

Perfluoropolymer Surface for Shock-Free Homeotropic Alignment of Smectic Liquid Crystals

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In order to use liquid crystals (LCs) in practical applications such as liquid crystal displays (LCDs) and photonic optical devices, a uniform director orientation of LC molecules is essential. In particular, vertical alignment (VA) of nematic LC molecules has been studied and applied in VA-mode LCDs, owing to their superior properties such as wide viewing angle and high contrast ratio compared to the conventional twisted-nematic display. Recently, an inorganic silicon oxide (SiO_x) layer has been intensely studied as a VA layer because of its robust properties and good performance even under harsh conditions, such as intense light and high temperature, that cause deterioration of organic materials.^[1–5] However, a vacuum process is not appropriate for large-area processing. Hence side-chain polyimide-coated surfaces are used for VA-LCDs. Here we demonstrate the advantages of an amorphous perfluoropolymer as a very stable VA layer for smectic LCs compared to conventional alignment layers.

Typically, low surface-energy substrates are preferred to obtain homeotropic alignment of LC materials because the minimized energy of the system is obtained when the LC molecules are in contact with each other rather than with the surface. Usually the homeotropic alignment of LCs is realized by the hydrophobic surface if there is no preferential orientation or surface roughness.^[6,7] One way to achieve such alignment of LCs is to adsorb a surfactant monolayer on the surface to render it hydrophobic.^[8,9] Geometrical factors can also be responsible; for example, LC molecules align parallel to the flexible long chains of a surfactant attached to substrate surfaces perpendicularly.^[10] However, the surfactant alignment is not stable because the small molecules of the surfactants gradually dissolve in the LCs. Hence side-chain polymers, in particular polyimides, are used in

practice, as mentioned above. It is well known that fluorine is effective for lowering the surface free energy chemically because fluorine has a small atomic radius and the largest electronegativity among the atoms, so that it forms a stable covalent bond with carbon.^[11] Various fluorine polymers, in particular polytetrafluoroethylene (PTFE), have been developed in many fields, because of their ultimate resistance to hostile chemical environments and high service temperatures owing to the high bonding energy of C–F (485 kJ mol^{-1}) and C–C (360 kJ mol^{-1}) bonds.^[12] However, PTFE is insoluble, which makes vacuum deposition indispensable.

The amorphous perfluoropolymer poly[perfluoro(4-vinyl-oxy-l-butene)] (PPFVB, also known under the commercial name Cytop) has been used for antireflective coatings and optical fibers because of its low refractive index of 1.34 and high transmittance over a wide wavelength range (200 nm to $2 \mu\text{m}$).^[13,14] It also has high solubility in perfluorinated solvents and is highly resistant to chemical and thermal stimuli. These properties make deposition

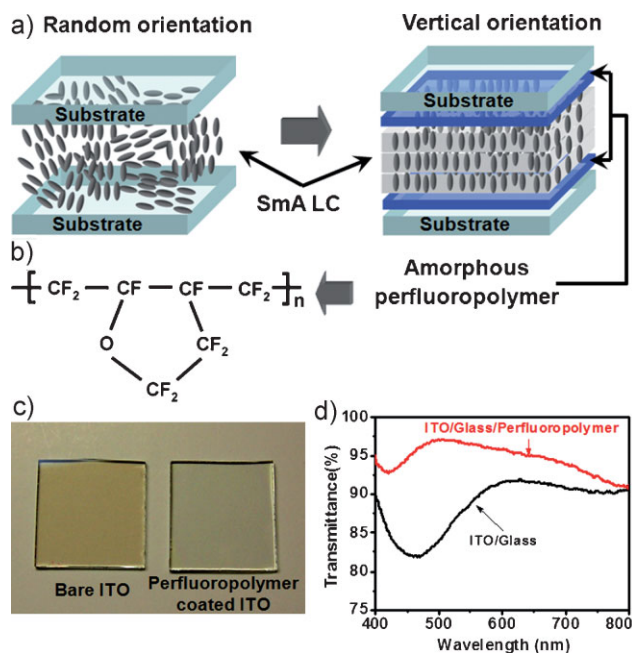


Figure 1. a) Schematic illustration of random (left) and vertical (right) orientation of smectic LCs. b) Molecular structure of the alignment layer, PPFVB, used in this work. Photograph (c) and transmittance spectra (d) of bare and perfluoropolymer-coated ITO glass.

