

Gradient polymer network liquid crystal with a large refractive index change

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Abstract: A simple approach for preparing gradient polymer network liquid crystal (PNLC) with a large refractive index change is demonstrated. To control the effective refractive index at a given cell position, we applied a voltage to a homogeneous cell containing LC/diacrylate monomer mixture to generate the desired tilt angle and then stabilize the LC orientation with UV-induced polymer network. By varying the applied voltage along with the cells' movement, a PNLC with a gradient refractive index distribution is obtained. In comparison with conventional approaches using patterned photomask or electrode, our method offers following advantages: large refractive index change, freedom to design specific index profile, and large panel capability. Potential applications include tunable-focus lenses, prism gratings, phase modulators, and other adaptive photonic devices.

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1. Introduction

Polymer network liquid crystals (PNLCs) have been investigated intensively and various photonic devices proposed [1–14]. For different devices, the functionality of polymer network could be quite different. For examples, polymer network could be used to stabilize the LC for an optical switch [1,2,5], shorten the LC response time [11]; broaden the temperature range of blue phases [7,14], or realize gradient refractive index distribution [8–10]. According to the PNLC morphologies, both uniform and nonuniform network distributions can be obtained. Through a proper fabrication process, the latter can generate a spatially gradient refractive index distribution, which is useful for adaptive lenses and prism gratings.

To obtain gradient polymer networks, conventional approach is to expose a homogeneous LC/monomer mixture with an *inhomogeneous* UV light (or laser beam). A denser (looser) polymer network is formed in the region with higher (lower) exposure intensity. When such a gradient PNLC is subject to an external voltage, the LCs in the looser (denser) polymer network region present a larger (smaller) tilt angle due to the weaker (stronger) anchoring force from the polymer network. Therefore, the distribution of gradient refractive index of the PNLC can be varied [8,9]. Because the gradient of PNLC is dependent on the intensity distribution of the exposure light, it is rather difficult to obtain a large refractive index change. Moreover, LCs in looser polymer network region could encounter two problems: slower response time and instability after long term operation. How to overcome these shortcomings is an urgent issue.

In this paper, we demonstrate a new approach to generate large refractive index change across a gradient PNLC cell. We applied a voltage to control the tilt angle of a homogeneous cell containing LC/monomer mixture and then stabilized the LC orientation by a UV light. By repeating the same process at different cell position and different voltage, a large refractive index change can be obtained. In addition, our PNLC exhibits a fast dynamic response, good stability and negligible scattering. These properties are attractive for adaptive lenses, prism gratings, spatial light modulators, and other photonic devices.

2. Device fabrication

Figure 1 depicts the fabrication procedures of the proposed PNLC. First, we injected the LC and diacrylate monomer to a homogeneous cell. The inner surface of the top and bottom substrates is over-coated with an indium-tin-oxide (ITO) electrode, followed by a polyimide alignment layer. The cell is placed on a photomask [Fig. 1(a)]. By applying a voltage ($V = V_1$) to the cell, the LCs and the monomers are reoriented along the electric field direction. The cell is then exposed to a UV light from the bottom side. The exposed area forms network after polymerization, which in turn stabilizes the oriented LCs [Fig. 1(b)]. Next, we lower the voltage to V_2 ($< V_1$) so that the tilt angle of the uncured LC is decreased due to the anchoring of the cell surface. After that, the cell is translated rightward with a short distance. After photo-polymerization, the LC in the exposed region is also stabilized by the formed polymer

network, but with a smaller tilt angle [Fig. 1(c)]. By repeating the same process, the remaining uncured LC can be stabilized by the polymer network in homogeneous state [Fig. 1(d)] if the voltage is below threshold ($V_3 < V_{th}$). Compared to conventional photomask approach, our new PNLC offers three attractive features: 1) maximum refractive index change ($n_e - n_o$) can be obtained, as illustrated in Fig. 1(d), 2) specific index profile can be generated by the applied voltage along with the cell's movement, and 3) a large PNLC panel can be fabricated.

