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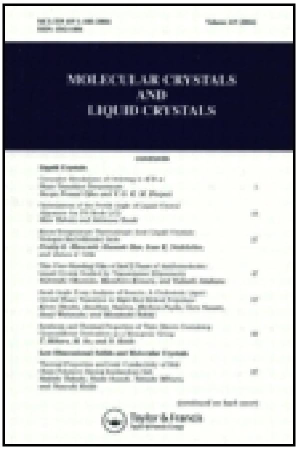

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Version of record first published: 22 Jul 2010

To cite this article: Sunnam Kim, Takahiro Shiozawa, Tomonari Ogata, Takamasa Nonaka & Seiji Kurihara (2009): Photo-Response Properties of Inverse Opal Infiltrated with Push-Pull Type Azobenzene Functionalized Polymer Liquid Crystals, Molecular Crystals and Liquid Crystals, 498:1, 40-48

To link to this article: http://dx.doi.org/10.1080/15421400802612102

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*Mol. Cryst. Liq. Cryst.*, Vol. 498, pp. 40–48, 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802612102

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# Photo-Response Properties of Inverse Opal Infiltrated with Push-Pull Type Azobenzene Functionalized Polymer Liquid Crystals

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*Azo-containing polymers,* poly*(DR1Mc),* poly*(Dc2AzMc) and their copolymers, having push-pull type of azo-group were prepared and their photo-orientation behaviors were investigated. They were infiltrated into silica inverse opal, and reversible Bragg reflection shift was induced by irradiation of light in a range of 500 nm to 600 nm. With linearly polarized light irradiation, Bragg reflection of inverse opal was shifted to longer wavelength region, because azobenzene compounds oriented perpendicular to the axis of incident polarized light and the refractive index contrast was changed. On the other hand, with unpolarized light, Bragg reflection was shifted to shorter wavelength region. This blue shift was due to the molecular orientation preferring parallel to the incident light direction.*

**Keywords:** azobenzene; Bragg reflection; inverse opal; photo response properties; push-pull

## INTRODUCTION

Three-dimensional (3D) photonic crystals (PCs) consisting of spatially periodic ordered dielectrics have attracted considerable attention due to their potential applications in confining and controlling light in all three directions of space [1–7]. The ability to control light is brought by an appearance of photonic band gap. The photonic band gap (PBG) mainly depends on lattice constants and refractive index contrast of the constructing materials as can be expressed by following

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Bragg's equation.

$$\lambda = 2(2/3)^{1/2} d(\mathrm{n}_{\mathrm{eff}}^2 - \sin^2\theta)^{1/2} \tag{1}$$

$$\mathrm{n}_{\mathrm{eff}} = \{\mathrm{n}_{\mathrm{sphere}}^2 f + \mathrm{n}_{\mathrm{void}}(1-f)\}^{1/2} \tag{2}$$

where, $\lambda$ is the wavelength of the diffracted light (or the so-called stop band), $\mathrm{n}_{\mathrm{eff}}$ is the mean refractive index of the crystalline lattice, $d$ is the interplanar spacing of the structure, and $\theta$ is the angle between the incident light and the normal to the surface of the crystals. The $\mathrm{n}_{\mathrm{eff}}$ is dependent on the consisting materials and filling factor. Any variations in either spacing or refractive index should result in an observable shift in the diffraction peak.

On the other hand, Disperse red 1 (DR1) azobenzene compounds are well known as materials for effective and high speed photo-response properties. Based on its rapid trans-cis-trans photoisomerization cycle, the azo groups can be easily aligned perpendicular to the polarization axis of the linearly polarized light irradiation, and also the random alignment can be restored by following circularly polarized light irradiation [8–13]. From this point of view, photo-tuning of PBG is possible by infiltration of azobenzene compound into the inverse opal regarding to the refractive index change via the photo-alignment property [7]. In this study, *poly*(DR1Mc-*co*-MnPBMe)s were synthesized with various composition and photo-response properties in the bulk films were investigated. In addition, copolymers were infiltrated into the $SiO_2$ inverse opal and the photochemical tuning of PBG was investigated.

