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Electrically surface-driven switchable wettability of liquid crystal/polymer composite film

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This study demonstrates the electrical control of the surface wettability of liquid crystal and polymer composite film. The application of external voltages significantly affects the surface wettability of the film. This study uses atomic force microscopy to quantitatively characterize the fundamental mechanism responsible for the structurally driven changes in surface properties at various applied voltages. The surface wettability transitions of the film are electrically driven, as shown by reorganized liquid crystal molecules. Measurements of the voltage-dependent surface wettability of the composite film suggest approaches to supporting control applications of future electro-optical nanotechnology devices. © 2010 American Institute of Physics. [doi:10.1063/1.3378688]

Tailoring the delicate interfacial wettability properties of complex anisotropic liquid and polymer soft materials is an important task in many optical devices, including liquid crystal displays, electrically tunable privacy windows using polymer-dispersed liquid crystals, and tunable focus liquid crystal lenses.¹⁻³ Recently-developed liquid crystal and polymer composite film (LCPCF) not only has the property of electrically tunable wettability but is also capable of aligning LC directors.⁴⁻⁷ According to Ref. 6, the increase in the transmission of the LCPCF when external voltages are applied to the film can be indicated that in-plane electric fields can switch the LC directors anchored between polymer grains. Therefore, the orientation and conformation of molecular units at the polymer surface is the fundamental mechanism responsible for the structurally driven changes in surface properties at various applied voltages. Reorganizing the LC molecules among the polymer grains in LCPCFs determines the interfacial properties and is responsible for the electrically surface-driven switchable wettability of these composite films. Under a spatial wetting gradient, the switchable surfaces of LCPCFs are highly promising for use in future microfluidic devices, liquid lenses, windshields, and polarizer-free displays. However, there is a lack of experimental research on the orientation of LC molecules at the LCPCF surface to support their potential applications in electro-optical nanotechnology devices.

A number of techniques have been used, with varying degrees of success, to determine how the reorientation of molecules affects the composite film interfacial surface. For example, researches have used ellipsometry and infrared spectroscopy to investigate rubbing-induced anisotropy on the surface of the film.^{8,9} Near-edge x-ray absorption spectroscopy reveals information on the orientational order parameter of a polymer surface.¹⁰ Further, sum-frequency generation vibration spectroscopy can demonstrate the chain orientation of a composite film surface.¹¹ However, these approaches are not very effective at locally characterizing the interfacial wettability properties of complex soft materials in real space on a nanoscale. Since scanning probe microscopy

is a highly effective means of locally characterizing nanoscale materials,¹² this study reports the application of the atomic force microscopy (AFM) technique not only to elucidate the liquid surface morphology of the film but also identify how the inherent physicochemical surface adhesion properties vary at various external voltages, and the physical mechanisms that govern the electrically switchable wettability of the LCPCFs.

LCPCFs were prepared by mixing a nematic LC mixture E7 (Merck) and a liquid crystalline monomer [4-(3-Acryloyloxypropoxy)-benzoic acid 2-methyl-1,4-phenylene ester, Merck] at various weight ratios. The extent to which the concentration of LC affected the surface property of the LCPCF was then investigated using E7-monomer blends with E7: monomer weight ratios of 69%. The LC/monomer mixture showed a nematic phase at room temperature. When the LC concentration exceeded 69%, the mixture of E7 and monomer at 70 °C was in the near phase transition state, thus limiting its applications.³

Figure 1(a) shows the LC molecule structures, while Figs. 1(b)–1(d) displays the device structures and the operating principles of the proposed electrically switchable wettability system. Figure 1(b) shows that the bottom electrodes of patterned indium tin oxide (ITO) stripes have a zigzaglike

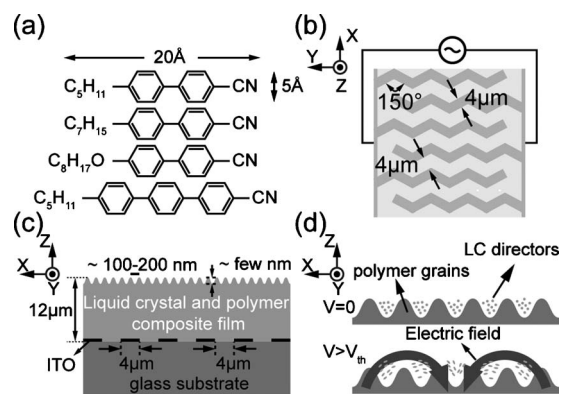


FIG. 1. Schematic illustration of (a) the LC molecules, (b) electrode design, and the surface of the LC/polymer composite film in (c) voltage-off, and (d) voltage-on states.