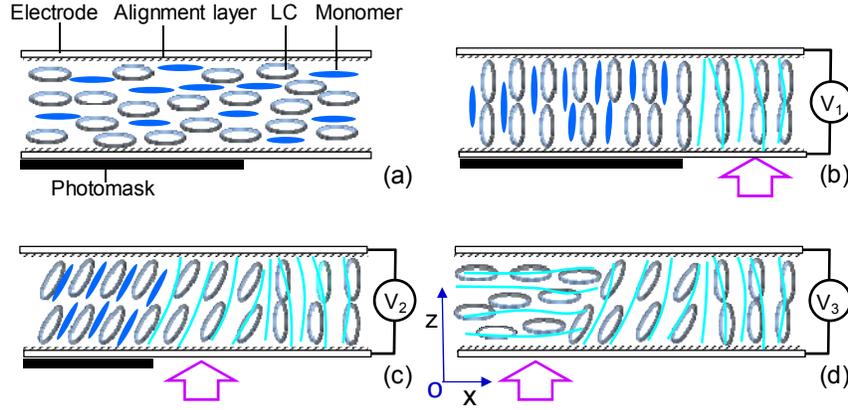


Fig. 1. The fabrication procedures of preparing a PNLC with variable tilt angles. (a) Homogeneous alignment, (b) At $V = V_1$, LC/diacrylate monomer are oriented along the electric field and the monomer in the region without photomask is exposed to UV light. (c) At $V = V_2 (< V_1)$, the cell moves a short distance to the right and the oriented LC is stabilized by the formed polymer network with a smaller tilt angle. (d) Repeat the step of (c) to get a homogeneous polymer-stabilized LC when the voltage is removed or lower than the threshold level.

From Fig. 1, if the applied voltage is decreased gradually and the cell is moved rightward smoothly during UV exposure, then the LC in the polymer network would exhibit a spatially varying tilt angle (or refractive index). For the LC stabilized in homeotropic [right edge of Fig. 1(d)] or homogeneous direction [left edge of Fig. 1(d)], the normally incident linear light (along x -axis) will see the ordinary refractive index (n_o) and extraordinary refractive index (n_e), respectively. Under such a condition, the refractive index change of the PNLC is the highest. Depending on the photomask patterns, various gradient PNLCs can be prepared. For example, an iris diaphragm can be used as a photomask. By gradually opening the iris diaphragm and changing the voltage from low (high) to high (low) during UV exposure, a centrosymmetric gradient PNLC can be obtained. The formed PNLC can function as a positive or negative circular lens.

From Fig. 1(d), the relative phase difference (referenced to n_o) of the normally incident linearly polarized light can be expressed as:

$$\Delta\phi = 2\pi d(n_\theta - n_o) / \lambda, \quad (1)$$

where d is the cell gap, λ is the incident wavelength, and n_θ is the refractive index of the LC with θ tilt angle. At $V = 0$, $n_{(\theta = 0^\circ)} = n_e$, and as $V \rightarrow \infty$, $n_{(\theta = 90^\circ)} = n_o$. From Eq. (1), the gradient of the PNLC is tunable. Due to the surface anchoring of the polymer network, the dynamic response of LC can be significantly improved. Without polymer network, the decay time (free relaxation process) of a homogeneous LC is expressed as [15]:

$$\tau_{o,LC} = \gamma_1 d^2 / (K \pi^2), \quad (2)$$

where γ and K are the rotational viscosity and elastic constant of the LC, respectively. When polymer network is induced in the LC bulk, along the z -axis direction, one can assume that the LC is separated into m equal-spaced layers by the polymer network, where m is determined by the averaged size of polymer network domain. This is an oversimplified model. From Eq. (2), if d is replaced by d/m , then the decay time of a PNLC can be expressed by

$$\tau_{o,PNLC} = \tau_o / m^2. \quad (3)$$

From Eq. (3), the decay time of the PNLC can be significantly decreased if the polymer network density is increased, but a tradeoff is the higher operation voltage [16].

3. Experiment

To fabricate a PNLC cell as Fig. 1(d) depicts, we chose BL038 ($\Delta n = 0.272$, $n_o = 1.527$, Merck) as LC host and RM82 as UV curable diacrylate monomer. Monomer RM82 with reactive double bonds at both sides has two desirable features: rod-like chemical structure and high reorientation order in the LC host. To increase the polymer network stability and minimize the light scattering, we prepared a precursor containing 88 wt% BL038, 11.7 wt% RM82, and 0.3 wt% photoinitiator (IRG-184). The mixture was thoroughly stirred and injected into an antiparallel-rubbed cell by capillary flow. The cell gap and the thickness of the glass substrate are $\sim 6.7 \mu\text{m}$ and 0.7 mm, respectively. In the voltage-off state, the LC and monomer present a homogeneous alignment, as Fig. 1(a) shows.