## EXPERIMENTAL

DR1Mc and MnPBMe were synthesized and copolymerized by using AIBN as initiator at 60°C for 48 h in DMF. The molecular weights and distributions were measured by GPC and the thermal properties were studied by DSC. Solid thin films of the copolymers were prepared by spin coating method and their photo-response properties were investigated with $Ar^+$ laser (LASER GAPHICS 165 LGS, $\lambda = 488$nm, 10 mW/cm$^2$) as a light source. The transmitted light intensity of He-Ne laser ($\lambda = 632.9$ nm) passed through the samples placed between crossed polarizers was measured under irradiation with $Ar^+$ laser. The copolymers were infiltrated into $SiO_2$ inverse opal. The $SiO_2$ inverse opal was prepared as follows: mono dispersed polystyrene (PS) spheres with diameters of 300 nm were arrayed well and subsequently the voids were filled with $SiO_2$ spheres (diameter,

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12 nm). Then, the PS opal infiltrated with $SiO_2$ was converted to macroporous $SiO_2$ inverse opal by heating at 500°C to remove PS spheres. Reflection behaviors of inverse opal infiltrated with copolymers were measured with CCD spectrophotometer (Ocean Optics USB2000, 250–800 nm) during irradiation of Xenon lamp (Ushio SX-UI500XQ, $\lambda = 500\text{–}600$ nm) as a light source.

## RESULTS AND DISCUSSION

Figure 1 shows reflection spectra of the PS opal film with sphere diameters of 300 nm and the silica inverse opal film which consists of air voids instead of PS spheres, and reflection peaks are located at 670 nm and 480 nm, respectively. According to Bragg's equation, the interval spacing and filling fraction were determined to be $d = 331.6$ and $f_{silica} = 0.590$ for PS opal, $d = 278.0$ nm and $f_{silica} = 0.118$ for silica inverse opal, respectively, by using refractive indices (n) of PS (1.59) and silica (1.45).

Copolymers of DR1Mc monomer with MnPBMe(n = 2,6) were prepared by varying the concentration of DR1Mc and spacer length linked to LC mesogen (Table 1). It is clear that the glass transition temperature (Tg) is dependent on the DR1Mc content in the copolymers. Therefore, in order to clarify the effect of the DR1Mc content on the thermal properties, Tg and melting point (Tm) are plotted as

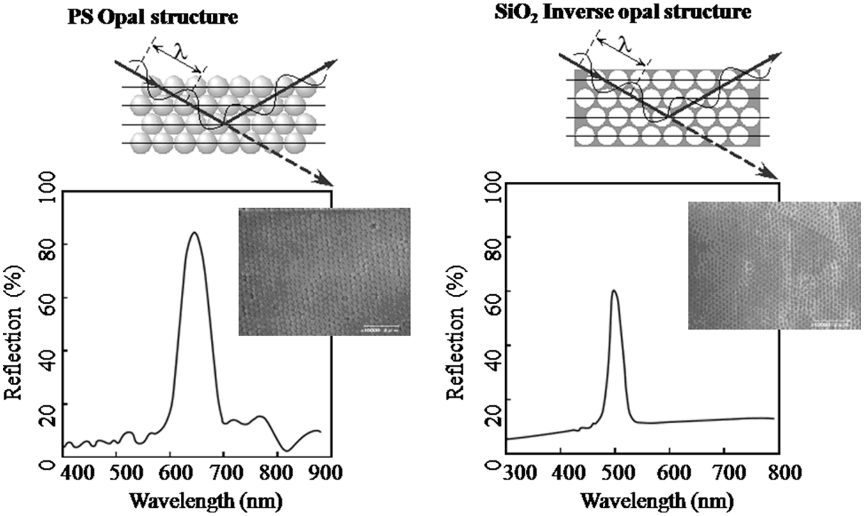

**FIGURE 1** Reflection spectra of opal structure (polystylene with diameter of 300 nm) and $SiO_2$ inverse opal structure and their SEM images.

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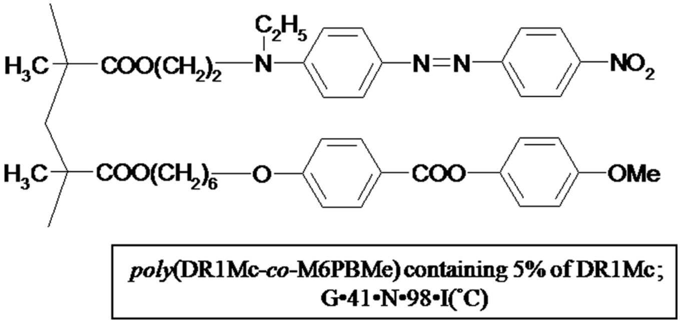

