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2011 Chinese Phys. B 20 024212

(http://iopscience.iop.org/1674-1056/20/2/024212)

Chin. Phys. B Vol. 20, No. 2 (2011) 024212

Electro-optical properties of polymer stabilized cholesteric liquid crystal film*

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(Received 27 May 2010; revised manuscript received 25 June 2010)

Liquid crystals (LCs) and polymers are extensively used in various electro-optical applications. In this paper, normal mode polymer stabilized cholesteric LC film is prepared and studied. The effects of chiral dopant and monomer concentrations on the electro-optical properties, such as contrast ratio, driving voltage, hysteresis width and response time, are investigated. The reasons of electro-optical properties influenced by the concentrations of the materials are discussed. Through the proper material recipe, the electro-optical properties of polymer stabilized cholesteric LC film can be optimized.

Keywords: liquid crystal, polymer, electro-optical property, cholesteric liquid crystal

PACS: 42.70.Df, 42.79.Kr, 61.30.Gd, 61.30.Pq **DOI:** 10.1088/1674-1056/20/2/024212

1. Introduction

Liquid crystals (LCs) and polymers have been extensively studied over the past decades. The LCs with chiral dopant and a certain amount of polymer ($<$ 10 wt%), i.e., polymer stabilized cholesteric LCs (Ch-LCs) have been developed for various applications such as displays,[1−3] optical switches,[4,5] light shutters,[6] polymer stabilized blue phases,[7] polymer stabilized isotropic displays,[8] broad reflection band materials[9,10] and gratings,[11,12] etc. The interests of fundamental researches and potential applications are still increasing. When mixed with monomers, the textures of Ch-LCs can be stabilized by polymerization induced phase separation (PIPS) method. The detailed investigations have been carried out for reverse mode polymer stabilized cholesteric texture (R-PSCT) that is transparent at zero voltage and is opaque under applied electric fields.[13] For R-PSCT, the switch between transparent and opaque state comes from planar texture (PT) and focal conic texture (FCT) of the Ch-LC. The formed polymer network is parallel to the cell surface because of the homogeneous alignment layer on the substrate. If the formed polymer network is perpendicular to the cell surface, normal mode PSCT can be obtained. The switch between transparent and opaque state comes from homeotropic texture (HT) and FC texture. Compared with R-PSCT, it is easier to prepare normal mode PSCT. No special surface alignment treatment is needed. The contrast ratio (CR) of the film is higher than that of R-PSCT film.

In this paper, electro-optical properties of normal mode polymer stabilized Ch-LC film were systematically studied, including voltage-dependent transmittance (V–T), CR, driving voltage, hysteresis width and response time (RT). The effects of the chiral dopant and monomer concentrations on the electro-optical properties were discussed. This work is helpful to fundamental understanding and application developments of polymer stabilized Ch-LC film.

2. Experiments

2.1. Materials

The Ch-LC was achieved by mixing a nematic LC BLO36 (from Merck, $\Delta n = 0.267$) and a chiral dopant R811 (from Merck). The pitch length P of the Ch-LC can be determined by

$$P = \frac{1}{HTP \cdot x}, \tag{1}$$

where x is the concentration of the chiral dopant and HTP is helical twisting power.[14] The HTP

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*Project partially supported by the National Natural Science Foundation of China (Grant Nos. 60736042, 60578035 and 50703039) and the Science Foundation of Jilin Province of China (Grant Nos. 20050520 and 20050321-2).

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of R811 in BLO36 is 9.5 μm^{-1}, which is measured by using Grandjean–Cano wedge-shaped cell. Liquid crystalline monomer RM257 (from Merck) was added into the Ch-LC. It is a bi-function monomer, which has a core chain and two carbon–carbon double bonds in the molecular structure. A small amount of photo-initiator 2, 2-dimethopxy-1, 2-diphenylethanone (IRG651, from TCI) was also added to initiate polymerization of the monomer, making the carbon–carbon double bonds of RM257 open and link each other to form polymer network. The amount of IRG 651 was 10 wt% of the concentration of RM257. The chemical structures of R811, IRG651 and RM257 are shown in Fig. 1.

