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Formation of polymer structure by thermally-induced phase separation for a dye-doped liquid crystal light shutter

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A B S T R A C T

A dye-doped LC/polymer light shutter with a polymer structure that is formed using the thermally-induced phase separation (TIPS) method is demonstrated. The TIPS method does not include any chemical reaction, and thus there is no degradation of the dye during the fabrication process. The light shutter can be fabricated quickly because the optical performance is not affected by the cooling time. The fabricated TIPS cell exhibits excellent optical performance, such as a low haze value of 0.5% in the initial transparent state, and a high haze value of 99.1% in the opaque state with a superior black color. This approach can be used for the high image quality of see-through displays using organic light-emitting diodes.

1. Introduction

See-through displays using organic light-emitting diodes (OLEDs) are gaining popularity as next-generation displays [1–3]. However, they cannot display the black color because of their see-through area. In addition, they suffer from poor image quality because the displayed images overlap with objects behind the display panel. Therefore, to realize the high-quality mode, a see-through display using OLEDs requires a light shutter, which can facilitate the display of the black color and hide the objects behind it.

Light shutters based on light absorption, such as electrochromic devices [4–6], suspended particle devices [7–9], and guest-host liquid crystal (LC) devices [10–22], have been studied for the control of the transmittance. However, it is difficult to hide the background completely with light shutters based on light absorption. To hide the background completely and display the black color simultaneously, LC light shutters based on simultaneous control of light scattering and absorption have been actively studied [11,12,15–21]. In particular, dye-doped LC/polymer composites have been widely investigated for this purpose [11,12,16–18].

In a dye-doped LC/polymer light shutter, polymerized-induced phase separation (PIPS) is widely used to form the polymer structure by UV curing inside the LC cell. However, degradation of dyes by free radicals, which are formed by the photo-initiator during the fabrication process, has been reported [18,19]. To solve this problem, fabrication of a dye-doped LC/polymer light shutter by thermal curing has been proposed [18]. However, since curing has to be performed within the temperature range of the nematic phase of the LC for the high optical performance of the fabricated light shutter, curing is performed at a low temperature. Therefore, the formation of the polymer structure is time-consuming. Moreover, although no degradation of the dye in thermally-cured LC/polymer composites has been reported, thermal curing also includes a chemical reaction that might cause degradation of the dye.

In this study, we report the fabrication of an initially-transparent dye-doped LC/polymer light shutter in which the polymer structure is formed by the thermally-induced phase separation (TIPS) method. TIPS is a method of forming a polymer structure in a cell without any chemical reaction. Therefore, the fabrication process is simple and there is no degradation of the dye. We confirm that the fabricated dye-doped LC/polymer light shutter can provide a superior black color as well as excellent optical performance. We expect that the proposed light shutter can be widely used for high visibility of see-through displays.

2. Cell fabrication and operation principle

Phase separation between the LC and polymer is important to form a proper polymer structure in an LC cell. PIPS is one of the most commonly used methods for the formation of the polymer structure inside an LC cell [23]. Initially, the pre-polymer or monomer and initiators are dissolved in the LC. After the bond of the initiator is homolytically cleaved into free radicals by external energy, such as heat or UV, free radicals initiate the process of polymerization. When the monomer becomes a polymer chain, it is no longer dissolved in the LC and phase separation occurs between the polymer and LC [23,24]. In this process, free radicals not only polymerize the monomers, but also oxidize other materials. Dye molecules in a dye-doped LC/polymer light shutter are degraded for this reason. If a low external energy or low reactivity initiator is used, degradation may not occur; however, the cell fabrication

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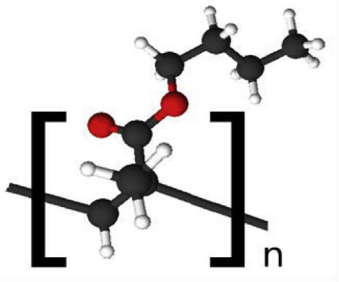

Fig. 1. Chemical structure of poly(butyl methacrylate).

