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# On-off switching properties of one-dimensional photonic crystals consisting of azo-functionalized polymer liquid crystals having different methylene spacers and polyvinyl alcohol

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ABSTRACT

In this paper, photoresponsive behavior of multi-bilayered films having precisely controlled layer thickness prepared by stacking an azo-functionalized polymer liquid crystal, PMAzXAc, and polyvinyl alcohol alternatively, PVA, is described. The multi-bilayered films were found to reflect a light of specific wavelength depending on the layer thickness and refractive index, and showed the reversible change in the reflection intensity by irradiation with visible and UV lights. The change in the reflection intensity was brought about by change in the molecular orientation of PMAzXAc between an out-of-plane orientation and a photo-induced isotropic state, and was strongly dependent on the number of methylene spacer of PMAzXAc linking the azobenzene side group with the acrylate polymer main chain. PMAz6Ac with hexa-methylene spacer showed the largest change in the reflection intensity, while smaller change in the reflection intensity was observed for PMAzXAc having shorter or longer methylene spacer than 6. The effect of the methylene spacers on the photochemical change in the molecular orientation of azobenzene chromophores in the multi-bilayered films will be discussed.



## 1. Introduction

The Photonic crystals exhibit photonic band gap (PBG), and have attracted much attention from both fundamental and practical points of view, because of their unique properties inhibiting the propagation of light due to PBG [1–3]. In particular, multi-bilayered films having precisely controlled layer thickness are known as one-dimensional photonic crystals (1D-PCs). In the case of 1D-PCs consisting of the multi-bilayered structure, both reflection peak wavelength and intensity of reflection depend on the periodicity of layered structure and refractive index of materials. The wavelength of reflection peak, $\lambda$, can be estimated according to Bragg diffraction equation as follows: [1,2,4]

$$m\lambda = 2a\sqrt{n_1^2\frac{d_1}{a} + n_2^2\frac{d_2}{a}} \tag{1}$$

where $a$ is the thickness of each bilayer, $n_1$, $n_2$ and $d_1$, $d_2$ are the refractive indices and the layer thicknesses of stacked materials 1 and 2 in each layer, respectively, and $m$ is the diffraction order integer. So, the wavelength of the reflection can be controlled by varying the thickness of each layer and/or the refractive index of the stacked materials.

In addition, peak reflectance, $R$, of the multi-bilayered films is given by the following equation for the normal incidence of light: [5]

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

where $n_H$ and $n_L$ are the high and low refractive indices of the stacked materials in each bilayer, respectively, $n_S$ is the refractive index of the substrate and $q$ is the number of bilayers. From equation (2), the reflectance will be increased with the increase in

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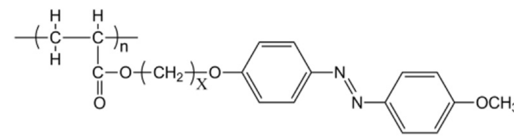
the difference between $n_H$ and $n_L$. In contrast the reflectance becomes extremely low when $n_H$, $n_L$ and $n_S$ are nearly equal. Therefore, an on-off switching of the reflection will be achieved by controlling the difference in the refractive indices of the stacked materials between the equal state ($n_H = n_L = n_S$) (Fig. 1A) and the different state ($n_H \neq n_L$) (Fig. 1B). Recently, we have successfully demonstrated that the on-off switching of the reflection of the multi-bilayered films by switching between the equal and different states [6]. In our previous work, we used polyacrylate having the azobenzene side group via hexamethylene spacer, PMAz6Ac ($X = 6$ in Scheme 1) and polyvinyl alcohol (PVA) as the stacked materials. PMAz6Ac was found to show spontaneous out-of-plane orientation in the multi-bilayered films fabricated by alternative spin coating of a PMAz6Ac/cyclohexanone solution and a PVA/water solution on a glass substrate. The multi-bilayered films reflected the light of specific wavelength which was depending on the difference between the refractive indices of PMAz6Ac (1.60, $n_{av}$) and PVA (1.49) layers, and the bilayer thickness, while the reflection band was disappeared by heating at 80 °C due to the out-of-plane orientation of PMAz6Ac (Fig. 1C), resulting in the decrease in the refractive index of the PMAz6Ac layer (1.48, $n_o$), which was nearly equal to that of the PVA layer. The reflection band was recovered by




**Scheme 1.** Azo-functionalized polymers used in this study, PMAzXAc.

irradiation with ultraviolet (UV) light to cause photoisomerization from the trans-form to cis-form, leading to the transformation from the out-of-plane orientation to the photo-induced isotropic state (see Supplementary Information Fig. S1) in the PMAz6Ac layer (Fig. 1 D). In this way, the on-off switching of reflection of the multi-bilayered films was achieved by the combination of thermal self-organization and photochemical disorganization of the azobenzene-functionalized liquid crystalline polymer.

