-47 at 50 °C; (b) CCN-47 during the first-order anchoring transition; (c) CCN-47 at 40 °C; (d) MBBA at 35 °C; (e) MBBA at 25 °C with flow direction (white arrow) making 45° with respect to the polarizer. The chemical structure of perfluoropolymer CYTOP is also shown at the upper right.

through a rubbed cell. Rubbing was made to have a uniform alignment in the planar state. The variation in the transmitted intensity is shown as a function of temperature in Fig. 2(a). The intensity in the nematic phase jumps at 45 °C and 50 °C on cooling and heating, respectively, with a large hysteresis of 5 °C. We also calculated the birefringence from the transmitted intensity using the formula, $I(T) = I_0 \sin^2 \frac{\pi \Delta n\, d}{\lambda}$, where Δn is the birefringence, d is the cell thickness, and λ is the wavelength of the light used. We show the variation in the birefringence as a function of temperature in both heating and cooling cycles in Fig. 2(b). It is noted that the birefringence jumps from 0.022 to 0 on cooling and from 0 to 0.019 on heating. The birefringence of the sample was also measured as a function of temperature in an independent cell treated with a homogeneous alignment agent (AL-1254, Nissan Chemicals). We confirmed that no anchoring transition was observed on this alignment layer. The data agree well with the data measured on cells treated with the perfluoropolymer. It may be pointed out that birefringence measured on perfluoropolymer is slightly less than the values reported on other polyimides [24,25] which are measured at 633 nm light. The lower value of birefringence measured on both perfluoropolymer and AL-1254 indicates that in the present cell (CCN-47), a sufficient pretilt angle of the director is generated due to rubbing the plates.

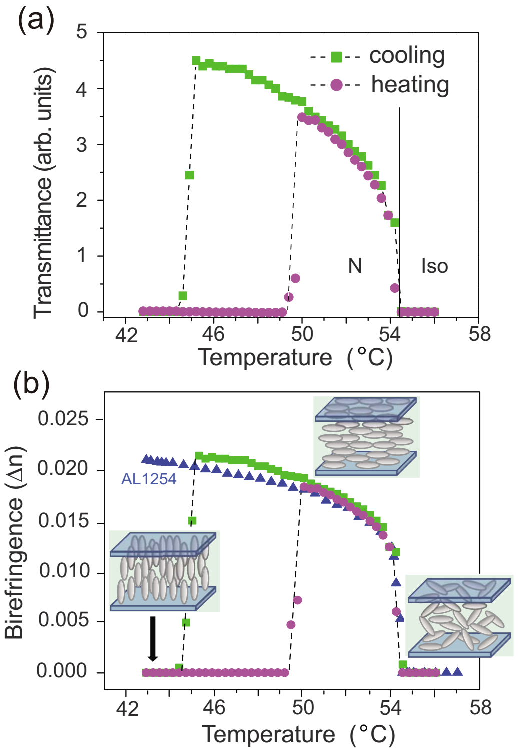

FIG. 2. (Color online) (a) Transmitted light intensity (in arbitrary units) of an orientated sample of CCN-47 between crossed polarizers as a function of temperature. (b) Calculated birefringence obtained from (a). Data for cooling and heating processes are shown by squares and circles, respectively. A large hysteresis in temperature is observed. Data corresponding to triangles are measured using the commercial homogeneous alignment agent AL-1254, which shows a pretilt from the vertical direction and no anchoring transition.

