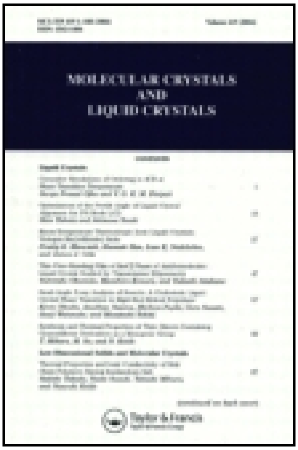

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Photoswitching Behavior of SiO_2 Inverse Opal Films Infiltrated with Azo-Tolane Copolymer: Effect of Polymer Main Chain Structure

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Photoswitching Behavior of SiO_2 Inverse Opal Films Infiltrated with Azo-Tolane Copolymer: Effect of Polymer Main Chain Structure

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Phototunable photonic band gap materials were prepared by infiltration of a liquid crystalline azopolymer into voids of a SiO_2 inverse opal film. Linearly polarized light irradiation resulted in a reversible and stable shift of the reflection band to longer wavelength region due to the transformation of azobenzene groups from random to anisotropic molecular orientation. Acrylate and methacrylate copolymers having both azobenzene and tolane groups in side chain have been synthesized in order to improve switching property. Upon irradiation of linearly polarized light SiO_2 inverse opal film infiltrated with methacrylate copolymer showed a larger wavelength shift of the reflection band compared to that of the composite film infiltrated with acrylate copolymer.

Keywords: azobenzene; birefringence; photonic crystal; tolane

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INTRODUCTION

Photonic crystals having a three dimensional periodic structure have attracted much attention from both fundamental and practical points of view, because of their unique properties in controlling the propagation of light [1]. One of the typical photonic band gap materials known as an opal structure can be prepared by self assembling spheres, showing a semi-photonic band gap. In case of the opal structure, Bragg's diffraction due to the semi-photonic band gap under normal incident condition can be expressed by Bragg's diffraction equation as follows:

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

where λ is the peak wavelength of diffraction, d is the diameter of the spheres, n_{sphere} and n_{void} are the refractive indices of the spheres and the medium in the voids of the opal structure, respectively and f is the volume fraction of the spheres. Thus, the peak wavelength can be tuned by controlling the diameter of spheres or refractive indices.

Recently, we have reported the preparation of a phototunable photonic crystal by infiltration of liquid crystalline azopolymers in a SiO_2 inverse opal film [2]. Molecular orientation of liquid crystalline azopolymers was controlled by irradiation with linearly (LP) and circularly polarized (CP) lights. Consequently, a birefringence which is the difference between the refractive indices of extraordinary and ordinary lights, $\Delta n = n_e - n_o$, could be induced [3]. In this system, irradiation with LP and CP lights resulted in a reversible transformation between a random and an anisotropic molecular orientations of azo-chromophores in the voids, leading to reversible and stable shift of the reflection band [2,4]. However, switching properties such as magnitude of the change in the wavelength of the reflection band were not enough. The shift width of the reflection band was dependent on the photoinduced birefringence of azopolymers in the voids of SiO_2 inverse opal films. So, a larger shift of the reflection band will be induced if liquid crystalline polymers with higher photoinduced birefringence are used as the infiltration material into the voids.

It is well known that tolane compound has higher birefringence because of its rigid π-conjugated electronic structure [5,6]. Therefore, in this study we prepared SiO_2 inverse opal films infiltrated with methacrylate and acrylate polymers having both azobenzene and tolane groups in the side chain, and investigated their photoresponsive properties.

EXPERIMENTAL

Materials

Monodispersed polystyrene (PS) spheres with a diameter of 300 nm were purchased from Duke Scientific Corp. An alcoholic colloidal solution of SiO_2 nano-spheres with a diameter of 12 nm was kindly supplied by Catalysis and Chemical Industries Co., Ltd. Other reagents were purchased and used without further purification.

