

Review

# Photochemical On–Off Switching of One-Dimensional Photonic Crystals Consisting of Azo-Functionalized Liquid Crystal Polymer and Polyvinyl Alcohol

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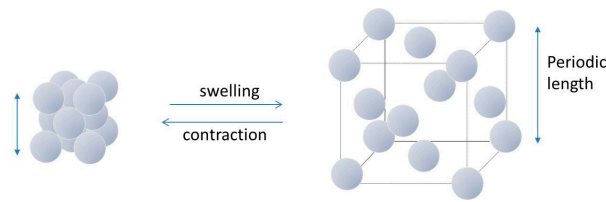
**Abstract:** One-dimensional (1D) photonic crystals (PCs) are prepared from multi-bilayered films stacked with alternating azo-functionalized liquid crystal polymer (PAz) films and polyvinyl alcohol (PVA) films. Reflection with a wavelength that depends on the thickness of the films is observed, and the reflection can be turned on and off by switching between the two states, based on whether there is a difference in the refractive index between the two films. The refractive index change of PAz can be photochemically caused by a phase transition, based on the alignment states of the liquid crystal (LC). In this review, we focused on an effective photo-induced on–off switching approach in 1D PCs using LC properties and described the basic optical and chemical principles, the experimental results, and further optimizations.

**Keywords:** photonic crystal; azobenzene; liquid crystal; multilayered film; molecular orientation; photochemical switching; refractive index

## 1. Introduction

The structural color that comes from the interaction of light with highly-ordered nanostructures is highly iridescent, vivid, and extremely resistant to oxidation and degradation. Some natural examples can be found in peacock feathers, Morpho butterflies, neon tetra fish, the shining wings of some insects, and natural opals. If a stimuli-responsive structural color could be artificially created, this material would be an excellent candidate for optical applications, such as photonic chips, optical transistors and circuits, and display devices. The artificial periodic structures are called photonic crystals (PCs) or photonic band gap (PBG) structures.

The structural color determined by the structural periodicity mainly depends on the refractive indices and periodic lengths of the constructed materials [1–5]. There are many reports on the tuning of structural color by deformation of PCs, with periodic length changes during swelling and contraction. For example, three-dimensional (3D) periodic structures are self-assembled by long-range electrostatic repulsions of colloidal particles [6–11]. PBG tuning can be achieved by controlling the spatial structure, as shown in Figure 1. This is usually accomplished by taking advantage of the volume phase transition of hydrogels, caused by temperature, pH, ionic state, or external mechanical forces [12–20]. However, imperfections in recovery and deformation in the order of micrometers are disadvantages for repetitive control of the lattice constant, resulting in difficulties in practical applications.



**Figure 1.** Lattice constant change of 3D photonic crystals (PCs) constructed by self-assembled colloidal particles.

On the other hand, PBG tuning can be achieved by refractive index changes. Since refractive index is an inherent property of materials, it can be changed by exchanging the material or using a birefringent material. Firstly, in the example of exchanging materials, it has been reported that PBG changes by infiltrating a different solvent into the voids of PCs [21,22]. This is interesting for color display applications that involve writing and erasing because the solvent that penetrates the voids can be used as ink. Secondly, liquid crystals (LCs) are well known as materials with birefringent properties. Since the birefringence of LCs is fairly large, usually 0.1 to 0.2, a change in refractive index, based on a change in LC molecular orientation, is sufficient for PBG switching. PBG tuning by refractive index change is not accompanied by structural deformation, so it is expected to have excellent repeated durability. In this review, we focus on 1D PCs and introduce the basic optical and chemical principles of PBG tuning by refractive index change, based on LC orientation. In addition, the experimental results and further optimizations are described [10,23–29].

## 2. PBG Tuning by Refractive Index Change

An example of a simple PC is a multilayered film with a refractive index difference between alternating layers. For multilayered films, such as 1D PCs, the wavelength of reflected light can be described by the Bragg–Snell law, expressed by the following equation [30]:

$$m\lambda = 2a \sqrt{n_1^2 \frac{d_1}{a} + n_2^2 \frac{d_2}{a}}, \quad (1)$$

where  $n_1$  and  $n_2$  are the refractive indices of 1 and 2, respectively,  $d_1$  and  $d_2$  are the thickness of single layers 1 and 2,  $a$  is the thickness of each bilayer in which 1 and 2 are stacked, and  $m$  is an integer termed the diffraction order. This suggests that the reflection wavelength ( $\lambda$ ) can be controlled by changing the film thickness and refractive index of the material.