In contrast to CCN-47, MBBA exhibits a continuous homeotropic to tilted transition. A typical homeotropic texture of compound MBBA at 35 °C under a polarizing microscope is shown in Fig. 1(d). While cooling, the transmitted intensity increases gradually without showing a birefringent color [Fig. 1(e)]. The transmitted intensity gradually increases/decreases with decreasing/increasing temperature in the nematic phase range as shown in Fig. 3(a). Clearly no hysteresis was observed. The increase in the transmittance indicates that the molecules are tilted with respect to the vertical direction. The transmittance varies by rotating the cell, showing the maximum when the flow direction in the sample introduction makes 45° with respect to the polarizer direction [Fig. 1(e)], indicating that the molecules tilt along the flow direction. In order to estimate the tilt angle we calculated the effective refractive index (n_{eff}) as a function of temperature by using the formula, $I(T) = \sin^2 \pi(n_{\mathrm{eff}} - n_{\mathrm{o}})d/\lambda$. The value of n_{eff} is used to calculate the tilt angle as a function of temperature by using the equation $\theta = \cos^{-1}\sqrt{(n_{\mathrm{e}}^2 - n_{\mathrm{eff}}^2)n_{\mathrm{o}}^2/(n_{\mathrm{e}}^2 - n_{\mathrm{o}}^2)n_{\mathrm{eff}}^2}$, where n_{o} and n_{e} are the ordinary and extraordinary refractive indices, respectively. The variation in the tilt angle as a function of temperature is shown in Fig. 3(b). The isotropic to homeotropic nematic transition takes place at around 38 °C. In the homeotropic phase the director has a small pretilt of ~1.5° from the vertical direction [Fig. 3(b)]. We found that the molecules gradually tilt from 88.5° at the nematic-isotropic transition point to 82.5° at room temperature.

Parsons [26] theoretically predicted a continuous transition from homeotropic to tilted which could perhaps explain

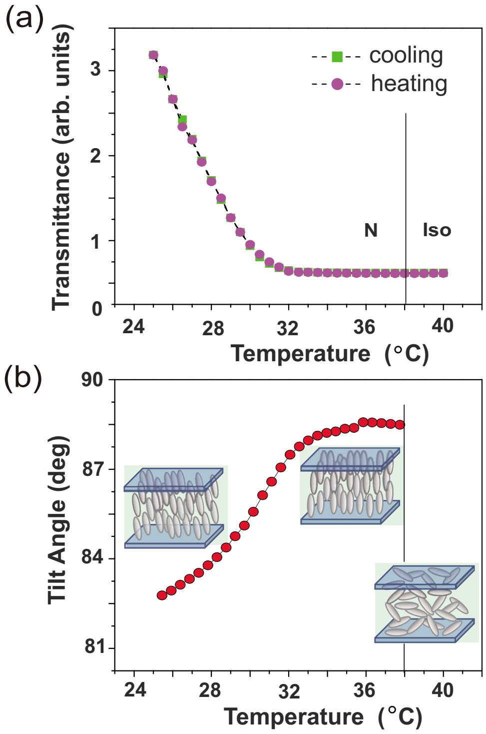

FIG. 3. (Color online) (a) Transmitted light intensity of an orientated sample of MBBA between crossed polarizers as a function of temperature. Data for cooling and heating processes are shown by squares and circles, respectively. No hysteresis is seen. (b) Calculated tilt angle as a function of temperature obtained from (a).

the transition in the case of MBBA in the present case. But this theory cannot predict the discontinuous transition as observed in the case of CCN-47. Kimura [9] studied the orientation of nonpolar rodlike molecules at hard flat walls using the mean-field approximation. He predicted a discontinuous planar-homeotropic transition and a continuous planar-tilt-homeotropic transition with decreasing temperature by taking into account isotropic van der Waals interaction (dispersion force) and steric interaction between liquid-crystal molecules and surface. In addition to that polar contribution must be included, since our two molecular systems with large and small transverse dipoles gave opposite results in the present study. The steric interaction and the dispersion force give planar and homeotropic orientations, respectively [9,27,28]. A short-range dipolar interaction tends to align the dipole moments perpendicular to the surface, leading to different molecular orientations between molecules with a transverse dipole (CCN-47) and a longitudinal one (cyanobiphenyl). A long-range electrostatic interaction between the polar groups of liquid-crystal molecules and surface also gives a different orientation for these molecular systems, i.e., surface tends to align the more electronically polarizable direction of liquid crystal parallel to the plane of the substrate. Therefore, liquid-crystal molecules with transverse and longitudinal dipoles align perpendicular and parallel to the surface, respectively [28]. Thus these four contributions have different orientational preference and show different temperature dependence. All of these factors could be responsible for anchoring transition in liquid crystals composed of polar molecules.