Synthesis of Copolymers

Acrylate azobenzene monomer (**MAz6Ac**), acrylate tolane monomer (**MTo6Ac**), methacrylate azobenzene monomer (**MAz6Mc**), and methacrylate tolane monomer (**MTo6Mc**), were synthesized according to the synthetic routes described earlier [7–9]. Copolymers of **MAz6Ac** and **MTo6Ac** (ATAc) and of **MAz6Mc** and **MTo6Mc** (ATMc) shown in Figure 1 were synthesized as follows: First, 0.75 mmol of azobenzene monomer, 0.75 mmol of tolane monomer, and 0.015 g (0.125 mmol) of benzylthiol as a chain transfer agent were dissolved in 10 ml of dimethylformamide (DMF) in a glass tube, and 10 mg (0.06 mmol) of 2,2′-azobisisobutyronitrile (AIBN) was added to the solution. After purging with nitrogen the tube was sealed and was placed in a water-bath with shaking. Polymerization was carried out at 60°C for 48 h. The reaction mixture was then poured into excess methanol. The precipitated product was collected and was purified by chloroform/methanol reprecipitation technique.

Properties of Copolymers

Thermal properties of the copolymers were examined by means of differential scanning calorimetry (DSC; Seiko SSC-5020) at a heating rate of 10°C/min and polarizing microscopic observation (Olympus BHSP polarizing microscope; Mettler FP80 and FP82 hot stage and controller). Molecular weights of copolymers were determined by gel permeation chromatography (GPC; Jasco 870-UV detector at 254 nm, Shodex KF-804 L column, tetrahydrofuran as eluent). Copolymerization ratio was determined by UV-Vis spectroscopy.

Photochemical Properties of Copolymers

Copolymer films having a thickness of 100∼200 nm were prepared by spin-coating the polymer solution in toluene on a glass substrate. Figure 2 shows the schematic representation of instrumental setup for investigating photoinduced birefringence of the copolymer films.

The polymer film was placed between crossed polarizers where the polarizing directions of the polarizers were set at an angle of 45° with respect to the polarizing direction of a pumping laser beam. An Ar^+ laser (488 nm, 80 mW/cm^2) and a He-Ne laser (633 nm) were used as the pumping and the probe light sources, respectively. A change in transmitted light intensity of the probe beam was monitored with a photo-detector. The photoinduced birefringence (Δn) of the copolymer films was estimated according to the method reported earlier [10].

Preparation of Copolymer/SiO_2 Composite Films

SiO_2 inverse opal film was fabricated on a glass substrate according to the method reported earlier [11,12]. A typical procedure was as follows: A hydrophilic glass substrate was vertically immersed into an aqueous suspension containing 0.5 vol% of monodispersed PS spheres with a diameter of 300 nm and was maintained at 50°C for 3 days to evaporate the solvent. The PS opal film was completely dried at room temperature, and heated at 80°C for 30 min to enhance the binding between the spheres or between the spheres and the glass substrate. Then, the film was immersed in an alcoholic colloidal solution of SiO_2 spheres having a diameter of 12 nm and lifted with a rate of 8 µm/s leading to infiltration of the SiO_2 spheres in the voids of PS opal structure. Finally, the PS opal film infiltrated with SiO_2 spheres was heated at 500°C for 5 h to remove the PS spheres, and to give the inverse opal film consisting of SiO_2. Then, each copolymer was infiltrated into the voids of the SiO_2 inverse opal film by heating above the melting point of the copolymer, and the obtained copolymer/SiO_2 composite film was cooled to room temperature.

Photochemical Properties of Copolymer/SiO_2 Composite Films

The reflection spectra of copolymer/SiO_2 composite films were explored by Bragg's reflection microscopy for incident white light with a CCD spectrometer (Ocean Optics USB2000). Reflection spectra of copolymer/SiO_2 composite films were measured with/without irradiation of LP and CP lights from an Ar^+ laser at various temperatures.

RESULTS AND DISCUSSION

Characterization of Copolymers

Copolymers having both azobenzene and tolane groups in the side chain were synthesized by radical polymerization and their structures

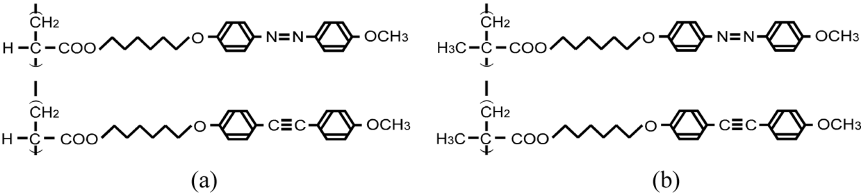


FIGURE 1 Structure of (a) ATAc and (b) ATMc.

are shown in Figure 1. Copolymerization ratio, molecular weight and thermal phase transition temperatures of the copolymers are given in Table 1. The copolymerization ratio was controlled by adjusting the feed ratio of azobenzene monomer to tolane monomer.