On the other hand, the reflectance,  $R$ , of the multilayer film normal to the incident light is given by the following equation [30,31]:

$$R = \left[ \frac{1 - (n_H/n_L)^{2q} (n_H^2/n_S)}{1 + (n_H/n_L)^{2q} (n_H^2/n_S)} \right]^2, \quad (2)$$

where  $n_S$  is the refractive index of the substrate,  $n_H$  and  $n_L$  are the high and low refractive indices of the materials in each bilayer, respectively, and  $q$  is the number of bilayers. From Equation (2), it can be seen that the greater the difference in refractive index between  $n_H$  and  $n_L$ , the higher the reflectance. In addition, if  $n_H$  and  $n_L$  are almost equal, the reflectance is very low. Therefore, reflection can be switched on and off by switching between two states, where the refractive indices of the two materials in the bilayer are equal ( $n_H \approx n_L$ ) and different ( $n_H \neq n_L$ ), as shown in Figure 2.

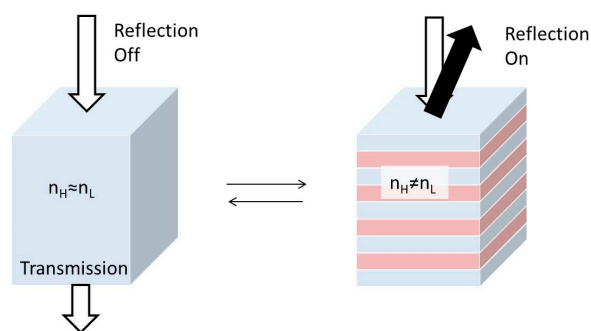


Figure 2. On–off switching of the reflection for the multilayered films of 1D PCs.

### 3. Refractive Index Change Based on LC Molecular Orientation

The refractive index of LC depends on the polarization direction. When anisotropic LC molecules are aligned vertically, linearly polarized light, with its electric vector oscillating in the vertical and horizontal directions, respectively, detects an extraordinary refractive index,  $n_e$ , and an ordinary refractive index,  $n_o$ , as shown in Figure 3. Thus, the birefringence of LCs,  $\Delta n = (n_e - n_o)$ , can be utilized by polarized observation [32]. On the other hand, the refractive index of isotropic states ( $n_{iso}$ ) is generally between  $n_e$  and  $n_o$ . Therefore, the difference in refractive indices is also caused by a phase transition between LC and isotropic phases.

