Flexible Vertically Aligned Polymer Network Liquid Crystal Using Transferred Spacers Bonded by Photoreactive Mesogens for Smart Window Films

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ABSTRACT

We have developed flexible vertical alignment polymer network liquid crystal using transferred spacers for smart window applications. We clarified that application of photoreactive mesogens to the substrates enabled bonding two substrates and control of the liquid crystal alignment and we achieved a small radius of curvature.

1. INTRODUCTION

Dimmable smart windows [1] can reduce the power requirement for lighting and air conditioning, and are expected to be useful in a wide range of applications, such as buildings, airplanes, and automobiles. Among the methods available for smart window light modulation, the use of alignment-controlled polymer network liquid crystals (PNLCs) [2] has attracted attention because of its high transmittance and high response speed when the voltage is turned off. The flexibility of PNLCs will allow their application to curved windows in automobiles and designer buildings, and thus expand the use of smart windows.

A challenge to the development of PNLCs using a plastic substrate is suppression of the flow of liquid crystal caused by deformation of the substrate that occurs during bending, which reduces the degree of orientation of the polymer in the PNLC. This results in the decrease of transmittance when the voltage is off [3]. Therefore, it is necessary to develop a PNLC structure that suppresses the deformation of the substrate due to bending. Furthermore, the establishment of an inexpensive manufacturing method, such as roll-to-roll, is also required for cost reduction.

We previously reported that a structure resistant to bending can be fabricated using a polymer wall spacer with bonding of the upper and lower substrates via the ultraviolet (UV) pattened exposure method using photomask [4]. However, this mask exposure method is difficult to apply to roll-to-roll production.

Here, we propose a PNLC device (Fig. 1) in which a post spacer is formed using the transfer method [5], which is a printing technology suitable for roll-to-roll production. Moreover, reactive mesogens (RM) is applied to the opposite substrate to control the bonding of both substrates and the alignment of the liquid crystal. We also verified the effectiveness of this device experimentally.

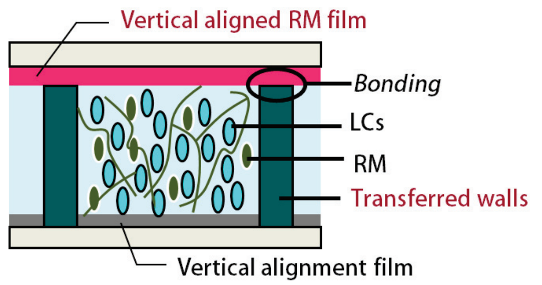

Fig. 1 Schematic diagram of PNLC cell structure with bonding transferred spacers.

2. PRODUCTION

The process for fabrication of the PNLC structure proposed in this study is shown in Fig. 2. Polycarbonate (PC) with an indium zinc oxide (IZO) transparent electrode was used as a plastic substrate.

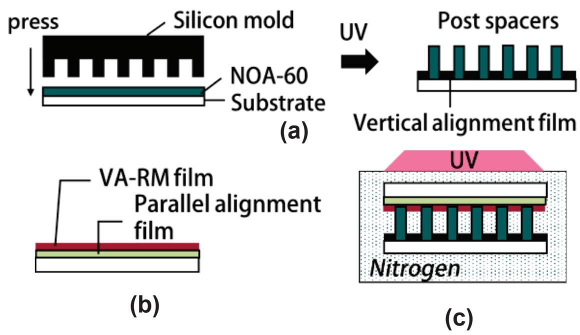

Fig. 2 Fabrication process.
(a) Post spacer transfer. (b) Apply RM on parallel alignment film. (c) UV irradiation under nitrogen atmosphere after superposition.

First, a UV polymerization monomer (NOA-60; Norland Products) was applied to one substrate, and a spacer structure was then transferred using a post spacer silicon mold. The column of this structure had a width of 10 μm, height of 15 μm, and pitch of 100 μm. After transferring the spacer structure, a vertical alignment film (SE-4811; Nissan Chemical Corporation) was applied. As NOA-60 is an insulator, the voltage applied to the liquid crystal dropped when the film thickness was large. To suppress this effect, the spin coating conditions for NOA-60 were optimized. Figure 3 shows a comparison of the Voltage-Haze characteristics among the coating thicknesses. The haze value is defined by the following formula:

$$\text{Haze} = \frac{\text{Diffuse transmission}}{\text{Total transmission}} \quad (1)$$

The results confirmed that the applied voltage can be reduced by setting the rotation speed to 6,000 rpm and the time to 120 s.

