FOCUS REVIEW

Azobenzene-containing polymers for photonic crystal materials

Sunnam Kim[1], Tomonari Ogata[2] and Seiji Kurihara[1,3]

Photonic crystals have attracted great attention because of their potential applications in optical materials. When an optically birefringent liquid crystal is incorporated in photonic crystals, structural coloration can be easily changed by external stimuli, such as electric field, annealing and light irradiation. In this review, our recent work on the phototunability of photonic crystals consisting of azobenzene-containing polymers is discussed, and their birefringence properties based on their polymeric molecular structures are reviewed.

INTRODUCTION

Tunable photonic crystals

Structural coloration is basically caused by the interaction between light and periodic nanostructured materials, and light absorption by dyes or pigments is not required for structural coloration. Consequently, structural color is extremely resistant to degradation such as oxidation. Structural coloration of various materials is found in nature, and structural colors are iridescent and very durable: for example, opal and peacock wings. If the wavelength or intensity of the structural color consisting of artificial nanostructured materials can be controlled and modulated by external stimuli, these materials will be candidates for optical applications.[1–4] Artificial periodic structured materials are called photonic crystals.

Azobenzene derivatives are well known as stable photoresponse liquid crystal (LC) materials, and their 'photochemical phase transition' between the liquid crystalline phase and the random state and 'birefringence' are very useful parameters for optical photonic crystal switching. In this review, we introduce one- and three-dimensional photonic crystal structures consisting of azobenzene-containing polymers and discuss the dependence of the photonic crystal phototunability on birefringence as well as structural periodicity. We also specifically mention the birefringence properties of the azobenzene-containing polymers based on their polymeric molecular structures.

Opal and inverse opal structures for three-dimensional photonic crystals. A typical material with a three-dimensional periodic structure, which is known as the opal structure, can be prepared by self-assembling spheres. The opal structure can be converted into a three-dimensional periodically porous material by infiltration with other materials, such as SiO_2, TiO_2 and Si, followed by the removal of the opal template.[5–9]

These porous materials are called an inverse opal structure. For the opal and inverse opal structures, the reflection wavelength (λ) under normal incident conditions is expressed by the Bragg diffraction equation as follows:[5,10]

$$\lambda = 2\sqrt{\frac{2}{3}}d\sqrt{n_{\text{sphere}}^2 f + n_{\text{void}}^2(1 - f)} \tag{1}$$

where d is the diameter of the sphere, n_{sphere} and n_{void} are the refractive indices of the sphere and the medium in the voids of the opal, respectively, and f is the volume fraction of the sphere. Thus, the peak wavelength can be roughly tuned by two approaches, either by controlling of the diameter of the sphere[11–18] or by controlling the refractive index.[19–25] When a nematic LC is infiltrated into the pore of the inverse opal structure, the optical birefringence can be tuned by external stimuli, and the resulting composite material will be a tunable photonic band gap material.

Multibilayered films for one-dimensional photonic crystals. On the other hand, one-dimensional photonic crystals can be prepared simply by using multibilayered films with a refractive index difference between the alternate layers. λ is also expressed by the following Bragg equation:[26]

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

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 the stacked materials 1 and 2 in each bilayer, respectively; and m is the diffraction order integer. In such multibilayered films, the wavelength of the reflection can be controlled by varying the thickness of each layer and/or the refractive index of the stacked materials.

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The reflectance, R, of the multibilayered films for the normal incidence of light is given by the following equation:[27]

$$R = \left[\frac{1 - (n_{\text{H}}/n_{\text{L}})^{2q}(n_{\text{H}}^2/n_{\text{S}})}{1 + (n_{\text{H}}/n_{\text{L}})^{2q}(n_{\text{H}}^2/n_{\text{S}})} \right]^2 \qquad (3)$$

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. Inspection of Equation (3) shows that the reflectance will increase with increasing 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 so that 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} and n_{s}) and the different state (n_{H} and n_{L}). As the wavelength and intensity of the reflection depended strongly on the changes in the birefringence of the materials, the study of the orientation behaviors of the azobenzene-containing polymers is very meaningful. In the following section, the dependence of the birefringence properties of azobenzene-containing polymers on their molecular structures will be discussed.

