Photoinduced Tuning of Optical Stop Bands in Azopolymer Based Inverse Opal Photonic Crystals**

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Photo-tunable photonic crystals were prepared from three dimensional (3D) colloidal crystal templates using a photosensitive azopolymer. For the preparation of azopolymer infiltrated photonic crystals, silica colloidal crystals were fabricated by gravity sedimentation, a self-assembly technique. The interstitial voids between colloidal particles were filled with azopolymer and azopolymer inverse opals were produced by treatment with aqueous hydrofluoric acid. These photonic crystals exhibited stop bands in their transmission spectra measured in the normal incidence to the (111) plane of face centered cubic (fcc). The photonic bandgap of the azopolymer infiltrated opal and inverse opal could be controlled by the refractive index change due to the photoinduced orientation of azobenzene chromophores. When the azopolymer photonic crystals were irradiated with linearly polarized light, their bandgap positions were shifted to shorter wavelength regions with increasing irradiation time. This behavior experimentally produced a photoinduced orientation of the azobenzene groups in parallel with the incidence of the excitation light. Through such an out-of-plane orientation of azo chromophores, parallel to the [111] fcc crystallographic axis, the effective refractive index of the photonic crystal medium was decreased. Therefore, a blue-shift in bandgap positions was consequently induced with 20–40 nm tuning ranges. The out-of-plane orientation was confirmed by angular resolved absorption spectral measurements.

1. Introduction

Photonic crystals (PCs)[1,2] which are arrays of dielectric materials with a one, two, or three dimensional periodicity have attracted considerable attention during the past decade. PCs have been considered to be one of the most promising materials for manipulating light in three dimensional spaces for all optical signal processing and optical integration technology.

Through numerous theoretical studies and experimental work, a complete photonic bandgap (PBG) has been introduced for a PBG material to cover all three dimensions. One possible approach is a three dimensional architecture such as artificial opal structures which are constructed from self-assembled colloidal spheres[3,4] such colloidal PCs have been widely investigated for other optical applications due to their low-cost and ease of fabrication. To open the full PBG in 3 dimensions, various attempts have been tried through the infiltration of several high refractive index materials into the nanoscale voids of the colloidal PC. Because the opaline structures based on a colloidal assembly can not have complete PBGs; they exhibit only a pseudo gap or optical stop band in a certain crystallographic axis[5,6].

Tunable PCs, the bandgap of which can be controlled through external parameters, such as physical extension, chemical treatment, an electric field, and light irradiation, have recently been investigated for use in tunable optical devices. PCs based on colloidal crystals have been good candidates for tunable PCs because of their macroporous structures to easily infiltrate other functional materials. Based on this infiltration technique, the concept of tunable PCs has been proposed, in which the PBG can be tuned as desired by controlling certain parameters such as lattice spacing, refractive index, and space-filling factor of colloidal PCs. Tunable PCs based on the concept of modifying the lattice constant have been reported. For example, an external mechanical force,[7,8] the volume phase transition,[9,10] change of temperature[11] or ionic strength,[12] light irradiation,[13] the order-disorder phase transition,[14] and anisotropic colloidal shape.[15] Other tunable PCs have been reported based on changing the refractive index contrast. Photo-tunable PCs by refractive index change due to photochromic reaction of a spiro dye,[16,17] and liquid crystal (LC) infiltrated opal and inverse opal PCs, have been demonstrated for tuning a band through external factors such as electrical field, thermal energy, and photochemical reaction.[18-23]

Kubo et al. recently demonstrated a tunable PC structure infiltrated with photosomerizable azobenzene dyes blended with LC molecules.[22,23] More recently, Ozin group demonstrated the tuning of defect modes using a photochemically and ther-
mally controllable planar defect layer composed of azo-chromophores.[24] Both studies illustrate important possibilities of azobenzene materials as a one of the bandgap engineering strategies in the PC field.

