Direct image of a molecular orientation of a liquid crystal using directional polymerization of photoreactive mesogen

You-Jin Lee,[1] Chang-Jae Yu,[1,2] Young-Ki Kim,[1] Soo In Jo,[2] and Jae-Hoon Kim[1,2,a]

[1]*Department of Information Display Engineering, Hanyang University, Seoul 133-791, Republic of Korea*
[2]*Department of Electronic Engineering, Hanyang University, Seoul 133-791, Republic of Korea*

We present a method for visualizing the geometrical distribution of a liquid crystal (LC) arrangement using the replication of the molecular orientation by a mixture of alignment layers. We found that the anisotropic diffusion of the reactive mesogen (RM) monomers, mixed with an alignment layer, in contact with the LC was governed by the LC director through application of external voltage and allowed the directional polymerization under ultraviolet light illumination. The directional polymerization of a RM transferred and visualized the LC arrangement even at optically indistinct LC distributions. © *2011 American Institute of Physics*. [doi:10.1063/1.3537959]

The directional ordering of anisotropic molecules, such as compacted DNAs, elongated RNAs, self-assembled supramolecules, and liquid crystals (LCs), has attracted much attention in studies of chromatin condensation,[1] conformational transitions of RNAs,[2] self-assembly of functionalized molecules,[3] and the physics of low dimensional crystals.[4] In fact, visualizing the ordering of highly complex biomacromolecules, such as DNAs, RNAs, and viruses, which have steric constraints that allow liquid-crystalline behavior,[1,5] has been extensively pursued in efforts to understand the mechanisms underlying order formation.[2,5–9] Particularly, the orientational ordering of LC molecules is governed by contact, not only with solid substrates of different chemical constitution, but also with other mesophases such as polymers.[10,11] It has long been known that LC orientation can be directed by the anisotropy of a surface, which can be introduced by surface modifications with various techniques.[11–13] However, the direct image of an arrangement of LC molecules, without the introduction of an external agent, has not been studied.

In this paper, we present a method for visualizing the geometrical distribution of an LC arrangement using the replication of the molecular orientation by a mixture of alignment layers. The direct image of the LC arrangement is visualized by reactive mesogen (RM) producing directionally polymerized RM filaments, which are directly governed by the underlying LC distribution. Moreover, we present an underlying mechanism for the nanofilament formation, in which the RM monomers on the alignment layer dissolve in the LC molecules and anisotropically aggregated by the gradient force of their monomer density.[14,15] We believe that this method has the potential to allow visualization of the arrangement of anisotropic molecules with steric constraints and replicate the alignment of these molecules.

Figure 1 illustrates the main steps in the fabrication process for the transcription of the director distribution of the LC molecules on a RM mixed homeotropic alignment layer (RMHAL). For RMHAL, AL60101 (Japan Synthetic Rubber Co.), RM257 (BASF), and Irgacure 651 (BASF) (20% of the RM) were used as a vertical alignment of LC, RM monomer, and initiator, respectively. The process begins with the preparation of two substrates which are coated of alignment layers

on indium-tin-oxide (ITO) glass substrates. The alignment layers were spin-coated at 3000 rpm for 20 s and baked at 100 °C for 10 min in a soft baking process and at 180 °C for 1 h in a hard baking process. The RM monomers with rodlike shape are randomly oriented in the alignment layer due to an isotropic anchoring property of a homeotropic alignment layer (HAL), without any additional treatment such as a rubbing process. The cell thickness of the assembled substrates is maintained by the use of 3 μm glass spacers. The LCs of MLC6610 (E. Merck) with negative dielectric anisotropy are injected into the assembled cell by capillary action in the isotropic phase and are aligned vertically with respect to the substrates in the nematic phase. When a voltage above a certain threshold voltage is applied between two ITO substrates, the LC molecules rotate parallel to the substrates (that is, perpendicular to the applied direction of the voltage). At this moment, LC molecules have no preference in the azimuthal direction due to the continuously degenerate boundary condition. After random planar transitions, the LC molecules tend to reorient to minimize the deformation energies, and two-dimensional (2D) singular points (defects) form on the surface. In such a situation, the RM monomers align along the LC molecules in the alignment layer to reduce the excluded volume.[4] Exposure to UV
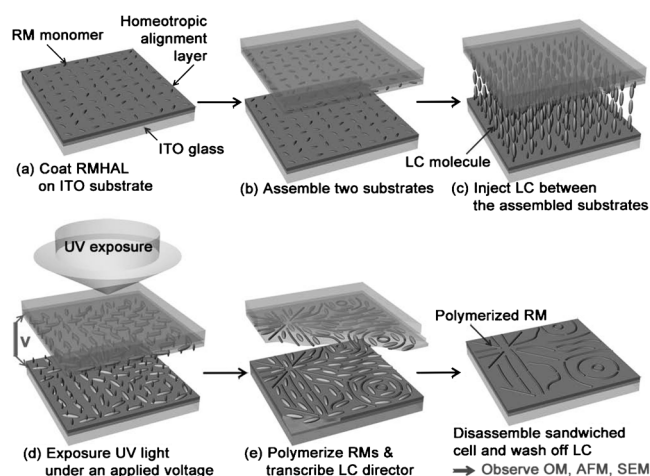

