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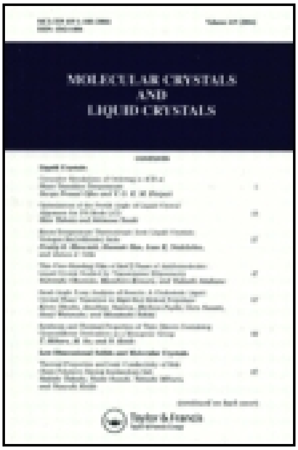

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Phototunable Liquid Crystalline Photonic Band Gap Material

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We fabricated phototunable photonic crystals by infiltrating an azobenzen liquid crystal polymer (PLC) into voids of an opal or an inverse opal film. Azochromophores of PLC could be oriented perpendicular to the polarization direction of incident light, causing a change in refractive index of the PLC domain. Consequently, photonic band gap could be reversibly shifted by using the photo-induced molecular orientation. In addition, the photonic band gap in the inverse opal film was sifted larger than that in opal.

Keywords: inverse opal; opal; photonic crystal

1. INTRODUCTION

Photonic crystals are periodic dielectric structures that can inhibit light propagation in certain directions in space for a certain frequency

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band known as a photonic band gap [1,2]. A typical photonic band gap material can be prepared by self assembling spheres, showing a semi-photonic band gap. It is generally called opal. In the case of the opal, Bragg diffraction due to the semi-photonic band gap is expressed by Bragg diffraction equation under normal incident condition [3],

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

where λ is the peak wavelength, d is the diameter of the sphere, n_{sphere} and n_{void} are the refractive indices of spheres and the medium in the voids of the opal, and f is the volume fraction of the spheres, respectively. According to the Eq. (1), the peak wavelength is cleary dependent on the diameter of the spheres, and the refractive indices.

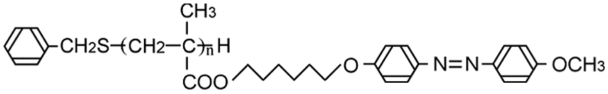
Recently, there are several works on tunable photonic band gap materials containing liquid crystals (LCs). LCs are well known to exhibit birefringence, and show good response to external stimuli. Therefore, if one can fabricate the photonic crystals from LCs, they will be promise of applications to optical devices such as recording, display and so on.

In this work, we fabricated photonic crystals containing a polymer LC having azobenzene groups. The photonic crystals were prepared by infiltration of the polymer LC in the voids of an opal and an inverse opal. The inverse opal was fabricated by using the opal as a template. Azobenzene molecules show a reversible photoisomerization between a trans-form and a cis-form. The trans-cis photisomerization of the azobenzene molecules in host LCs is known to disorganize LC molecular orientation. Therefore, we investigated the effects of the photoisomerization of the azobenzene LC polymer relating to the shift of the Bragg diffraction of the opal and the inverse opal.

2. EXPERIMENTAL

2.1. Fabrication of SiO_2 Opal Film and SiO_2 Inverse Opal Film

The SiO_2 opal and SiO_2 inverse opal films were fabricated on a glass substrate according to the method reported earlier [4]. Typical procedure was as follows. Opal films composed of SiO_2 particles with a diameter of 300 nm were prepared by vertical deposition method. In the case of SiO_2 inverse opal films, opal films composed of polystyrene (PS) particles with a diameter of 300 nm were fabricated by the same method described above. Then, the films were immersed in an alcoholic colloidal solution of SiO_2 particles with a diameter of 12 nm and lifted with a rate of 8 μm/s, leading to the infiltration of SiO_2



SCHEME 1 Structure of poly(MAz6Mc).

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particles in the voids of the PS opal films. Then, the PS opal films infiltrated with SiO_2 particles were calcined at 500°C for 1 h to remove the PS particles and to give an inverse opal structure consisting of SiO_2. The structure of the opal and the inverse opal films was examined by scanning electron microscopy (SEM).

2.2. Synthesis of Polymer LC

Polymer LC, poly(MAz6Mc), was synthesized by polymerization of azobenzene monomer in the presence of both benzylthiol as molecular weight controlling agent and 2,2′-azobisisobutyronitrile as radical initiator, respectively, in *N,N*-dimethylformamide at 60°C for 48 h. The structure of poly(MAz6Mc) is shown in Scheme 1.

2.3. Characterization and Photoresponsive Behavior

Thermal properties of the polymer were examined by means of differential scanning calorimetry (DSC; Seiko SSC-5020) and polarizing microscopic observation (Olympus BHSP polarizing microscope; Mettler FP80 and FP82 hot stage and controller). The scan rate of DSC measurements was 10°C/min of heating. Molecular weight of poly (MAz6Mc) was determined by gel permeation chromatography (GPC; Jasco 870-UV detector at 254 nm, Shodex KF-804F column, tetrahydrohuran, THF as eluent).