**SCHEME 1** Molecular structure of *poly*(DR1Mc-*co*-M6PBMe).

a function of DR1Mc content in Figure 2. For both copolymers, Tg were increased with increasing in the DR1Mc content. On the other hand, Tm and enthalpy change at Tm were decreased with increasing in the DR1Mc content. In particular, the decrease in Tm is tremendous for *poly*(DR1Mc-*co*-M6PBMe). Basically, no Tm was observed for homo-polymer of DR1Mc. This may be strong electrostatic interaction between azobenzene groups, because the azobenzene groups possess push-pull groups at both ends of the molecule. Therefore, it can be assumed that the intermolecular interaction between the polymer chains is enhanced by the introduction of DR1Mc groups in the copolymers. Consequently, the melting of the copolymers disappeared by increasing in the DR1Mc content in the copolymers. All copolymers containing DR1Mc more than 10 mol% could not be infiltrated in the

**TABLE 1** Copolymerization of *poly*(DR1Mc-*co*-M*n*PBMe) ($n = 2{,}6$)

| Initial feed (mol%) (DR1Mc: M2PBMe: M6PBMe) | | | Molecular weight Mn ($\times 10^3$) | Tg (°C) | Yield (%) | DR1Mc content (mol%) |
|---|---|---|---|---|---|---|
| 100 | 00 | – | 6.1 | 122 | 85 | 100 |
| 70 | 30 | – | 8.7 | 113 | 91 | 53 |
| 50 | 50 | – | 8.6 | 94 | 92 | 35 |
| 30 | 70 | – | 10.8 | 89 | 94 | 25 |
| 10 | 90 | – | 10.0 | 84 | 91 | 13 |
| 5 | 95 | – | 9.0 | 88 | 93 | 5 |
| 00 | 100 | – | 11.6 | 90 | 90 | 0 |
| 70 | – | 30 | 8.6 | 97 | 96 | 52 |
| 50 | – | 50 | 7.8 | 70 | 86 | 37 |
| 30 | – | 70 | 10.6 | 62 | 87 | 23 |
| 10 | – | 90 | 15.0 | 50 | 88 | 10 |
| 5 | – | 95 | 15.0 | 41 | 82 | 5 |
| 00 | – | 100 | 14.4 | 41 | 86 | 0 |

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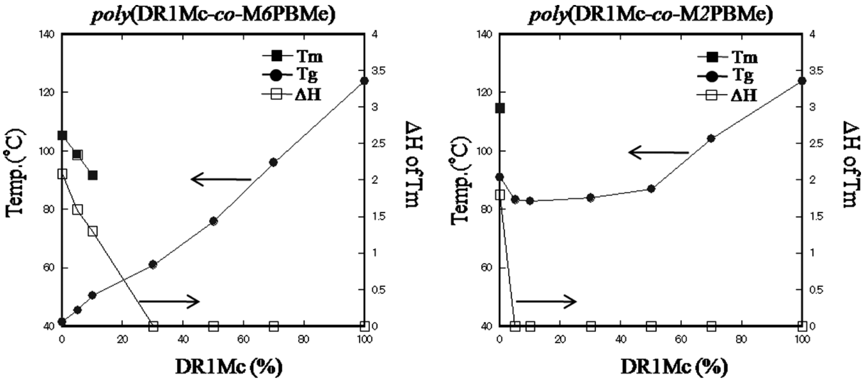

(a) (b)

**FIGURE 2** Thermal properties of *poly*(DR1Mc-*co*-M6PBMe) (a) and *poly* (DR1Mc-*co*-M2PBMe) (b) on the various compositions. It is plotted by DSC measurement.

$SiO_2$ inverse opal. Only *poly*(DR1Mc-*co*-M6PBMe) containing 5% of DR1Mc was successfully infiltrated in the $SiO_2$ inverse opal. So prior to investigate the photo-response properties of the $SiO_2$ inverse opal infiltrating with *poly*(DR1Mc-*co*-M6PBMe), the photo-orientation behavior of the solid film made of *poly*(DR1Mc-*co*-M6PBMe) containing 5% of DR1Mc was explored by irradiation of linearly polarized light with $Ar^+$ (488 nm) as shown in Figure 3. The birefringence was

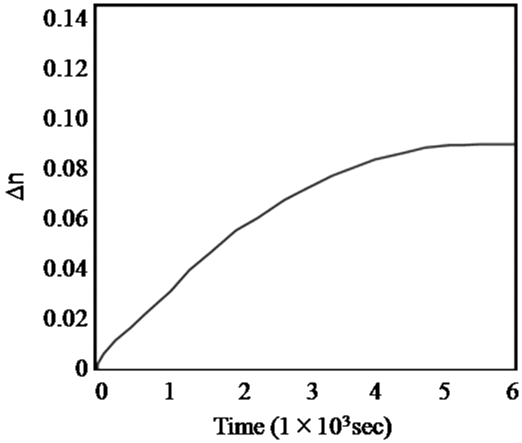

**FIGURE 3** Birefringence of *poly*(DR1Mc-*co*-M6 PBMe) containing 5% of DR1Mc under linearly polarized light. The film thickness is 100 nm.