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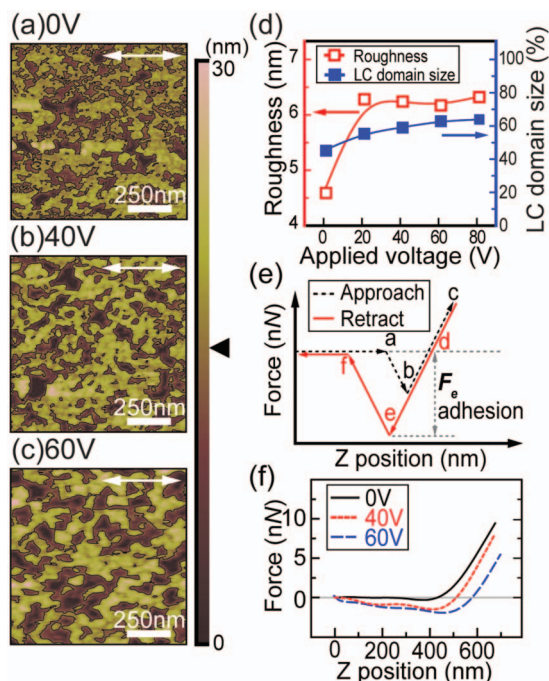


FIG. 2. (Color) AFM topography images of 69 wt % LC concentrations at different external voltages of (a) 0 V, (b) 40 V, and (c) 60 V. White arrows inside the figures indicate the rubbing direction of the PI layer. (d) Statistical results concerning roughness and total LC domain size of the film surfaces at different external voltages. (e) Idealized F - D curve of the composite film. The black curve represents the approach, while the red curve represents the departure. (f) The corresponding F - D curves on the adhesion property measurements for 69 wt % LC concentration at 0, 40, and 60 V.

pattern along the y -axis, parallel to the rubbing direction of the polyimide (PI) layer. This study set the distance between the working electrode and counter electrode at $4.0 \pm 0.5 \mu\text{m}$. Additionally, the zigzag ITO electrode strips have a corner angle of 150° .⁴

The LCPCF surfaces were probed by trapping mode AFM (Dimension 3100, Digital Instruments) at room temperature in air. Silicon nitride tips (Nanosensors) with a resonant frequency of 260 kHz were used. The cantilevers were excited just below their resonant frequency. Additionally, to determine the dependence of liquid surface adhesion on the external ac voltage ($f=1$ kHz), each force (F) curve was measured as a function of the displacement of the cantilever (D) at the position above the electrode, and recorded using a constant-diameter AFM probe tip in a complete approaching and separating cycle. Notably, the force-distance (F - D curve) relationship or the surface wettability is dependent on the probing position under an applied voltage. Generally, the transition of the surface wettability in the film is principally dependent on the location of the LC domain but is not significantly influenced by the location of the polymer region. In this study, the surface adhesion of the film is measured only at the positions above the electrode.

Figure 2 shows AFM topographical images of the experiments for external applied voltage-dependent investigations. To prevent electric fields from disturbing the piezo drive, we used external applied voltages of less than 80 V for the device. The surface morphologies possessing topography nanometer-to-micrometer-scale were quantified at various voltages for 69 wt % LC concentrations by simply analyzing the structural configurations of LCPCFs through the root-

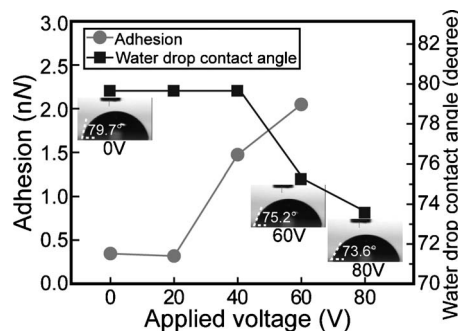


FIG. 3. Variations of analyzed average adhesion force (gray circles) and water drop contact angle (black squares) for the composite film as a function of the external voltages at 69 wt % LC concentration.

mean-square (rms) roughness of the film surfaces and the variance of the total area of LC domain size (%) at various applied voltages. The rms roughness of the LCPCF surface was 4.5 nm without external voltages applied. However, under an external applied voltage, the surface roughness and the total LC domain size (%) of the LCPCF surface does not show dramatic variance even when applying the external voltage is 60 V [Fig. 2(d)]. These experimental results indicate that a significant electrical reorganization change of the LCs anchored between polymer grains instead of the LC microstructure pattern on the surface. The orientation changes in the LCs anchored between polymer grains at different electric fields might serve as the fundamental mechanism of structurally-driven changes in surface properties at various applied voltages.