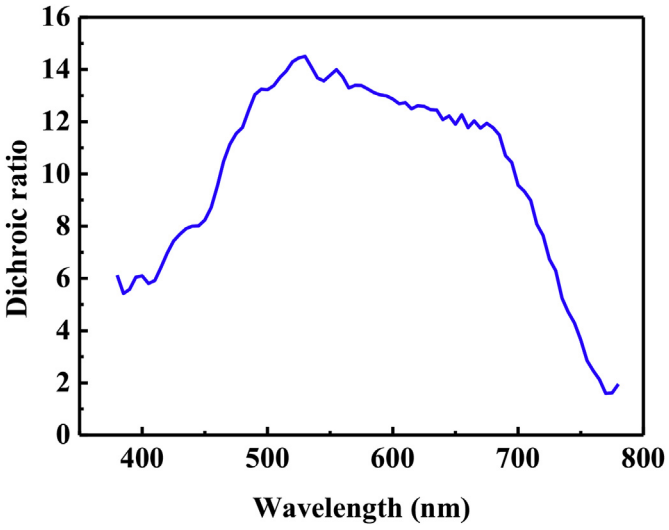

Fig. 2. Wavelength dependence of dichroic ratio of X12.

time increases [18,19,25].

In contrast, TIPS is a method for the formation of a polymer structure using a thermoplastic polymer. The polymer is dissolved in an LC that acts as a solvent at a high temperature [26]. When the solution is cooled, solidification occurs and the polymer is no longer miscible with LC. Finally, a polymer structure is formed in the cell. As mentioned above, the fabrication process in the TIPS method does not include any chemical reaction that can degrade the dichroic dye. The cell fabrication is simple because it only requires cooling of the cell from a high temperature to room temperature.

To fabricate a dye-doped LC/polymer light shutter using the TIPS method, we mixed a negative nematic LC mixture (SP0-001, Silchem, China) with poly(butyl methacrylate) (PBMA, Sigma-Aldrich, USA) (Fig. 1) and 1 wt% of dichroic dye (X12, BASF, Germany). Dichroic ratio of X12 is shown at Fig. 2. Since the initially-transparent light shutters must be transparent in the initial state, the haze value should be low. The haze of the cell in the initial state can be decreased by index matching [27,28]. For a low haze in the initial transparent state, we chose PBMA because its refractive index (n = 1.483) is similar to the ordinary refractive index of the LC mixture used. The physical parameters of the negative LC mixture, SP0-001, are as follows: optical anisotropy, Δn, of 0.282 (n_e = 1.783 and n_o = 1.501 at 589.3 nm and 20 °C) and dielectric anisotropy, $\Delta\varepsilon$, of −4.8 ($\varepsilon_{\parallel}$ = 3.5 and $\varepsilon_{\perp}$ = 9.3 at 1 kHz and 25 °C). The solution was mixed in a glass vial by stirring continuously for 24 h at 130 °C. The complete fabrication process is shown in Fig. 3(b). Indium-tin-oxide glass substrates were coated with a homeotropic alignment polyimide using a spin coater, and then baked at 230 °C for 1 h for curing. To maintain the cell gap, an empty cell was assembled using silica spacers with a diameter of 10 μm. Then, the solution was filled into an empty cell through capillary action at 130 °C. The cell was cooled from 130 °C to room temperature over 5 min.

To compare the electro-optic characteristics of a TIPS cell, a reference cell with a polymer structure formed by the PIPS method using UV light was fabricated. The concentration of the polymer and dye in the two cells was identical in order to compare the performance at an identical total transmittance. We mixed 93.8 wt% of negative nematic LC mixture with 5 wt% of reactive mesogen (RM 257, Merck, Germany), 0.2 wt% of photo-initiator (Irgacure 651, BASF, Germany), and 1 wt% of dichroic dye (Fig. 1). The complete fabrication process is shown in Fig. 3(a). The mixture was filled into an empty cell through capillary action at room temperature. The LC cell was exposed to UV light of 5 mW/cm^2 for 60 min. PIPS cells can be fabricated much faster if they are fabricated with a higher-intensity UV radiation. However, this may cause degradation of the dye molecules.

