A novel approach of realizing the transmittance-tuning mechanism based on the topographic localization of the liquid crystals (LCs) within the polymer network is proposed. The photopolymerization of chiral LC (CLC)/reactive mesogen (RM) mixtures without a photoinitiator in the bulk induced the gradual phase separation of the CLC and RM, producing a submicron-scale porous morphology in the polymer network. An achiral LC, which was injected after the removal of the residual mixture, was localized in the porous polymer network. In the state without an applied voltage, the localized LC molecules were homogeneously aligned along the adjacent polymer ordering, enabling the transmissive state to be achieved. Under the applied electric field, the reorientation of the LC molecules distributed the effective refractive index to scatter the incident light. The authors' concept of localizing LC molecules in the submicron scale will be applicable for the new type of smart window applications.

1. Introduction

Smart windows that regulate the optical and thermal transmission and/or are capable of harvesting energy from heat and sunlight play a crucial role in making the indoor environment comfortable and sustainable [1–3]. Recently, many research groups realized the tuning capability of optical transmission using a variety of external stimuli, such as an electric field [4–9], light [10–12], temperature [13–16], and mechanical stress [17–20]. The stability of materials, on/off cycling durability, linearity, uniformity in a large scale, and cost-effectiveness are key issues that such devices have to address for their practical application. Among the various existing approaches, systems based on liquid crystals (LCs) are promising because they offer a superb optical transmission tuning capability, a long-range order, and reliability [8,16,21–24]. In general, localization techniques that spatially confine and manipulate LCs as droplets in a polymeric medium are widely employed [21,23,25–28]. Localized LC molecules, driven by the electric field, can provide the transparent state in an index-matching scheme, or the scattering state through the distribution of the effective refractive index. The distribution of the effective refractive index in the visible wavelength regime is essential to the realization of a strong light scattering state. The localization of LCs up to the submicron scale is currently limited, however, due to the dewetting of LCs in an isotropic medium. Therefore, it is desirable to develop a new mechanism that embeds LCs in the submicron scale and achieves fully tunable transmittance.

Demonstrated herein is the topographic localization of LCs within a polymer network produced from the gradual phase separation of a chiral LC (CLC)/reactive mesogen (RM) mixture during the photopolymerization process. Figure 1(a) shows the principle of the topographic localization of LC molecules in a polymer network. The growth of the polymer network was initiated from the photoinitiator-doped surface. In the initial state of the photopolymerization process, the homogeneous dispersion of the RM in the CLC first produced the chiral scaffold [29–31]. The chiral scaffold is capable of inducing the memorized chiral nematic phase to the reinjected
achiral LC. The absence of the photoinitiator in the bulk decreased the photopolymerization speed, which gradually induced the phase separation of the RM and CLC. The phase separation resulted in a porous morphology in the submicron scale where the reinjected achiral LC molecules were localized. Along the direction of polymer growth, the ratio of the in-plane porous region increased, and the optical axis rotated in the azimuthal plane. Under this configuration, the reorientation of localized LC molecules through electrical modulation can induce a strong distribution of the effective refractive index to scatter the incident light, as shown in Figure 1(b).

2. Experiment details

Four liquid crystalline mixtures ($M_1$, $M_2$, $M_3$, and $M_4$) containing the negative nematic LC (MJ981185) ($n_e =$ 1.5957, $\Delta n = 0.1102$; Merck), the RM (RM257) ($n_e =$ 1.687, $\Delta n = 0.179$; Merck), and the chiral dopant (R811, Merck) in various ratios were prepared as shown in Table 1.

| Table 1. Four liquid crystalline mixtures ($M_1$, $M_2$, $M_3$, and $M_4$) containing the negative nematic LC, the RM, and the chiral dopant in various ratios. |
|---------------------------------|---------------|---------------|---------------|---------------|
| M1                              | M2            | M3            | M4            |
| LC (%)                           | 71.68         | 62.78         | 51.75         | 40.81         |
| RM (%)                           | 10.43         | 20.15         | 30.05         | 41.62         |
| Chiral dopant (%)                | 17.89         | 17.07         | 18.20         | 17.57         |

The mixtures were heated at 100°C and were vigorously stirred. The RM was homogeneously dispersed in the host CLC so that it would follow the chiral nematic phase, and all the mixtures exhibited a circular Bragg reflection in the red-colored region.

An indium-tin-oxide (ITO)-evaporated glass substrate was spin-coated with a homogeneous alignment material (AL22620, JSR Co.) doped with a 1 wt.% 4-(dimethylamino)-benzophenone photoinitiator (Sigma Aldrich) at a 3000 rpm rate for 30 s, followed by thermal annealing at 180°C for 1 h. Another ITO-evaporated glass substrate was coated with the AL22620 intrinsic alignment layer. The two alignment layers were then rubbed in an anti-parallel direction. The empty cell was assembled using a 10 μm silica microsphere spacer. The prepared mixtures ($M_1$, $M_2$, $M_3$, and $M_4$) were infiltrated by the capillary action at a temperature ∼1°C lower than the clearing point of each mixture. The substrate with a doped alignment layer was irradiated with ultraviolet (UV) light, and photopolymerization was carried out at 20 mW/cm² for different doses (20, 40, 60, and 80 s). After forming a polymer network, the remaining mixture was washed by immersing the cell in acetone for 24 h, and the positive nematic LC (ZLI-5400-075) ($n_e =$ 1.6549, $\Delta n = 0.1544$; Merck) was reinjected into the cell. The reinjected LC was subsequently localized in the polymer network.