In addition to analyzing the results of molecular rearrangement in the nanometer scale, this study also attempts to realize the electrically surface-driven switchable wettability of the LCPCFs. Quantitative analyses of the F - D curve during a complete approach and separate cycle [Fig. 2(e)] suggest various schemes for determining the equilibrium state in the composite film with various external voltages.¹³ The retractive force F_e in the departure process can be physically defined as the value of adhesiveness and the variance of the LCPCF surface can be observed at various voltages executed clearly. Figure 2(f) magnifies portions of a complete cycle in the departure process at various voltages.

Due to the chemical heterogeneity of the surface of the composite films, the average adhesiveness as a function of applied voltage (V) on the LCPCF can be expressed as

$$F_e(V) = f_{lc} \cdot F_{e,lc}(V) + f_p \cdot F_{e,p}(V), \quad (1)$$

where f_{lc} and f_p are the fractions of LC and polymer grains for the measured average adhesiveness $F_{e,lc}$ and $F_{e,p}$ in several locations at a specific external voltage applied, respectively. Figure 3 summarizes those results showing that the adhesion force increases noticeably as the increases at applied external voltages for 69 wt % LC concentration. Since a significant change in the surface adhesion was locally recorded from the force-distance (F - D) relationship at a specific LC domain using a probe with a ~ 10 nm apical radius, the variance of the local wettability measurement confirmed again from the LC reorientation. In addition, the quantitative analysis of LC orientation at various voltages can be deduced from the F - D curve.¹⁴

Based on the LC molecular configuration in the work [refer to Fig. 1(a)] the bond polarity of CN terminal groups

is larger than that of the C_nH_{2n+1} and the benzene groups. Therefore, the CN-terminal groups were identified as possessing high adhesion, which in turn produces a high degree of wettability. Therefore, we suggest that the application of a voltage to the composite films causes a transition in the orientation of the LC molecules, rotating the long axis of the LC. This implies the CN-terminal groups rotate out of the plane of the surface significantly, subsequently yielding dramatic adhesion characteristics of the film. Based on the adhesiveness function, the underlying mechanism for electrically surface-driven switchable wettability of the LCPCFs can be developed. In addition, the switchable wettability of the LCPCFs under in-plane electric fields was also correlated with contact angle measurements using a $\sim 3 \mu\text{l}$ drop of de-ionized water deposited on the film surfaces.^{6,15} The wettability experiments also provides evidence that the electric fields preferentially align the LC molecules with the CN-terminal groups up instead of down. In Fig. 3, a larger adhesive implies a lower contact angle of a water droplet on the surface. However, since a $\sim 3 \mu\text{l}$ water droplet should cover over several electrode stripes, the primary discrepancy between the wettability experiment and the adhesion measurement in Fig. 3 is primarily due to the dependence of the surface adhesion on the probing position under an external applied voltage.

This study characterized the surface wettability properties of LCPCFs using AFM with LC concentrations at 69 wt %, and further discusses the physical mechanism of the surface adhesion of nanosized molecules. Typically, the associated surface adhesion was significantly varied and was depended strongly on the orientation of LC molecules at the surface. The tunable wettability of the LCPCF, and the chemical structures of the outermost layers can be modified to trigger various interfacial behaviors, which can be exploited in future technologies.

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- ¹³In the approaching step, the tip reached the surface when it was extended to point *a* and, then, deflected to point *b* under the van der Waals force. Beyond point *c*, the tip departs from the surface of the composite film. While passing point *d* prior to removal from the liquid, the tip breaks free from the liquid with an adhesion force F_e . Upon further retraction, the tip completely departs from the liquid surface to a distance beyond point *e*, and the cantilever returns to zero force at point *f*.
- ¹⁴We suggest the adhesiveness F_{\parallel} and F_{\perp} for the long and the short axis of LC molecules, respectively. The molecule is rotated through the *z*-axis by an angle θ . The quantitative analysis of LC orientation at various voltages can be deduced by the equation $F(\theta) = F_{\parallel}F_{\perp} / \sqrt{F_{\parallel}^2 \sin^2 \theta + F_{\perp}^2 \cos^2 \theta}$, where F is the adhesiveness measured from the *F*-*D* curve.
- ¹⁵See supplementary material at <http://dx.doi.org/10.1063/1.3378688> for images of the water droplet contact angle experiment observing by charge coupled device.