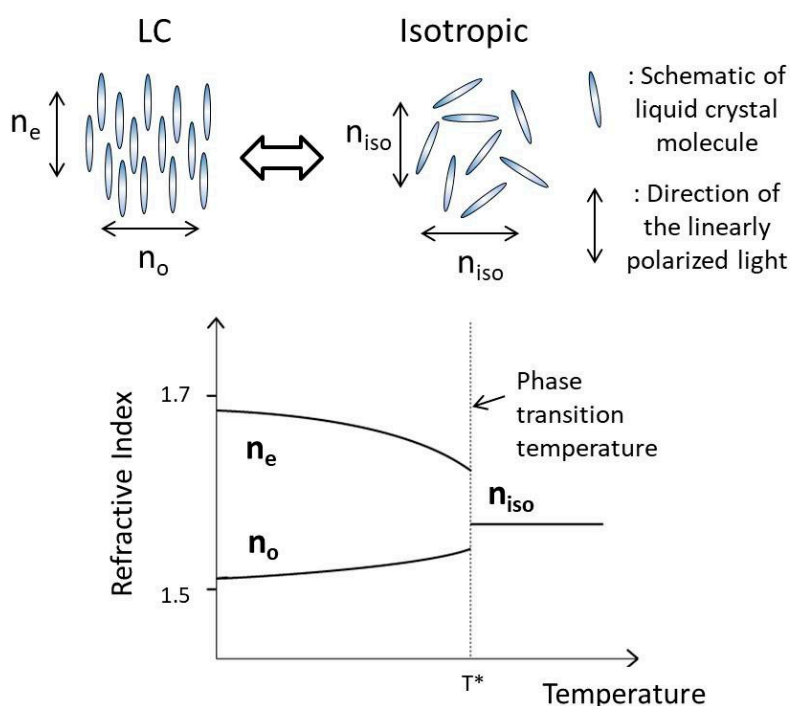


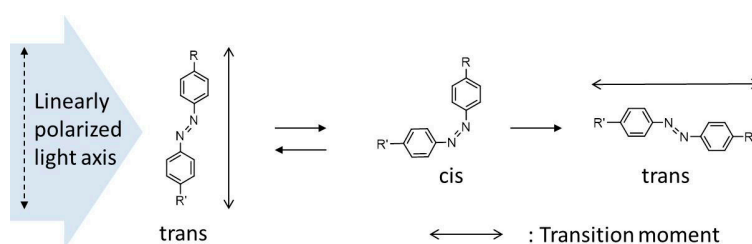
Figure 3. The refractive index change based on the molecular orientation of azobenzene liquid crystals (LC).

The Azobenzene group exhibits excellent photochromic properties and is also well known as a command material for the LC orientation [33–35]. The trans form of the azobenzene group has a rod-like shape, which stabilizes the aligned LC phase, while the cis form, as the isomer, has a bent shape and tends to destabilize the alignment state formed by the trans form, ultimately leading from the LC state to the random state. In other words, phase transition can be induced isothermally by photochemical reaction under light irradiation. The cis form generated by UV light is converted to the

thermally stable trans form. However, the cis-to-trans isomerization that occurs in the random state hardly changes the refractive index.

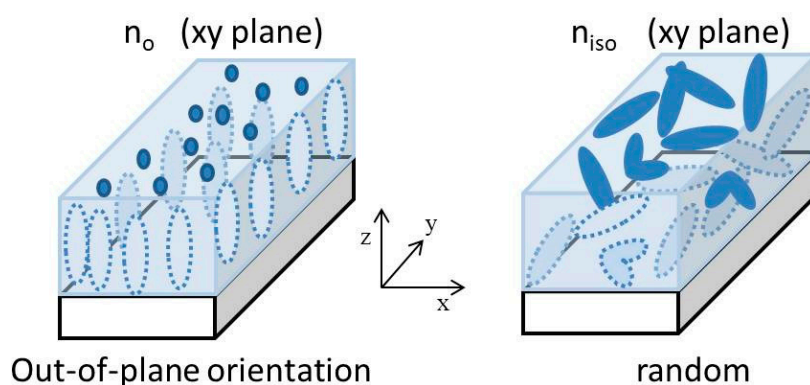
#### 4. Photoselective Molecular Orientation

The refractive indices of LC films are determined by molecular orientation states, and the molecular orientation of azobenzene molecules can be easily controlled by polarized light. When the transition moments of trans azobenzene molecules are parallel to the polarization direction, they are very effectively activated to the excited state, leading to trans-to-cis isomerization. If the transition moments are perpendicular to the polarization direction, the actinic light is inert to isomerization. As shown in Figure 4, as a result of repeated trans–cis–trans isomerization cycles, there will be an accumulation of azobenzene molecules aligned perpendicularly to the polarization direction, because the  $\pi$ – $\pi^*$  transition moment of the azobenzene group is almost parallel to the long axis of the molecule. This angular dependence on linearly polarized light is known as the Weigert effect [36,37].



**Figure 4.** Photoselective orientation of azobenzene molecules via photoisomerization.

On the other hand, for unpolarized light, only the propagation direction is generally perpendicular to the electric vector of the light. When irradiated with unpolarized visible light, the azobenzene molecules are expected to align only in the direction of propagation of the actinic light, indicating out-of-plane orientation behavior of the trans azobenzene molecules [38]. When the monitoring light is perpendicular to the film plane, the refractive index of the plane normal to the monitoring light is involved in the monitored reflection. Therefore, as shown in Figure 5, the effective refractive indices for the out-of-plane orientation and random state, respectively, correspond to  $n_o$  and  $n_{iso}$ , which generally exhibit different values. This means that the difference in refractive indices is detectable without a polarizer. In this sense, actinic unpolarized light is simple and is expected to lead to a new methodology for 3D molecular manipulation using light.

