Flexible polymer network liquid crystals using imprinted spacers bonded by UV-curable reactive mesogen for smart window applications

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ABSTRACT
We propose junction-type, vertically aligned polymer network liquid crystals using plastic substrates for flexible smart windows, in which the spacers are formed with the imprinting method and are bonded to the substrate surface by UV-curable reactive mesogen (RM). We clarified that the optical property can be improved by suppressing the aggregation of RMs around the spacers through thinning of the coating of the RM and the simultaneous improvement of the wettability of the parallel alignment film. We achieved excellent haze properties of 3.0% with voltage off and 92.7% with voltage on, and high curvature performance with a small curvature radius of 9.0 mm.

1. Introduction
Dimmable smart windows [1–4] reduce the power required by lighting and air conditioning in buildings, aircraft, and automobiles. Of the various methods used to modulate the light performance of smart windows [5–10], vertically aligned polymer network liquid crystals (PNLCs) [11–16] have attracted considerable attention because of their high transmittance in the voltage-off state, and high haze values and fast switching speeds in the voltage-on state. Flexible PNLCs using plastic substrates are in high demand; their flexibility allows for their application to the curved windows of automobiles and designer buildings. However, achieving mechanical stability of PNLC films using flexible plastic substrates is challenging; the liquid crystal (LC) flow caused by the substrate deformation during bending must be suppressed because it affects the orientation of the PNLC and can decrease transmittance in the voltage-off state. The PNLC must be able to suppress the substrate deformation caused by bending [17]. Furthermore, an inexpensive manufacturing method for large smart windows, such as a printing process [18,19], is essential.

We previously reported that polymer spacers formed in LCs via ultraviolet (UV) light patterning suppressed substrate deformation during curvature by bonding the top and bottom substrates [20–22]. This bonding technique can be used to develop flexible PNLCs [23,24]. However, patterning using a photomask is difficult on a large screen, which is needed to reduce costs, during the printing process.

In this paper, we discuss our development of a junction-type PNLC device with columnar spacers formed using the imprinting method [25–30], instead of polymer spacers formed by UV patterning (Figure 1). The top and bottom substrates were bonded using UV-curable reactive mesogen (RM) [31,32] applied to the counter-substrate to provide highly flexible PNLCs. Unlike conventional acrylic monomers, with RM polymerization, the individual molecules are aligned. Thus, RM can serve as an alignment film for PNLCs. We aimed to create high-quality, flexible, vertically aligned PNLCs. We optimized the fabrication conditions and experimentally demonstrated the effectiveness of the device.

2. Experimental methodology
We fabricated PNLC cells with imprinted spacers and thin RM layers. We used a polarizing microscope (BX-50; Olympus) with a crossed-Nicols polarizer to evaluate the LC alignment. The dark and bright regions indicated optically isotropic, vertically aligned LCs and birefringent tilted LCs, respectively, which allowed us to determine the uniformity of their alignment. We measured the light diffusion, represented by the haze value of the...
Figure 1. The junction-type PNLCs. The imprinted spacers were bonded to the substrate with reactive mesogen (RM).

PNLCs, using a haze meter (HM-150; Murakami Color Research Laboratory). We calculated the haze value, which is the ratio between the total and diffused light transmittance, as follows:

\[ \text{Haze} (\%) = \frac{\text{Diffused light transmittance}}{\text{Total light transmittance}} \times 100 \]  

Figure 2 illustrates the fabrication of a PNLC cell with imprinted spacers. We fabricated a prototype spacer via photolithography and created a mold by applying polydimethylsiloxane (PDMS; Dow Corning) to the spacer, followed by curing at 60°C. The spacer was columnar in structure, with a width of 10 μm, a pitch of 110 μm, and a height of 15 μm. Then we spin-coated a low-viscosity (300 cps) UV-curable acrylic monomer (NOA60; Norland Products) onto a substrate with transparent indium zinc oxide (IZO) electrodes, after which we imprinted the spacer structure by pressing the PDMS mold and performing UV light irradiation (JATEC Co., Ltd.). As the UV light energy was 20 J/cm², it fully polymerized the monomer. The center wavelength was 365 nm, and the light was normally incident to the cell substrate. Then we spin-coated a vertically aligned polyimide film (SE-4811; Nissan Chemical Industries) onto the substrates and baked them at 120°C for 10 min.

We coated the counter substrate with a parallel alignment polyimide film (AL-1254; JSR) that exhibited high wettability when exposed to the substrate, after which we performed rubbing treatment. Then we spin-coated RM (UCL-011-K1; DIC) onto the parallel-alignment film and fabricated empty cells, which we irradiated with UV light in a nitrogen atmosphere to polymerize the RM and bond the top and bottom substrates. The total UV light energy was 30 J/cm².