Photoinduced Birefringence of Copolymer Thin Films

Copolymer films with thickness of 100 to 200 nm were prepared by spin-coating the polymer solution in toluene. Figure 3 shows the changes in birefringence of copolymer films by irradiation with LP and CP lights from an Ar^+ laser at various temperatures. Birefringence of both copolymer films was increased with an increase in irradiation time of LP light, and was decreased by following irradiation with CP light at all the temperatures studied. This might be due to reversible transformation of side chain groups between a random state and a uniaxially-oriented state upon irradiation with LP and CP light. Although the changes in birefringence of ATAc and ATMc are in similar trend, the photoinduced birefringences of ATAc at 60°C and above were remarkably depressed compared to that of ATMc. In case of ATMc, the depression of the photoinduced birefringence was also observed at temperatures above 80°C. These results revealed that temperature dependence of the photoinduced birefringence is related to the flexibility as well as the mobility of polymer chain segments of the copolymers. Namely, the higher the flexibility and mobility, the

TABLE 1 Characterization of Copolymers

Copolymer	Copolymer composition (mol%)	M_n ($\times 10^3$)	M_w ($\times 10^3$)	Phase transition temperatures (°C)
ATAc	MAz6Ac: MTo6Ac = 50:50	3.6	4.6	G 47 S 70 N 111 I
ATMc	MAz6Mc: MTo6Mc = 51:49	6.8	11	G 69 N 108 I

M_n: number-average molecular weight; M_w: weight-average molecular weight; G: glassy; S: smectic; N: nematic; I: isotropic.

higher the birefringence. However, micro-Brownian motion of polymer chain segments at temperatures higher than the glass transition temperature (Tg) lowers the stability of molecular orientation of the side groups, resulting in the decrease of the birefringence at higher temperatures. Tg of ATAc was lower than that of ATMc (Table 1). This might be a reason for exhibiting the difference in the temperature dependence of the photoinduced birefringence of copolymer films. In addition, an apparent increase of the birefringence was observed after light was turned off. The reason behind the increase of the birefringence in the dark is not clear to us. It is assumed that it may be due to an incomplete orientation of azobenzene and tolane side groups because of continuous photoisomerization of the azobenzene groups during the irradiation of Ar^+ laser [13]. In the dark after irradiation with LP light, some incompletely-oriented chromophores may tend to be aligned parallel to the dominant molecular orientation direction due to a cooperative effect. The incomplete orientation and the cooperative effect attributed to the curious increase in the birefringence after the LP light was turned off.

Photochemical Properties of Copolymer/SiO_2 Composite Films

In order to investigate the effect of the photoinduced orientation of azobenzene and tolane groups on the reflection spectra of the

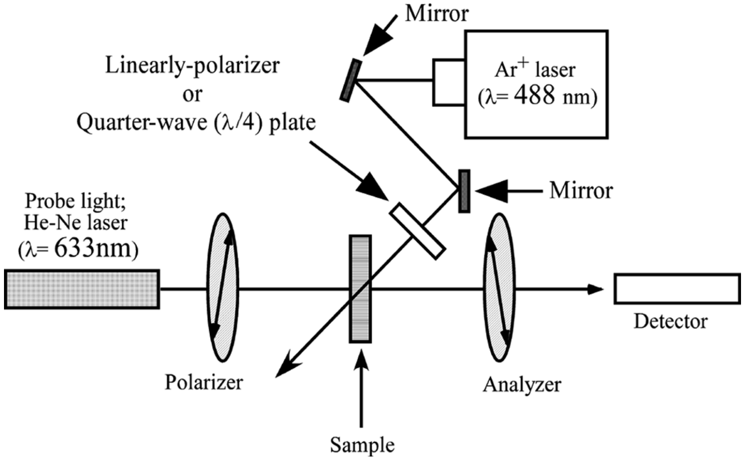


FIGURE 2 Experimental setup for the measurement of photoinduced birefringence.