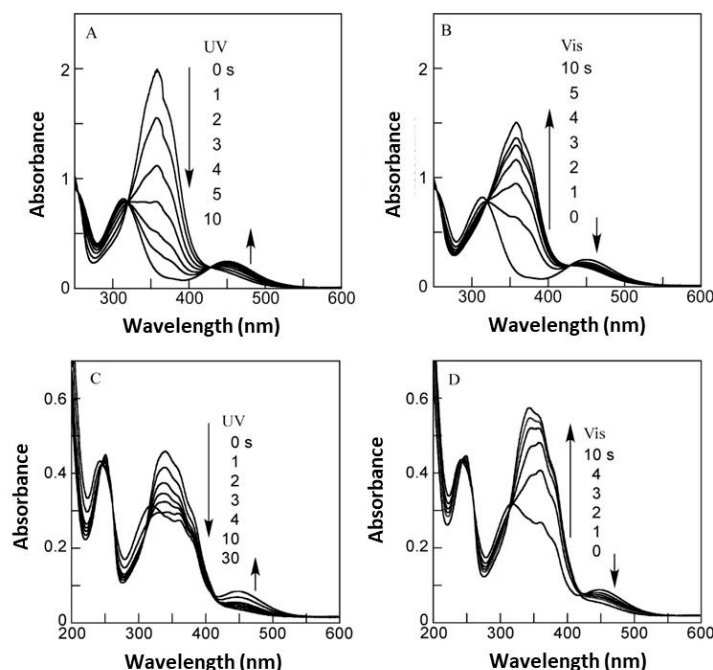


**Figure 5.** Refractive indices of the out-of-plane orientation and random state. The film plane (xy plane) is normal to the monitoring light.

## 5. Out-of-plane Orientation of Azobenzene LC Polymer

For azo-functionalized liquid crystal polymer (PAz) solid films stored at room temperature, below  $T_g$ , the alignment remains almost unchanged even after several years. This is one of the reasons that PAz is expected to be useful in optical applications. However, unlike low molecular weight LCs, orientation characteristics and photoresponse properties of polymeric LCs are greatly affected by the polymeric structure, such as the backbone chain structure, side-chain spacer length, and end groups [37,39–41]. For example, the out-of-plane orientation characteristics of azobenzene polymers are completely different only by the difference in the main chain of methacrylate and acrylate [29,39]. Herein, the dependence of the out-of-plane orientation of PAz on the different methylene spacer lengths of the side-chains is specifically described.

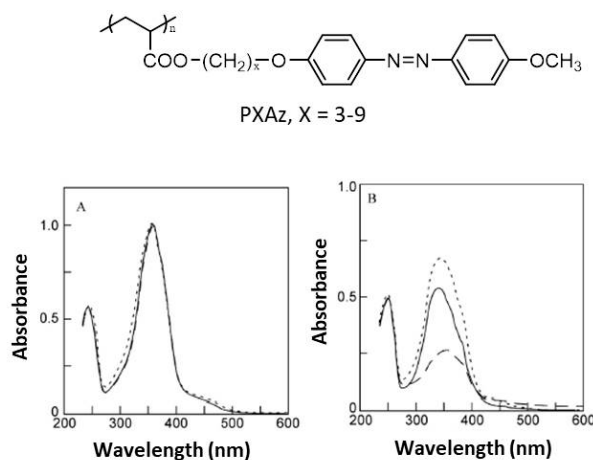
As shown in Figure 6, the absorption spectra of solutions and films containing azobenzene molecules are characterized by a strong  $\pi$ – $\pi^*$  transition band at around 360 nm and a weak band at around 450 nm, corresponding to  $n$ – $\pi^*$  transition. Irradiation with ultraviolet (UV; 365 nm) light decreased the absorbance at 360 nm but slightly increased the absorbance at 450 nm, indicating trans-to-cis photoisomerization. Conversely, the opposite situation was observed by irradiation of visible light (436 nm).