Photoisomerization behavior of poly(MAz6Mc) in THF were examined by monitoring change in absorption spectra with an UV/visible spectrometer (Shimazu UV-1600) at room temperature under ultraviolet and visible light irradiation. The solid films of the polymer were prepared by spin-coating using THF as solvent. The photoisomerization of azobenzene groups between the trans-form and the cis-form was performed by using a 500-W high pressure Hg lamp (Ushio SX-UI 5000) equipped with a cut filter (Sigma, UTVAF-35U) for UV irradiation (365 nm), and a 500-W Xe lamp (Ushio SX-UI 500XQ) equipped with a cut filter (Sigma, DIF-50s-GRE) for visible light. The power densities of the incident light were 58 mW/cm^2 for UV and 58 mW/cm^2 for visible light, respectively.

Photoinduced anisotropy of the poly(MAz6Mc) films was investigated by using the conventional pump-probe method. In our experiments, Ar+ laser (488 nm) and He-Ne laser (633 nm) were used as pumping laser and probe light, respectively. The polymer films prepared by spin-coating were placed between two crossed polarizers in the path of the probe light, where the polarization direction of the polarizers was set at an angle of 45° with respect to the polarization direction of pumping laser. Under irradiation with the pumping laser, the change in transmitted light intensity of the probe light was monitored with a multichannel photo-detector with an Ocean Optics USB2000 spectrometer.

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2.4. Infiltration of poly(MAz6Mc) into SiO_2 Opal and Inverse Opal Films

Opal and inverse opal films infiltrated with poly(MAz6Mc) were prepared by heating SiO_2 opal and inverse opal films at 130°C on a hot plate, and following injection of the polymer at the temperature.

2.5. Photoresponsive Properties of Opal and Inverse Opal

The photoresponsive properties of the opal and inverse opal films infiltrated with poly(MAz6Mc) were explored by measuring reflection spectra with an Ocean Optics USB2000 spectrometer under irradiation of polarized light with Ar+ laser (488 nm, 80 mW/cm^2), using incident white monitor light normal to the surface of the films.

3. RESULTS AND DISCUSSION

3.1. Characterization and Thermal Properties

The molecular weights of poly(MAz6Mc), Mn and Mw, were 5800, and 12000. The polymer showed liquid crystalline phases as follows; $G \cdot 51^{\circ}C \cdot S \cdot 86^{\circ}C \cdot N \cdot 124^{\circ}C \cdot I$, where G, S, N and I represent glass, smectic, nematic and isotropic phases, respectively.

3.2. Opal and Inverse Opal Films Infiltrated with Poly(MAz6Mc)

Figures 1 and 2 show reflection spectra of SiO_2 opal and inverse opal films, and their SEM images. Comparison of these spectra and change in the reflection band filled with various solvents revealed that the periodic parameter (d) and volume fraction (f) of SiO_2 are 325 nm,

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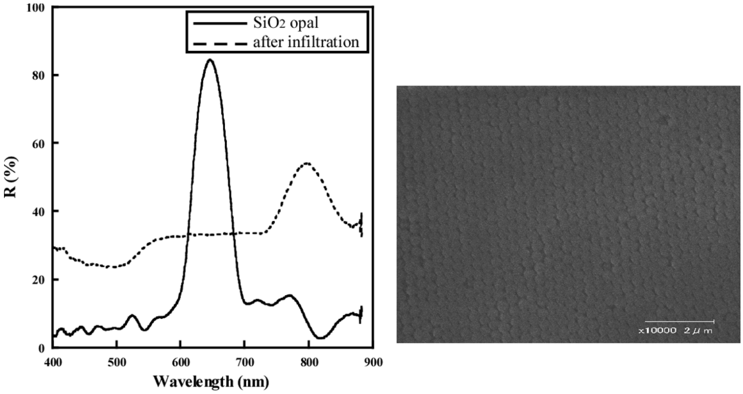

FIGURE 1 Reflection spectra of the opal and after infiltrated by MAz6Mc telomer (left) and SEM image if the opal film (right).

0.60 for the opal film, and 278 nm, 0.12 for the inverse opal film, respectively. The infiltration of poly(MAz6Mc) in the opal and inverse opal films caused a shift of the reflection peak; 680 nm to 797 nm for the opal film and 480 nm to 710 nm for the inverse opal film as shown in Figures 1 and 2. According to the Bragg diffraction equation, the refractive index of poly(MAz6Mc) in the voids, n_{void}, was estimated to be 1.58, and 1.58 for the opal and inverse opal films. This value is almost consistent with the refractive index of poly(MAz6Mc) without any alignment treatment (1.56). Therefore, the mesogenic molecules of poly(MAz6Mc) can be considered to align randomly in voids of both films.