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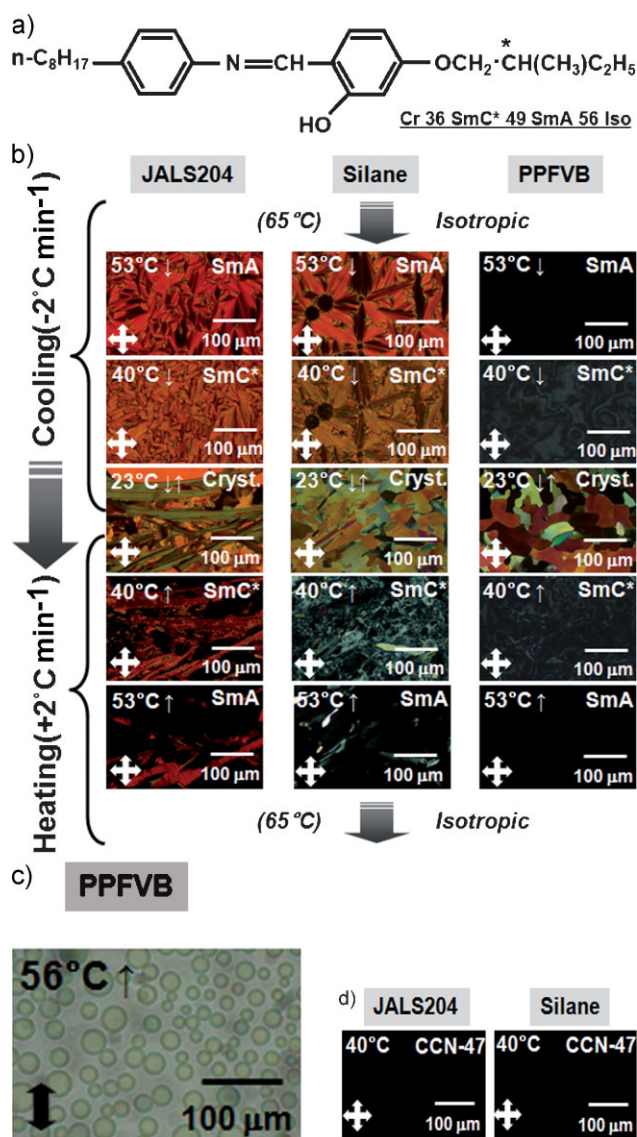


Figure 2. a) Molecular structure and the phase sequence of the smectic LC (MBRA-8) used. b) Photomicrographs under crossed polarizers of MBRA-8 during cooling and heating processes in JALS204-, silane-, and PPFVB-coated cells. Note that we manually increased the brightness of the SmC* photos to visualize Schlieren textures. c) Photomicrograph of the phase transition from SmA to the isotropic state in a PPFVB-coated cell without polarizers. d) Photomicrographs of a vertically aligned nematic LC (CCN-47) in JALS204- and silane-coated cells at 40 °C.

of indium tin oxide (ITO) and nanoimprint lithography (NIL) possible for photonic application in organic light-emitting diodes (OLEDs),^[15] lasing,^[16] and biological applications.^[17] In this Communication we propose and demonstrate a new application of PPFVB as a VA layer for smectic LCs.

Smectic LCs have a one-dimensional (1D) positional order, namely a layer structure, although they are liquid-like within each layer. Generally, the methods for homeotropic alignment of nematic LCs can be applied for smectic phases. Therefore, normally better alignment can be achieved in SmA LCs if materials have the phase transition sequence Iso–N–SmA than for