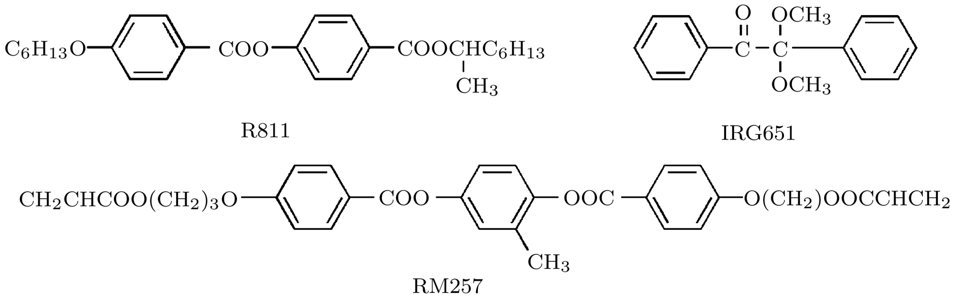

Fig. 1. Chemical structure of R811, IRG651 and RM257 in the experiment.

2.2. Preparations of the samples

The homogeneous mixture was filled into a 15-μm thick indium-tin oxide (ITO) glass cell by capillary action in a vacuum chamber or on a hot plate and was irradiated by a UV light (3.5 mW/cm^2, 1 hour) for polymerization. There was no alignment layer on the substrate. During the polymerization, a sufficiently high electric voltage (80 V) was applied to align the LCs in the homeotropic texture. The monomers are aligned with the LCs since they are both rod-shaped liquid crystalline molecules. Therefore perpendicular polymer network was obtained after phase separation and polymerization.[15] In this experiment, sample series A–D were prepared. The concentrations of the chiral dopant R811 were 8, 9, 11 and 13 wt% respectively. The pitches of series A–D were 1.32, 1.17, 0.96 and 0.81 μm respectively. The concentrations of R811 and RM257 are shown in Table 1.

Table 1. Concentration of the samples.

concentration/wt%					
sample	R811	RM257	sample	R811	RM257
A1	8	2.16	C1	11	2.5
A2	8	2.5	C2	11	3.0
A3	8	3.0	C3	11	3.5
A4	8	3.5	D1	13	2.5
B1	9	2.0	D2	13	3.0
B2	9	2.45	D3	13	3.5
B3	9	3.0	D4	13	4.0

2.3. Measurements

The electro-optical performances were investigated by an opto-electrical measurement system, as shown in Fig. 2. A 50-W halogen lamp (from Ushio) powered by a power supply (from Oriel) was used. The output light was collected to a photodiode detector by a battery of lens. Because of the involved scattering light, the transmittance of the sample varies with the collection angle of the detector.[16] A pinhole was placed in the light path to fix the collection angle as 2°. The driving of the sample and the recording of the light transmittance were controlled by a computer.

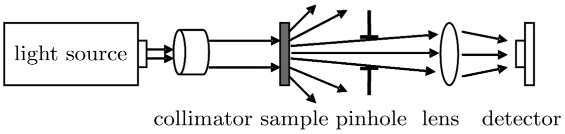

Fig. 2. Opto-electrical system to measure the electro-optical properties of the samples.

3. Results and discussion

As shown in Fig. 3, the film is in off-state when no electric field is applied whereas it is in on-state when an electric field is applied. The PSCT film is optically opaque in the off-state, where the liquid crystals in the FCT are randomly oriented within multi-domains. The incident light is scattered by the different refractive index matrix. When an electric field is applied (on-state), the liquid crystals in the HT are uniformly aligned to the direction which is perpendicular to the substrate. The refractive indices of the liquid crystals and the polymers are matched. Therefore the film becomes highly transparent.[17,18] The polarized light with different direction all works. No polarizer is required.[19]

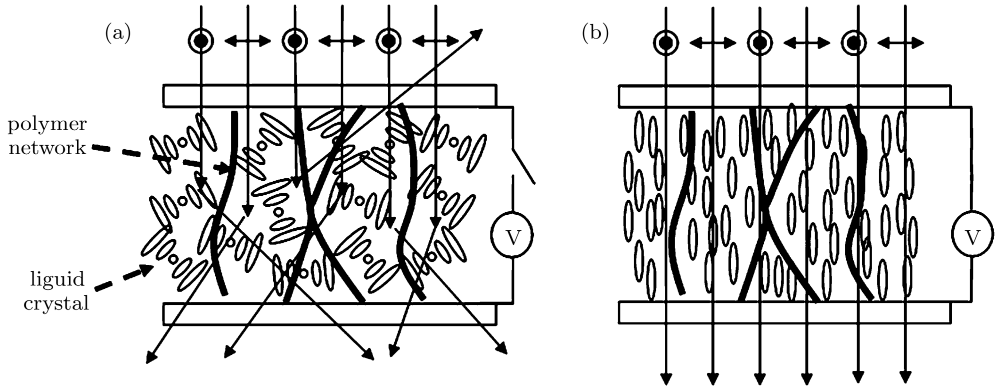

Fig. 3. Schematic principles of the PSCT: (a) off-state, (b) on-state.