These azobenzene-functionalized materials have very useful controllability and processibility for refractive index processing because of their efficient photodynamic properties. For that reason, azo dyes and polymers have been widely studied for various optical properties such as the optical alignment[25] or refractive index modulation.[26,27] Thus, the manipulation of azo materials can offer an opportunity to control refractive indices and optical signals.[28] Azobenzene moieties exist in two geometric isomers, trans and cis forms, in which the isomerization reaction is a light- or heat-induced interconversion of the two isomers. A photo-orientation of azobenzene molecules within the trans↔cis photoisomerization also occurs when these molecules are photo-selected by linearly polarized light with an appropriate wavelength. The azobenzene molecules experience successive cycles of trans↔cis photoisomerization and eventually become aligned perpendicular to the plane of polarization of the irradiation.[29,30] In particular, in the case of azobenzene-functionalized polymers, they show more efficient and stable photodynamic properties than an azo dye molecule, because the light induced ordering of azo chromophores in the polymer case can be effectively restored after switching off the laser light compared with the case of the azo molecule itself.

In our system, we introduced an azobenzene-functionalized polymer as a route for the modification of refractive index contrast in the colloidal crystal based PCs. The resulting azobenzene based colloidal PCs can exhibit tunable optical stop bands due to the photoinduced molecular orientation of photoresponsive azobenzene-functionalized polymer. In addition, an azopolymer macroporous structure, namely, an inverse opal, exclusively composed of an azobenzene-functionalized polymer was demonstrated in this paper. This approach is a simple and easy method for the bandgap engineering of colloidal PC structures by varying the light induced refractive index contrast. Furthermore, the stop band tunability dependent on the irradiation times for the excitation of the azobenzene chromophores is also investigated. The possible mechanism for the bandgap tuning by the photoresponsive azobenzene is proposed; based on the concept of effectively changing the refractive index by a photoinduced orientation of an azopolymer.

2. Results and Discussion

2.1. Morphologies in the Bare, PDO3 Infiltrated and Inverse Opal

A scanning electron microscopy (SEM) image of the top surface of the bare silica colloidal crystal is shown in Figure 1a. Monodispersed silica particles were closely packed on the substrate by gravity sedimentation. A face-centered-cubic (fcc) lattice similar to a natural opal was observed which was similar to previous reports employing the sedimentation method.[31] In our case, colloidal crystals could be obtained on a millimeter scale laterally and the thickness of colloidal crystal was about 60 μm, corresponding to about one hundred colloidal layers. This 3D opaline structure generally has a filling ratio of 74:26 for silica and air. Throughout these porous structures, the precursor solution continuously flowed and diffused by capillary force, filing the void regions with the Poly(disperse orange 3) (PDO3) polymer after evaporation of the solvent. The well pe-

![Figure 1. SEM images of bare, infiltrated and inverse opals: a) top (111) surface of bare opal; b) top (111) of infiltrated opal; c) the cleaved edge plane of an infiltrated opal; d) top (111) of inverse opal. All inset pictures are high magnification images. e) transmission spectra of bare, infiltrated, and inverse opals.](image-url)
netrated and infiltrated azopolymer throughout the interconnected nano-void channel of the bare silica crystal was observed as shown in Figure 1b. In Figure 1c, the cross section image of the azopolymer infiltrated structure clearly shows that the PDO3 polymer was completely filled to the bottom of the colloidal crystal. No significant change in the crystallinity of the colloidal crystal was observed before and after infiltration. The crystal lattice might be very slightly shorter than that of a bare opal structure after the infiltration process because of the volume shrinkage of the PDO3 polymer during the polymerization. However, this slight lattice change due to the volume shrinkage of the polymer was negligible, as shown in our previous reports concerning the case of PMMA.[32,33]

In the case of the preparation of the PDO3 inverse opal structure, the infiltrated opal was immersed in a hydrofluoric acid (HF) aqueous solution and the SiO2 spheres were etched out. During this process, the exposed surface of the silica colloidal template was initially dissolved and the melting flow continuously streamed out through the 3-dimensionally interconnected nano-voids, and finally developed as a solubilizing solution. After thoroughly rinsing with DI water and drying in a vacuum oven (10−2 Torr) at room temperature, the resulting PDO3 inverse opal structure was clearly shown in Figure 1d. This ordered macroporous structure, called an inverse opal, is a 3D inverted fcc array. Recently, Li et al. reported an azo polymeric porous structure induced by a sphere-pore inversion of azopolymer colloidal arrays.[34] Their mesoporous films were obtained from a solvent treatment due to a hydrophobic core and a hydrophilic corona of polymeric colloidal sphere. The pore size of their porous structures was shrunk, while the pore of our PDO3 inverse opal was almost not changed as shown in Figure 1d.