4. Results and discussions

To determine the bias voltage for UV curing (Fig. 1), we measured the transmittance of the LC cell at $\lambda = 633 \text{ nm}$ (He-Ne laser). The cell was placed between two crossed polarizers with its LC directors oriented at 45° to the optic axis of the front polarizer. The cell was driven by a computer-controlled LabVIEW data acquisition system and the transmitted light intensity was detected by a photodiode. Figure 2 shows the voltage-dependent transmittance (VT) curve of the LC cell. The threshold behavior is smeared because of the relatively large pretilt angle. The total available phase change of the LC cell is $\sim 5.67\pi$ and the decay time was measured to be $\sim 580 \text{ ms}$. To cure the cell with multi-step procedures, we placed the cell on an opaque photomask and used a single-axis translation stage to move the cell in one direction. In each step, we first changed the applied voltage and then translated the cell. After achieving a new stable reorientation, we turned on the UV light to illuminate the unshielded LC/monomer. The UV light intensity was measured to be $\sim 20 \text{ mW/cm}^2$. The relationship among the applied voltage, the traveling distance, and the curing time are shown in Fig. 3. The cell moved six steps in one direction and the traveling distance for each step was $\sim 0.4 \text{ mm}$. The voltage applied to the cell started at $V = 10 V_{\text{rms}}$ and the UV curing time for each step was 1 min, as Fig. 3 shows.

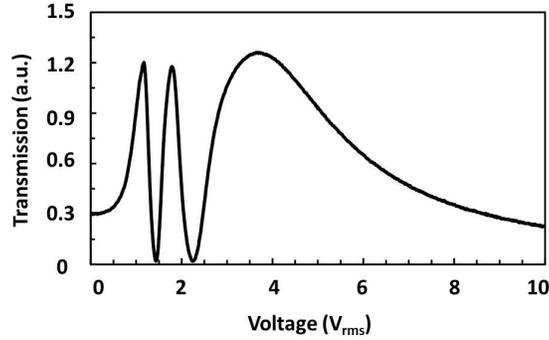


Fig. 2. Measured VT curve of the PNLC cell (before UV curing) between crossed polarizers. $\lambda = 633$ nm.

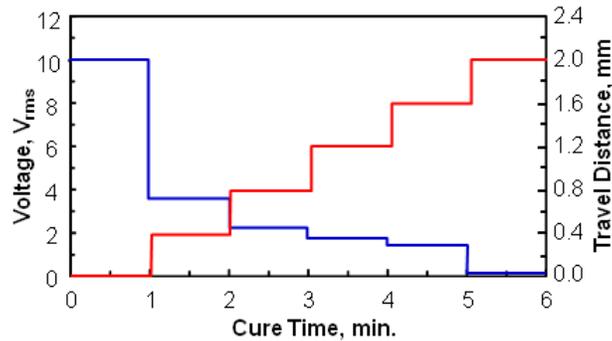


Fig. 3. The voltages applied to the cell (blue), the movement of the cell (red), and the curing time.

The prepared PNLC cell is highly transparent in the voltage-off state ($V = 0$). To check how the applied voltage affects the formed PNLC, we observed the birefringence colors under a polarizing optical microscope (POM) in the transmissive mode. The cell was placed on the microscope stage between two crossed polarizers. The rubbing direction of the cell was oriented at 45° with respect to the transmission axis of the linear polarizer.

Figures 4(a) and 4(b) show the observed birefringence color stripes at $V = 0$, in which the stripes are taken in a consecutive region and a total of seven color stripes are presented. The top-left stripe in Fig. 4(a) was cured at $V = 10$ V_{rms} (1 kHz) and the bottom-right stripe in Fig. 4(b) was cured at $V = 0$. From the top-left to bottom-right, the colors are distributed in the order of orange, red, blue, green, orange, magenta, and green, implying the tilt angles of LCs in the PNLC are different and the oriented LCs are well stabilized by the polymer network. Different from conventional PDLC whose scattering at $V = 0$ is over 90%, in a PNLC we used a rod-like monomer (RM82) with a ~ 12 wt% concentration. Because of surface rubbing, the LC domains present homogeneous-like alignment. Since the LC domains are not fully confined by the formed polymer network, light scattering can be suppressed to below 10% [17].