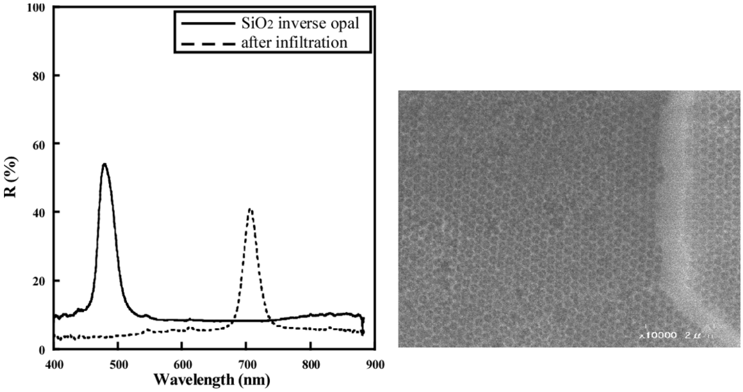

FIGURE 2 Reflection spectra of the inverse and after infiltrated by MAz6Mc telomer (left) and SEM image if the inverse opal film (right).

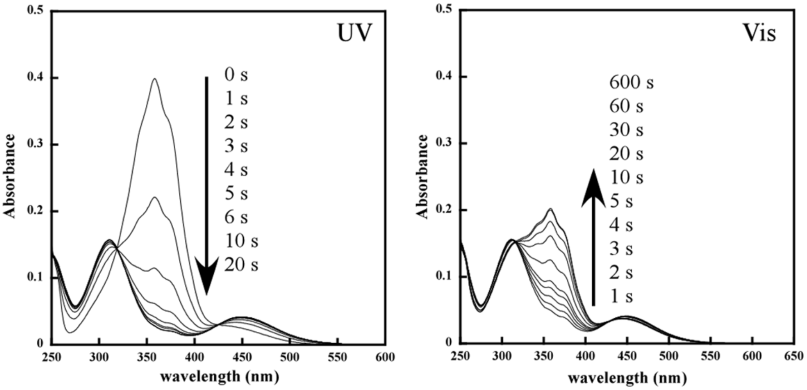

FIGURE 3 Changes in absorption spectra of MAz6Mc telomer in solvent THF.

Figure 3 shows changes in absorption spectra of poly(MAz6Mc) in THF solution by UV and visble light irradiation. Two absorption peaks were observed at 358 nm corresponding to π-π^* transition, and at 448 nm corresponding to n-π^* transition before irraiation. Upon UV irradiation, the peaks at 358 and 448 nm were decreased and increased, indicating the photoisomerization of the azobenzene groups from the trans-form to the cis-form. Reverse photoisomerization from the cis-form to the trans-form could be cuased by visible light irradiation.

It is well known that linearly polarized light irradiation on amorphous polymers having azobenzene groups can induce a birefringence, because of reorientation of the chromophores perpendicular to the direction of the light polarization [5]. The trans-cis-trans photoisomerization cycle is required for the reorientation of the azo-chromophores. In this study, we used a light of 488 nm for the reorientation, because there is a weak absorbance at 488 nm for both trans-form and cis-form as can be seen in Figure 3. Figure 4 shows change in birefringence of the poly(MAz6Mc) solid film by irradiation of polarized light of 488 nm with Ar+. It is clearly seen that the transmitted light intensity increased with the irradiation. In addition, the light intensity was decreased by irradiation of circularly polarized light of 488 nm. These resultes indicate that the azo-chromophores can be aligned perpendicular to the polarization direction of polarized light, and the photochemical alignment is reversible by irradiation of linearly and circularly polarized light irradiation. The refractive index of the aligned state is larger that the random state. Therefore, it is

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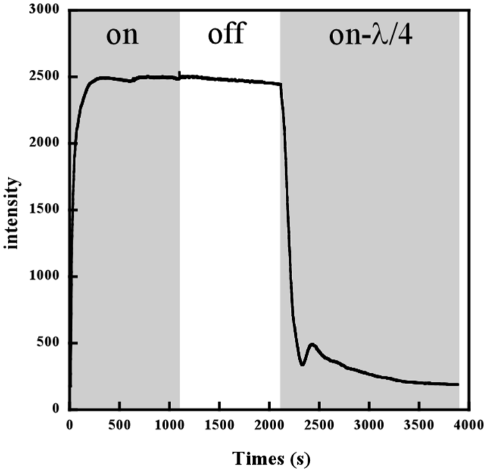

FIGURE 4 Change in birefringence by linearly, and circularly polarized Ar+ laser (488 nm).

expected that the reflection band from the opal and inverse opal films infiltrated with poly(MAz6Mc) can be tuned by the irradiation of linearly and circularly polarized light of 488 nm.