2.2. Stop-Band Formation in Bare, PDO3 Infiltrated and Inverse Opal

Optical properties of the colloidal PC structures were evaluated by transmission measurements at the normal incident direction to the fcc (111) plane. For the artificial opal structures, fcc PCs made of colloidal spheres, the PCs generally do not have a complete photonic bandgap, and a bandgap occurs only at the [111] crystallographic axis. This incomplete bandgap is often referred to as a pseudo gap or stop band because it only appears in the transmission spectrum along a certain direction of propagation.[5,6] Band gap widths are subject to refractive index contrast, while gap positions are governed by the effective refractive index and lattice parameter.[15]

The optical stop band is determined by Bragg’s law satisfied by multiple Bragg reflection conditions that is \( \lambda_{max} = 2d_{111}\sqrt{n_{eff}^2 - \sin^2 \theta} \), where \( d_{111} = \sqrt{2/3D} \) is the lattice spacing of the (111) planes in the fcc, \( D \) is diameter of spheres, respectively. \( n_{eff} = \sqrt{n_p^2 + (1-f)n_v^2} \) is the effective refractive index, \( n_p \) and \( n_v \) are the refractive indices of the colloidal particles and the interstitial void region, respectively, \( f \) is the filling factor of the fcc close-packed structure, and \( \theta \) is incident angle. Ideally, bare silica opals are comprised of 74% silica and 26% air. The refractive indices of silica and air are known to be 1.45 and 1.00 @ 589 nm, respectively. The transmission spectrum was obtained when the probe beam was normal incident to the (111) plane of the fcc colloidal crystal. The bandgap of a bare silica opal is observed at around 1540 nm where the transmission is noticeably decreased in the transmission spectrum (Fig. 1e). This measured maximum peak wavelength of stop bandgap, \( \lambda_{max} \) was well matched with the calculated one using a 700 nm lattice spacing.

In the case of PDO3 infiltrated opal, the \( \lambda_{max} \) was observed at about 1580 nm as shown in Figure 1e. The peak position was shifted to a longer wavelength than the \( \lambda_{max} \) of the bare opal due to the increase in effective refractive index in the infiltrated PC. After the azopolymer was infiltrated into the void instead of air, the refractive index of colloidal crystal medium, \( n_r \) was changed. The refractive index of PDO3 was determined as 1.59 @ 633 nm, as evidenced by ellipsometry measurements (EPI, Nanofilm Technologie GmbH). The calculated effective refractive index of the infiltrated opal medium was increased from 1.35 to 1.49. In addition, the stop band width of the infiltrated opal was accordingly reduced to 39.5 nm compared to the bare opal case, 52.6 nm. The reason for why this band width change is caused is due to the less coherent scattering strength[36] based on the low index contrast from SiO2/air to SiO2/PDO3.

When the silica colloidal template was removed by the HF etching process, the PC structure changed to a macroporous inverse opal structure. At the transmission spectrum of an inverse opal, the stop gap position was measured to be about 1320 nm caused by a decrease in the effective index. The index contrast was dramatically increased by the air fraction, ~74%, created by etching and the band width was widened due to the strong coherent scattering strength, compared to bare or infiltrated opals. The measured band width of the inverse opal was observed as 72.4 nm. Moreover, the peak attenuation at the \( \lambda_{max} \) was also noticeably increased due to the enhanced index contrast.