The schematic of the structure and operating principle of a dye-doped LC/polymer cell is shown in Fig. 4. In the initial state, the LC and dye molecules are aligned perpendicular to the substrate. Therefore, the light scattering and absorption by the LC and dye molecules are minimized so that the light shutter is transparent. When a vertical electric field is applied, the LC and dye molecules are randomly oriented to maximize light absorption and scattering. The composite cell blocks the

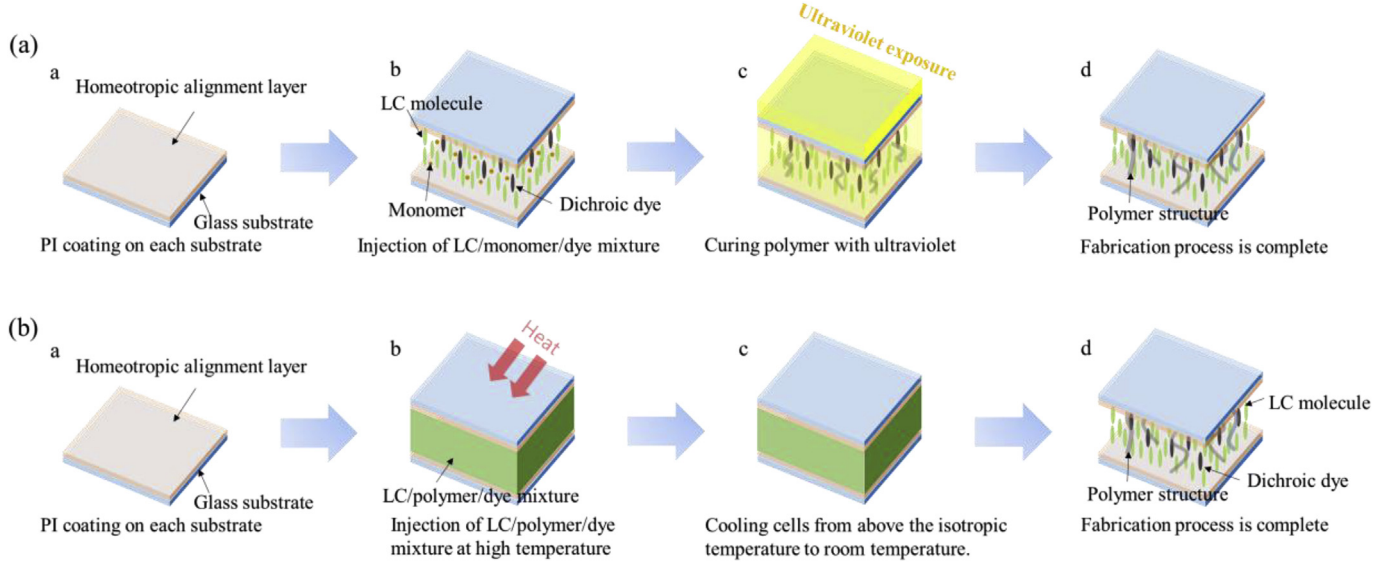

Fig. 3. Fabrication process using the (a) PIPS and (b) TIPS methods.

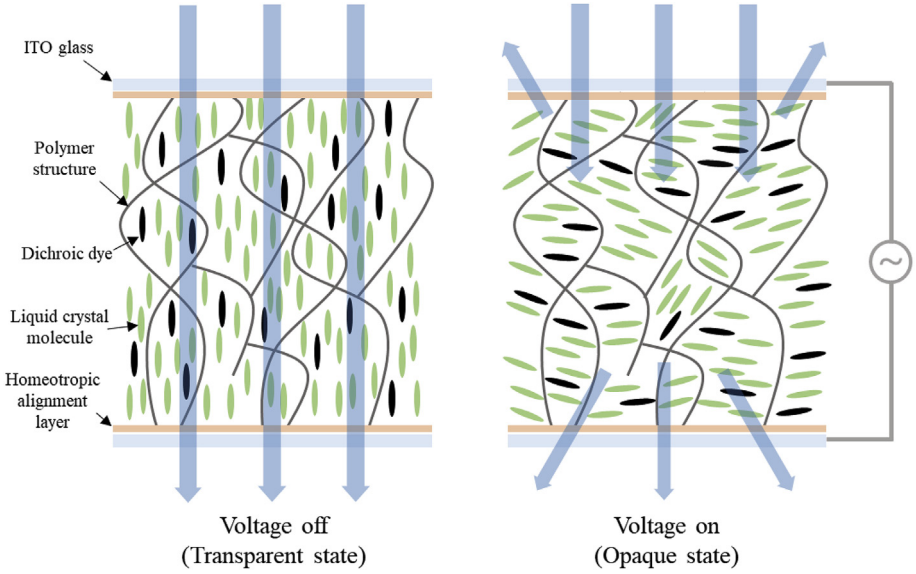

Fig. 4. Operating principle of an initially-transparent dye-doped LC/polymer cell.