FIG. 1. Enumeration of steps for the visualization of the orientational distributions of the LC molecules using the RMHAL. The red ellipses, green ellipses, and red rods are the RM monomers, LC molecules, and directionally polymerized RMs, respectively.

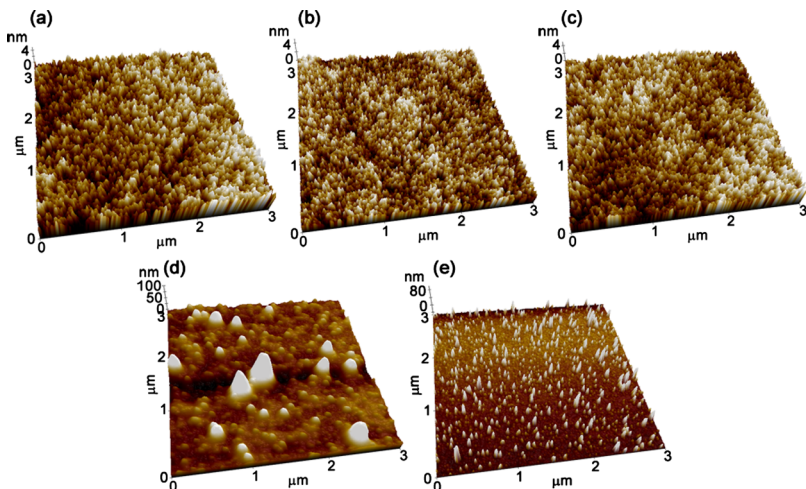[a]Author to whom correspondence should be addressed. Electronic mail: jhoon@hanyang.ac.kr.

FIG. 2. (Color online) Topographic structures of the HALs with/without the RMs. The AFM images of (a) the pure HAL and (b) the UV illuminated RMHAL in contact with ambient air. The AFM images of the RM-HALs polymerized in contact with (c) DI water, (d) PGMEA solvent for the RM, and (e) LC molecules during UV illumination.

light from a xenon lamp (Newport Co.) at 100 W for 30 min under an applied voltage of 10 V directionally polymerizes the aligned RM monomers along the LC alignment. The polymerized RMs may form filament patterns that transcribe the LC directors. As a result, by observing the RM filaments with a polarizing microscope (Eclipse E600 POL, Nikon), it is possible to visualize the LC director distribution directly and distinguish all defect patterns (even optically indistinguishable defects) without complicated methods of observation.

When the voltage is applied to the conventional vertically aligned (VA) LC sample with a pure HAL, it produces a Schlieren texture under a polarizing microscope due to the continuously degenerate boundary condition on the pure HAL. The textures result from singular points (defects) that are classified into four types, with an index m of ± 1 and $\pm 1/2$, depending on the configuration of LC directors.[4] The geometric distribution of LC molecules with m$= \pm 1$ cannot easily be determined by polarizing microscopy because the defects are optically equivalent. Moreover, the textures change with each voltage application because the LC molecules are aligned in temporarily stable states on the pure HAL.

Topographic structures of the RMHALs were observed by modulating the contact environments with the RMHALs during UV exposure/RM polymerization to understand the underlying mechanism of the RM nanofilament formation. Figures 2(a) and 2(b) are AFM images of the substrates with pure HAL and RMHAL, respectively, illuminated by UV light under ambient air environment. Both morphologies were very smooth and indistinguishable. Also, in the substrate with RMHAL illuminated in contact with deionized (DI) water, a similar morphology was observed, as shown in Fig. 2(c). Because the RM monomers are insoluble in ambient air and DI water, they polymerize by UV exposure without diffusion and/or drift. On the other hand, when the RMHAL is kept in contact with propylene glycol methyl ether acetate (PGMEA), which is a solvent for the RMs, the protrusions of the polymerized RMs can be seen, as shown in Fig. 2(d). The protrusions are formed by aggregation and polymerization of RM monomers during UV exposure, similar to the diffusive polymerization reported in photopolymer composite systems.[14,15] In this case, the RM monomers in the alignment layer dissolve and diffuse in the PGMEA solvent. When these dissolved RM monomers are exposed to UV