2.3. Photo-Induced Stop-Band Tunability in a PDO3 Infiltrated and an Inverse Opal

In order to analyze the light-induced optical properties of colloidal PC structures based on PDO3, the azopolymer infiltrated opal was exposed to an Ar+ laser beam at 488 nm. The stop gap position \( \lambda_{max} \) of the infiltrated and inverse opal was shifted to a shorter wavelength as the irradiation time increased (Fig. 2). No additional blue-shift could be observed with the irradiation time longer than 25 min because photo-induced orientational motion of azo molecules probably was saturated.

As mentioned earlier, the gap position is determined by the lattice spacing and the refractive index contrast. Because the lattice spacing was fixed at about 700 nm, as shown in SEM images of the infiltrated opals (Fig. 1a and b), the blue-shifted stop band of the infiltrated opal could be due to the decrease of the effective refractive index. The change of refractive index of a PDO3 medium can be caused by photoinduced reorientation of azo groups. This behavior also implies that the azo mol-
molecules were oriented parallel to the direction of propagation of the excitation light, by the irradiation of light. In the infiltrated or inverse opal based on the azopolymer, the out-of-plane orientation of azobenzene molecules, parallel to the incident direction of excitation light, leads to a decrease in the average refractive index of the azo medium.

Before the irradiation of light, the refractive index of the azopolymer in a nano-void region should be macroscopically averaged because of its isotropic state, random orientation of azo molecules. However, if the azobenzene molecules start to be aligned by the irradiation, the out-of-plane orientation becomes partially dominant with the irradiation time increased, the ratio of the aligned molecules normal to the surface, out-of-plane orientation would be increased. Consequently, the average index of the azopolymer part was decreased in the void region. Similar refractive index modulation behaviors can be observed in the previous works about LC infiltrated tunable PCs by a electric field modulation.[19–21] In the case of LC infiltrated PC, based on the electrically orientational change of the active molecules, the effective refractive index can be controlled in the infiltrated LC domains, and the bandgap of the PC can be consequently manipulated.[22,23]

They have been widely studied and characterized for the photoinduced orientational behaviors of azo-chromophores effect on the average indices of anisotropic media. In general, azobenzene molecules can be efficiently photo-oriented when the azopolymer is initiated by the photochemically induced anisotropy by the irradiation. There are two types of orientation modes, as extreme cases; one is the uniaxial in-plane orientation of the azobenzene with an electric transition dipole moment parallel to the plane of the film surface when the linearly polarized light which is parallel to a normal to the film surface, the other is the out-of-plane orientation along the propagation direction of light. There are a number of reports on the photoinduced out-of-plane reorientation of azobenzenes.[37–41] Moreover, spectroscopic evidence reported to date is consistent with the out-of-plane orientation of azobenzene molecules, reorientation of azobenzene chromophores toward the direction of propagation of the excitation light.[42,43] In order to evaluate the photoinduced in-plane and out-of-plane orientations of azobenzene chromophores, angular resolved absorption spectra of photoirradiated films were usually measured with various incident angles of probe light, which are defined as the angles between the propagation direction of light and the surface normal. From the angular resolved absorption spectra with p- and s-polarized probe light, two major contributions could be employed to confirm the out-of-plane photo-orientation, one is the $\pi -$ $\pi ^*$ absorption maximum of the azobenzene groups taken by p- and s-polarized probe light, the other is the absorbances of the monomeric species and H-aggregates.[43]

2.4. Out-of-Plane Orientation of Azobenzene Chromophores in PDO3 Based Colloidal Crystals

In the case of the PDO3 infiltrated opal, the total bandgap tuning range was about 40 nm after irradiation with a fixed laser power, 100 mW cm$^{-2}$ for 25 min as shown in Figure 2a. In addition, the photo-induced $\lambda_{\text{max}}$ tunability of the PDO3 inverse opal was also evaluated under the same conditions as were used for the infiltrated opal. As shown in Figure 2b, the stop gap peak was also shifted to a shorter wavelength with increasing irradiation time with similar tendency as the infiltrated opal case. The total tuning range of the PDO3 inverse opal was measured about 20 nm.