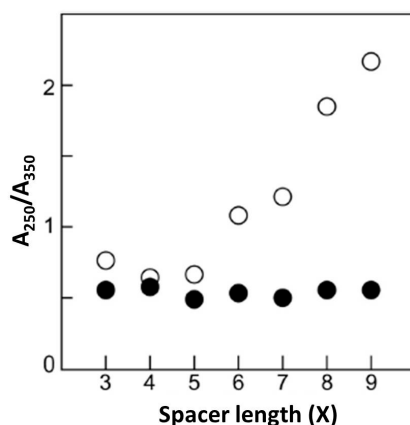
**Figure 6.** Changes in the absorption spectra of azo-functionalized liquid crystal polymer with six of the methylene spacer length (P6Az) in chloroform solution (A,B) and solid film (C,D) by irradiation of UV light (365 nm, 10 mW/cm²) (A,C) and following visible light (436 nm, 58 mW/cm²) (B,D). Source: Yagi et al. 2014 [42]. Copyright 2014. Reprinted with permission from Elsevier Ltd.

On the other hand, the absorbance of the films can give information about the out-of-plane orientation. The relative intensities of the  $\pi$ – $\pi^*$  absorption band at around 350 nm to the  $\sigma$ – $\sigma^*$  absorption band at around 250 nm is indicative of the degree of the out-of-plane orientation of the azobenzene molecules in solid film [42]. As shown in Figure 7, absorption at 360 nm decreases with longer spacer length for the freshly prepared film. When plotting the relative intensities of the absorbance at 250 and 350 nm ( $A_{250}/A_{350}$ ), it is apparent that it increases with increasing spacer length, as shown in Figure 8. As a result, it is demonstrated that the azobenzene polymer with longer methylene spacers tends to be in the out-of-plane orientation. It is considered that the effects of polymer

chain motion on side-chain motion, and the flexibility of side-chain groups, are largely involved in the formation of the out-of-plane orientation.



**Figure 7.** Schematic molecular structure of the azo-functionalized liquid crystal polymer with the different methylene spacer length (PXAz, X is the methylene spacer length, 3 to 9) and the absorption spectra of PXAz (X = 3, 6, 8) in chloroform solution (A) and film (B). Source: Yagi et al. 2014 [42]. Copyright 2014. Reprinted with permission from Elsevier Ltd.



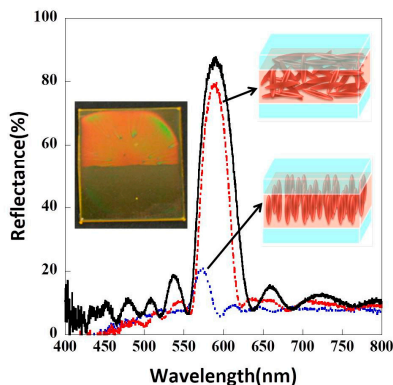
**Figure 8.** The plot of intensities of absorbance at 250 nm relative to absorbance at 350 nm ( $A_{250}/A_{350}$ ) of the chloroform solution (closed circle) and solid film (open circle) against the PXAz methylene spacer length, X. Source: Yagi et al. 2014 [42]. Copyright 2014. Reprinted with permission from Elsevier Ltd.

## 6. On–Off Switch of PBG Based on Molecular Orientation State

The multi-bilayered films with azo-functionalized liquid crystal polymer with different methylene spacer length (PXAz, X is the methylene spacer length of 3 to 8) and polyvinyl alcohol films (PVA) could be fabricated by alternative spin coating, due to the immiscible properties between hydrophobic and hydrophilic solutions [30,42–46]. The refractive indices of the randomly oriented PAz film and PVA film are 1.60 and 1.49, respectively. The thickness of the stacked bilayers of PAz and PVA layers was adjusted to be about 1/4 of a reflection wavelength, according to Equation (1). For the freshly prepared 20-multi-bilayered films of P6Az and PVA, the apparent initial reflectance was about 90%. This is consistent with the result calculated in Equation (2), when P6Az was expected to be randomly oriented.

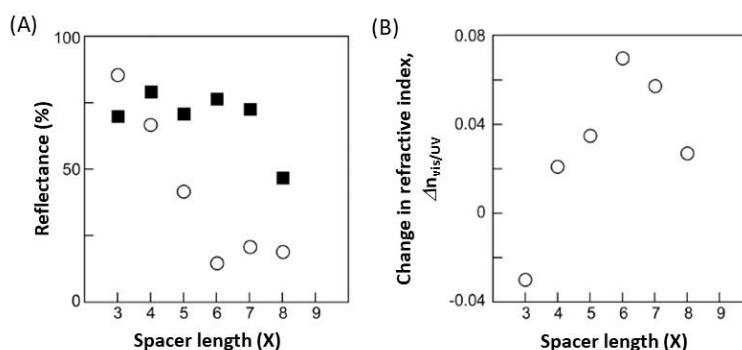
On the other hand, by irradiation of visible light, the reflectance was decreased, as shown in Figure 9. It is assumed that the reason for this is that the refractive index gap between the PAz and PVA layers disappeared. By irradiation of visible light normal to the plane, the random orientation of P6Az is converted to the out-of-plane orientation, as described in Section 4. The ordinary refractive indices