RESULTS AND DISCUSSION
Azobenzene side-chain polymers with different methylene spacer lengths
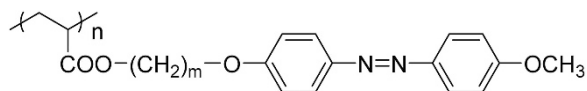

(1) m=3
(2) m=6
(3) m=11

As the methylene spacer becomes smaller, the interaction between the azochromophores becomes easier.[28] However, the motion of the azobenzene chromophores is more restricted when the length of the methylene spacer is decreased because of the coupled motion between the main chain segments and the side chains.[29] As a result, the orientational order of compound (1), which has three methylene spacers, was lower than that of compound (2), which has six methylene spacers. However, the photoresponse of compound (3), which has 11 but much longer methylene spacers, was extremely poor compared with the other polymers and exhibited the lowest birefringence.[28] This poor performance is likely to be due to the aggregation of the azochromophores.

The birefringence values obtained for the composite films, SiO$_2$ inverse opal films infiltrated by compounds (1–3), were estimated based on Bragg's law using the observed reflection peak wavelengths with the perpendicular and parallel polarizers to the polarization direction of the linearly polarized light. The obtained values were smaller than those obtained for the solid films, implying that the photo-orientation of the azobenzene chromophores in the inverse opal films was weaker than that in the solid films. It is known that the surface of a substrate influences the LC arrangement, and this distortion effect is dependent on the distance from the surface.[30] In the case of the composite films, the LC orientation is induced in confined spaces with spherical surfaces and is more affected by the surface potentially causing LC distortion. This spatial effect contributes to a lower photo-orientation of the polymers in the composite films.

Copolymer with azobenzene and tolane groups

(4)
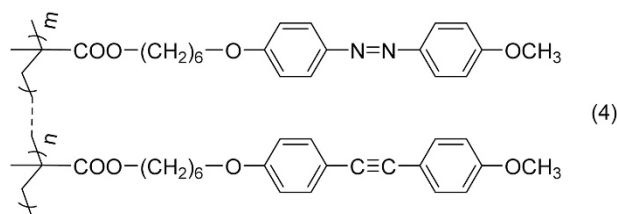
A tolane group shows a larger birefringence because of its rigid π-conjugated electronic structure.[31–33] Furthermore, azobenzene copolymers with tolane groups were reported to show a cooperative molecular reorientation during light irradiation.[34–38] For SiO$_2$ inverse opal films containing compound (4), a copolymer with azobenzene and tolane groups, reversible switching of the reflection peak was achieved by irradiation with linearly polarized and circularly polarized light. However, the shift width of the reflection peak was almost comparable to that of the azobenzene homopolymer at room temperature. However, it was improved at higher temperature below the glass transition temperature because of the increasing flexibility of the polymer segment at higher temperatures. The segment flexibility is advantageous for the orienting movement when the non-photo-responsive tolan groups aligned along the orientation direction of azobenzene groups. As the refractive index is increased relative to the cooperative orientation of the mesogen units, the shift of the reflection wavelength increases, as described in Equation (1). As a result, a larger shift width in the reflection peak wavelength was achieved for the SiO$_2$ inverse opal film infiltrated with azobenzene and tolane copolymers than that of azobenzene homopolymer.

