

Electrically tunable birefringence of a polymer composite with long-range orientational ordering of liquid crystals

Byeongdae Choi,^{1,2,*} Seongkyu Song,¹ Soon Moon Jeong,¹ Seok-Hwan Chung,¹ and Anatoliy Glushchenko²

¹Nano & Bio Research Division, Daegu Gyeongbuk Institute of Science and Technology (DGIST), 50-1 Sang-Ri, Heyonpung-Myeon, Dalseong-Gun, Daegu 711-873, South Korea

²Center for Advanced Technologies & Optical Materials, University of Colorado at Colorado Springs, 1420 Austin Bluffs Parkway, Colorado Springs, CO 80918, USA

*bdchoi@dgist.ac.kr

Abstract: We report an optical film with electrically tunable birefringence in which the liquid crystals (LCs), mixed with the host polymer, form long-range ordering. The film was prepared through polymerization without phase separation between the LCs and polymers. Driving voltage below 30 V for full switching of birefringence is achieved in a 6 μm -thick film. Electro-optical investigations for the film suggest that the long-range ordering of the LCs mixed in the film caused by polymerization lead to rotations of the LCs as well as optical anisotropy in the film. These films with electrically tunable birefringence could have applications as flexible light modulators and phase retardation films for 2D–3D image switching.

©2014 Optical Society of America

OCIS codes: (160.0160) Materials; (160.3710) Liquid crystals; (230.3720) Liquid-crystal devices; (120.2040) Displays; (130.4110) Modulators.

References and links

1. J. Stöhr and M. Samant, “Liquid crystal alignment by rubbed polymer surface: a microscopic bond orientation model,” *J. Electron Spectrosc. Relat. Phenom.* **98–99**, 189–207 (1999).
2. N. A. J. M. van Aerle, M. Barmentlo, and R. W. J. Hollering, “Effect of rubbing on the molecular orientation within polyimide orienting layers of liquid crystal displays,” *J. Appl. Phys.* **74**(5), 3111–3120 (1993).
3. D.-H. Chung, T. Fukuda, Y. Takamishi, K. Ishikawa, H. Matsuda, H. Takezoe, and M. A. Osipov, “Competitive effects of grooves and photoalignment on nematic liquid-crystal alignment using azobenzene polymer,” *J. Appl. Phys.* **92**(4), 1841–1844 (2002).
4. S.-C. Jeng, C.-W. Kuo, H.-L. Wang, and C.-C. Liao, “Nanoparticles-induced vertical alignment in liquid crystal cell,” *Appl. Phys. Lett.* **91**(6), 061112 (2007).
5. F. Nemoto, I. Nishiyama, Y. Takamishi, and J. Yamamoto, “Anchoring and alignment in a liquid crystal cell: self-alignment of homogeneous nematic,” *Soft Matter* **8**(45), 11526–11530 (2012).
6. O. Sato, T. Kasai, M. Sato, K. Sakajiri, Y. Tsujii, S. Kang, J. Watanabe, and M. Tokita, “High-density poly (hexyl methacrylate) brushes offering a surface for near-zero azimuthal anchoring of liquid crystals at room temperature,” *J. Mater. Chem. C* **1**(48), 7992–7995 (2013).
7. H. Ren and S.-T. Wu, “Anisotropic liquid crystal gels for switchable polarizers and displays,” *Appl. Phys. Lett.* **81**(8), 1432–1434 (2002).
8. Y.-C. Hsiao, C.-Y. Tang, and W. Lee, “Fast-switching bistable cholesteric intensity modulator,” *Opt. Express* **19**(10), 9744–9749 (2011).
9. S. J. Lee, C. K. Morizio, and M. Johnson, “Novel frame buffer pixel circuits for liquid-crystal-on-silicon microdisplays,” *IEEE J. Solid-State Circuits* **39**(1), 132–139 (2004).
10. F. Yaras, H. Kang, and L. Onural, “State of the art in holographic displays: a survey,” *J. Display Technol.* **6**(10), 443–454 (2010).
11. J. Vogelsang, J. Brazard, T. Adachi, J. C. Bolinger, and P. F. Barbara, “Watching the annealing process one polymer chain at a time,” *Angew. Chem. Int. Ed. Engl.* **50**(10), 2257–2261 (2011).
12. M. Vacha and M. Habuchi, “Conformation and physics of polymer chains: a single-molecule perspective,” *NPG Asia Mater.* **2**(4), 134–142 (2010).
13. M. W. J. van der Wielen, M. A. Cohen Stuart, G. J. Fleer, D. K. G. de Boer, A. J. G. Leenaers, R. P. Nieuwhof, A. T. M. Marcelis, and E. J. R. Sudhölter, “Order in thin films of side-chain liquid-crystalline polymers,” *Langmuir* **13**(17), 4762–4766 (1997).