The voltage-dependent transmittance curves (V–T curves) of sample series A–D are shown in Fig. 4. The transmittances of the samples in the on-state were very high. According to Fig. 4, we can obtain the parameters such as CR, threshold voltage and hysteresis width.

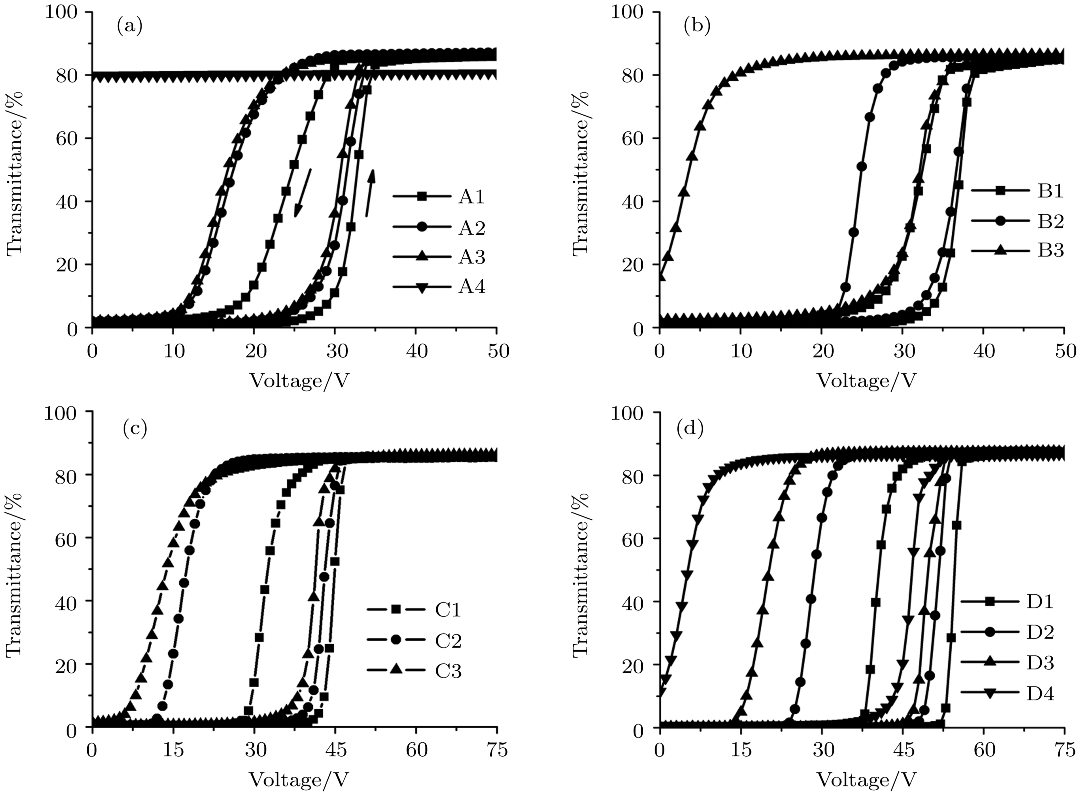

Fig. 4. Voltage-dependent transmittance curves of the samples.

3.1. Contrast ratio

The CR is defined as the ratio of the transmittance in the on-state and off-state. The CR is sensitive to the transmittance in the off-state, we can find that the CR increases with the increase of chiral dopant concentration. For example, the CRs were 173:1, 211:1, 397:1 and 541:1 for the samples A1, B1, C1 and D1 respectively (Fig. 5). Higher CR results from the smaller pitch of the Ch-LC. When the chiral dopant concentration is higher, the pitch is smaller. The domain size of the FCT is smaller. Therefore the scattering of the sample is stronger and the CR is higher.