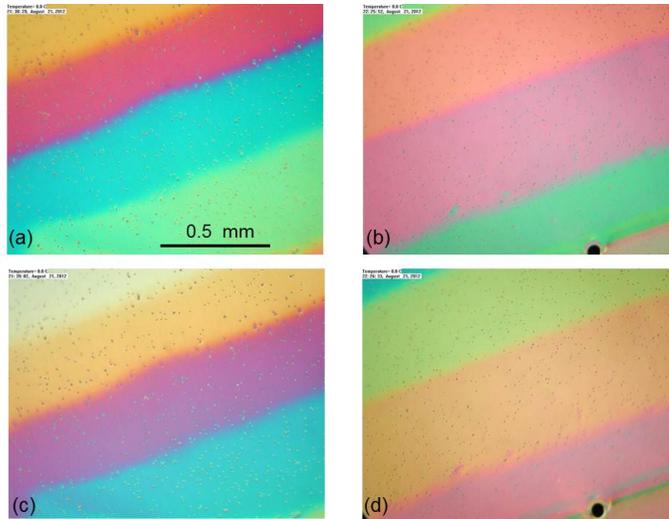


Fig. 4. The UV cured cell observed using POM: (a) and (b) show the color of seven stripes at $V = 0$ (Media 1, Media 2), (c) and (d) show the color of seven stripes at $V = 50 V_{rms}$.

When a voltage is applied to the cell, the LC directors are reoriented by the electric field. As a result, the color of each stripe is changed. Figures 4(c) and 4(d) show the color change of each stripe at $V = 50 V_{rms}$. Again from the top-left in Fig. 4(c) to bottom-right Fig. 4(d), the colors are distributed in the order of mutual grey, orange, red, blue, green, orange, and magenta. The color of the stripes shifts along the direction from the top-left (high curing voltage) to the bottom-right (low curing voltage). To visually observe the color change of the stripes, two movies were recorded in Fig. 4(a). At 40V square pulses, the color of each stripe shifts to that of its adjacent stripe (Media 1), while at 60V square pulses, the color of each stripe jumps over that of the neighbor stripe and move to the next (Media 2). As shown in the two movies, the PNLC sample can fully return to its original state in each cycle. We also tested the stability of the PNLC cell and found that after several hundreds of cycles (from 0 to 60 V_{rms}) the PNLC can still return to its original state. Due to the high density of polymer network, the response time of our stripe-patterned PNLC is very fast. For a π phase shift, the decay time was measured to be ~ 1 ms. From Eq. (2) and Eq. (3), m is calculated to be ~ 24 and the average domain size is estimated to be $\sim 0.27 \mu\text{m}$.

A PNLC with stripe (or zone) patterns is favorable for Fresnel lens and grating [18–20]. In addition, a gradient PNLC can also be prepared if the applied voltage and the cell's traveling distance are linearly changed during UV exposure. To prepare such a PNLC, the same LC/monomer mixture was filled into another 6.7- μm -thick homogeneous cell. Figure 5 shows the relationship between applied voltage, cell's traveling distance and curing time. The travelling velocity of the cell is $\sim 5 \mu\text{m/s}$. The highest bias voltage applied to the cell is 3V and the traveling distance is 1.5 mm.

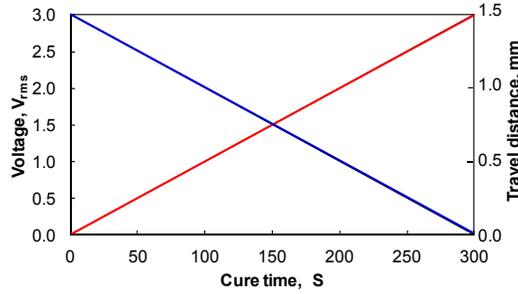


Fig. 5. The voltage applied to the cell (blue), the movement of the cell (red), and the curing time.