14. M. Schadt, H. Seiberle, A. Schuster, and S. M. Kelly, "Photo-induced alignment and patterning of liquid crystalline polymer on single substrates," *Jpn. J. Appl. Phys.* **34**, L764 (1995).
15. J. M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Patel, "The mechanism of polymer alignment of liquid-crystal materials," *J. Appl. Phys.* **62**(10), 4100–4108 (1987).
16. M. F. Toney, T. P. Russell, J. A. Logan, H. Kikuchi, J. M. Sands, and S. K. Kumar, "Near surface alignment of polymers in rubbed films," *Nature* **374**(6524), 709–711 (1995).
17. Y. R. Shen, "Studies of liquid crystal monolayers and films by optical second harmonic generation," *Liq. Cryst.* **5**(2), 635–643 (1989).
18. W. Chen, M. B. Feller, and Y. R. Shen, "Investigation of anisotropic molecular orientational distributions of liquid-crystal monolayers by optical second-harmonic generation," *Phys. Rev. Lett.* **63**(24), 2665–2668 (1989).
19. S. H. Hwang, K. J. Yang, S. H. Woo, B. D. Choi, E. H. Kim, and B. K. Kim, "Preparation of newly designed reverse mode polymer dispersed liquid crystals and its electro-optic characteristics," *Mol. Cryst. Liq. Cryst.* **470**(1), 163–171 (2007).
20. H. K. Shin, J. H. Lee, J. W. Kim, T. H. Yoon, and J. C. Kim, "Fast polarization switching panel with high brightness and contrast ratio for three-dimensional display," *Appl. Phys. Lett.* **98**(6), 063505 (2011).
21. J. H. Oh, W. H. Park, B. S. Oh, D. H. Kang, H. J. Kim, S. M. Hong, H. J. Hur, and J. Jang, "Stereoscopic TFT-LCD with wire grid polarizer and retarder," *Proc. SID Int. Symp. Dig. Tech. Pap.* **39**, 444–447 (2008).
22. V. Belyaev, A. Solomatin, and D. Chausov, "Phase retardation vs. pretilt angle in liquid crystal cells with homogeneous and inhomogeneous LC director configuration," *Opt. Express* **21**(4), 4244–4249 (2013).
23. H. G. Jerrard, "Optical compensators for measurement of elliptical polarization," *J. Opt. Soc. Am.* **38**(1), 35–59 (1948).
24. S.-J. Sung, E. Ae Jung, K.-J. Yang, Y. Tae Park, J.-K. Kang, and B.-D. Choi, "Liquid crystal alignment properties of inorganic SiO₂ layers prepared by reactive sputtering in nitrogen-argon mixtures," *Mol. Cryst. Liq. Cryst.* **507**(1), 137–149 (2009).
25. J.-M. Jin, K. Parbhakar, and L. H. Dao, "Polymerization induced phase separation (PIPS) in a polymer dispersed liquid crystal (PDLC) system: A Monte-Carlo simulation approach," *Liq. Cryst.* **19**(6), 791–795 (1995).
26. C. H. Gooch and H. A. Tarry, "The optical properties of twisted nematic liquid crystal structures with twist angles ≤ 90 degrees," *J. Phys. D* **8**(13), 1575–1584 (1975).