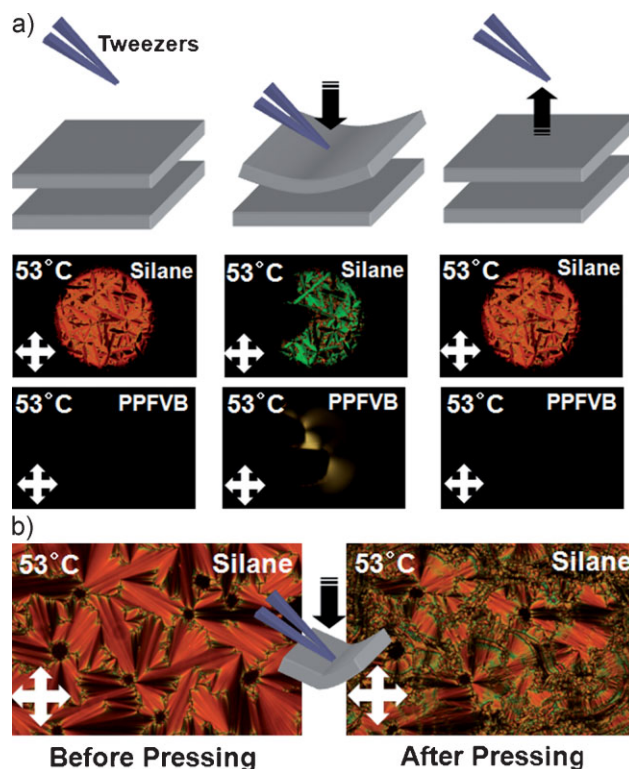


Figure 3. a) Mechanical pressing test by tweezers. Spontaneous self-recovery to vertically aligned SmA LCs is realized in a PPFVB-coated cell. b) Magnified optical images before (left) and after (right) pressing for a silane-coated cell. Cracking is observed and there is no recovery.

materials exhibiting the direct Iso–SmA transition.^[18] However, alignment of smectic LC molecules is still very difficult and is easily upset by mechanical shock, particularly in homogeneous (planar) alignment^[19] because of the 1D periodic structure and limited fluidity. So far, vertically aligned smectic LCs have not been applied practically, although recently a display application using vertically aligned smectic LCs such as bent-core SmAP_R LCs,^[20,21] and ferroelectric SmC* LCs has been proposed.^[22,23] However, it would be useful to have a good alignment layer for vertically aligned smectic LCs for future applications.

Figure 1a shows a schematic illustration of random orientation and VA of SmA LCs. We employed a flat amorphous PPFVB layer with low surface energy to achieve uniform VA. The molecular structure of PPFVB is depicted in Figure 1b. PPFVB forms a highly transparent film on an ITO-coated glass substrate owing to its antireflection characteristic, as shown in Figures 1c and d.

To examine the superiority of the PPFVB layer over other alignment layers for aligning smectic LCs, we prepared three kinds of substrates treated with a commercial homeotropic alignment layer (JALS204, Japan Synthetic Rubber), a silane coupling agent (AY43-021, Dow Corning Toray), or PPFVB, and observed the textures using a polarizing optical microscope (POM). We chose a smectic LC material, 4-*O*-(2-methyl)-butylresorcyldene-4'-octylaniline (MBRA-8), shown in Figure 2a. The material exhibits the phase transition sequence Isotropic (56 °C) SmA (49 °C) SmC* (36 °C) Crystal and was introduced into empty cells at a temperature above the isotropic phase transition (ca. 65 °C).

Figure 2b shows POM images of MBRA-8 sandwiched by JALS204-, silane-, and PPFVB-coated substrates during cooling and heating. Broken fan-shaped texture was observed for JALS204- and silane-coated cells. By contrast, we obtained very good alignment in SmA if we used PPFVB-coated substrates. Good alignment was retained even in SmC*, and then a typical pattern of birefringent colors in random domains emerged in the crystal phase. Quite surprisingly, the smectic layer seems to realign parallel to the PPFVB surface in SmC* and finally perfect VA results in SmA. Such recovery is not possible using normal homeotropic alignment agents, as shown by the textures in JALS204- and silane-coated cells. To confirm that this dark image represents vertically aligned SmA at 53 °C, and not the isotropic phase, a texture of a PPFVB-coated cell was taken at 56 °C without polarizers during the heating process. The phase transition from SmA to the isotropic phase was clearly observed, as shown in Figure 2c, indicating good VA in the SmA phase. It should be noted that JALS204 and silane act as good alignment layers for nematic LCs, as exemplified by Figure 2d for the nematic LC 4'-*trans*-butyl-4-cyano-4-*trans*-heptyl-1,1'-bicyclohexane (CCN-47, Merck) with negative dielectric anisotropy and the following phase sequence: Isotropic (57.3 °C) N (28.2 °C) SmA (25.6 °C) Crystal; both surfaces serve as good homeotropic alignment layers.