Figure 2c shows the stop band tuning ranges of the PDO3 infiltrated and inverse opal, respectively. Based on the bandgap tuning range, the calculated effective index decrease was about
0.034 in the azopolymer medium of the infiltrated opal by simple evaluation from Bragg’s law. On the other hand, the effective refractive index decrease in the azopolymer medium of the inverse opal could be expected to be about 0.016. As expected, this value is rather small compared to the case of the infiltrated opal. Probably, this relatively small change could result from the strong scattering process due to the larger refractive index contrast in the inverted azopolymer and air interface. That is, the excess light scattering for azobenzene excitation wavelength could occur due to their macroporous structure nature, the only small portion of the azo-chromophores located in the vicinity of the surface in the azopolymer inverse opal would accordingly undergo photoinduced isomerization. In addition, there is another possibility that the azopolymer could be damaged during the HF treatment when removing the silica template. Thus, the estimated effective index values of PDO3 infiltrated and inverse opal seem to be rather high considering the amorphous nature of the PDO3 azopolymer material used in this study. Generally, these highly out-of-plane orientations in amorphous azopolymers are not expected. Even in the in-plane orientation of amorphous azopolymers by linear polarized irradiation, it is usually not easy to obtain an effective index change by photoinduced alignment of PDO3 polymer that corresponds to 0.034 in the in-plane birefringence. Furthermore, while a number of studies on the in-plane alignment of amorphous azopolymer have been carried out, there are no proper reports that investigate the out-of-plane orientational motion of an amorphous azopolymer to date.

Recently, in the LC azopolymer case, Yaroshchuk et al. found that the irradiation of non-polarized light with a low intensity (11 mW cm–2) on an LC azopolymer with polar groups did not change the orientational distribution of azo-chromophores. However, they observed homeotropic alignments when irradiated with a high intensity beam (90 mW cm–2). Moreover, the irradiation of an LC azopolymer with alkyl groups increased the out-of-plane ordering in the orientation of azo-chromophores, especially, out-of-plane orientation. The molecular motion of azo-chromophores in the amorphous conformation seems to be somehow affected by closely packed 3D colloidal crystal structures.

2.5. Angular Resolved Absorption Spectrum Measurement

Therefore, for a further investigation of the photoinduced orientation of PDO3 amorphous azopolymer in a physically confined structure, absorption spectra were obtained at various incident angles of linearly polarized probe light. It is possible to evaluate the spatial orientation of azobenzene chromophores through angular resolved absorption spectra measurements using p- and s-polarized light. The probe light was polarized into p- and s-polarization, respectively. Figure 3 shows the schematic of p- and s-polarized light incidence with respect to out-of-plane alignment direction of azo-chromophores. p-Polarized light with the electric vector parallel to the plane of incidence is sensitive to an out-of-plane orientation, while s-polarized light with an electric vector perpendicular to the plane of incidence is relatively insensitive. The spectroscopic information obtained using p- and s-polarized light was evaluated by the following two parameters. One is \( A_{p420}/A_{s420} \), whereas \( A_{p465} \) and \( A_{s465} \) are π–π* absorption maximum of the azobenzene groups from p- and s-polarized light, respectively. Here, \( A_{p465}/A_{s465} \) is \( A_{p400}/A_{s400} \) in our system because absorption maximum of PDO3 is located at 465 nm wavelength. The other parameter is \( A_{H-aggregated}/A_{monomer} \) that corresponds to \( A_{p465}/A_{s420} \) in our case. Here, \( A_{p420} \) corresponding to existence of monomeric species denote as the p-polarized absorbance at around 420 nm. \( A_{p400} \) corresponding to H-aggregates defined as the p-polarized absorbance at around 400 nm. \( A_{p400}/A_{p420} \) was used to reveal the aspects of the H-aggregated azobenzene groups. The absorption spectral blue-shift is considered to result from the H-aggregation, which consists of a cofacial card-packed orientation of azobenzene chromophores.