1. Introduction

The orientational ordering phenomena of liquid crystals (LCs) on the surfaces of polymers have been intensively investigated because LC alignment provides optical anisotropy useful in optical devices such as optical modulators for optical communications and displays [1–10]. The long-range orientational ordering of LCs in a binary mixture of the LC molecules and polymer chains is a required characteristic for preparing a film with optical anisotropy. Especially, the long-range orientational ordering of LCs in bulk polymers is important for the fabrication of flexible devices with tunable optical anisotropy. However, few studies have reported the ordering interactions between LCs and polymers in a binary mixture. In this paper, we report a polymer composite with long-range orientational ordering of LCs and that LCs in a mixture with pre-polymers can form electrically rotatable long-range ordering during polymerization.

Polymers can form long-range ordering during the reaction process because of their long chain structure [11, 12]. Passive-type phase retardation films with birefringence have been prepared using this long-range ordering property of polymers [13, 14]. Although these films have optical anisotropy, they cannot be useful for active devices such as flexible light modulators because the LC forms a composite by conjugating with the polymer, and thus cannot rotate when an external voltage is applied. In order to provide LC motion in the composite, the mixture of LC molecules and polymer chains needs to form a homogeneous solution without chemical reaction or phase separation. To enable this, long-range ordered LCs need to be mixed in the polymer matrix.

On the other hands, LCs can align with orientational order on the substrate surface by anchoring, which is influenced by the surface topology and the chemical nature of the surface [15, 16]. Nematic LC bulk alignment is fully determined by the orientational ordering of the LC monolayer deposited on a polyimide (PI) film surface [17, 18]. Based on these observations, our hypothesis is that nematic LCs in a mixture of LCs and pre-polymers could align in a specific direction by polymerization with orientational ordering. We considered that the LC molecules could align in a specific direction by adsorbing on the surface of a forming

polymer that has orientational order. It is noted that the process for producing polymer-dispersed liquid crystals (PDLCs) satisfies these conditions [19]. No chemical reaction or phase separation between the LCs and the polymer can occur under the controlled condition. We also examined the ordering characteristics of the LCs during polymerization with orientational ordering in this solution. The results show that LCs in a mixture with pre-polymers can form long-range ordering during polymerization. Moreover, the LC in the resulting film rotates according to an externally applied voltage. Using this property, the phase of polarized lights can be modulated. The driving voltage required for modulation decreases with increasing LC content in the mixture. We believe that the present result will provide a breakthrough for fabrication of optical devices including flexible light modulators and active phase retardation films for 2D–3D image switching [20, 21].

2. Experimental

LC-polymer composite cells were prepared by using a solution of LCs (E7, $n_o = 1.5024$, $n_e = 1.697$ Merck, $\Delta\epsilon = 14.3$, 50 wt%) and pre-polymers (PN393, $n_p = 1.473$, Merck, 50 wt%). Glass cells (10×10 mm, 6 μm gap) with (Cell #1) or without (Cell #2) PI films rubbed in anti-parallel and crossed (Cell #3) directions on the glass surface coated with ITO were filled with the solution by a capillary method under ambient atmosphere. The detail procedure for the capillary method can be found elsewhere [19]. We then irradiated the cells with 100 mW/cm^2 UV light (345 nm) for 10 min to induce the polymerization of the pre-polymers. In order to examine the effects of LC content on electro-optical property, we additionally prepared LC-polymer composite cells (6 and 20 μm gap) with a solution of LCs and pre-polymers at the various wt% ratios (80:20, 70:30, 60:40, 40:60, and 30:70). To prepare the flexible LC-polymer composite film, a volume of 10 cc of the LC and pre-polymer mixture (50:50) was dropped by pipette onto the ITO-coated polyarylate film (AryLite A200HC, retardation < 10 nm, Ferrania technologies). This was followed by stacking the polyarylate films with ITO surface coatings and leveling with a roll coater, in sequence. The sample was then exposed to UV light (345 nm) with an intensity of 100 mW/cm^2 for 10 min at room temperature to induce polymerization.

A transmittance polar plot of the cells between the two crossed polarizers was used for evaluating LC ordering. The electro-optical properties of LC-polymer composite were measured using a photodiode, and a He-Ne laser with wavelength of 632.8 nm at the voltage range of 0 to 40 V AC. The voltage was directly applied to the ITO coatings through power cables. The internal structure and the cross-section of the LC-polymer composites were investigated with optical microscope (Nikon, LV-100) and scanning electron microscope (SEM, SU8020, Hitachi), respectively.