3.3. Photo-Tuning Behavior of Reflection Band

Figure 5 shows changes in the reflection spectra for both opal and inverse opal films infiltrated with poly(MAz6Mc) by the irradiation of linearly polarized light for 80 min at 500 mW/cm^2. The irradiation on both films resulted in a shift of the reflection peaks to longer wavelength region as can be seen in the figure. The magnitude of the shift of the inverse opal film was larger that that of the opal film. The difference in the magnitude of the shift may be due to the difference in the volume fraction of poly(MAz6Mc) in the films; 0.6 for the opal film and 0.12 for the inverse opal film. Namely, the more content of poly(-MAz6Mc) increases, the more shift of the reflection peak becomes. The reflection band could be returned to the initial state by irradiation of circularly polarized light. In addition, no change in the reflection spectra was observed in the dark over than 24 h. These results demonstrate good stability and reversibility of the photo-tuning of the reflection band.

In order to explore the mechanism for the shift, the reflection spectra were measured with a polarizer for the inverse opal film. As shown in Figure 6, the peak and shoulder of the reflection band after the

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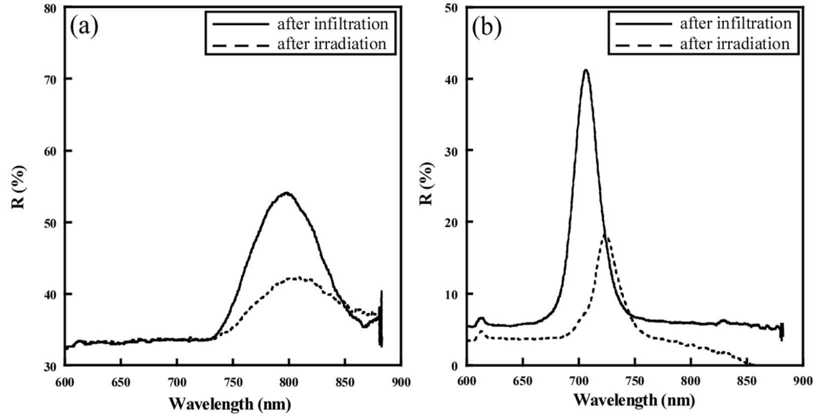

FIGURE 5 Change of reflection spectra of MAz6Mc telomer infiltrated opal (a) inverse opal and (b) film by photo-isomerization.

linearly polarized light irradiation is likely to be combination of reflections observed by using a polarizer perpendicular and parallel to the direction of the light polarization. On the contrary, before the irradiation no change in the reflection band was observed with a

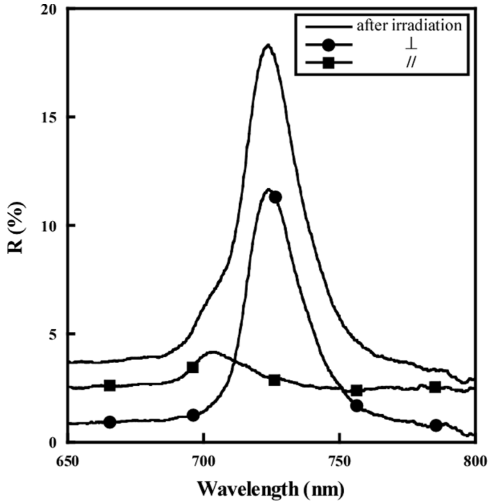

FIGURE 6 Reflection spectra with a ploarizer of MAz6Mc telomer infiltered inverse opal film after irradiation. ⊥ and // indicate perpendicular and parallel direction to the direction of the light polarization, respectively.

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polarizer. On the basis of the results, the shift of the reflection band is interpreted in terms of a formation of anisotropic molecular orientation of poly(MAz6Mc) in the voids by the linearly polarized light irradiation. After the linearly polarized light irradiation, the refractive indices of MAz6Mc polymer in the voids, n_e and n_o, were estimated to be 1.61 and 1.56, respectively from the wavelength of the reflection bands.

4. CONCLUSION

We have fabricated photochemically tunable photonic crystal by infiltration of the polymer LC having azo-chromophores in an opal structure and an inverse opal structure. The linearly polarized light irradiation caused the shift of the reflection band. The spectroscopy indicates clearly that the shift of the reflection band is attributed to the photochemical transformation from the random structure to the anisotropic structure. The switched state was stable in the dark, and reversible switching of the reflection band can be achieved by the linearly and circularly polarized light irradiation.

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