Comparing with uniform azopolymer film, photo-induced alignment of azobenzene chromophores in a 3D colloidal crystal structure was investigated by collecting angular resolved polarized absorption spectra. Figure 4 shows the angular resolved polarized \( A_{p400}/A_{s400} \) in the PDO3 azopolymer film and infiltrated opal, respectively. The irradiation time for these two samples was fixed at 25 min. The solid line is drawn simply as an eye guide. As shown in Figure 4, the quite distinctive angular dependence on the π–π* absorption maximum of the PDO3
was observed in the infiltrated opal structure. Comparing with PDO3 infiltrated opal case; the clear angle dependence due to the formation of the photoinduced out-of-plane orientation was not observed in the uniform PDO3 azopolymer film under the same irradiation conditions. When the azobenzene chromophores are oriented in the normal to the surface, the values of $A_{p400}/A_{s400}$ are remarkably increased with increasing incident angle because the photoinduced out-of-plane orientation is sensitive to p-polarized light and is a function of the incident light angle. This result implies that photoinduced alignment of azobenzene chromophores in the physically confined structure such as colloidal PC seems to be more favorable toward the out-of-plane direction. As shown in Figure 5a and b, the $A_{p400}/A_{p20}$ and p-maximum peak position also clearly shows the angular dependence, respectively. The $A_{p400}/A_{p20}$ in PDO3 infiltrated opal was less sensitive to incidence angle variation compared to the polymer film case. These behaviors indicate that PDO3 polymer in the colloidal PC structure has a relatively small amount of aggregated azobenzene groups compared with the polymer film sample. This result seems to be reasonable because the polymer chains with azo-chromophores would be expected to have a more condensed conformation in the azopolymer film case. In other respects, since the microscopically confined structures such as close-packed colloidal spheres may constrain aggregations between azo-chromophores, the more uniform distribution of polymer backbones with azo-chromophores would be expected in the infiltrated opal sample. As shown in Figure 5b, angular dependence on the p-maximum peak wavelength was shifted to shorter wavelength with increasing incident angle. These blue-shift behaviors provide the information on H-aggregation. That is, the aggregations between azo-chromophores in the polymer film are more severe than those in an infiltrated opal sample. In addition, Figure 5c shows the effect of the H-aggregation on the p-absorption with the incident angle after the same irradiation time, 25 min. In the case of the polymer film, the blue-shift tendencies of absorption spectra were much more prominent than the infiltrated opal case. Considering this plot, it is easier to understand that the formation of the card-packed H-aggregates could be microscopically hindered in the infiltrated opal.

While the efficient out-of-plane alignment of azobenzene chromophores can be explained using a concept corresponding to the aggregation behavior based on the material properties, we can also describe orientations of azo-chromophores in terms of the interaction between the excitation light and the sample structure. One possible explanation can be the depolarization of the excitation light due to excess light scattering through the 3D PC structure. Actually, the polarized excitation light can be largely depolarized by excess scattering in the PC medium, although we used linearly polarized light for the photoisomerization of the PDO3 sample. Unfortunately, due to this unavoidable excess scattering in the PDO3 PC structure, a series of reasonable results corresponding to angular resolved absorption spectra in the PDO3 inverse opal sample could not obtained. The detectable signal in the spectrometer was too weak to systematically analyze the spatial alignment of azobenzene chromophores because of the excess light scattering due to the large refractive index contrast between the PDO3 polymer and air. Yaroshchuk et al. observed a photoinduced out-of-plane orientation of azo-chromophores by unpolarized light, while the efficient out-of-plane alignment of azobenzene chromophores was not observed in the uniform PDO3 azopolymer film under the same irradiation conditions.
as an extreme case of an out-of-plane orientation.[27] They proposed that unpolarized light can effectively induce an out-of-plane alignment. Thus, when exposed to unpolarized light, the alignment of azo-chromophores prefers an out-of-plane orientation rather than an in-plane orientation. Under considerations based on the aggregation azobenzene chromophores as well as the light interaction in the PDO3 PC structure, the large amount of out-of-plane orientation of azochromophores suggested in our system seems to be more convincing.