Finally, we prepared a mixture of nematic LCs (SKE-150N; Δn = 0.09) and UV-curable monomers (UCL-011-K1; DIC) at a weight ratio of 93:7 and injected these into the cells via capillarity. Finally, we irradiated the cells with UV light (6 J/cm²) to fabricate junction-type PNLC cells.

3. Results and discussion

3.1. Optimization of the thickness of the acrylic monomer coating

The acrylic monomer used to form the spacer structure was a dielectric material, so any residual layer created during the imprinting could have increased the driving voltage. To prevent this, we controlled the thickness of the monomer coating by varying the spin-coating speed and the sample temperature. Then we investigated the
The effect of the coating thickness on the driving voltage, i.e., the voltage at which the haze value was highest. As shown in Figure 3, the driving voltage decreased as the coating became thinner. The \( \leq 1 \mu m \) coating thickness prevented the residual layer from affecting the driving voltage. Using confocal laser microscopy, we found that the fabricated columnar spacer (VK-9710; Keyence) had an average height of 14.4 \( \mu m \) and an average width of 12.3 \( \mu m \). We confirmed that the structure was imprinted as designed even with a thin coat.

### 3.2. Optimization of the RM coating conditions

To confirm the alignment of the RM coating onto the parallel alignment film, we assessed the angle-dependent phase retardation with a spectroscopic ellipsometer (M-2000; J. A. Woolam), and calculated the pre-tilt angle through curve fitting (Figure 4). The experimental and theoretical values had a good agreement; the tilt angle at the air interface side was 88°, which confirmed that the RM was hybrid-aligned on the parallel alignment film. We also confirmed that the RM alignment was perpendicular to the air interface, so it served as a vertically aligned film for the PNLCs.

We then evaluated the uniformity of the RM alignment in the empty cells after UV irradiation. Figure 5 shows a polarization micrograph of an empty cell taken under the crossed-Nicols condition. It can be seen that the RM was aggregated near the spacers after the substrate stacking, which was attributed to the differences in the wettability of the RM, the spacer, and the parallel alignment film. The spacer showed high wettability, and the aggregated RM molecules were vertically aligned on its surface (Figure 6).

We also investigated the effect of the RM aggregation on the haze values of the PNLC cells. We injected the LC mixture into the empty cells and assessed the haze after UV irradiation (Figure 7). The haze values in the voltage-off and -on states were 10.2% and 76%, respectively. These values were higher and lower, respectively, than those of the non-junction-type LC cells without RM (3% and 95%, respectively). The increased haze in the voltage-off state is attributable to the light scattering caused by the difference in the refractive index between the spacer and the RM aggregates, and between the RM aggregates and the LCs. Also, the voltage did not drive the aggregation, and the haze value decreased in the voltage-on state. Therefore, the RM aggregation had to be suppressed to improve the optical properties of the PNLCs.
3.3. Reduction of the RM aggregation around the spacers

To reduce the RM aggregation around the spacers, the LC flow from the substrate to the spacer had to be suppressed during the substrate stacking using the following methods:

1. Reduction of the RM coating thickness and
2. Control of the wettability of the parallel alignment film.

3.3.1. Reduction of the RM coating thickness

The aggregation of RM on the spacer was evaluated according to the thickness of the RM coating (Table 1). The haze decreased in the voltage-off state as the aggregation radius and the film thickness decreased. The haze increased in the voltage-on state as the aggregation radius decreased, but the haze decreased once the coating thickness reached 329 nm. To further investigate this decrease, the PNLC alignment was analyzed under a polarizing microscope (Figure 8). A crossed-Nicols polarizer with a polarization axis of 45° relative to the rubbing direction was used. For comparison, we also show the results of the PNLC cell fabricated via RM film polymerization before substrate stacking. When the RM at the air interface was polymerized before substrate stacking, it was vertically oriented, as revealed by the low crossed-Nicols transmittance. On the other hand, interference colors, which reflected the LC birefringence, were observed in the cells where RM was polymerized after substrate stacking. Thus, the RM flowed after the stacking, which reduced the film thickness, whereas the RM at the air interface became tilted because of the anchoring force imparted by the parallel alignment film. Therefore, the PNLC was no longer vertical (Figure 9). If PNLCs are not vertically aligned, the tilt direction in the voltage-on state is fixed and light scattering depends on the incident polarization. Thus, the haze decreases. As there is a trade-off between the suppression of the RM aggregation by controlling the coating thickness and the haze in the voltage-on state, the thickness of the RM coating must be optimized.

3.3.2. Controlling the wettability of the parallel alignment film

If a parallel alignment film has high wettability, the RM aggregation on the spacers and the haze in the voltage-off state can be reduced. Therefore, the PNLCs remain in vertical alignment and the haze value is high in the voltage-on state. After measuring the contact angles of the AL-1254 (JSR), RN-2322 (Nissan Chemical Industries), and PA1 (Nissan Chemical Industries) parallel alignment films using a dedicated device (LSE-ME3; Nick) (Table 2), we used the high-wettability RN-3222 alignment film to create junction-type PNLC cells.