3. Results and discussion

3.1. Long-range ordering of LCs in polymer composite

Figure 1 shows the optical activity (phase retardation) by the birefringence of the cells with rubbed PI films [Fig. 1(a), Cell #1] and without PI films [Fig. 1(b), Cell #2]. Figure 1(c) schematically illustrates the configuration of the cells positioned between the two cross polarizers. Cell #1 has the PI films rubbed in anti-parallel directions [see Fig. 1(c)], and it can be seen that the polarized lights via Cell #1 transmit through the crossed polarizer (Analyzer) [Fig. 1(a)]. The cell is position between the two crossed polarizers, and the intensity of transmitted light was changed by the rotation of the cell.

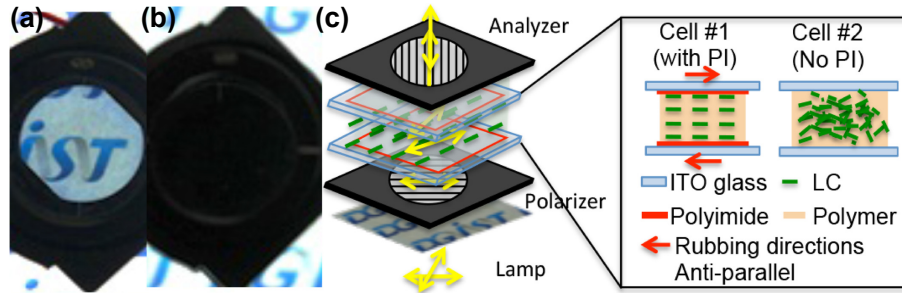


Fig. 1. Phase retardation of the cells filled with LC-polymer composite. (a) Cell #1 with rubbed PI films, (b) Cell #2, no PI film, and (c) schematic illustration for the configuration of Cell #1 and Cell #2.

The digital photograph was taken when the angle between the rubbing direction and polarizers reached 45° . In contrast, no transmitted light was observed by the rotation of Cell #2 [Fig. 1(b)] that has no PI films, regardless of optical axis. This result indicates that the phase of the polarized light is retarded only in Cell #1. We considered that the long-range orientational ordering of the LCs caused the birefringence of Cell #1 because the LC molecule has refractive index anisotropy. In the cell with the orientational ordering of the LCs, the retardation angle $\Delta\varphi$ is given by:

$$\Delta\varphi = \frac{2\pi\Delta n d}{\lambda} \quad (1)$$

where Δn is the birefringence, λ is the wavelength, and d is the thickness of the cell-gap [22]. The intensity after the analyzer is given by:

$$I(\theta) = I_o \sin^2(\Delta\varphi/2) \sin^2(2\theta) \quad (2)$$

where I_o is the intensity of the light after the first polarizer [23]. Therefore, the long-range orientational ordering of the LCs was explicated by a simple method using the polar plot for transmittance of the LC cell in the two-crossed polarizers [24].

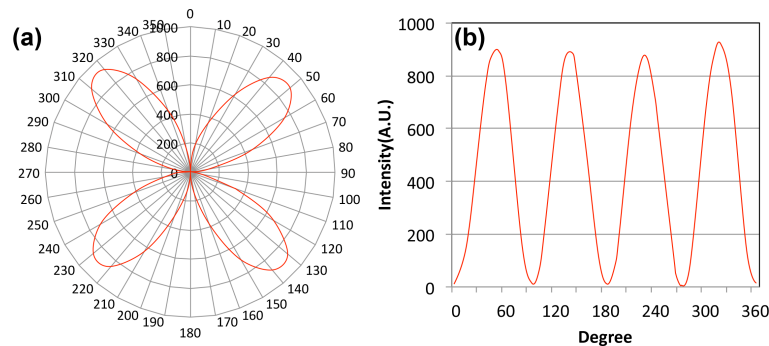


Fig. 2. Phase retardation by birefringence of the cells (Cell #1) with anti-parallel rubbing directions. (a) the polar plot for transmittance along the rotation angle and (b) the corresponding intensity.