light, the polymerized RM seeds grow into protrusions due to the free lateral diffusion of RM monomers in solvent. However, the polymerized RM does not have azimuthally-ordered structure because the PGMEA solvent is isotropic. In the RMHAL sample in contact with the LC, the RM monomers easily dissolve in the LCs and diffuse, similar to the behavior seen in PGMEA solvent, due to the liquid crystalline properties of RM. However, because the lateral diffusion is partially prohibited by the excluded volume effects of the RMs in the ordered LC molecules, the pikes in the LCs are smaller and denser than the protrusions in PGMEA solvent, as shown in Fig. 2(e). From observing the topographic structures of the RMHALs corresponding to the molecular directions of the LCs, we also found the underlying mechanism of the RM nanofilament formation. Applying an external voltage and illuminating UV light to a VA LC sample with RMHALs, the shape of the polymerized RMs strongly depends on the applied voltage governing the LC director distribution as shown in Fig. 3. The directional polymerization of the RMs is governed by the anisotropic diffusion of the RM monomers which strongly depends on the molecular direction of the LC. Below a certain saturation voltage, the LC molecules still remain vertically and thus the RM monomers are diffused and polymerized isotropically [see Fig. 3(a)]. With increasing the applied voltage, the polymerized RMs were elongatedly formed because the LC molecules were gradually fallen down and the RM monomers were anisotropically diffused as shown in Figs. 3(b) and 3(c). Note that the pikes are not observable under a polarizing microscope, because the sizes of the pikes are much smaller than the wavelength of visual light, as shown in the AFM images.

With increasing density of RM monomers, the structure of polymerized RMs under an applied voltage elongates and
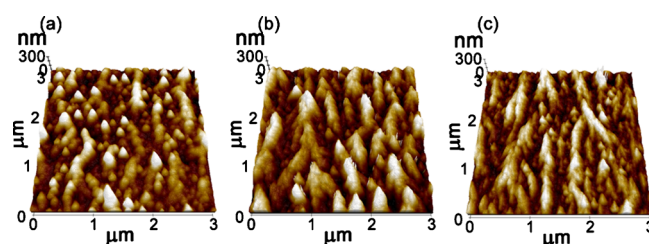

FIG. 3. (Color online) The AFM images of the disassembled RMHAL samples, after the RMs were polymerized under UV exposure with applied voltages of (a) 4.1, (b) 4.6, and (c) 10 V.
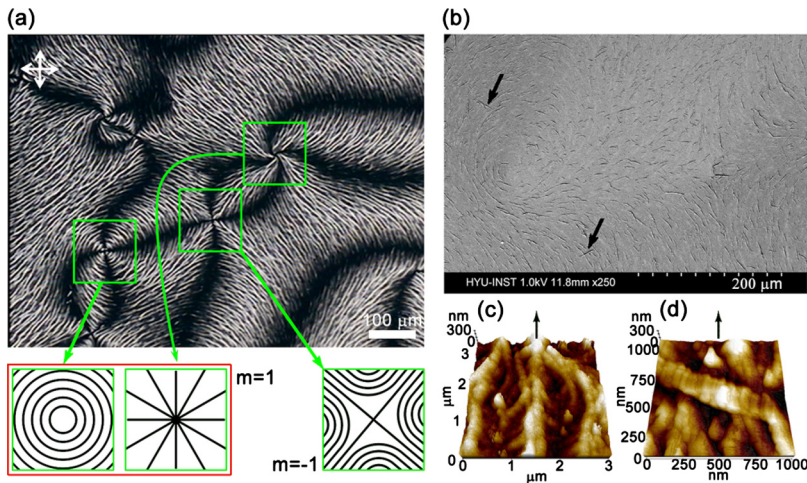
FIG. 4. (Color online) Transcription and visualization of the liquid crystal directors with the directionally polymerized RM filaments. (a) OM image of an LC cell, prepared by polymerization of the RMs under UV exposure at 10 V, imaged with crossed polarizers in the absence of the applied voltage. (b) SEM image of the disassembled substrate, which shows two defects in a circular pattern (m=1) and a hyperbolic pattern (m=−1). (c) and (d) AFM images of the polymerized RMs with different positions and magnifications.