Azobenzene-disubstituted polymers


(5)

(6)
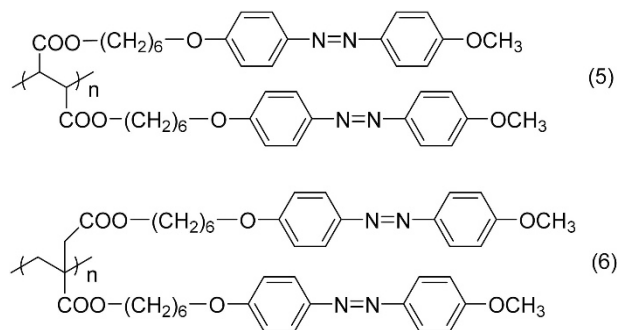
Polymers with high segment density are very attractive because of their interesting properties, such as reduced viscosity, good solubility, low glass transition temperature and fast response to external stimuli.[39] Motivated by great interest in polymer architecture with high segment density, disubstituted fumarate and itaconate polymers with the same azobenzene molecules in the side chain, compounds (5) and (6), were prepared by radical polymerization.[40] Although the azobenzene-disubstituted monomers did not show LC phases, their polymers did. Comparing both polymers, which differ only in the substitution positions of the two mesogenic groups relative to the backbone, compound (5) showed higher LC phase stability based on the high phase transition temperature. However, the restricted and rigid stereogeometric structure led to poor solubility and film fabrication ability. By contrast, compound (6) was less rigid and showed similar isomerization behavior and anisotropic properties compared with the polymer with a single azobenzene side group as a unit, compound (2). Therefore, it was found that the stabilities of

mesophase LC states depended on the degree of the substitution and the positions of the backbone chain; it was also found that the isomerization behavior was largely dependent on the substitution position. In addition, it is considered that the 6-methylene spacer of the mesogen is sufficiently long for the mesogen side groups to be decoupled from the backbone chain.

Poly(ethylene imine)s having azobenzene side groups
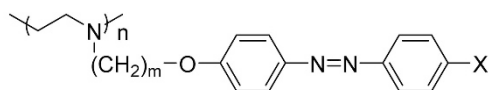
(7) m=6, X=OCH$_3$
(8) m=6, X=CN
(9) m=6, X=C$_4$H$_9$
(10) m=6, X=NO$_2$
(11) m=8, X=OCH$_3$

(12)
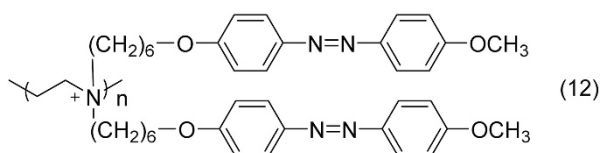
The molecular orientational properties largely depended on the backbone structure; compared with the other polymers, the out-of-plane orientation tendency was high for the ethylene imine backbone structure. Ujiie's group reported that some polyethylene imines (PEIs) with azobenzene groups as the side groups show liquid crystalline phases and spontaneously align perpendicularly to the substrate by heating and subsequent cooling.[41,42] Since it is expected that a spontaneous out-of-plane molecular orientation will open a door for new functions or new materials, we synthesized polyethylene imine with substituted azobenezene side-chain groups with the different azobenzene end groups, such as methoxy, cyano, buthyl and nitro groups and six or eight methylene spacer lengths (compounds (7–11)).[43–45] Compounds (9) and (10), bearing buthyl and nitro end groups, respectively, showed higher-order parameter values on annealing than those obtained for compounds (7) and (8), which have methoxy and cyano end groups, respectively, indicating a well-pronounced tendency for the development of out-of-plane order. With the exception of the compound (10) film, the other PEI films showed reversible alignment behavior on annealing and upon irradiation by UV and non-polarized visible light. For compound (10), which has electron-donating and -withdrawing substituents at each end of the azobenzene group, the random orientation state was not induced after the out-of-plane orientation. This observation may be explained in terms of a rapid reverse reaction from the *cis* form to the *trans* form, supported by the very small change in the absorption spectra on prolonged UV irradiation despite the photoinduced orientation. These results indicate that the molecular orientation behavior of the PEIs greatly depends on the structure of the azobenzene side-chain end groups.