The result for Cell #1 shown in Fig. 2 presented 4-fold symmetry, which represents the typical pattern that appeared in the cells filled with the aligned LCs. When the nematic LC cell with homogeneous planar alignment was placed between two crossed polarizers, the intensity of the transmitted light depended on the angle between the LC optical axis and the polarizers and reached maximum at 45° . This implies that the LCs in Cell #1 have orientational ordering in a specific direction. The configuration of Cell #1 and Cell #2 [see

Fig. 1(c)] indicates that the PI film rubbed in anti-parallel directions on the surface of the ITO glasses seeds the ordering of the LCs, although we realized that the PI film does not seed the ordering of LCs in the solution directly since the ordering of LCs was not observed before polymerization. The PI film was able to seed the ordering of the polymer, which then aligns the LC in a specific direction. In order to test the above idea, we prepared Cell #3, which had crossed rubbing directions. If the LCs in the solution directly align in the rubbing directions, it is easy to consider that the polarized light transmits to the analyzer when the rubbing directions for the upper and the bottom layers are in parallel with the analyzer and the polarizer, respectively, because the LCs could form a twisted structure that is typically seen in twisted-nematic (TN) LC devices.

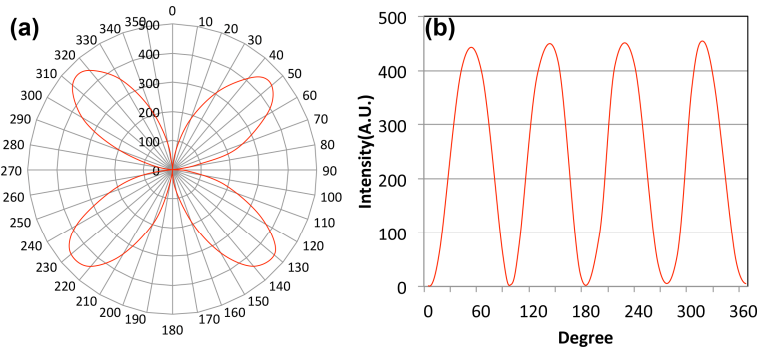


Fig. 3. Phase retardation by birefringence of the cells (Cell #3) with crossed rubbing directions. (a) the polar plot for transmittance along the rotation angle and (b) the corresponding intensity.

However, the result shows that the intensity is maximized when the angle between the polarizers and the rubbing directions reaches about 45° [Figs. 3(a) and 3(b)]. This indicates that the LCs in the mixture align not in a twisted manner but in homogeneous planar direction. The polar plots for the transmittance of Figs. 2(a) and 3(a) show that the alignment direction of the LCs in Cell #3 is the same as that of Cell #1, which has anti-parallel rubbing directions.

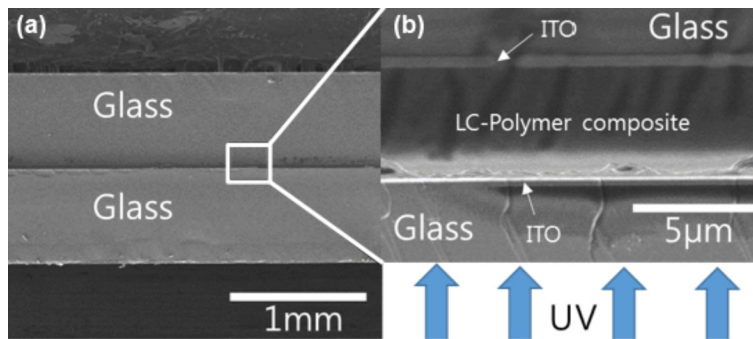


Fig. 4. Cross-sectional SEM images the cell with a $6\ \mu\text{m}$ cell-gap filled with the 50%-LC composite. (a) low magnification and (b) high magnification.

