http://dx.doi.org/10.5012/bkcs.2012.33.8.2806

Photopolymerization-Induced Vertical Phase Separation and Homeotropic Alignment in Liquid Crystal and Polymer Mixtures

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Received June 15, 2012, Accepted June 21, 2012

Key Words : Liquid crystals, Photopolymerization, Phase separation, Homeotropic alignment, UV irradiation

For decades, studies on the alignment of liquid crystal (LC) molecules have been of significant interest due to their immediate applications for display devices and the intriguing physiochemical properties they exhibit at the surface of mixtures.[1] Usually, homeotropic (or vertical) alignment, in which the long axes of the LC molecules are oriented in a direction perpendicular to the surface, is achieved by using surfactants such as lecithin, silanes or polyimide.[2-6] Recently homeotropic alignment of liquid crystal molecules was achieved by irradiating photosensitive polymers, by doping nanoparticles into LC, by utilizing nano/micro patterns, or by incorporating self-assembled monolayers (SAMs).[7-14] However, a clear understanding about the alignment mechanism is still elusive. In this paper, we report a novel method for homeotropic alignment of LC by utilizing the phase separation of LC/polymer mixtures.

Figure 1 shows orthoscopic and conoscopic polarized optical microscopy (POM) images of the LC/NOA65 cells with mixing ratios ranging from 99:1 (LC:NOA65) to 80:20, under UV exposure with an intensity of 30 mW/cm^2 (λ~365 nm) for 20 min. The POM image of the cell, made from LC and NOA65 in a weight ratio 99:1, exhibited homeotropic alignment with some defects, as shown in Figure 1(a). Note that the distinct Maltese crosses (insets in Fig. 1) in the conoscopic POM images indicate the homeotropic alignment of the LC molecules. Cells with a weight ratio of 97:3 and 97:5 showed a highly uniform homeotropic alignment over the entire area of the cells, as shown in Figure 1(b) and 1(c). However, cells with higher polymer contents (90:10 and 80:20) showed no alignment. At higher polymer content levels, the photoinitiated-polymerization-induced phase separation creates a fibrillar network or elongated domain of the polymer in the bulk, which hinders the ability of the LC molecules to align uniformly. The results are consistent with the observations reported elsewhere.[15-19]

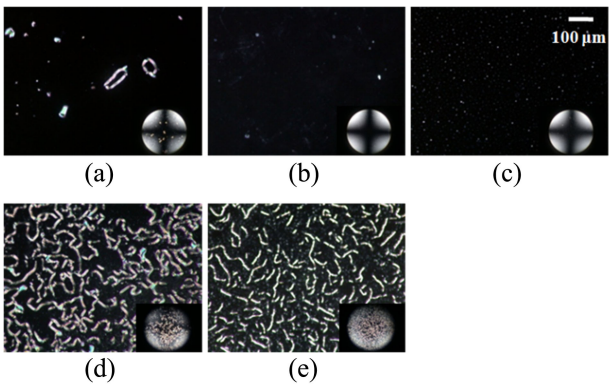

Figure 1. Orthoscopic and conoscopic (inset) POM images of the LC/NOA65 composite cells with the LC and NOA65 mixing ratio ranging from (a) 99:1, (b) 97:3, (c) 95:5, (d) 90:10, and (e) 80:20, respectively.

Figure 2 illustrates the possible scenario of phase separation of the photocurable monomer NOA65 and the LC mixed in the isotropic state (Fig. 2(a)). When the cell is exposed using an unpolarized UV light, the photocurable polymer NOA65 is cured, and the LC/NOA65 mixture undergoes photoinitiated-polymerization-induced phase separation in the vertical direction. The vertical phase separation in the LC/NOA65 mixture is believed to be driven by the differences in the surface energy of each component.[20-23] At a certain proper range of NOA65 concentration, a polymer network forms at the substrates and the LC molecules orient perpendicularly from the surface as shown in Figure 2(b).