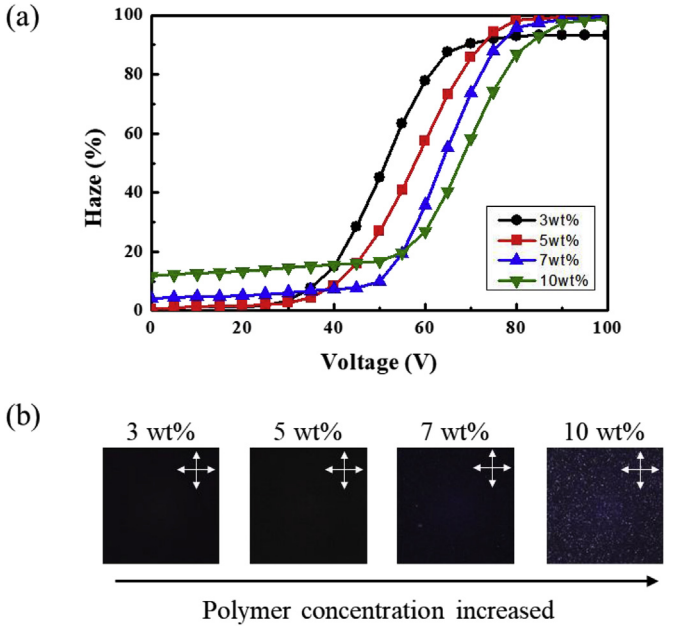

Fig. 5. (a) Measured voltage-haze curve of TIPS cells fabricated using 3, 5, 7, and 10 wt% of polymer (without dye), (b) Polarized optical microscope image of TIPS cells in the transparent state.

Table 1
Measured haze values of TIPS cells at different polymer concentrations.

		Polymer concentration			
		3 wt%	5 wt%	7 wt%	10 wt%
Haze (%)	Transparent state	0.5%	0.5%	4.2%	11.9%
	Translucent state	93.3%	99.3%	99.5%	98.7%

background completely. When the applied voltage is removed, the cell returns to its initial transparent state [29].

3. Experimental results and discussion

To confirm the scattering characteristics, the electro-optic properties of all the fabricated samples were measured with a haze meter (HM-65W, Murakami Color Research Laboratory) capable of measuring the total transmittance, specular transmittance, and haze. The total transmittance (T_t) is the sum of specular transmittance (T_s), and diffuse transmittance (T_d). The haze (H) can be calculated as $H = T_d/T_t$.

In LC/polymer composite devices, the polymer concentration is an important factor in determining the optical properties of the device [24,26,30]. To optimize the polymer concentration, we fabricated TIPS cells with different polymer concentrations without dichroic dye, and measured the haze of the cells. The voltage-haze curves of the TIPS cells are shown in Fig. 5(a) and the detailed values are shown in Table 1. When the polymer concentration is 3 or 5 wt%, the initial haze was less than 1%, as expected. For a polymer concentration higher than 7 wt%, the haze value of the cell increased. We can observe the light leakage in the polarized optical microscopy image shown in Fig. 5(b). To block the background completely, the light shutter must have a high haze in the opaque state. The haze values of the cells with polymer concentrations of 5, 7, and 10 wt% approached 99%. We chose the cell with a polymer concentration of 5 wt% because it exhibited a low haze of 0.5% in the transparent state and a high haze of approximately 99% in the translucent state.