In addition, we investigated the cross-section of the samples to examine LC phase segregation at the opposite side of UV illumination. If LC phase segregates during polymerization, the ordering of the LCs can be induced by the PI film in top layer. Figure 4 shows the cross-sectional images by SEM at low [Fig. 4(a)] and at high [Fig. 4(b)] magnification of the cell with the 50%-LC composite. Figure 4(b) indicates no LC phase segregation at the opposite side of UV illumination, which implies that the PI film in the top layer is not effective for the ordering of the LCs. In contrast, the results strongly support that only the PI film in the bottom layer where polymerization starts influences the orientational

ordering of the LCs. The LC alignment in a composite has been investigated for a wide range of LC contents until the composition reaches to the critical value (m_c) for the phase separation of the LC and polymer to form PDLCs [25]. This can be evaluated by the transmittance of the composites. We investigated the transmittance of the cells prepared with the solution of LCs and polymers at the various ratios, and the effects of alignment layer on the transmittance by using glass cells with and without PI film.

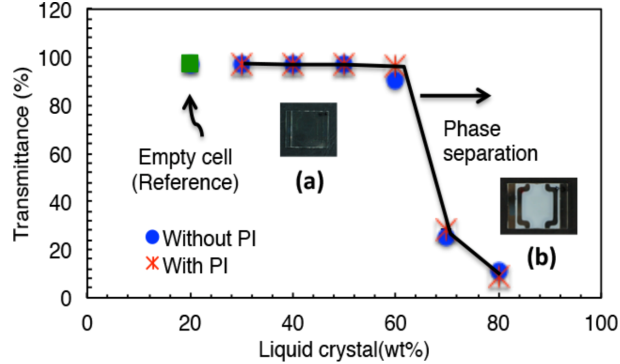


Fig. 5. Transmittance of the cells according to LC content. (a) transparent cell (b) milky cell.

Figure 5 shows the transmittance of the cells according to LC content and PI film. The transmittance over 90% at low LC content drastically decreases at around 70% LC content ($\sim m_c$) with regardless of PI film because the LC phase and polymer separate to form PDLCs [see Figs. 5(a) and 5(b)]. It is also known that PI layers do not degrade the transmittance of the cell. This is because the PI layer does not cause the phase separation between the LC and polymer.

3.2. Development of LC ordering in polymer composite

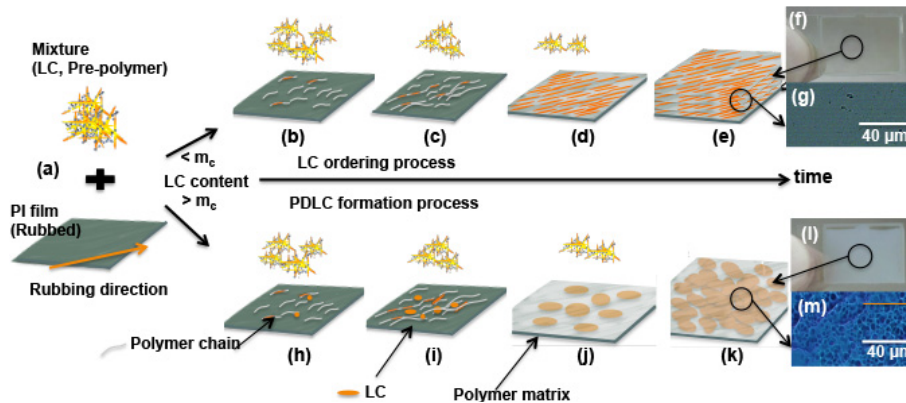


Fig. 6. Schematic illustration of polymerization and long-range ordering of LCs in the mixture of LCs and polymer.

Determining the detailed ordering mechanism of the LCs in a mixture of polymers is very helpful for considering these materials for device applications, and also for further understanding the nature of LCs. In this system, two types of processes for polymerization can be considered. When the content of LC is smaller than the m_c ($LC < m_c$, LC ordering process), the mixture of the LCs and pre-polymers [Fig. 6(a)] starts to polymerize and the PI film in the bottom layer seeds polymer chains with orientational ordering, which then adsorb LC molecules [Figs. 6(b) and 6(c)]. The ordering of polymer chains is considered because of the interaction with mechanically rubbed PI film surface. Asymmetric LC molecules could