of P6Az,  $n_o$ , were estimated to be 1.48. As a result, the refractive index of the P6Az layer is almost the same as that of PVA [29], which means that there is no difference in refractive indices between PAz and PVA layers. Conversely, it was demonstrated that the reflectance was recovered by UV-light irradiation to induce the random state from the out-of-plane orientation of P6Az.



**Figure 9.** Change in reflection spectra of the P6Az/polyvinyl alcohol films (PVA) 20-multi-bilayered film before (black solid line) and after irradiation of unpolarized visible light (436 nm, 140 mW/cm<sup>2</sup>, 10 min; blue dotted line) and following UV light (365 nm, 40 mW/cm<sup>2</sup>, 10 min; red dash-dot line) [42].

When on–off switching of the reflection by UV and visible light, the photochemical changes in the refractive indices of the PXAz ( $X = 3–8$ ) layers,  $\Delta n_{\text{vis/UV}}$ , are plotted against the spacer length, as shown in Figure 10B. The plot is described by calculation according to Equation (2), using the reflectance given in Figure 10A, which is the experimental data [42]. With the increase in the spacer length up to 6,  $\Delta n_{\text{vis/UV}}$  was increased and P6Az showed the highest  $\Delta n_{\text{vis/UV}}$ . The spacer length of 6 is proper for the photo-induced random state from the out-of-plane orientation by UV-light irradiation. On the other hand,  $\Delta n_{\text{vis/UV}}$  decreased as the spacer length of PXAz ( $X = 3–8$ ) increased beyond 6. It is assumed that the azobenzene groups that have longer spacers have stronger molecular interactions between azobenzene groups, and thus, a weak dissociation effect of trans–cis isomerization led to a poor response. Therefore, it is demonstrated that the order of the out-of-plane orientation, as well as the molecular motion to destroy molecular interactions, are important factors for on–off switching using refractive index differences.



**Figure 10.** Change in reflectance of the PXAz ( $X = 3–8$ )/PVA 20-multi-bilayered film by irradiation with unpolarized visible light (436 nm, 140 mW/cm<sup>2</sup>, 15 min; open circle) and following UV light (365 nm, 40 mW/cm<sup>2</sup>, 15 min; closed square) (A) and calculated refractive indices (B) of PAz against the methylene spacer length from three to eight. Source: Yagi et al. 2014 [42]. Copyright 2014. Reprinted with permission from Elsevier Ltd.

## 7. Cooperative Orientation of LC Copolymer

In order to further improve the photoresponse characteristics, it is necessary to solve the problem that most of the incident light is absorbed near the surface, blocking the transmission due to azobenzene molecules with high absorbance. As the azobenzene molecule is well known as a command molecule for LC orientation, it is considered that the concentration of azobenzene molecules can be reduced by utilizing the cooperative effect between LC molecules.

On the other hand, when the azobenzene copolymer with LC mesogen groups is employed for multi-bilayer film, LC mesogen must be selected in consideration of a high refractive index, as well as good cooperative motion with azobenzene groups. The diphenylacetylene (tolane) group has been reported to exhibit a high extraordinary refractive index based on high conjugation along the molecular long axis, contributing to an increase in the average refractive index and birefringence of the azobenzene copolymer containing the tolane group, P6Az–tolane (Figure 11) [47–50]. Figure 12 shows the improvement of light response properties for multi-bilayered films consisting of P6Az–tolane instead of P6Az [51]. For 436 nm visible light, the reflection for all films decreased and the response speed of reflection was faster for the P6Az–tolane copolymer than the P6Az homopolymer, indicating improvement of out-of-plane orientation behaviors in the multi-bilayered films. For 365 nm UV light, the light response of the P6Az–tolane copolymer was faster than that of the P6Az homopolymer, indicating improvement of random orientation behavior attributed to light penetration deep inside. Furthermore, during photo-induced on–off switching, the P6Az–tolane copolymer showed improvement of the reflection contrast as shown in Figure 13, owing to a better orientation behavior and higher refractive index. The reflection change by alternate irradiation of UV and visible light can be performed without any degradation and structural deformation, providing the reliability advantage.