At $V = 0$, the observed color stripes of the PNLC under POM are shown in Fig. 6(a). The top-left region (red color) was cured at $3 V_{\text{rms}}$ and the bottom-right region (red color) was cured at $V = 0$. Along the diagonal direction, this PNLC shows nearly two cycles of the color change (from red to red) and the color changes continuously in each cycle, implying that the PNLC presents a gradient phase (or refractive index) difference. The transmittance (normalized to two parallel polarizers) of the PNLC cell between two crossed polarizers is expressed by [21]:

$$T = \sin^2 \frac{\pi d (n_{\theta} - n_o)}{\lambda}, \quad (4)$$

From Eq. (4), the red stripes will appear when the effective refractive index (with tilt angle θ) satisfies the following relation:

$$n_{\theta} = n_o + \left(p - \frac{1}{2}\right) \frac{\lambda_{\text{red}}}{d}, \quad (5)$$

where p is an integer and λ_{red} is the wavelength of the red light. If $\lambda_{\text{red}} = 0.65 \mu\text{m}$, $d = 6.7 \mu\text{m}$, when $p = 1, 2$, and 3 , n_{θ} is calculated to be $1.58, 1.67$, and 1.77 , respectively. These three refractive indices are obtainable for LCs oriented with a small or zero tilt angle (BL038 $n_o = 1.527$, $n_e = 1.799$). Also from Eq. (5), the phase difference between two adjacent red stripes is 2π , so the phase difference within three red stripes at $V = 0$ is $\sim 4\pi$, which is very close to that shown in Fig. 2 ($\sim 4.2\pi$ phase retardation when the voltage increases from 0 to $3 V_{\text{rms}}$). Compared to the previous fabrication procedures of gradient PNLC, in which the gradient refractive index distribution is formed by exposing UV light through a patterned photomask [8] or hole-patterned electrodes [22], our approach offers a possibility to get PNLC with the largest refractive index change (i.e., from n_e to n_o) under a given precursor.

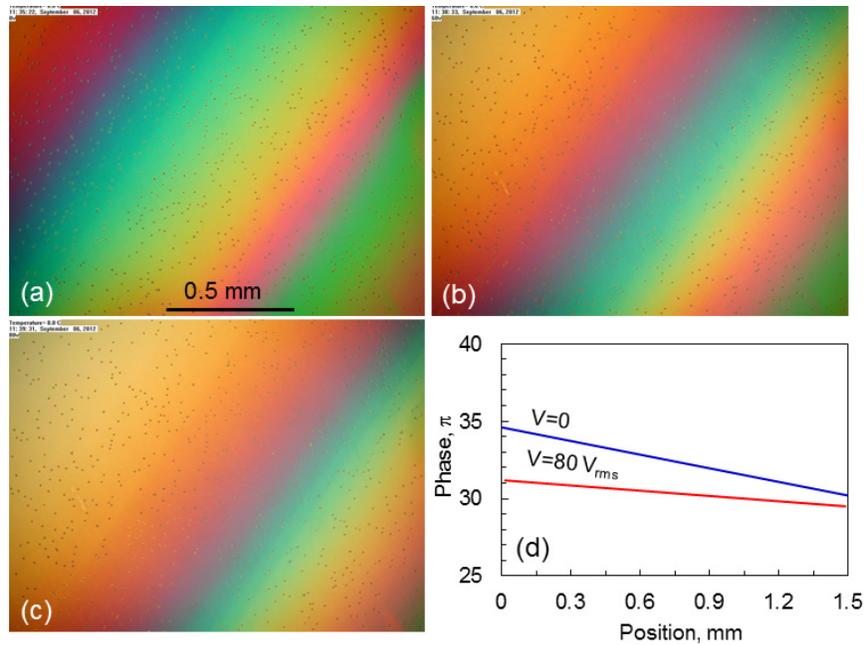


Fig. 6. The observed PNLC color at (a) $V = 0$, (b) $V = 50 V_{rms}$ (c) $V = 80 V_{rms}$ (Media 3), and (d) the measured phase difference across the cured region with a 1.5-mm width (travel distance).