align in parallel with polymer chain to reduce electrostatic energy. The polymer chains grow continuously and this process repeats to form a LC-polymer composite with long-range ordered LCs [Figs. 6(d) and 6(e)]. Figures 6(f) and 6(g) show the digital photo image of the LC-polymer composite cell and the corresponding matrix image by optical microscopy, respectively. In the case of $LC > m_c$ (PDLC formation process), the mixture of the LCs and pre-polymers starts to polymerize and the LCs and polymer phase separate [Figs. 6(h) and 6(i)] on the PI film, forming PDLCs [Figs. 6(j) and 6(k)]. Figures 6(l) and 6(m) represent the digital photo image of the LC-polymer composite cells and the corresponding matrix image by optical microscopy, respectively.

3.3. Electro-optical properties of LC-polymer composite with the long-range orientational ordering of LCs

Understanding the electro-optical properties as well as birefringence and transmittance are very important for finding potential applications for the composite. Therefore, we evaluated the electrical response of the LCs in the composite, as electrical performance is unquestionably a required characteristic for fabricating active devices. Strikingly, we observed that the LC in this composite rotates when exposed to external electric fields.

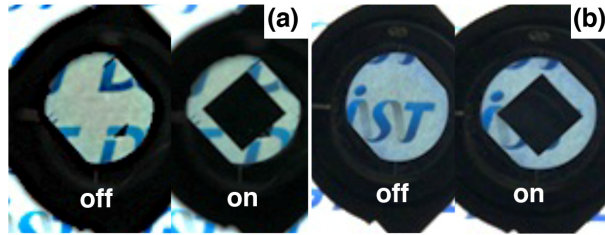


Fig. 7. Electrical switching of the transmitted light. (a) digital photo images for the cell with a 6 μm cell-gap filled with pure LC (reference sample) and (b) with the 50%-LC composite (Cell #1).

The response time was about 1 s in the cell with a 6 μm cell-gap, which was much greater than that of pure LC about 60 ms. We applied 30 V AC to the cells for driving the direction of the LCs. Figure 7 compares the resulting digital photographs of the transmittance with electric voltage for the cells with a 6 μm cell-gap filled with pure LC [reference sample, Fig. 7(a)] and with the composite with 50% of LC [Fig. 7(b)], respectively.

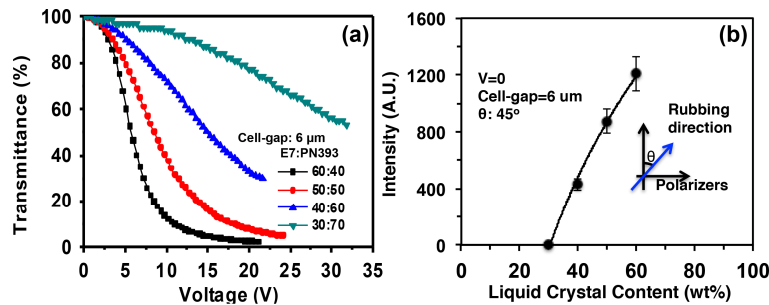


Fig. 8. Electrical switching of the transmitted light. (a) V–T curves of the cells filled with the composite according to LC content and (b) intensity of the transmitted light according to the content of LC.

In this test, we obtained the saturation of transmittance at a driving voltage as low as 30 V. The detailed voltage–transmittance (V–T) curve for the cells filled with the composite is presented in Fig. 8(a). The saturation voltage decreases with increasing LC content, this is because the anchoring force between the LCs and polymer decreases with increasing LC content. The phase retardation of the polarized lights is determined by the birefringence,

which is also a function of the LC content in the mixture, is considered another reason. According to Gooch and Terry, this depends on $\Delta n \cdot d$ in the Mauguin limit $\Delta n \cdot d \gg \phi \lambda / \pi$, where Δn is birefringence of the liquid crystal, d is the thickness of the liquid crystal layer, ϕ is the twist angle of the liquid crystal, and λ is the wavelength of the light [26]. Figure 8(b) shows that the initial transmittance ($V = 0$) increases as a function of LC content, which means the phase retardation increases with increasing LC content, and the driving voltage required to obtain the same phase retardation decreases with increasing LC content.