3. Results and discussion

The scanning electron microscopy (SEM) images of the polymer networks formed using $M_1$ under several photopolymerization conditions (20, 40, 60, and 80 s UV exposure at 20 mW/cm²) are shown in Figure 2(a). The intensity gradient of the UV light in the CLC/RM mixture initiated the polymer network growth from the top alignment surface [32]. The doping of the photoinitiator in the top alignment layer was found to have increased the polymerization speed. The photoinitiator molecules on the surface of the alignment layer, being unbound, may promote the initial photopolymerization process. The increase of the doping ratio (2 wt.% of the photoinitiator), however, made little difference in the thickness of the polymer network in the same UV dose. In the case of the relatively low-dose UV exposure, the polymer
network had a homogeneous morphology, which corresponds to the chiral scaffold, while the polymer network became more porous as the exposure time increased. This means that phase separation between the RM and the CLC gradually occurred during the photopolymerization process. Figure 2(b) shows the SEM images of the polymer networks that were formed using the four aforementioned mixtures (M1, M2, M3, and M4) at a higher-dose UV exposure (80 s). Porous morphologies similarly appeared in all the cases, but the density of the pores decreased in the case with a higher RM ratio due to the elongated thickness of the chiral scaffold. Note that the diffusion of the RM plays a key role in determining the degree of phase separation that will occur during the polymerization process [33].

Each fabrication step was observed using M4, under the reflection mode of polarized optical microscopy (POM). In step 1, M4 exhibited a circular Bragg reflection in the red-colored region, as shown in Figure 3(a). The photopolymerization process (20 mW/cm² for 20 s) in step 2 led to the pitch gradient of the chiral scaffold along the thickness. As shown in Figure 3(b), the variation of the POM images between the top and bottom sides confirmed the redistribution of the effective refractive index arising from the gradient of the RM density. After the removal of the remaining unpolymerized mixture, the sample lost the circular Bragg reflection (step 3) because the chiral scaffold became optically inactive. The circular Bragg reflection appeared again, however, after the reinjection of the achiral LC (step 4).

Considered next are the geometry and optical properties of the polymer network. As shown in Figure 4(a), the thickness of the polymer network was saturated due to the decreased photopolymerization speed. In the case of step 4, under a longer UV light exposure, the overall transmittance decreased owing to the light scattering at the porous region, as shown in Figure 4(b). In the case where M1 or M2 was used, the circular Bragg reflection was not realized due to the low thickness of the chiral scaffold. Figure 4(c) shows the transmittance spectra in each M4 fabrication step. In step 2, band broadening of the reflection was observed due to the pitch gradient of the chiral scaffold (see Figure 3(b)). In step 4, the chiral scaffold induced a chiral nematic phase to the reinjected achiral LC. The central wavelength of the circular Bragg reflection in the chiral phases was determined to be $n_a p$, where $n_a$ and $p$ are the average ordinary and extraordinary refractive indices of LC molecules and the helical pitch of the chiral scaffold, respectively. As the chiral scaffold and the reinjected LC formed a homogeneous composite system, $n_a$ can be estimated as $n_p \phi_c + n_{LC}(1 - \phi_c)$, where $n_p$, $n_{LC}$, and $\phi_c$ are the average refractive index of the chiral scaffold, the average refractive index of the reinjected LC, and the volume ratio of the chiral scaffold, respectively [34,35]. Depending on the swelling of the chiral scaffold in the LCs, the value of $\phi_c$ can be varied to shift the bandwidth of the circular Bragg reflection [36]. The chiral nematic phase, however, was unwinding at the localization site, and the mismatch of the refractive index between the localized LC and the polymer network decreased the overall transmittance.

To characterize the electro-optic properties, transmittance was observed as a function of the wavelength at several applied electric fields. Figure 5(a) and (b) show the transmittance-tuning capability of the devices where polymer networks were constructed using M4 under UV light exposure at 20 mW/cm² for 20 and 80 s, respectively. Under no applied voltage, there was no significant difference in transmittance between the low- and
high-UV-dose samples. In the case of the short UV exposure (20 s), the LC was not localized, and as such, the transmittance was maintained irrespective of the applied electric field, as shown in Figure 5(a). The transmittance-tuning capability, however, was much enhanced in the longer-UV-exposed cell. It is clear that the light scattering becomes dominant under the applied electric field. Also, the LC in the chiral scaffold, which corresponds to the bottom region of the polymer network, was stable under the applied voltage; as such, the transmittance decreased in all the wavelength regions without any change in the Bragg band. The polymer network can be constructed
using a nematic mixture for the electrically tunable transmittance without coloration.

4. Concluding remarks

The topographic localization of liquid crystal (LC) was demonstrated through the gradual phase separation of the polymer network to produce the transmittance-tuning mechanism. The growth of the polymer network, which was selectively initiated from one side of the surface, allowed the gradient of polymerization. Therefore, phase separation, represented as a porous morphology, was spontaneously achieved. The localized LC molecules in the porous region were reoriented under the applied electric field to distribute the effective refractive index. The proposed transmittance-tuning mechanism between the light scattering and transmissive states can be directly extended to smart window applications and a new class of electro-optic devices in a monolithic architecture.

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