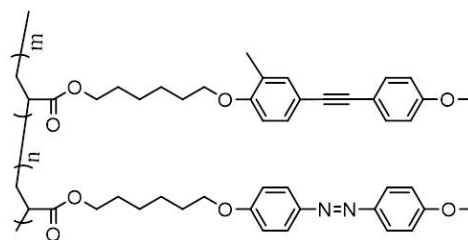


Figure 11. Schematic molecular structure of the P6Az–tolane copolymer.

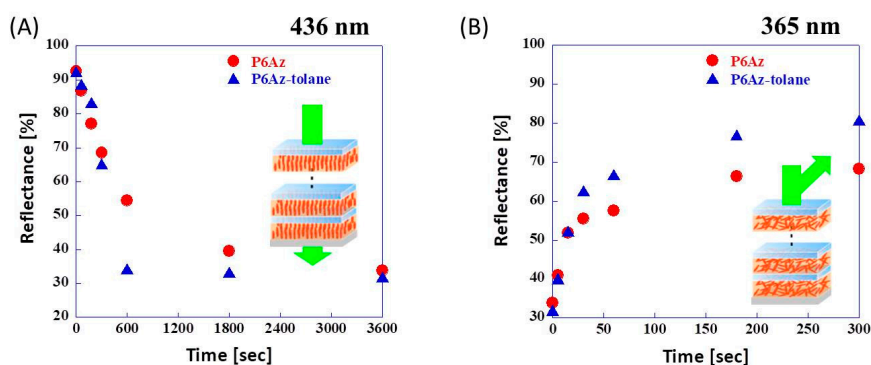
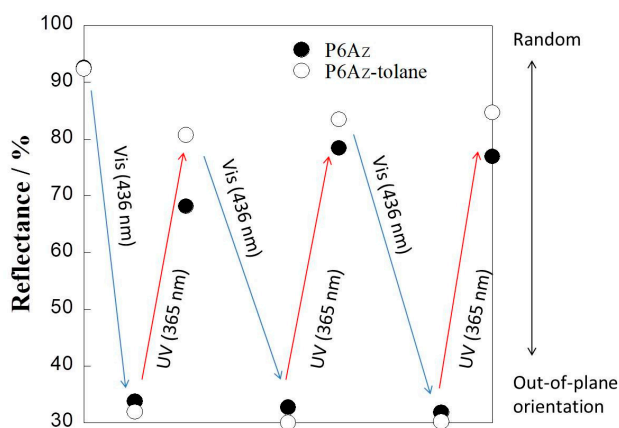


Figure 12. Reflectance change of the P6Az/PVA 20-multi-bilayered film and P6Az–tolane/PVA 20-multi-bilayered film under (A) visible light (436 nm) and (B) UV light (365 nm). Source: Kim et al. 2017 [51]. Copyright 2017. Reprinted with permission from Royal Society of Chemistry.



**Figure 13.** Reflectance change of the P6Az/PVA 20-multi-bilayered film and P6Az-tolane/PVA 20-multi-bilayered film during on-off switching by visible light and UV light. Source:Kim et al. 2017 [51]. Copyright 2017. Reprinted with permission from Royal Society of Chemistry.

## 8. Conclusions

The artificial structural color created by periodic structures consisting of azo-functionalized LC polymers was tuned by refractive index change, depending on the LC molecular orientation state, which was not accompanied by any deformation of the structure. On-off switching using unpolarized light to control LC molecular orientation states, between the out-of-plane orientation and random state, is an excellent method, and is expected to open up a new methodology to manipulate molecules in a three-dimensional manner. From the experimental results, it was found that the photochemical out-of-plane orientation properties of the azo-functionalized LC polymer were highly dependent on the methylene spacer length of the azobenzene side-chain. In addition, further improvement of photoresponse properties for PBG tuning could be achieved by introducing the cooperative effect of the LC mesogen group.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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