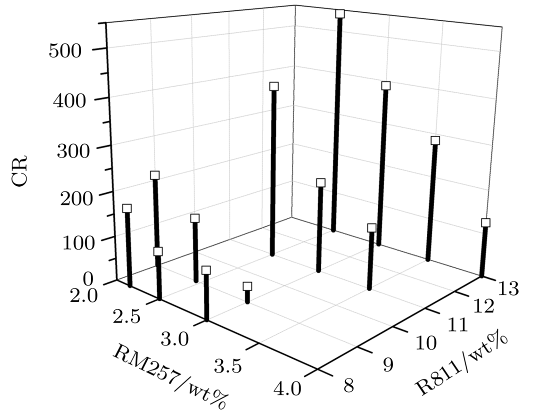

Fig. 5. The CRs of the samples.

The polymer concentration is important to obtain better CR. If the polymer concentration is too much, the LCs would be frozen in the HT by the aligning effect of the perpendicular polymer network.[6,20] For example, there was no FCT when the polymer concentration was 3.5 wt% for A4 sample. The polymer concentration of A4 was so much that there was no electro-optical response in this sample, as illustrated in Fig. 4(a). The film was transparent in the off-state due to the LCs aligned in the HT by the perpendicular polymer network. The electric field cannot reorient the LCs.

3.2. Saturation voltage

The helical structure of the Ch-LC is unwound by an applied electric field. The driving voltage of the LC cell can be described by

$$V_{\text{th}} = \frac{d\pi^2}{P}\sqrt{\frac{K_{22}}{\varepsilon_0\,|\Delta\varepsilon|}}, \tag{2}$$

where V_{th} is the threshold voltage of unwinding the helical structure, d is the cell thickness, K_{22} is the twist elastic constant of the LC, ε_0 is dielectric constant of free space and $\Delta\varepsilon$ is the dielectric anisotropy of the LC.[13] The saturation voltages (V_{90}, a driving voltage at the transmittance of 90% in the increasing V–T curve from the FCT to the HT) of the samples are recorded in Fig. 6. From Eq. (2) and Fig. 6, we can find that the driving voltage increases with the increase of chiral dopant concentration because of the smaller pitch of the Ch-LC. When the film thickness is constant, higher energy (electric field) is required to unwind the smaller helical structure. Therefore the driving voltage is higher.

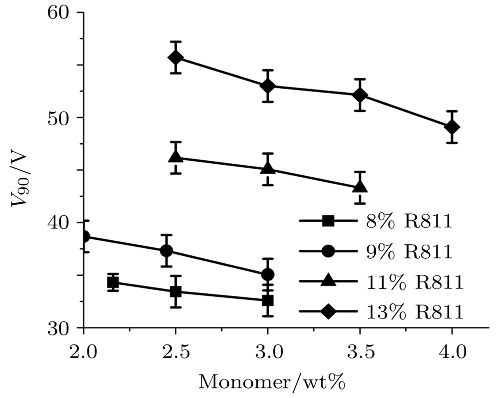

Fig. 6. Saturation voltages of the samples.

Another trend of the saturation voltage is that it decreases with the increase of polymer concentration. This is due to the aligning effect of the polymer fibre on the reorientation of the LCs.[20,21] The aligning effect of the polymer F is proportional to the surface area of the polymer network S and $F \propto S = N2\pi rd$, where N is the numbers of polymer bundles and r is the average radius of the polymer fibre. More polymers give more aligning ability to the LCs to align them perpendicularly. Therefore the driving voltage is lower for the sample with more polymers. The SEM (scanning electron microscope) photos (Fig. 7) with different polymer concentration verify that the polymer network density is higher and the r is bigger when the concentration of the monomer RM257 is higher.

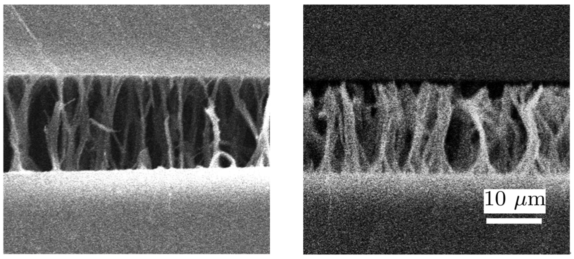

Fig. 7. Side-view SEM pictures of the sample B2 with 2.45 wt% monomer concentration (left) and B3 with 3 wt% monomer concentration (right).

3.3. Hysteresis

The hysteresis width (ΔV) is defined as the width between the half maximum transmittance of the increasing and the decreasing V–T curves. It mainly comes from the polymer aligning effect and does not change significantly with chiral dopant concentration.