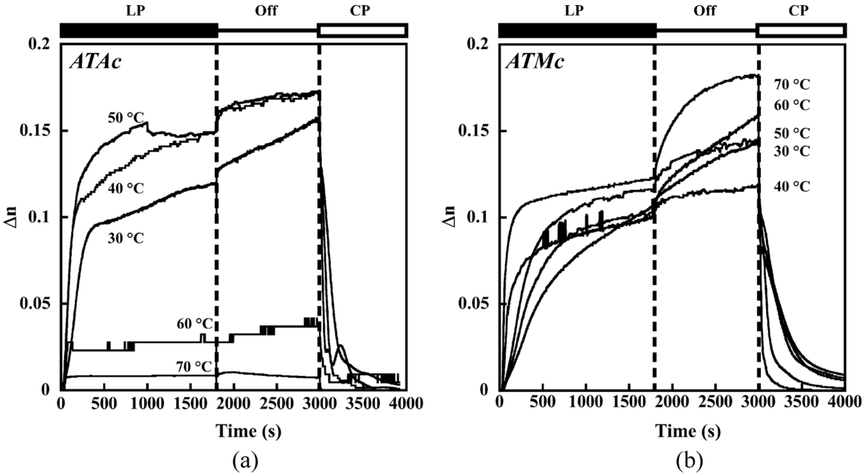


FIGURE 3 Photoinduced birefringence of (a) ATAc; and (b) ATMc copolymer films by irradiation with LP and CP lights from an Ar^+ laser at various temperatures.

copolymer/SiO_2 composite films, the composite films were irradiated with LP light at 488 nm from an Ar^+ laser. Figure 4 shows the changes in reflection spectra of the ATMc/SiO_2 composite film by irradiation with LP light at room temperature. The significant change in the reflection spectra was observed by irradiation with LP light for 60 min, leading to a shift of the reflection band to longer wavelength region by 11 nm. In addition, the wavelength of the reflection band was returned to the initial wavelength by following irradiation with CP light.

Polarized reflection spectra were measured in order to explore the mechanism for the shift of the reflection band. As shown in Figure 4, the shape of the reflection band after the LP light irradiation is roughly coincident with the combination of reflection bands observed by using a polarizer perpendicular or parallel to the polarization direction of the LP light. According to the Bragg's law, it is assumed that the small peak appearing at shorter wavelength region is related to lower refractive index, n_o, corresponding to the short molecular axis of azo chromophores, and the reflection peak at longer wavelength region is attributed to higher refractive index, n_e, along the long molecular axis of the chromophores. Therefore, the reversible shift of the reflection band can be interpreted in terms of the reversible transformation between the random and the anisotropic molecular orientation

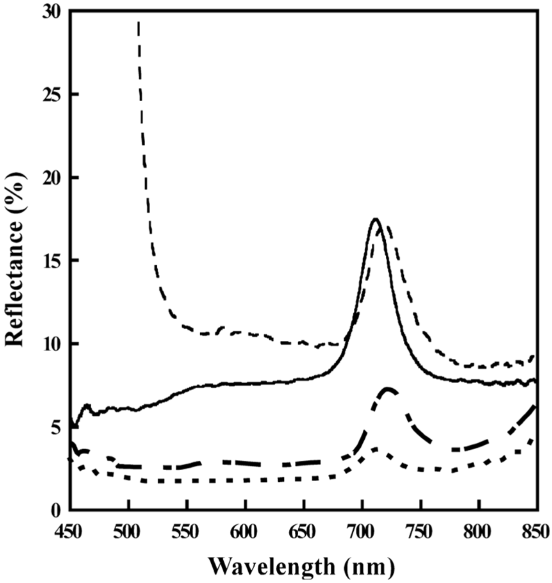
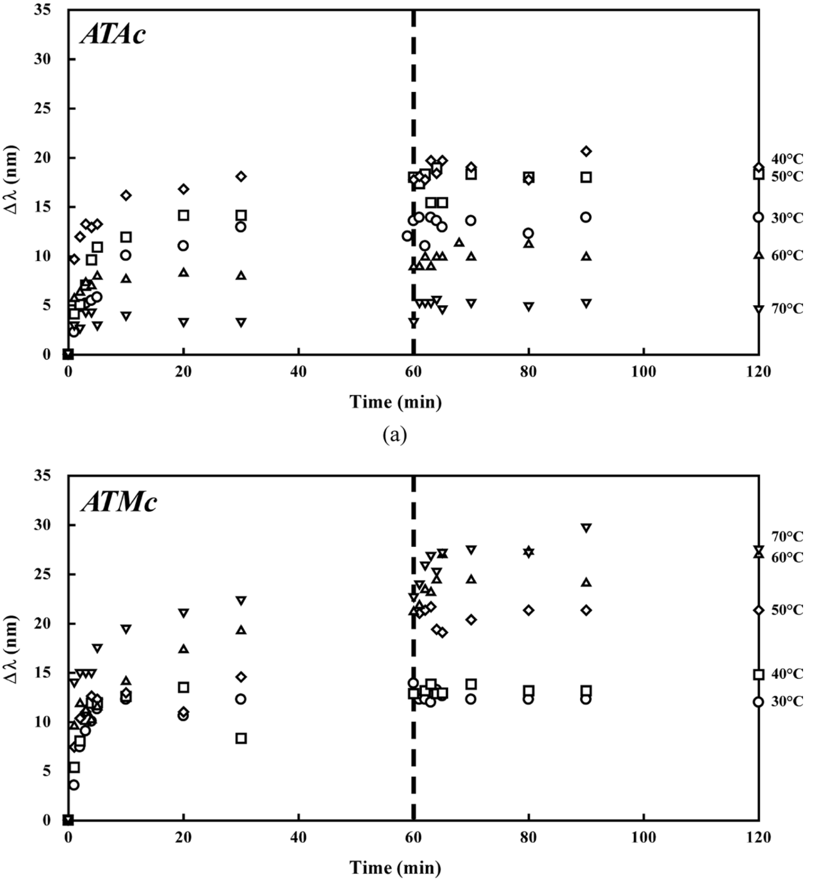