In the initial stage of this study on the bandgap tuning by using the photo-induced amorphous azopolymer, such a series of the spectroscopic results that support the more favorable alignment toward out-of-plane of an amorphous PDO3 azopolymer in the microscopically confined structure, was not expected. However, we have found that the photo-induced effective refractive index change of the azopolymer colloidal PCs could be understood in aspects of the large amount of the out-of-plane orientational motion.

3. Conclusions

We demonstrated azopolymer colloidal photonic crystal structures in which the optical stop band can be tuned by photo-orientation of the azobenzene molecules. When the tuning of the bandgap frequency was performed through irradiation with linearly polarized light, the out-of-plane orientation of the azo-chromophores parallel to the incident light increased with increasing irradiation time. In terms of out-of-plane space, the effective refractive index of the azopolymer, PDO3 region was decreased by the increase of the out-of-plane orientation. As a result, the photonic bandgap of the azopolymer PCs was shifted toward a shorter wavelength with increasing irradiation time. Optically band tunable PCs, especially, photoinduced bandgap controllable PCs offer an opportunity of realizing photonic applications with a greater controllability, while conventional tunable PCs by the physical or thermal variation have a drawback in terms of controllability, device damage, and so on, for the practical applications. In addition, the unexpectedly large amount of out-of-plane orientation of azochromophores in our system was observed in the evaluation process of the stop band tuning. Through the angular polarized absorption measurements of PDO3 uniform films and infiltrated opals, the more favorable alignment behavior of azochromophores toward out-of-plane was concluded to be due to a hindrance to the aggregation of azobenzene chromophores and a scattering induced depolarization effect by the 3D photonic crystal structure. Since this resulting large amount of out-of-plane orientational behavior, order of $10^{-2}$, is difficult to observe in amorphous azopolymer materials, we believe that our photonic crystal structure based on an azopolymer can be useful for studies of the photoinduced molecular behavior of the azobenzene functionalized materials in amorphous polymers as well as a promising approach in bandgap engineering in the photonic applications.

4. Experimental

**Synthesis of Poly(disperse Orange 3) (PDO3):** A well known azopolymer was synthesized from bisphenol A diglycidyl ether and disperse orange 3 following the literature procedure [47]. Bisphenol A diglycidyl ether was purchased from Tokyo Chemical Industry. The sample showed a molecular weight of 340.42 g mol$^{-1}$ and a melting point of 40–44 °C. Disperse orange 3 was purchased from Sigma-Aldrich Co. Its molecular weight was 242.24 g mol$^{-1}$ with a melting point of 200 °C. Equimolar amounts of Bisphenol A diglycidyl ether and disperse orange 3 were mixed homogeneously and polymerized at 120 °C for 24 h. The polymerized mixtures were dissolved in tetrahydrofuran (THF) and reprecipitated by adding methanol and cooling at room temperature. The precipitate was filtered and dried in a vacuum oven at 70 °C for 24 h.

**Preparation of the Inverse Opal Based on the Azopolymer:** Silicon dioxide (silica) colloidal micro-spheres (nominal diameter of 0.7 μm, 0.73 ± 0.04 μm) suspended in water were purchased form Duke Scientific Co. A silica colloidal suspension was diluted with aqueous solution (7:3 ethanol/deionized (DI) water) substrate and well mixed as sonicator for 30 min. The resulting solid content in this diluted suspension was 0.1 vol%. Substrates were used as fluorinated tin oxide (FTO) coated glass substrates for a preparation of the azopolymer inverse opal structure. Because FTO layer plays role of a protecting glass substrate in the preparation of the inverse opal, etching step of the silica spheres. The dimensions of FTO substrates were with 25 mm x 37.5 mm. All substrates were cleaned overnight in a 6:1 H2O/H2O2/HCl solution and then thoroughly rinsed in DI water. Finally, an oxygen plasma treatment was performed for 30 min. The colloidal crystals were fabricated by the typical sedimentation technique. The colloidal suspension was loaded on the cleaned surface of substrates, colloidal crystals were obtained after evaporation of an aqueous solution for 48 h during the spontaneously self-organization of silica colloids by the gravity sedimentation. These colloidal crystals were used as templates for preparing azopolymer infiltrated and inverse opal structures. Consequently, the crystallized silica opals were treated at 110 °C for 12 h to remove the remaining aqueous solvent. In the infiltration process, the mixture of Bisphenol A diglycidyl ether and disperse orange 3 were homogeneously mixed and dissolved in THF to 3 wt %. This resulting precursor solution was filtered (0.02 μm) and infiltrated into the inside of the macroporous colloidal crystal structure at room temperature for 12 h and polymerized at 120 °C for 24 h in convection oven. Finally, an inverse opal structure was fabricated by selectively removing silica colloidal spheres of the azopolymer infiltrated colloidal crystal. The infiltrated colloidal crystal was immersed in a 20 wt % HF aqueous solution for 24 h.