As shown in Fig. 8, the driving voltage of the increasing V–T curve decreases and that of the decreasing V–T curve decreases dramatically when the monomer concentration increases, resulting in big hysteresis width value. The values of series D especially can represent the hysteresis phenomenon. For example, the hysteresis width ΔV of the samples D1–D4 were 14, 23, 30 and 42 V with the monomer concentration of 2.5, 3.0, 3.5 and 4.0 wt% respectively. More polymers give more aligning ability to the LCs to prevent them relaxing back to the original focal conic state. Therefore the hysteresis width value is bigger when the polymer concentration is higher. Using this property, the bistable operating method can be realized through a bias voltage in the hysteresis loop.[21] However, a small ΔV value is good to achieve a fast response PSCT.

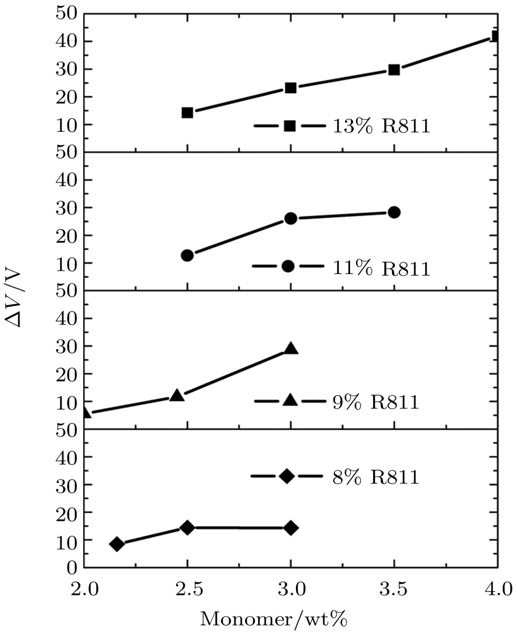

Fig. 8. Hystereses widths of the samples.

3.4. Response time

The response time of turn-on $\tau_{\rm on}$ (applying voltage pulse to make the LCs switch from the FCT to the HT) and turn-off $\tau_{\rm off}$ (removing voltage pulse to make the LCs switch from the HT to the FCT) of samples are expressed as

$$\tau_{\rm on} = \frac{\gamma_1}{\varepsilon_0 \left|\Delta\varepsilon\right| E^2 - K_{22}\pi^2/P^2}, \tag{3}$$

$$\tau_{\rm off} = \frac{\gamma_1 P^2}{K_{22}\pi^2}, \tag{4}$$

where γ_1 is rotational viscosity of the LCs.[13] Typical response time curves of the sample C2 are shown in Fig. 9. The voltage pulse width was 500 ms (from 100 to 600 ms on the time-axis) and the frequency of the electric field was 1 kHz. The turn-on time is defined as the time switched up to 90% of the maximum transmittance from the minimum transmittance (0%–90%). The turn-off time is defined as the time switched down to 10% of the maximum transmittance from the maximum transmittance (100%–10%). From Eqs. (3), (4) and Fig. 9, we can find that the turn-on time is related to the amplitude of the applied field. The higher the applied voltage is, the faster the turn-on time is. The $\tau_{\rm on}$ of the sample C2 were 185, 81 and 52 ms for 50-, 60- and 70-V pulse respectively. The turn-off time is less dependent on the applied field. The $\tau_{\rm off}$ were 44, 45 and 46 ms for the 50-, 60- and 70-V pulse respectively.

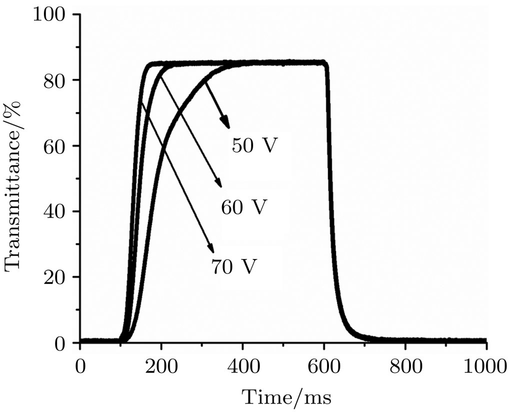

Fig. 9. Typical response times of the sample C2.