In the case of the PIPS cells with thermal curing, the time required to form the polymer structure can be reduced by curing at a high temperature or using free radicals that react strongly. However, for a high transmittance in the initial state of an initially-transparent light shutter, polymer curing should be carried out while the LC molecules are oriented perpendicular to the substrates. Therefore, the curing temperature of the polymer is limited to within the temperature range of the nematic phase. In addition, the condition for reducing the time of polymerization can cause a greater reaction of the free radicals; this can cause degradation of the dye [25]. Therefore, the thermal curing of the polymer is usually time-consuming (over an hour). In contrast, the optical performance of the TIPS cell was not significantly affected by the cooling time. We cooled the cell from 130 °C to room temperature over 5 min. For this reason, the fabrication time is considerably shortened in comparison with the thermal curing.

Fig. 6 shows the measured total transmittance, specular transmittance, and haze values of the TIPS and PIPS cells. The detailed values of the measured electro-optical properties for the transparent and opaque states are summarized in Table 2. The fabricated TIPS cell exhibits excellent optical properties with a low haze value of 0.5% in the initial

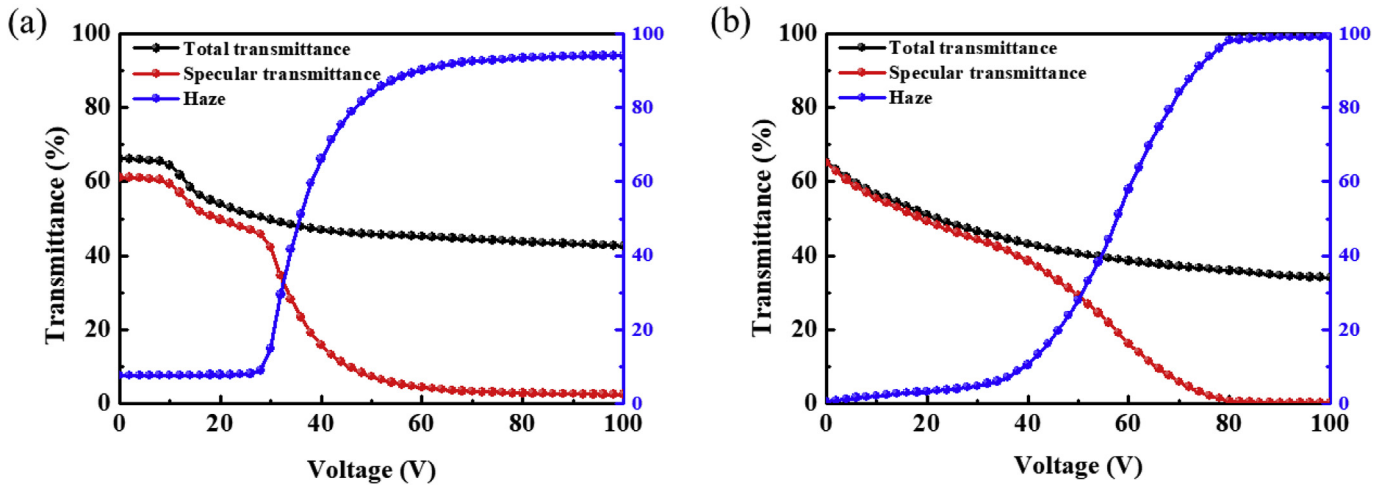

Fig. 6. Measured total transmittance (T_t), specular transmittance (T_s), and haze of (a) PIPS and (b) TIPS cells.

Table 2
Measured total transmittance, specular transmittance, and haze of TIPS and PIPS cells.

		PIPS	TIPS
Transparent state	Total transmittance	66.2%	65.4%
	Specular transmittance	61.1%	65.1%
	Haze	7.6%	0.5%
Opaque state	Total transmittance	42.6%	34.1%
	Specular transmittance	2.5%	0.3%
	Haze	94.1%	99.1%

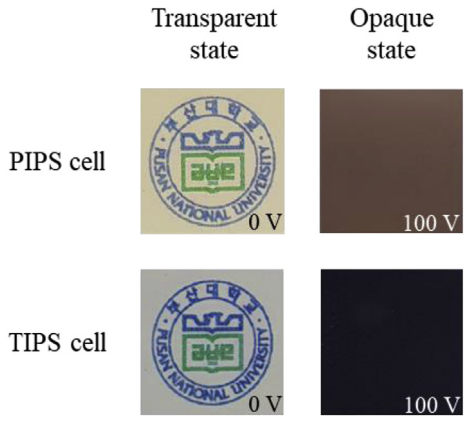

Fig. 7. Images of TIPS and PIPS cells placed on printed paper.