By applying various voltages to the PNLC cell, the phase gradient of the PNLC can be changed as well. At $V = 10 V_{rms}$, the color starts to shift along the direction from top-left to bottom-right. At $V = 50 V_{rms}$, a distinct color shift is observed (Fig. 6(b)), indicating that the phase gradient of the PNLC is decreased. At $V = 80 V_{rms}$ the gradient of the PNLC is largely decreased as a much loose color distribution is observed (Fig. 6(c)). LCs in the top-left region is highly reoriented along the electric field, so this region presents a mutual color. Media 3 shows the dynamic color change of the PNLC when it is switched between 0 and $80 V_{rms}$. Similar to the first PNLC cell, the second cell can be driven cycle by cycle with good color stability, fast response time and negligible light scattering. The measured phase gradient of the PNLC is shown in Fig. 6(d). At $V = 0$, the PNLC exhibits the largest phase gradient. At $V = 80 V_{rms}$, the phase gradient is largely decreased. If the voltage is continuously increased, the phase gradient can be further decreased.

In Fig. 6(a), the color distribution in the PNLC across the 1.5-mm-width of the cured region is quite loose. To contract the color distribution, one approach is to decrease the cell's traveling distance and increase the voltage gradient during UV exposure. Another approach is to increase the cell gap, as depicted in Eq. (1). As a result, the phase difference ($\Delta\phi$) across the cured region can be increased, but the voltage to tune the gradient of the PNLC will increase accordingly. Depending on the photomask patterns, our gradient PNLC can be used to prepare various adaptive photonic devices, such as prism gratings and Fresnel-zone/circular/lenticular lenses. Due to high diacrylate monomer concentration, the formed PNLC presents good stability, fast response and negligible light scattering.

Exposure time, UV intensity and LC concentration do affect the electro-optical properties (response time, operating voltage) and the gradient refractive index distribution (stripe colors) of the formed PNLCs. In our experiments, since the UV intensity is $\sim 20 \text{ mW/cm}^2$ the exposure time is already long enough to fully polymerize the monomer and fix the oriented LC molecules. A longer curing time will not cause too much difference in the polymerization. But if the UV intensity is too high, the operating voltage will increase due to a thinner and denser polymer network. If it is too low, the monomers cannot be fully polymerized and the

polymer network structure will not be stable. Moreover, LC (or monomer) concentration is also a critical parameter for the polymer network structure. Generally speaking, a high LC concentration will induce large polymer domains along with light scattering and performance degradation. While a low LC concentration will lead to fast relaxation, high operating voltage and small effective phase shift. In our experiments, ~88 wt% BL038 concentration is close to the optimal condition. Detailed investigation about the impact of UV curing time, UV intensity and LC concentration is certainly important, but it is beyond the scope of this paper.

For a given precursor, the number of steps, distance of each step and applied voltage during UV exposure play important roles in establishing the gradient of the refractive index change across the curing range. Here we just give two examples of the proposed approach: 1) 6 steps of 0.4 mm each (Fig. 3) and 2) continuous traveling (Fig. 5). The voltage applied to the cell during UV exposure can be determined according to the VT curve shown in Fig. 2 and it affects the maximal phase change of the PNLC. As shown in Figs. 5 and 6, when the applied voltage decreases from 3 V_{rms} to zero, the maximal phase change of the PNLC decreases to $\sim 4\pi$. Therefore, our approach offers more freedom to design the moving trail along with the voltage applied to the cell during UV exposure, based on the specific requirements. The cell's travelling speed itself does not affect the formed PNLC morphology. However, given a fixed total traveling time a faster travelling speed leads to a smoother gradient of the refractive index change. While given a fixed travelling distance, a faster travelling speed leads to a shorter curing time. It is not a concern if the UV intensity is high enough to fully polymerize the monomers, otherwise, the formed polymer network structure will not be stable. Because the phase separation process is rather complicated, it is challenging to optimize all the parameters (e.g. LC/monomer concentration, curing time/intensity, moving trail/speed, applied voltage) at once.

5. Conclusion

We have demonstrated a simple approach to prepare a gradient PNLC with large refractive index change, in which the LCs are first reoriented by voltages and then stabilized by the UV-induced polymer network. The spatial refractive index change of such a PNLC depends on the applied voltage along with the cell's movement during UV exposure. Based on this approach, various PNLCs can be prepared by using different photomasks. Due to uniform distribution and high density of polymer network, our PNLC shows good stability and fast response. To enlarge the refractive index change of PNLC, two simple methods can be considered: decreasing the cell's travel distance during UV exposure and increase the cell gap. Our PNLC with a large refractive index change has attractive applications in prism gratings, adaptive lenses, Fresnel zone lenses, and other adaptive photonic devices.

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