Figure 3 shows how effective the PPFVB layer is as a homeotropic alignment layer for the SmA phase of MBRA-8. During POM observation, we used tweezers to exert mechanical

pressure on silane- and PPFVB-coated glass samples filled with MBRA-8 to clarify the difference. While being pressed, the silane-coated cell exhibited birefringence color because bending of the upper glass substrate induced distortion of the smectic LC layers. Bending-induced birefringence was also observed in the PPFVB-coated cell. However, after the pressure had been released, the layer deformation rapidly recovered to the original vertically aligned state. As shown in the magnified picture in Figure 3b, however, the smectic layer of MBRA-8 in the silane-coated cell exhibited cracks after being pressed with tweezers and never returned to its original state. This is the natural behavior arising because of the limited fluidity in SmA LC cells with a conventional surface alignment layer. These results can be explained by the different interfacial surface energies between LCs and alignment layers. Owing to the low surface energy of PPFVB, the interaction between the LC and the alignment layer decreases and intermolecular interaction among LC molecules increases. Hence, vertical orientation of LC is much more favorable on an alignment layer with low surface energy.^[6,7]

Now we need to explain this phenomenon in more detail because the alignment of LC is induced by complex physicochemical interactions between the LC molecules and the aligned films. To explain the orientational recovery to VA, several types of interactions must be considered, including π - π electron coupling, geometric effect, dipole-dipole interaction, and van der Waals interaction. We assume that the dipole-dipole interaction can be neglected because the polarity of the PPFVB