In contrast, for compound (11), which have eight methylene spacers, multiple reorientation behaviors were observed. Upon UV irradiation, the azobenzene group aligned randomly on the glass substrate (S = 0.02). After annealing, the out-of-plane order parameter value increased from 0.02 to 0.41, and after irradiation with 435 nm non-polarized visible light, the order parameter value changed from 0.02 to 0.46. The reversibility of the alignment behavior of azobenzene

groups was achieved by changing conditions such as annealing, UV and non-polarized visible light irradiation.

For another quaternized PEI with an ionic backbone structure created by the disubstitution of the azobenzene side groups, compound (12), only the smectic phase in a much broader range, between 53 °C and 170 °C, was observed, and the thermal stability was significantly improved relative to that of compound (7). However, the thermally induced out-of-plane reorientation tendency was lower than that of the other PEIs because of the restricted mobility of the azobenzene side groups based on the steric hindrance with the bulky structure of the backbone chains.

**Copolymer having azobenzene and LC mesogen groups**

(13)
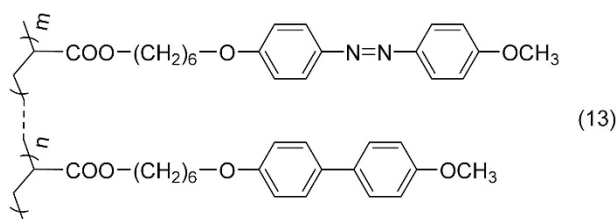
Recently, we reported the photochemical on–off switching of the reflection intensity of a one-dimensional photonic crystal that was fabricated by alternative spin coating of polyacrylates with an azobenzene side-chain group and polyvinyl alcohol (PVA) on a glass substrate, giving multibilayered films with a precisely controlled layer thickness.[46–47] For the 20-bilayered fresh film incorporating compound (2), the reflection intensity was ~ 90% because of the large difference in the refractive indices between PVA (n = 1.50) and compound (2) with a random orientation (n = 1.60). The change in the reflection intensity was achieved via the reversible change in the molecular orientation between the out-of-plane (n = 1.48) and photo-induced random orientations (n = 1.60) by a combination of thermal annealing and irradiation with UV light, as shown in Figure 1.