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increased by irradiation of the linearly polarized light, indicating the transformation from random state to uniaxially oriented state; the photo-induced birefringence was 0.09.

By infiltrating of *poly*(DR1Mc-*co*-M6PBMe) containing 5% of DR1Mc into $SiO_2$ inverse opal, the Bragg reflection band was shifted from 500 nm to 698 nm due to increase of $n_{eff}$. As shown in Scheme 1, *poly*(DR1Mc-*co*-M6PBMe) containing 5% of DR1Mc shows liquid crystalline phase. It was reported that the Bragg reflection of the $SiO_2$ inverse opal infiltrated with low molecule weight liquid crystal was influenced by varying temperature [6]. As shown in Figure 4, reflection band at 698 nm of $\lambda$max was decreased and shifted to the longer wavelength (709 nm) by heating in the range of nematic phase(∼100°C) and then turned to the shorter wavelength (700 nm) by continuous heating above isotropic temperature. By the cooling, the reflection band was restored to the original position undergoing

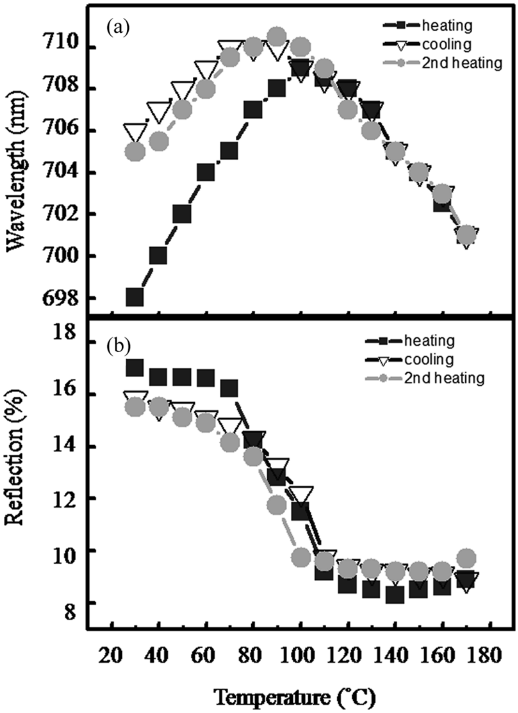

**FIGURE 4** Thermal effect on the Bragg reflection band. Dependence of reflection wavelength (a) and reflection intensity (b) on the temperature during heating and cooling of inverse opal infiltrated with *poly*(DR1Mc-*co*-M6PBMe).

the opposite course of heating, although reflection band position was slightly different according to the cooling rate.

In order to explore the photo-tuning of the PBG properties, reflection spectra were measured under irradiation of polarized/unpolarized light and shown in Figure 5. Under linearly polarized light irradiation, reflection band was shifted to longer wavelength region, and contrary, under unpolarized light irradiation reflection band was shifted to shorter wavelength region. This result was induced by the refractive index change via the photochemical molecular orientation. As shown in Scheme 2, when molecular orientation was induced perpendicular to the polarized axis of the incident light under linearly polarized light irradiation, Bragg reflection is related to the major axis component ($n_e$) and the minor axis component ($n_o$). On the other hand, in the case of unpolarized light irradiation, molecular orientation parallel to the incident light direction was induced, only minor axis component ($n_o$) influenced the wavelength of the

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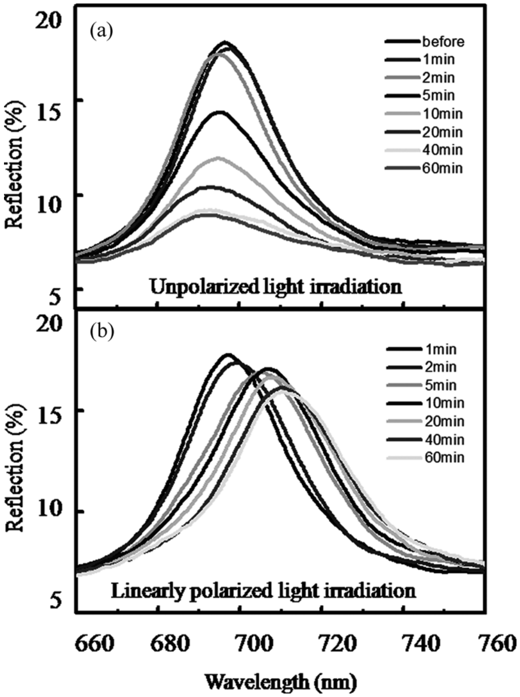

**FIGURE 5** Time course of reflection spectra of *poly*(DR1Mc-*co*-M6PBMe) containing 5% of DR1Mc under irradiation of unpolarized light (a) and polarized light (b).