In order to confirm the mechanism of the homeotropic alignment *via* phase separation in the cell of the LC/NOA 65 mixture, the morphology and wettability of the film were measured using SEM and a contact angle measurement apparatus. Figure 3 shows the SEM images and the water drop images. The top and bottom substrates of the LC cells were carefully separated and the LC was selectively removed using solvents. Figures 3(d) and 3(e) reveal top-view and tilted-view SEM images of the top substrate of an LC/

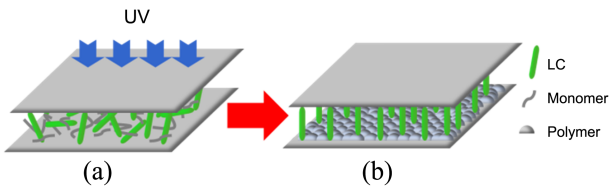

Figure 2. The schematic of homeotropic LC alignment from the phase separated polymer thin film through UV irradiation; (a) before UV irradiation, (b) after UV irradiation.

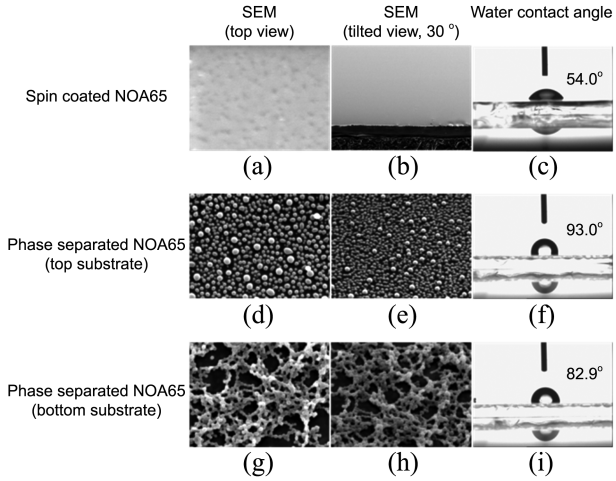

Figure 3. (a) Top view and (b) tilted view SEM images and (c) water contact angle image of the spin coated NOA65 thin film. (d) Top view and (e) tilted view SEM images and (f) water contact angle image of the top substrate of the 95:5 LC/NOA65 composite cell. (g) Top view and (h) tilted view SEM images and (i) water contact angle image of the bottom substrate of the 95:5 LC/NOA65 composite cell.

NOA65 mixture cell. Figures 3(g) and 3(h) show the SEM images of the bottom substrate of the LC/NOA65 mixture cell. In those images, the gravel pattern from the phase separated NOA65 can be seen at the top substrate, while the network pattern can be observed at the bottom substrate. To compare the surface roughness, we performed a contrast experiment using substrates coated with pure NOA65 film. Figures 3(a) and 3(b) show the surface texture from the substrate of the pure NOA65 film. As can be seen, the pure NOA65 surface is smooth without any noticeable patterns. This confirms that the gravel and network patterns were obtained through the phase separation process.

As shown in the third column of Figure 3, the water contact angle of the substrate of pure NOA65 was found to be 54.0° while the water contact angles of the top and bottom substrates of the LC/NOA65 mixture were found to be 93.0° and 89.2°, respectively. The water contact angle increases by 43.0° and 28.9° in the top and bottom substrates. The change of contact angle implies changes in the properties of the surface. It is well known that a low surface energy, the hydrophobic character of the surface, or low wettability results in high contact angles.[24] The LC molecules are oriented perpendicular to the substrate if the surface energy of the substrate (γ_S) is smaller than the surface energy of LC (γ_L); $\gamma_S < \gamma_L$.[25] In our experiment, polymer aggregates resulting from the phase separation of LC/NOA65 affect the surface roughness and, thereby, induce a higher contact angle. As a result, homeotropic alignment of LC molecules was obtained in the LC/NOA65 cells, where network or gravel textures had formed at the substrates due to phase separation. On the other hand, the substrates of the pure NOA65 film induce *random* planar alignment of the LC molecules due to their relatively low water contact angle.