However, a long irradiation time was required for the switching of the reflection of the multibilayered films because of the higher absorbance in the UV region due to the azobenzene chromophores in the multibilayered films. To improve the light penetration depth in
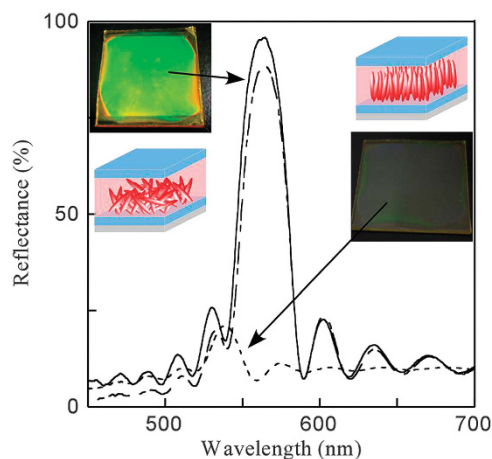
Figure 1 Change in reflection spectra of 20-bilayered films containing compound (13) by thermal annealing (80 °C for 10 min; dotted line) and irradiation with UV light ($\lambda = 365$ nm, 28 mW cm^{-2} for 120 s; dot and dashed line). The solid line represents the fresh film.[46] It exhibits a green color, and each layer is ~ 57 nm in thickness.
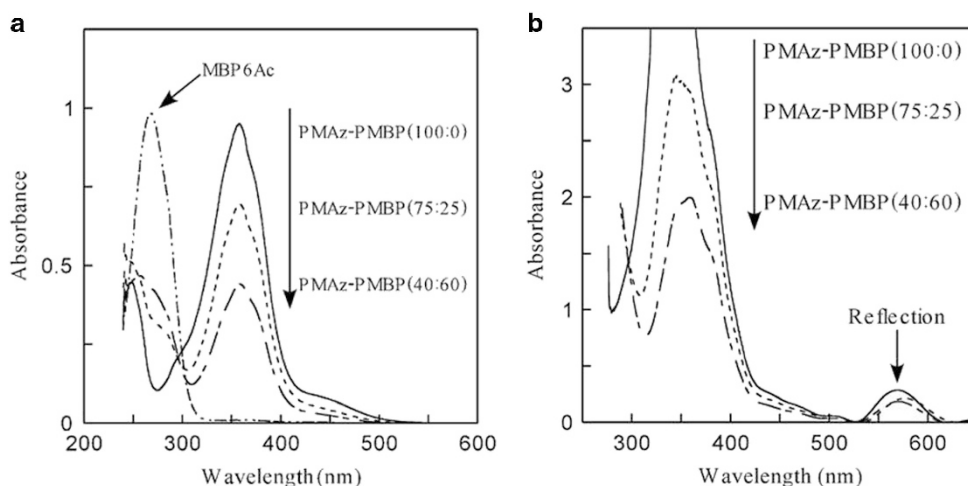
Figure 2 Absorption spectra of compound (**13**) with various molar ratios of azobenzene and biphenyl groups for solutions (**a**) and solid films (**b**).
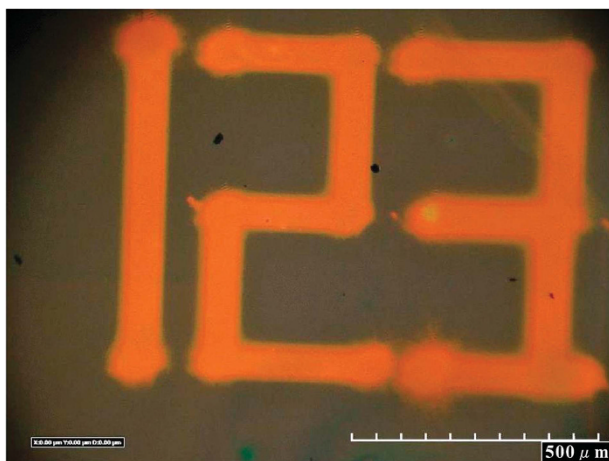
Figure 3 Photograph of numbers written on 20-bilayered films containing compound (**13**) with a UV laser (375 nm, 250 mW cm^{-2}) at the scan of 130 µm s^{-1}. Scale bar, 500 µm.[46] The sample exhibits a red color, and each layer is ~ 64 nm in thickness.

the films, a polyacrylate copolymer bearing azobenzene and biphenyl side-chain groups, compound (**13**), was employed.[48] As shown in Figure 2, absorbance at 360 nm for the solution and the solid films decreased with the increasing molar ratio of the biphenyl group. As the concentration of the azobenzene chromophores was reduced by the incorporation of the LC mesogen group undergoing the accompanying alignment behaviors, the photoisomerization of the azobenzene chromophores could be carried out throughout the film. The difference in the response speed was elucidated under low-intensity UV light irradiation (5 mW cm^{-2}). For the case of multibilayered films containing compound (**13**) where each layer was ~ 57 nm thick, a green color was found and required only 120–300 s of UV light irradiation for coloration, whereas 900 s of UV light irradiation was required for the coloration of the multibilayered films containing compound (**2**); and the irradiation time required for the coloration was reduced to one-third or less. In addition, it was possible to write letters on multibilayered films containing compound (**13**) ($m = 0.75$, $n = 0.25$) using a UV laser (375 nm, 250 mW cm^{-2}) at a scan speed of 130 µm s^{-1} (Figure 3). These films will be candidates for recording materials, such as a substitute material for paper.

SUMMARY

The birefringence and orientation behaviors of azobenzene-containing LC polymers were largely dependent on their molecular structures, such as their backbone structure, spacer length and end groups. Such optical information about polymer materials is a key for optical device technology. By incorporation of the azobenzene-containing LC polymers in periodic structures, smart and durable tunability of the photonic band gap was achieved without any memory effects. As various colors are realized and their on–off switching becomes possible, these materials will be candidates for use as recording materials, such as a substitute material for paper.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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