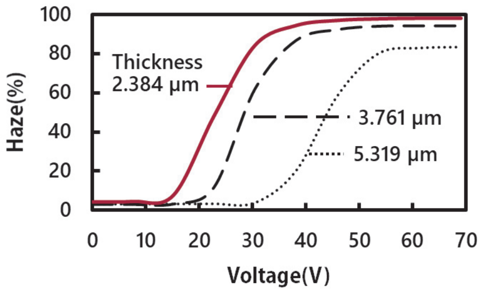

Fig. 3 Voltage-haze characteristics when the coating thickness of UV-polymerized monomer changes.

Next, a polyimide alignment film for horizontal alignment (AL-1254; JSR) was formed on the counter substrate by spin coating, and after rubbing, RM (UCL-011; DIC) was spin-coated at 6,000 rpm for 120 s at room temperature. To evaluate the orientation distribution of the UCL-011 film, angle-phase difference measurement was performed using a spectroscopic ellipsometer (M-2000, J. A. Woolam). The results are shown in Fig. 4. When compared with the trial hybrid alignment cell, we speculated that the UCL-011 film had hybrid-alignment on the horizontal alignment film.

These observations confirmed that the UCL-011 film also functions as a vertical alignment film, because RM molecules are vertically aligned at the air interface.

After combining both substrates, the RM was cured by UV irradiation in a nitrogen atmosphere. Figure 5 shows the results of observation of the cell after curing with a polarizing microscope under crossed nicols. As shown in the figure, the RM was aggregated around the post spacer due to the difference in wettability between the alignment

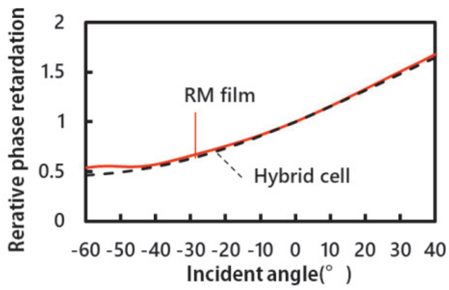

Fig. 4 Incident angle-retardation characteristics of RM film.

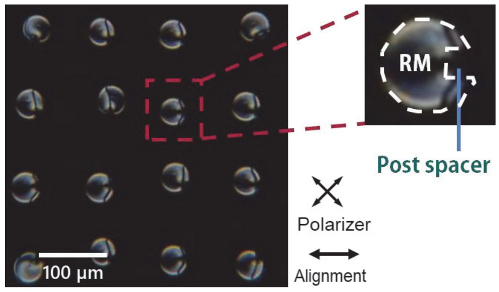

Fig. 5 Appearance of junction cell after UV curing without liquid crystal.

film and the spacer. To determine whether the aggregation was affected to the optical characteristics, liquid crystal was injected into the junction cell and the non-junction cell, and the haze was measured when the voltage was turned off. As a result, the haze in the junction cell was 7.9%, versus 3.0% in the non-junction cell; light scattering occurred when the voltage was turned off, indicating that the haze was higher. This aggregation was considered to depend on the RM coating thickness, and the coating conditions were thus optimized. Table 1 shows changes in film thickness when the spin coating time was fixed at 120 s while the temperature was varied (50°C, 75°C, 100°C, or 150°C). In consequence, the film thickness was found to decrease with increasing temperature. Table 2 shows changes in film thickness when the spin coating temperature was fixed at 100°C, while the spin coating time was varied (200, 300, 400, or 500 s). As the spin coating time increased, the film thickness decreased, up to 400 s. The lack of any further decrease after 400 s was considered to be due to the balance between interfacial tension of RM molecules and the centrifugal force of the spincoat when the film thickness exceeded a certain threshold. If the film thickness was too small, the anchoring force of the "parallel alignment film" suppressed the hybrid alignment of RM molecules toward the air interface so that the RM film lost its function as a vertical alignment film. Based on these results, when the junction cell was fabricated under the optimum conditions (temperature of 100°C and rotation

Table.1 Relationship between spin coat temperature and UCL-011 film thickness.