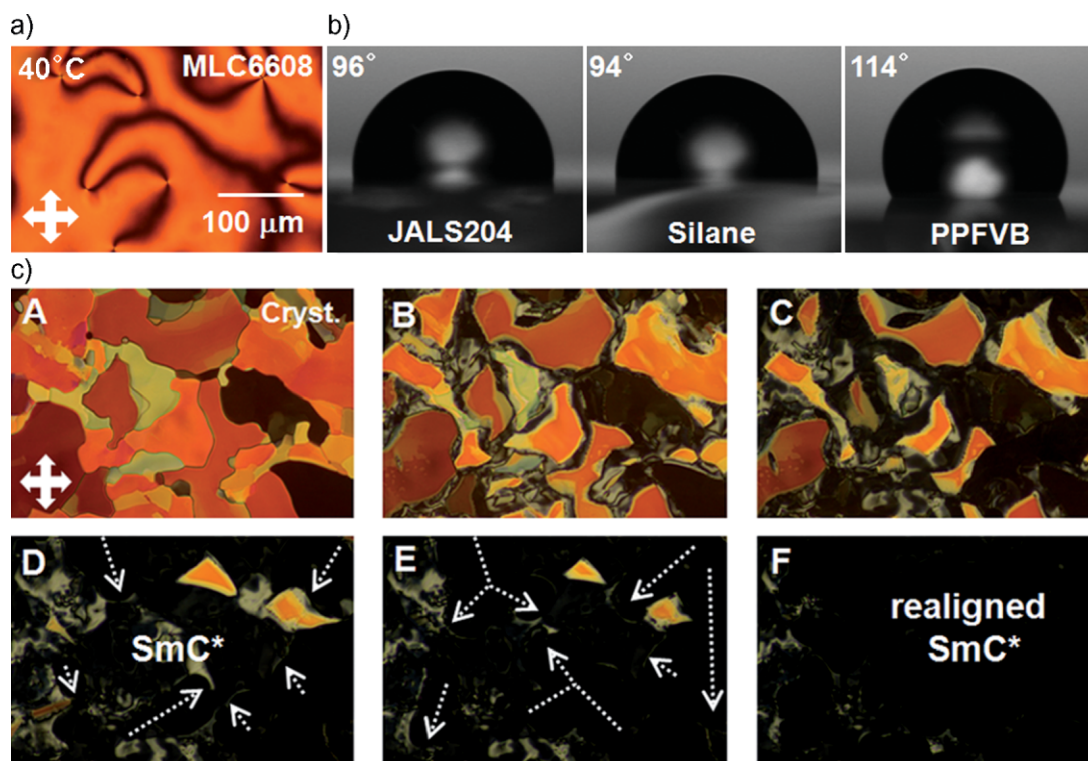


Figure 4. a) POM image of MLC6608 at 40 °C in a PPFVB-coated cell. b) Contact angles on JALS204-, silane-, and PPFVB-coated glass substrates. c) Progress of the phase transition with time from crystal to SmC* phase. A–C) The transition starts from the grain boundary region. D–F) Realigned SmC* regions are also formed (indicated by dotted arrows) and increase in volume over the whole sample area. Note that (D–F) were taken under an overexposed condition compared with (A–C) to visualize Schlieren texture.

surface is known to be very low. Low polar surface energy in fluorinated amorphous carbon supports our hypothesis.^[24] We also neglect the effects of π - π electron coupling and the geometric effect because the spin-coated PPFVB layer was not rubbed and it has a flat surface with high lubricity. The van der Waals interaction is an attractive potential given by $V = -\lambda/r^6$ between molecules and by $V = -\lambda/r^3$ between a surface and a molecule,^[25,26] where r is the distance between two objects and λ is a constant depending on the properties of the objects. The value of λ is proportional to the product of the polarizabilities of the alignment layer and the LC medium.^[3] As the polarizability is derived from its dielectric constants, $(\epsilon(\omega) - 1)/(\epsilon(\omega) + 2)$,^[27] PPFVB has very low polarizability because of its low dielectric constants ($\epsilon = 2.1$). Hence, van der Waals interaction can also be neglected.

Consequently, the smectic LC alignment on the PPFVB layer cannot be explained by the competition of various interactions between the alignment layer and LC molecules. Of course there might be a preferred interaction, but this is insufficient to explain homeotropic alignment of smectic LCs with limited fluidity because the preferred force must be very strong. Recently, we found that CCN-47 shows a discontinuous anchoring transition from homogeneous to homeotropic with decreasing temperature; some nematic LCs are homeotropically aligned on PPFVB, and others are not.^[28] To examine the alignment of nematic LCs on PPFVB, we also made POM observation of MLC6608 (Merck, Nematic (90 °C) Isotropic, with negative dielectric anisotropy) sandwiched between PPFVB-coated glass substrates. As shown in Figure 4a, Schlieren texture was observed, indicating homogeneous alignment. However, PPFVB shows stronger hydrophobicity (contact angle 114°) than JALS204 (96°) or silane coupling agent (94°), as shown in Figure 4b. These results indicate that homeotropic alignment of nematic LCs cannot be obtained simply by low surface energy of the alignment layer. On the other hand, smectic LCs strongly favor homeotropic alignment, as mentioned above. Hence, the strong ability of PPFVB to cause smectic LCs to align homeotropically must be explained in light of the difference between smectic and nematic LCs; namely, different fluidity due to the existence or otherwise of a layer structure. We simply employ a large driving force arising from the different interfacial surface energies between the LCs and alignment layers. The layered smectic plane is favorable to minimize contact area with PPFVB owing to its low surface energy. It should be noted, however, that this can be different for nematic LCs, because the nematic phase usually has enough fluidity that each molecule can interact with the alignment layer and LC molecules.

From this hypothesis the question arises as to how the crystal phase is transformed to the SmC* phase with minimized free energy even though crystals have almost no fluidity. Figure 4c shows how the crystal transforms to SmC* with time. The transition starts from the grain boundary region and the area grows (A–C) because the grain boundaries are relatively unstable. However, realigned regions (indicated by dotted arrows) also appear and propagate to other grain regions to make SmC* realigned over the whole sample area (D–F). (Note that D–F of Figure 4c were taken under an overexposure condition compared with A–C of Figure 4c to visualize the textures.) This means that LC molecules in layered planes reorient gradually with time to