FIGURE 4 Reflection spectra of the ATMc/SiO_2 composite film before (solid line) and after (dashed line) irradiation with LP light from an Ar^+ laser and polarized reflection spectra of the same composite film after LP light irradiation by using a parallel (dotted line) or perpendicular (dashed-dotted line) polarizer to the polarization direction of the LP light.

of azobenzene and tolane groups in the voids by irradiation with LP and CP lights [3].

The shift width of the reflection band of both ATAc and ATMc composite films after LP light irradiation was smaller than that infiltrated with azobenzene homopolymer (ca. 30 nm). This may be due to the presence of the rigid and plane tolane group having less photoresponsive property. However, photo-orientation was found to be strongly dependent on temperature as mentioned above. Therefore, in order to clarify the temperature dependence of the photo-tuning behavior of the composite films, the shift widths ($\Delta\lambda$) of the reflection peak wavelength at various temperatures were plotted in Figure 5, where $\Delta\lambda$ is the difference in the reflection peak wavelength before and after irradiation. The temperature dependence was similar to that of the photoinduced birefringence shown in Figure 3. The flexibility and mobility of the side groups in the copolymers are one of the important factors influencing the photoresponsive properties of the composite films. Thus, $\Delta\lambda$ was increased with an increase in temperature because of higher flexibility as well as higher mobility of the polymer segments of the



(a)

(b)

FIGURE 5 Changes in $\Delta\lambda$ of (a) ATAc; and (b) ATMc/SiO_2 composite films by irradiation with LP light from an Ar^+ laser at 30°C (circular), 40°C (square), 50°C (diamond), 60°C (triangle), and 70°C (inversed triangle).

copolymers. The ATMc composite film showed a larger wavelength shift than the ATAc composite film; $\Delta\lambda$ was 30 nm for ATMc and 20 nm for ATAc, respectively.

CONCLUSION

We have fabricated phototunable photonic crystal by infiltration of the liquid crystalline copolymers having both azobenzene and tolane groups in the SiO_2 inverse opal structure. The irradiation with LP and CP lights resulted in the reversible transformation between a random and an anisotropic molecular orientations of the azobenzene and tolane groups in the voids. Consequently, a reversible and stable shift of the reflection band to longer wavelength could be achieved. The shift width of the reflection band of the copolymer/SiO_2 composite films was smaller than that of azobenzene homopolymer/SiO_2 composite film at room temperature. The introduction of the tolane group having higher birefringence exhibited little effect on improvement of the photoresponsive properties. This may be related to the rigid structure of tolane group and its less photo-orientation property due to their strong laterally intermolecular interaction. In addition, the photoresponsive properties were found to be dependent on the flexibility and mobility of the polymers infiltrated in the composites.

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