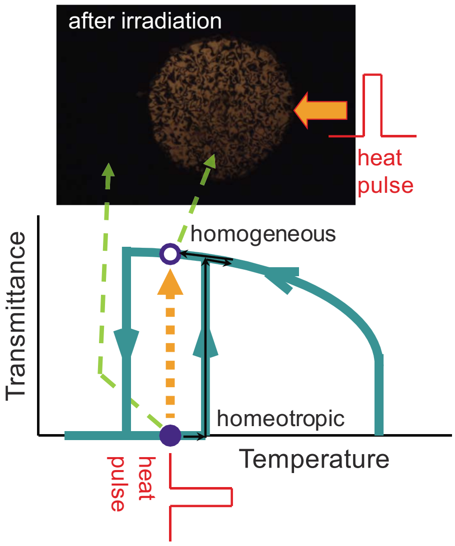

FIG. 4. (Color online) Principle of a bistable switching device using discontinuous anchoring transition and an actual image showing performance. On laser light irradiation to a cell at 49 °C, a homeotropic state (closed circles) switches to a homogeneous state (open circles) via thin black arrows. In the middle of a microscope image, where light irradiation is made, schlieren texture is observed.

In the present case both the liquid crystals exhibit negative dielectric anisotropy and CCN-47 has a strong dipole moment of about 3.1 D [25] along the transverse direction of the long molecular axis. Both the strong dipolar interaction and the steric interaction prefer a parallel (homogeneous) alignment in CCN-47 just below the nematic-isotropic transition. As the temperature is lowered the electrostatic interaction becomes comparatively stronger due to the increased polarizability anisotropy and the more polarizable direction (short axes of the molecules) prefers to align parallel to those of the large polarizable direction of the alignment layer. As a result the molecules are oriented vertically with respect to the surface. In the case of MBBA, the dipolar interaction is weaker compared to the van der Waals interaction due to the small values of dipole moment, and a vertical alignment is preferred just below the nematic-isotropic transition. Small continuous change to a tilted orientation may come from the temperature dependence of these interaction forces. Thus the relative strength of the four forces may also determine the nature of the transition. We also observed small continuous transition in penthylcyanobiphenyl (5CB) from homeotropic to planar with decreasing temperature. More detailed theoretical calculation accounting the physiochemical nature of the interface is needed to understand the phenomenon completely. It may be pointed out that a stable homeotropic alignment was also observed in smectic liquid crystals without any anchoring transition. The details will be reported elsewhere.

Finally we propose and demonstrate a possible device utilizing the bistability of homogeneous and homeotropic orientations in the CYTOP/CCN-47 system. The principle is shown in Fig. 4. We realized homeotropic orientation (closed circle) in the bistable temperature region at 49 °C, which shows completely black under crossed polarizers. Then we exposed the center of the cell to an Ar-ion laser light (488 nm) beam to increase the temperature above 50 °C. Photoinduced transition from homeotropic to homogeneous orientations occurred, and the change was easily recognized under an optical microscope, as shown in Fig. 4. We confirmed that this pattern remained unchanged at least for 1 day. We also found that the irradiation intensity can be brought down to a few milliwatts to write a spot if we doped CCN-47 with a small amount (0.5 wt) of 4-(dicyanomethylene)-2-methyl-6(4-dimethylaminostryl)-4H-pyran (DCM). Further studies for fabricating memory and light-driven display devices are under way.

In conclusion, we showed two different anchoring behaviors on the same alignment layer depending on the strength of dielectric anisotropy, i.e., discontinuous planar to homeotropic transition and gradually homeotropic to tilting state. This is a report of strong discontinuous anchoring transition on unrubbed and rubbed cells as well as opposite types of transition in a single surface. These results can be qualitatively explained on the basis of four temperature-dependent competing forces at the liquid-crystal/solid substrate interface. The observation of discontinuous anchoring transition in rubbed cell is unique in the sense that it provides an interesting system for application. The discontinuous first-order anchoring transition with large hysteresis facilitates bistable homogeneous and homeotropic orientations, which can be controlled by heat or light pulses, providing us with memory devices and light-driven display devices. Preliminary experiment has been made successfully. The details will be reported elsewhere. Further experimental investigation on the effect of electric field on the anchoring transitions and the measurement of pretilt angle that arise due to rubbing are under way.

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