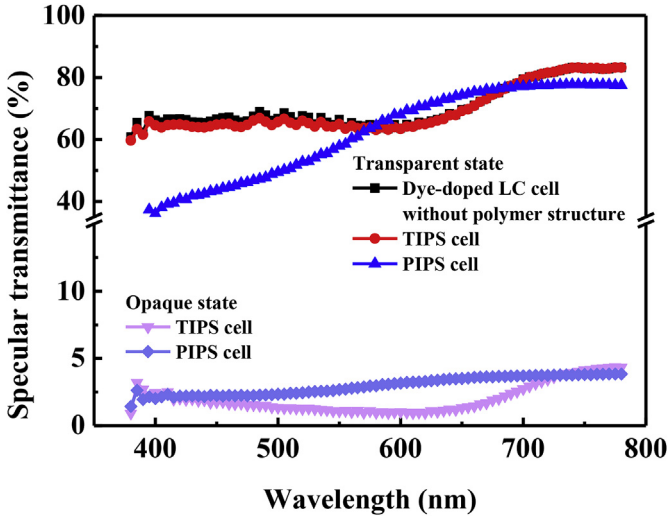

Fig. 8. Measured transmission spectra in the transparent and opaque states of a TIPS cell, a PIPS cell, and a dye-doped LC cell without polymer structure.

transparent state and a very high haze value of 99.1% in the opaque state. Despite the presence of the polymer structure in the TIPS cell, it has a low initial haze because the refractive index difference between the LC and the polymer is very small, as mentioned in Section 2. In the transparent state, the haze value of the PIPS cell is higher than that of the TIPS cell. The haze of the transparent state can be lowered by reducing the amount of polymer or by lowering the curing temperature [31]. The haze value in the opaque state is almost identical because the polymer concentrations of both cells were identical. For high haze, we need to apply a rather high voltage of 80 V to a TIPS cell. However, the operation of a light shutter is independent of the operation of an OLED display panel. Each pixel of an OLED panel is driven with thin-film transistors, but a light shutter can be driven simply by a voltage source. However, lowering of the operation voltage is still necessary to reduce energy consumption.

When a 1 kHz voltage wave of 85 V was applied to a TIPS cell for switching from the transparent to opaque state, the measured turn-on and turn-off times were 1 ms and 37.92 ms, respectively. There may be some concerns about the turn-off time of TIPS cell slower than an OLED panel. However, the operation of a light shutter does not require the switching speed of an OLED. The light shutter is not used to display moving pictures. It is used only for switching between the see-through mode and the high visibility mode. When it is opaque for the high visibility mode, we can enjoy high-quality displayed images by hiding the background objects behind an OLED panel. On the other hand, when it is transparent for the see-through mode, we can see-through the background objects overlapped with the displayed images. Moreover, compared with previous studies, the switching speed of our TIPS cell is not slow [20,21].

There is no significant difference in the total transmittance in the transparent state of the two cells because we used the same dichroic dye at identical concentrations in both cells. In the opaque state, however, the TIPS cell exhibited a lower total transmittance than the PIPS cell. The reason for this can be seen in Fig. 7, which shows the images of TIPS and PIPS cells placed on a printed image. When the LC cell is transparent, we can identify the printed images through the cell. Although the colors of the cells in the transparent state are slightly different, this has little effect on the total transmittance. When a voltage is applied, the cell becomes opaque such that we cannot identify the