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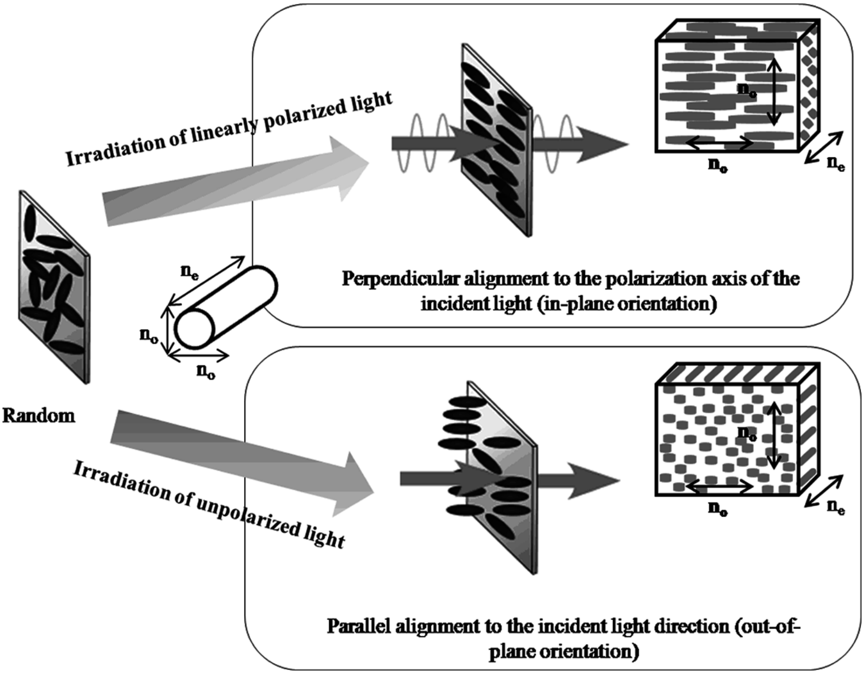

**SCHEME 2** Molecular orientation by linearly polarized light and unpolarized light irradiation.

Bragg reflection band. Figure 6 shows the reflection behaviors for two polarized components under irradiation of linearly polarized light. Reflection band was observed at 698 nm by rapid cooling. During linearly polarized light irradiation, Bragg reflection band was detected in the two opposite ways corresponding to the refractive indices parallel and perpendicular to the molecular orientation direction. The reflection band for the major axis component ($n_e$) of the alignment was red shifted as 12 nm due to the refractive index increase, while the reflection band for the minor axis component ($n_o$) was blue shifted as 10 nm due to the refractive index decrease.

## CONCLUSIONS

Azo-containing polymers, *poly*(DR1Mc-*co*-MnPBMe)s, having push-pull type of azo-group and phenyl benzoate ester group were infiltrated into silica inverse opal. With irradiation of light to the inverse opal, reversible Bragg reflection shift was observed by the change of refractive index contrast regarding to the azobenzene alignment.

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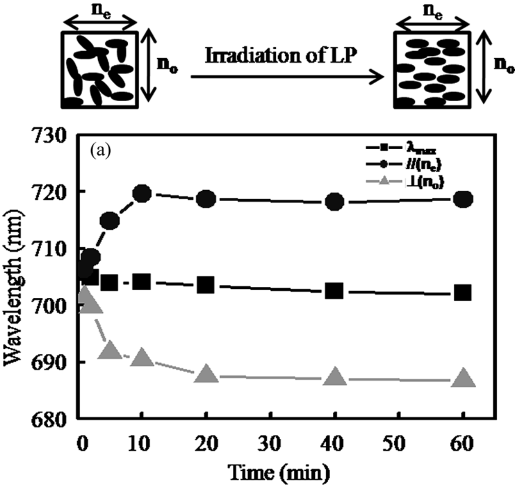

**FIGURE 6** Reflection spectra of *poly*(DR1Mc-*co*-M6PBMe) containing 5% of DR1Mc under linearly polarized light irradiation. Dependence of reflection wavelength on irradiation time.

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