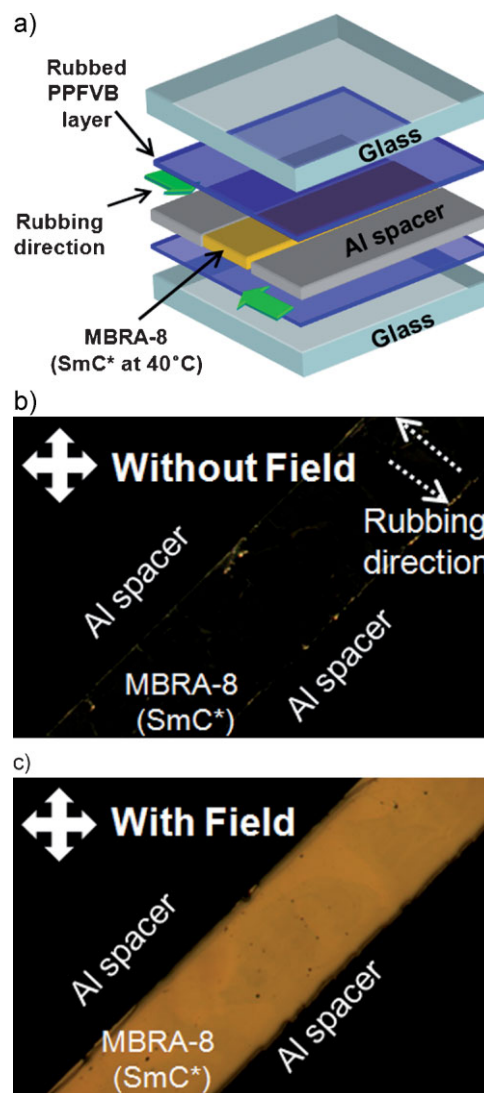


Figure 5. a) Schematic illustration of a PPFVB-coated switching cell filled with MBRA-8. Note that electric field was applied in the in-plane rubbing direction. b,c) POM images of MBRA-8 at 40 °C in the PPFVB-coated cell without (b) and with (c) electric field.

decrease interfacial free energy with the layered structure maintained. This results in perfect VA in the SmA phase over the whole sample area.

Finally, we introduce a possible SmC* display device using PPFVB as an alignment layer. Figure 5a shows a sample structure filled with MBRA-8 sandwiched between PPFVB-coated glass substrates. After antiparallel rubbing, two pieces of aluminum foil were used as spacers to make a 13 μm thick cell as well as electrodes with a 200 μm gap. The SmC* LC molecules aligned vertically and formed a helical structure with the helix axis along the surface normal, so that an optically isotropic view was observed when no voltage was applied, as shown in Figure 5b. When a voltage was applied along the rubbing direction, polar switching occurred to achieve uniform c -director orientation perpendicular to the electric field. A uniform bright view was obtained, since the crossed polarizers were 45° to the field direction, as shown in Figure 5c. This device, which uses surface

alignment by PPFVB, has advantages over devices using other surface alignment layers, namely, stable VA and self-recovery from orientational damage caused by mechanical shock.

In summary, we have demonstrated VA of a SmA LC (MBRA-8) with the direct Iso–SmA transition by employing an amorphous perfluoropolymer (PPFVB) as an alignment layer. The self-recovery to VA of SmA LCs was observed from deformed layer orientations caused by crystallization or external pressure. The high alignment ability for LC materials with Iso–SmA phase transition and the spontaneous recovery effect are remarkable if we consider the limited fluidity in the smectic phase. We believed that these results have their origin in the strongly hydrophobic surface of PPFVB, which has low polarity and low polarizability.

Experimental

The PPFVB used in our experiments is a mixture of PPFVB solution (CTX-809A, purchased from Asahi Glass Co.) and fluorinated solvent (CT-Solv.180). The solution CTX-809A contained 9 wt% PPFVB and was diluted with the solvent to make a 3 wt% solution. The PPFVB alignment layers were fabricated by spin-coating the solution onto the glass substrate and were cured for 30 min at a temperature of 100 °C in an oven. The thickness of PPFVB film was ca. 95 nm, as determined by a Dektak³ST (Veeco) surface profiler. The sample cell was made of PPFVB-coated glass substrates and was supported by a spacer (ca. 5 μ m). The LCs were introduced into an empty cell using capillary action in the isotropic phase. The texture was observed under a polarizing microscope (Nikon, Optiphot-Pol) equipped with a temperature-controlled Mettler-Toledo FP90 hot stage. The cooling and heating speed was ± 2 °C min⁻¹. For voltage-dependent POM images of the switching cell, a rectangular voltage (2 kV, $f = 3$ kHz) was applied.

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