On the other hand, it has been reported that variety of molecular orientation can be realized by changing polarization and wavelength of light, consequently the out-of-plane orientation is also produced by irradiation of non-polarized light on an amorphous polymers containing azobenzene groups [7,8]. If the on-off switching of reflection can be achieved by only irradiation of light

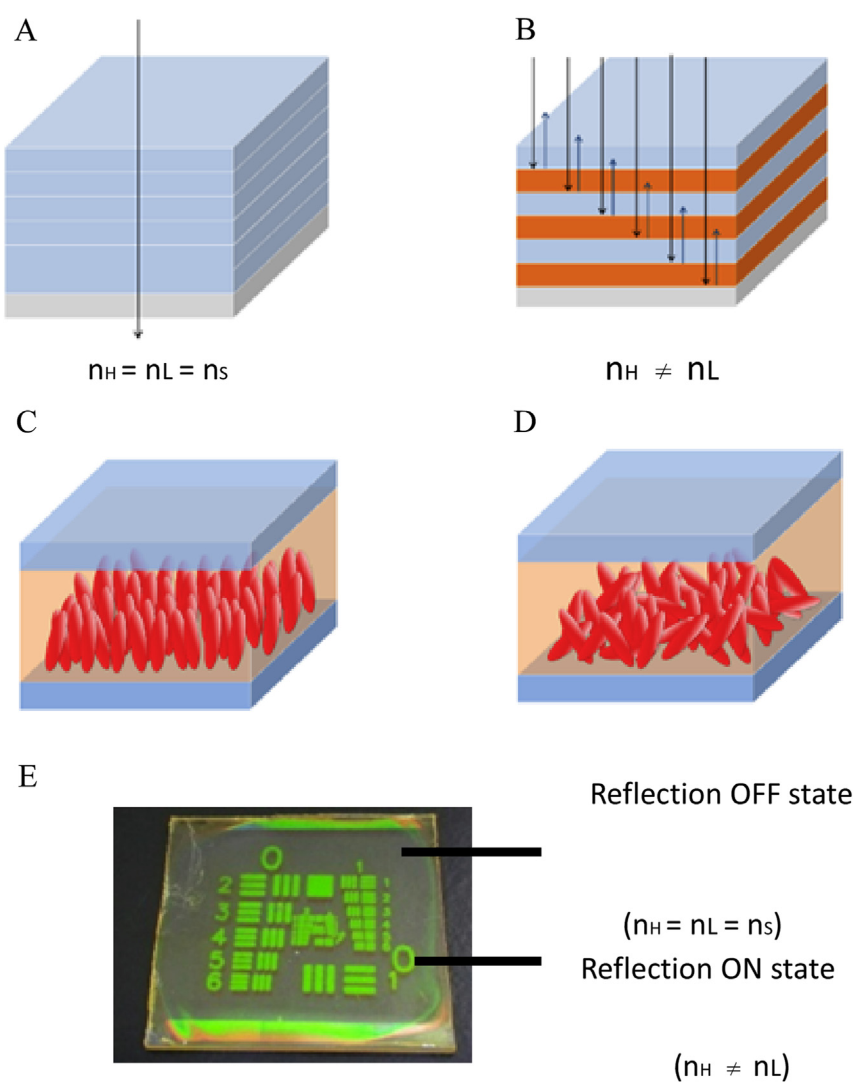



**Fig. 1.** Diagram of on-off switching of reflection by changing molecular orientation of azobenzene molecules. (A) On state of reflection of multi-bilayered film ($n_H = n_L = n_S$), (B) off state ($n_H \neq n_L$), (C) out-of-plane orientation, (D) random orientation (or photo-induced isotropic state), (E) patterned multi-bilayered film.