A 50-V pulse (500 ms, 1 kHz) was used to drive the sample series A–C and a 70-V pulse (500 ms, 1 kHz) was used to drive the sample series D to measure the response time. The $\tau_{\rm on}$ and $\tau_{\rm off}$ are shown in Fig. 10. These results indicate that the turn-on time decreases and the turn-off time increases when the monomer concentration increases whereas the turn-on time increases and the turn-off time decreases for the samples with same driving pulse and monomer concentration when the chiral dopant concentration increases. We think that the polymer aligning effect influences these response behaviours severely. When the polymer concentrations are same, it needs more energy to unwind the helical structure for the sample with high chiral dopant concentration, therefore the turn-on time increases. On the other hand, it is easier to recover back to the helical structure from the HT to the FCT for the sample with high chiral dopant concentration. Thereby the turn-off time decreases.

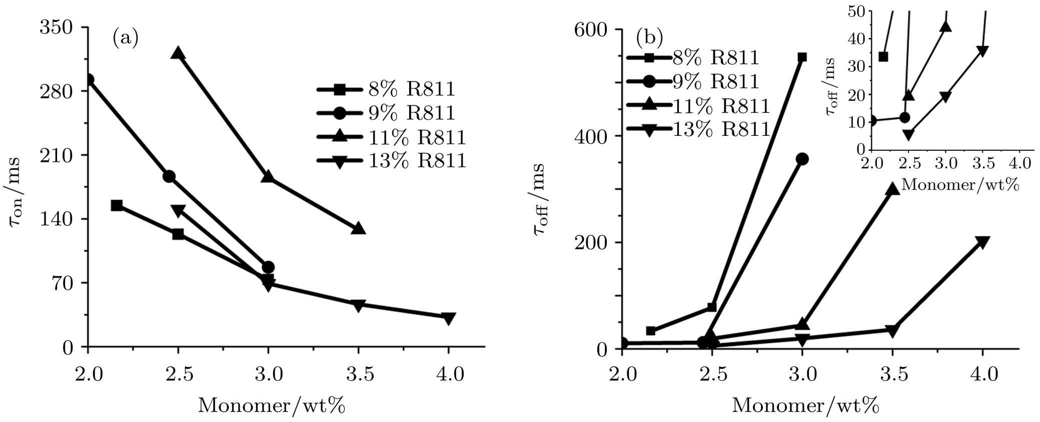

Fig. 10. Response times of the samples: (a) $\tau_{\rm on}$ and (b) $\tau_{\rm off}$. Insert: $\tau_{\rm off}$ from 0 to 50 ms.

Finally, we give a prototype of a switchable normal mode PSCT shutter (15-μm thick, 5 by 6 inch^2) by using the recipe of the sample A1 (see Fig. 11). The off-state showed highly scattering state and the on-state was highly transparent. The CR was 173:1, response times were 155 ms ($\tau_{\rm on}$) and 34 ms ($\tau_{\rm off}$), saturation voltage V_{90} was 34 V and the hysteresis width was 8.5 V. It exhibited good electro-optical properties and these results were achieved under the consideration of each optimized parameter.

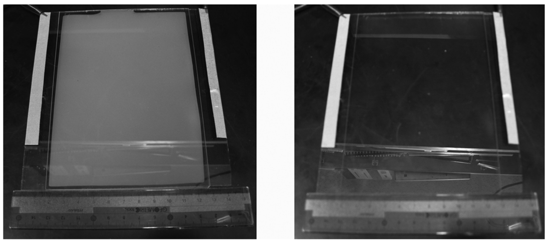

Fig. 11. A prototype switchable shutter in the off-state, $V = 0$ V (left) and in the on-state, $V = 50$ V (right).

4. Conclusions

In conclusion, we studied the effects of chiral dopant and monomer concentrations on the electro-optical properties of normal mode polymer stabilized Ch-LC film. These results illustrate the relationship between the material concentrations and the electro-optical properties of CR, driving voltage, hysteresis width and response time. The CR of the film increases with increasing chiral dopant concentration. The saturation voltage increases with increasing chiral dopant concentration and decreases with increasing polymer concentration. Monomer concentration is critically important for the property of the hysteresis. The value of the hysteresis width is bigger when the monomer concentration is higher. The turn-on response time decreases whereas the response turn-off increases with increasing monomer concentration. When the chiral dopant concentration is higher, the turn-on response time increases whereas the turn-off response time decreases. According to these results, the optimal electro-optical properties can be obtained.

Acknowledgements

The author Ji Ma would like to thank professor D. K. Yang of Kent State University for the helpful advice and discussion.

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