Table 1. Aggregation radius and haze values according to the RM thickness.

| RM Thickness (nm) | 1175 | 1050 | 752 | 329 |
|-------------------|------|------|-----|-----|
| Aggregation radius (um) | 30 | 23 | none | none |
| Haze (%) Off state | 10.2 | 9.3 | 4.9 | 3.5 |
| Haze (%) On state | 76 | 85.7 | 90.6 | 38.9 |

Table 2. Haze values of various parallel alignment films according to the contact angle.

| Alignment film | PA1 | AL-1254 | RN-2322 |
|----------------|-----|---------|---------|
| Contact angle (deg.) | 20 | 6 | < 3 |
| Haze (%) Off state | 5.5 | 4.9 | 3.4 |
| Haze (%) On state | 89.6 | 90.6 | 92.7 |
4. Fabrication of flexible PNLCs on plastic substrates

Using the conditions described above, we fabricated flexible PNLCs on plastic substrates. Polycarbonate (thickness = 80 μm) was used as the substrate material due to its high glass transition temperature (Tg > 215°C) and transmittance (T > 90%). Figure 10 shows a polarization micrograph of the fabricated junction-type PNLC cells under a crossed-Nicol polarizer. No monomer aggregation was observed around the spacers, and the PNLCs were uniformly aligned. Figure 11 shows the voltage-haze properties of our fabricated flexible PNLCs and the haze values of the PNLC cells without an RM layer (the non-junction-type LC cells) for comparison. Our flexible PNLC cell had a haze value of 3.8% in the voltage-off state and 92.7% in the voltage-on state, whereas the non-junction-type LC cell had a haze value of 3.0% in the voltage-off state and 95.1% in the voltage-on state. Therefore, the flexible PNLC cell had the same optical properties as the non-junction-type LC cell.

Next, we measured the radius of curvature of a curved LC cell of length L, along with the length d at which the orientation of the polymer network alignment changed due to the curvature deformation of the plastic substrates (Figure 12). The radius of curvature R was derived using the following equations:

\[ L = R \times \theta \]  \hspace{1cm} (2)
\[ d = 2 \times R \times \sin \left( \frac{\theta}{2} \right) \]  \hspace{1cm} (3)

where \( \theta \) is the angle between the center of curvature and the curved PNLC cell. The uniformity in the alignment of the non-junction-type LC cell decreased at a radius of curvature of 100 mm, but we were able to curve our PNLC cell to a radius of curvature of < 10 mm without any performance loss.

Finally, we derived the bending resistance of our curved PNLC cell at a bending radius of 10 mm (Figure 13). The flexible PNLCs controlled the haze value even when curved, allowing for a high haze value in the voltage-on state. Therefore, even when we used post spacers, we were able to suppress the substrate deformation by bonding the upper and lower substrates using the RM thin film, such that the structure resisted bending.

5. Conclusion

We developed flexible, vertically aligned junction-type PNLCs using a plastic substrate and spacers formed with the imprinting method and then bonded to the substrate via RM. By using a UV-curable monomer with a ≤ 1μm-thick coating to form the imprinted spacers, we were able to suppress increases in the driving voltage; and by decreasing the thickness of the RM coating and improving the wettability of the parallel alignment film, we reduced the RM aggregation into the spacers. Thus, we created vertically aligned, flexible PNLCs with excellent haze values of 3.0% and 92.7% in the voltage-off and
-on states, respectively, and with high ‘curvature performance’ due to a small radius of curvature (9.0 mm). Our flexible junction-type PNLCs have the advantages of high transmittance, high haze values, and high flexibility, and will be applied to future smart window applications.

Notes on contributors

Takahiro Ishinabe received his B.S., M.S., and Ph.D. degrees in Electronic Engineering from Tohoku University in Sendai, Japan in 1995, 1997, and 2000, respectively. From 2000 to 2002, he was a Research Fellow of the Japan Society for the Promotion of Science. From 2003 to 2012, he was an Assistant Professor at the Department of Electronics of the Graduate School of Engineering of Tohoku University, where he is now an Associate Professor since 2013. He has served as Chair of the Japan Chapter of the Institute of Electrical and Electronics Engineers (IEEE) Consumer Electronics Society in 2015–2016, and has been a fellow of the Institute of Image Information and Television Engineers of Japan (ITE) since 2016. He received the 2001 Best Paper Award and the 2013 Electronics Society Award from (IEICE); the 2001 and 2015 Best Paper Awards from the Japanese Liquid Crystal Society; and the 2003 and 2009 Niwa-Takayanagi Best Paper Awards from ITE. His current field of interest is flexible liquid crystal displays.

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