**Preparation of a Bare Azopolymer Film:** A bare azopolymer film was prepared to analyze photo-alignment and orientation behavior compared with azopolymer infiltrated or inverted opal structures. The synthesized PDO3 was dissolved in THF to 20 wt % and filtered (0.02 μm). This polymer solution was spun at 800 rpm for 30 s. The sample was dried in a vacuum oven for 30 min to remove residual solvent. The resulting uniform azopolymer film was measured by means of a profilometer to be 3 μm thick. The thickness of azopolymer film was optimized to have similar absorption coefficient of azopolymer infiltrated colloidal crystal samples.

**Irradiation Setup of Azopolymer Photo-Orientation:** The experimental setup for the photo-orientation is shown in Figure 6. An Ar$^+$ laser (Coherent innova 300c) of 488 nm wavelength where has relatively high absorption coefficient of azo-chromophores was used. The laser beam was passed through a polarizer and a half-wave plate, and was expanded by a spatial filter and an objective lens, and was then collimated. This linearly polarized light was directly incident on the samples. The intensity of the collimating beam with p-polarization was fixed at 100 mW cm$^{-2}$.

**FE-SEM Measurement and Transmission Measurement of Stop Band Shift in a Near IR:** Field emission SEM (FE-SEM, S-4700 Hitachi) was used to evaluate the crystallinity of bare, infiltrated and inverse colloidal crystals. The optical stop band properties of colloidal PCs were
characterized using a transmission measurement system as shown in our previous reports [32,33]. The setup of the transmittance measurement system was constituted as follows: light from a single-mode optical fiber (SMF) from a white light source (AQ4303B, Ando) was focused on the sample using an objective lens. The light transmitted through the sample was focused on a multi-mode fiber (MMF)-SMF coupled to an OSA (Optical spectrum analyzer, Agilent 86140B). The resolution bandwidth and sensitivity of the OSA was set at 0.5 nm and -80 dBm, respectively. Using this arrangement, the spot size in the measurement could be determined by adjusting the focal plane to the sample position between the input and output optical fibers (<0.5 mm²). All transmission spectra of PCs were obtained at a normal direction to the (111) plane of the colloidal PC structures. A sample was mounted in a perpendicular direction to the incident light and could be moved in the x, y, and z directions by the x–y–z motorized stage system.

**Polarized UV-vis Spectroscopic Measurement:** The polarized UV-vis spectroscopy (Cary 1E, Varian) was measured for the absorption spectra of PDO3 films and PDO3 infiltrated colloidal crystals. The samples were photoinduced oriented by linearly polarized light irradiation, the anisotropic absorbance using a polarized probe light with electric vectors perpendicular or parallel to polarization of the excitation light was measured. To obtain information concerning the spatial orientation of azo-chromophores, angular resolved absorption spectra of azopolymer films and infiltrated opals that have been exposed to lineation of azo-chromophores, angular resolved absorption spectra of light was measured. To obtain information concerning the spatial orientation of azo-chromophores, angular resolved absorption spectra of azo-chromophores, angular resolved absorption spectra of azopolymer films and infiltrated colloidal crystals. After the spectroscopy (Cary 1E, Varian) was measured for the absorption spectra of PDO3 films and PDO3 infiltrated colloidal crystals. After the stop band tuning of azopolymer infiltrated and inverse opals.