To further investigate the proper condition required for homeotropic alignment, we varied the irradiation time of the UV exposure. Figure 4 shows orthoscopic and conoscopic POM images of LC cells with a 95:5 mixture ratio under the following UV irradiation times: 0, 1, 3, 5, 10, 20, and 30 min. At 0 min, random planar alignment was observed. At up to 5 min the cells showed homeotropic alignment with some defects. Due to incomplete polymerization, uniform alignment was not obtained during shorter exposure times. However, uniform homeotropic alignment in the entire cell area was observed during longer exposure times ($t > 5$ min).

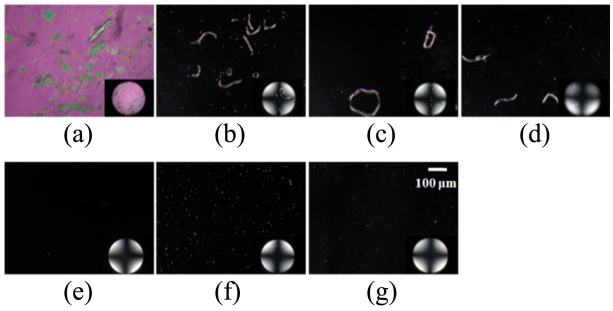

Figure 4. Orthoscopic and conoscopic (inset) POM images of the LC cells made by using a mixing ratio of LC and NOA65 with a weight ratio ranging from 95 to 5, then changing the UV (30 mW/cm^2) irradiation time from (a) 0, (b) 1, (c) 3, (d) 5, (e) 10, (f) 20 and (g) 30 min, respectively.

In conclusion, we presented a novel method for the homeotropic alignment of LC by using the irradiation of UV light on the LC/NOA65 mixture cell, in which the photo-initiated-polymerization-induced phase separation lowers the surface energy. When the amount of polymer content is sufficiently small, the gravel and network patterns were formed at the substrates *via* the vertical phase separation. We found that surface roughness plays an important role in the formation of the homeotropic alignment of LC. We also observed the alignment transition of the cells by varying the mixing ratio of LC/NOA65 or the UV radiation time. Furthermore, the present proposed method has great potential for application in display devices.

Experimental

We prepared a series of LC/polymer composites by mixing a negative dielectric anisotropic liquid crystal (MLC-7026-000; $n_e = 1.5577$, $n_o = 1.4755$ and $\Delta\varepsilon = -3.7$, Merck Co. Inc) and a photocurable prepolymer (NOA65, Norland Products Inc.). Various concentrations (1-20 wt %) of NOA65 were used to prepare the LC/NOA65 mixtures. The cells were made by sandwiching the mixtures between two glass substrates, which were separated by a 20 μm spacer. To initiate the photopolymerization, the cell was then exposed using an unpolarized UV light at an elevated temperature.

The POM images of the LC cells were taken from an optical microscopy (Nikon, Eclipse E600 POL) equipped with polarizers and a digital camera (Nikon, Coolpix 995). For conoscopic observation the Bertrand lens was inserted in the microscopy. To obtain the scanning electron microscope

(JEOL, JMS-6360) measurement, the sample was prepared by disassembling the UV-cured LC/NOA65 cells and using solvents to remove the LC. The contact angles were measured with a Kruss DSA10 contact angle analyzer equipped with drop shape analysis software. The Owens-Wendt's equation was applied to calculate the surface energies from the contact angles.[26]

Acknowledgments. This work was supported by the Soongsil University Research Fund (2009). Authors express their gratitude to Prof. J.-C. Lee at Seoul National University and Mr. J. S. Park at MD-Tech Corp. for sample preparation and useful discussions.

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