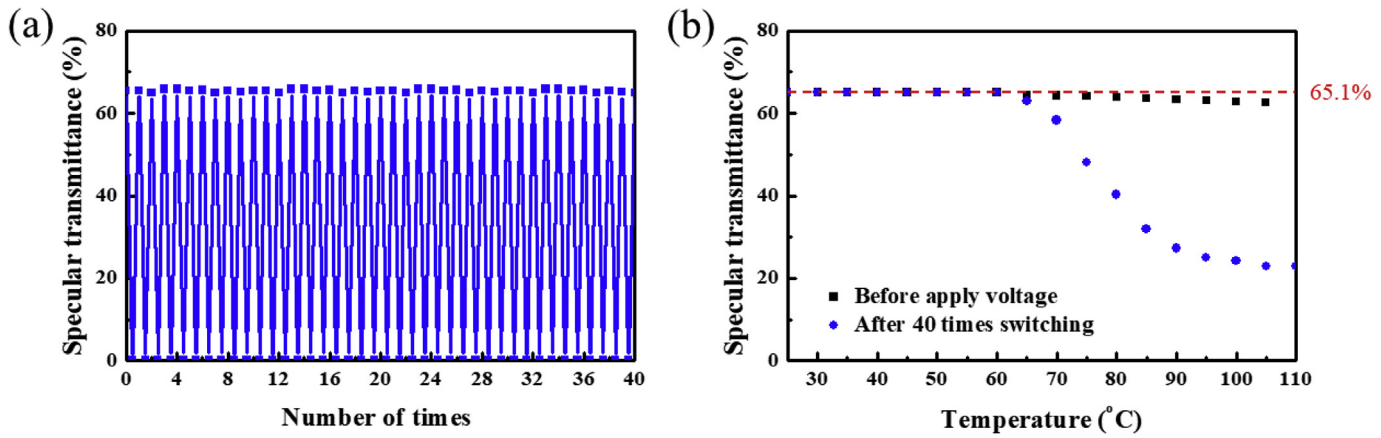

Fig. 9. The measured specular transmittance of the TIPS cell (a) under repeated electrical switching at 60 °C, (b) before and after 40 times of electrical switching as functions of the temperature.

printed images behind it. The TIPS cell displays black color as intended, whereas the PIPS cell displays a dark brown color because the oxidation reaction degraded the dye during the fabrication process. Therefore, in the opaque state, the total transmittance of the PIPS cell is higher than that of the TIPS cell.

Fig. 8 shows the transmission spectra of a TIPS cell, a PIPS cell, and a dye-doped LC cell without polymer structure. In the transparent state, the transmission spectrum of a TIPS cell is almost the same as that of a dye-doped LC cell without polymer structure. Therefore, we can conclude that the dye molecules are not degraded during the cell fabrication by the TIPS method. On the other hand, the specular transmittance of the PIPS cell is slightly lower than that of the TIPS cell for wavelengths shorter than 565 nm. In the transparent state, the specular transmittance of the PIPS cell is slightly lower than that of the TIPS cell for wavelengths shorter than 565 nm. Conversely, the transmittance of the PIPS cell is higher for wavelengths ranging from 565 to 685 nm. Because of this, the PIPS cell appears to be light brown. In the opaque state, the transmittance of the PIPS cell is higher than that of the TIPS cell. Although there is no significant difference in the transmittance of the blue wavelength in the TIPS and PIPS cells, there is a substantial difference in the transmittance of the red and green wavelengths, which makes the PIPS cell appear dark brown. In contrast, the TIPS cell exhibits a superior black color and blocks the background completely.

To check the stability of the vertically-aligned PBMA, we measured the specular transmittance after switching of the fabricated TIPS cell between the transparent and opaque state for 40 times. To test the thermal stability, the specular transmittance was measured as we increase the temperature. If the vertically-alignment of PBMA is not maintained, the specular transmittance will decrease after repeatedly switching because the vertical alignment of dichroic dyes and LCs will not be maintained. Fig. 9(a) shows that the specular transmittance of the TIPS cell remained almost the same even after repeated switching for 40 times at 60 °C. However, the specular transmittance of the TIPS cell did not return to the initial value after repeated switching at a temperature higher than 65 °C, as shown in Fig. 9(b). The structure of PBMA was deformed and the initial vertical alignment was not maintained. This result might be sufficient for general use as a light shutter in a see-through display, but this may limit its use at a high temperature.

4. Conclusions

We fabricated an initially-transparent dye-doped LC/polymer light shutter with a polymer structure formed using the TIPS method. Compared with the PIPS method, the TIPS method simplifies the fabrication process and reduces the fabrication time without any degradation of the dye. The fabricated cell exhibits an excellent optical performance with very low haze in the initial transparent state, and high haze in the opaque state with a superior black color. We expect that the proposed light shutter can be used for the high-visibility mode in see-through displays using OLEDs.

Acknowledgments

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