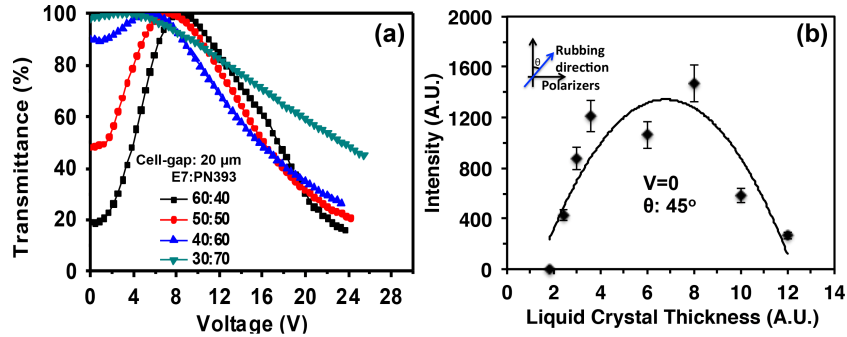


Fig. 9. Electrical switching of the transmitted light. (a) V-T curves of the cells filled with the composite according to LC content for a 20 μm cell-gap and (b) the intensity of the transmitted light according to the content of LC, which depends on the thickness of LC as sine function.

By the way, in the cell with a gap 20 μm we obtained the result that the initial transmittance inversely depends on the LC content [see Fig. 9(a)]. This strongly suggests that the intensity of the transmitted light depends on the phase retardation ($\Delta\phi$) as $I \propto \sin^2(\Delta\phi/2)$, and the phase of the polarized light is retarded in the range over $\pi/4$ in these cells. We summarized the relation between LC thickness and the initial transmittance in Fig. 9(b), which clearly shows that it depends on the thickness of LC in the composite as sine function. This result is also the evidence for the long-range orientational ordering of the LCs in the composite.

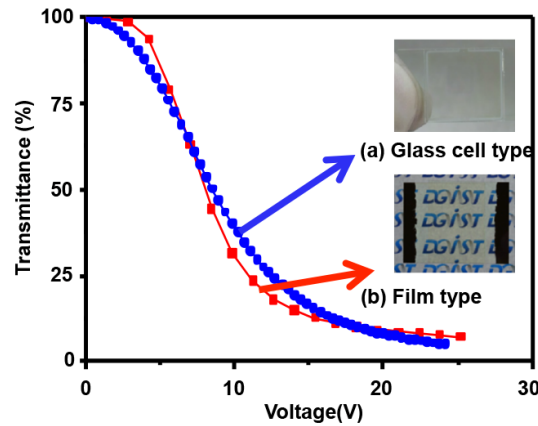


Fig. 10. V-T curves of the composite in (a) glass cell and (b) polyarylate films.

Finally, we applied this concept to a film substrate, which would be applicable in devices such as flexible light modulators and active retardation films for 2D-3D image switching. We prepared 6 μm -thick mixtures of LC and pre-polymers (50:50) on a polyarylate film (AryLite A200HC, retardation < 10 nm, Ferrania technologies) using a roll printing method. Then, polymerization was induced by exposure to 100 mW/cm^2 UV light (365 nm) for 10 min. The

performance shown by the V–T curve (Fig. 10) is nearly the same with that of the glass cell. This result implies that active phase retardation film is achievable with this LC-polymer composite film.

4. Conclusions

In summary, we explained an optical film with electrically tunable birefringence in which the liquid crystals (LCs), mixed with the host polymer, form long-range ordering. The film was prepared through polymerization without phase separation between the LCs and polymers. Driving voltage below 30 V for full switching of birefringence is achieved in a 6 μm -thick film. Electro-optical investigations for the film suggest that the long-range ordering of the LCs mixed in the film caused by polymerization lead to rotations of the LCs as well as optical anisotropy in the film. These films with electrically tunable birefringence could have applications as flexible light modulators and phase retardation films for 2D–3D image switching.

Acknowledgments

This work was partially supported by the basic research program (14-NB-05) through the Daegu Gyeongbuk Institute of Science and Technology (DGIST), funded by the Ministry of Science, ICT, and future planning of Korea.