Temperature (℃)	50	75	100	150
Film thickness(μm)	1.039	0.781	0.681	0.529

Table.2 Relationship between spin coating time and UCL-011 film thickness.

Time(sec.)	200	300	400	500
Film thickness(μm)	0.486	0.436	0.329	0.328

Table.3 Contact angle and haze of each alignment film to UCL-011.

Alighment layer	AL-1254	RN-3222	PA1	PA2
Contact angle(°)	6.06	< 3	19.92	< 5
Haze(%)	6.9	3.8	5.5	3.3

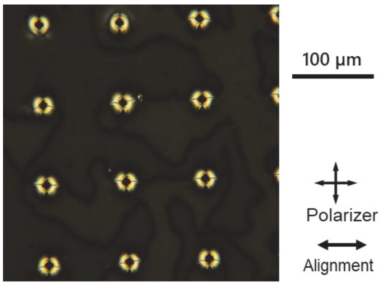

Fig. 6 Appearance of a junction cell fabricated using RN-3222 after liquid crystal injection.

time of 300 s), monomer aggregation was suppressed and the haze was 6.9%.

Furthermore, to suppress haze in the transmissive state, we investigated horizontal alignment films that could easily wet UCL-011. We examined the following horizontal alignment films, AL-1254, RN-3222 (Nissan Chemical Corporation), and two other photo-alignment films (PA1 and PA2). To evaluate wettability, after applying these alignment films to the substrate, UCL-011 was dropped by 2.0 μm and allowed to stand for 10 minutes. The contact angle was measured, together with the haze of the junction cell fabricated using the alignment films (Table 3). The results clarified that the haze decreased as the cell was made of a material having better wettability than UCL-011, and RN-3222 was adopted as the alignment film.

Finally, an LC mixture was prepared by mixing 93 wt% of negative liquid crystal and 7 wt% of UCL-011, and injected into the cell prepared under optimized conditions by capillary action. The appearance of the cell was examined, and it was confirmed that monomer aggregation has disappeared and the liquid crystal was uniformly aligned when no voltage was applied (Fig. 6).

3. CHARACTERIZATION

3.1. Electro-Optical properties

Fig. 7 shows the voltage–haze characteristics of the fabricated PNLC device. For comparison, a non-junction vertically aligned PNLC was prepared. The non-junction cell had a haze value of 3.0 % when OFF and 95.1% when ON; the corresponding values of the junction device were 3.8 % and 92.7 %, respectively. The result showed that a junction cell with optical properties close to that of a non-junction cell can be achieved.

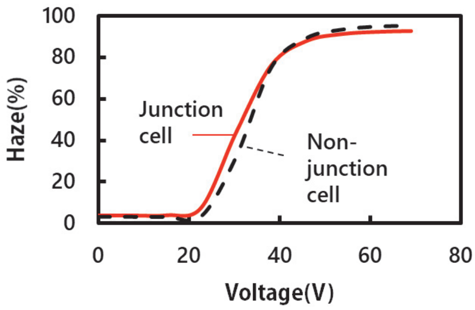

Fig.7 Comparison of haze characteristics of junction cell and non-junction cell.

3.2 Bondability evaluation by bending

A bending resistance test was performed on the junction device. Fig. 8 shows that the transparent and scattering states could be switched in the curved state. Next, the radius of curvature was examined and the results confirmed that it was possible to curve the device, with a radius of curvature of about 10 mm. In the case of the unbonded post-spacer-type vertically aligned PNLC, the radius of curvature was about 100 mm and the optical characteristics were degraded. Therefore, even with the transferred post spacers, it was possible to suppress deformation of the substrate by bonding the upper and lower substrates and to thus achieve a structure resistant to bending.

(a) 0 V (b) 70 V

Fig.8 Voltage drive of junction cell in curved state with a bending radius of 10 mm.

4. CONCLUSIONS

We proposed a vertical-aligned PNLC structure using plastic substrates with a transferred spacer bonded by RM. Consequently, we clarified that it is possible to produce PNLCs with good haze properties and bending resistance by suppressing liquid crystal aggregation during substrate bonding when using an alignment film with high-wettability to RM. In addition, it was confirmed that the junction-type device had almost the same optical characteristics as the unbonded PNLC using post spacers, and that achieved small radius of 10 mm. Therefore, application to various flexible smart windows is expected.

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