is visible under a polarizing microscope. Figure 4(a) shows the microscopic texture under a polarizing microscope of the RMHAL, fabricated with UV exposure at 10 V, in the absence of an applied voltage. Due to the high concentration of RM, the characteristic diffusion length decreases and the polymerized RM forms elongated nanofilament structures that follow the LC alignment during UV exposure. The white stripes reflect the elongated RM filaments with anisotropy corresponding to the LC director distribution. From Fig. 4(a), we find that various defect structures with four black brushes corresponding to m= ± 1 are clearly classifiable by observing the direction of stripes. In boxes, we represent the distribution of LC alignment by black curves and/or lines that have the same distribution of white stripes. Because the defect structures with integer indices are optically equivalent, one cannot easily distinguish them by observation under a polarizing microscope. In the RM mixed alignment layer, however, we can easily distinguish the geometric arrangement of LC molecules with m= ± 1 as well as two different arrangements with same index of m=1. Figures 4(b)–4(d) show the surfaces of the disassembled sample, imaged by SEM and AFM. The sample was carefully disassembled and the LC molecules were gently washed from the disassembled substrate with hexanes. Figure 4(b) represents the SEM image of two defect structures with m= ± 1. Although some RM filaments washed away during the preparation of the disassembled substrate, the twig patterns are clearly observed. Figures 4(c) and 4(d) show the AFM images of polymerized RM structures with different magnifications and positions. Most elongated micron-sized structures correspond to the LC alignment as shown in Fig. 4(c) (a black arrow represents a direction of the LC alignment). However, few elongated microstructures are formed in directions different from their neighbors, as indicated by the black arrows in Fig. 4(b). Figure 4(d) shows a magnified AFM image of the microstructure. We find that nanosized elongated structures are formed even on the differently aligned micron-sized filament structures. This implies that RM monomers are ordered parallel to the ordering of LC molecules due to the excluded volume effect. From these results, we conclude that the RM monomers are directionally polymerized, following the LC alignment. The reverse process, therefore, may also be possible (i.e., aligned RM will align LC molecules).[16,17]

In conclusion, RMs, polymerized in an alignment layer under UV exposure and under a certain saturation voltage,

are useful for the direct visualization and transcription of the distribution of LC directors even with optically indistinguishable defects. The polymerized RM filaments form by dissolving the RM monomers in the alignment layer of LC molecules and aggregating them by the gradient force of the monomer density. The anisotropic diffusion of the RM monomers is dynamically governed by the LC director through application of external voltages. Exploring applications using the dynamic control of the directionally polymerized RM filaments, and optimizing the conditions associated with the materials and layouts, are promising topics for future work.

[1] F. Livolant, A. M. Levelut, J. Doucet, and J. P. Benoit, Nature (London) **339**, 724 (1989).
[2] Q. Zhang, A. C. Stelzer, C. K. Fisher, and H. M. Al-Hashimi, Nature (London) **450**, 1263 (2007).
[3] L. Li, E. Beniash, E. R. Zubarev, W. Xiang, B. M. Rabatic, G. Zhang, and S. I. Stupp, Nature Mater. **2**, 689 (2003).
[4] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, New York, 1993).
[5] P. J. Yoo, K. T. Nam, J. Qi, S.-K. Lee, J. Park, A. M. Belcher, and P. T. Hammond, Nature Mater. **5**, 234 (2006).
[6] R. Galletto, I. Amitani, R. J. Baskin, and S. C. Kowalczykowski, Nature (London) **443**, 875 (2006).
[7] T. Hirose, T. Ohtani, H. Muramatsu, and A. Tanaka, Photochem. Photobiol. **76**, 123 (2002).
[8] M. Jonsson, B. Åkerman, and B. Nordén, Biopolymers **27**, 381 (1988).
[9] R. Duggal and M. Pasquali, J. Rheol. **48**, 745 (2004).
[10] A. A. Sonin, *The Surface Physics of Liquid Crystals* (Gordon and Breach Science, Amsterdam, 1995).
[11] S. Masuda, T. Nose, and S. Sato, Jpn. J. Appl. Phys. **34**, L1055 (1995).
[12] J.-H. Kim, M. Yoneya, and H. Yokoyama, Nature (London) **420**, 159 (2002).
[13] J. M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Patel, J. Appl. Phys. **62**, 4100 (1987).
[14] T. Qian, J.-H. Kim, S. Kumar, and P. L. Taylor, Phys. Rev. E **61**, 4007 (2000).
[15] M. Y. Jin, T.-H. Lee, J.-W. Jung, and J.-H. Kim, Appl. Phys. Lett. **90**, 193510 (2007).
[16] Y.-J. Lee, Y.-K. Kim, S. I. Jo, J. S. Gwag, C.-J. Yu, and J.-H. Kim, Opt. Express **17**, 10298 (2009).
[17] Y. Reznikov, O. Ostroverkhova, K. D. Singer, J.-H. Kim, S. Kumar, O. Lavrentovich, B. Wang, and J. L. West, Phys. Rev. Lett. **84**, 1930 (2000).