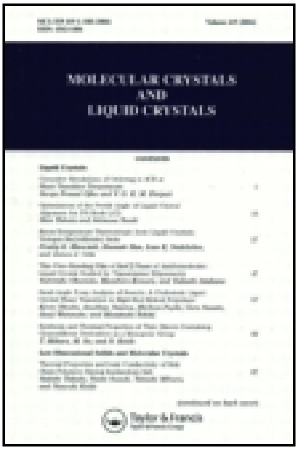


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterization of Photochromic Liquid Crystalline Polymer Beads

Sun Nam Kim [a], Masaki Moritugu [a], Tomonari Ogata [b], Takamasa Nonaka [b] & Seiji Kurihara [b]

[a] Graduate School of Science & Technology, Kumamoto University, Kumamoto, Japan

[b] Department of Applied Chemistry & Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto, Japan

Version of record first published: 31 Jan 2007

To cite this article: Sun Nam Kim, Masaki Moritugu, Tomonari Ogata, Takamasa Nonaka & Seiji Kurihara (2005): Synthesis and Characterization of Photochromic Liquid Crystalline Polymer Beads, Molecular Crystals and Liquid Crystals, 443:1, 127-135

To link to this article: http://dx.doi.org/10.1080/15421400500247078

Mol. Cryst. Liq. Cryst., Vol. 443, pp. 127–135, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500247078

Synthesis and Characterization of Photochromic Liquid Crystalline Polymer Beads

Sun Nam Kim
Masaki Moritugu
Graduate School of Science & Technology, Kumamoto University, Kumamoto, Japan

Tomonari Ogata
Takamasa Nonaka
Seiji Kurihara
Department of Applied Chemistry & Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto, Japan

Sub-micron sized liquid crystalline polymer beads containing azo groups and mesogenic groups were synthesized in order to develop 3D array showing photoinduced stimulus response properties. The size of beads was dependent on the polymerization temperature and the molar ratio of the azo and mesogenic groups. Films of the polymer beads were prepared by casting the suspension liquid on a glass plate. By irradiation of polarized light (488 nm) on the film of the polymer bead assembly, the photoisomerization effect of azo groups on the shape of the polymer beads as well as the molecular orientation of the mesogenic groups in the beads was investigated.

Keywords: azobenzene; monodisperse particles; photoisomerization; photonic crystal

INTRODUCTION

Many colors occur in nature that cannot be explained simply by the absorption and reflection of light. Examples found in nature are the shimmering wings of butterflies and iridescent opals. These colors arise from the interaction of light with highly ordered structures of sizes of the order of the wavelength of visible light. Periodicity and refractive index contrast in photonic crystals results in an appearance

Address correspondence to Seiji Kurihara, Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, 2-39-1 Kurokami Kumamoto-si, Kumamoto 860-8555, Japan. E-mail: kurihara@gpo.kumamoto-u.ac.jp

of photonic band gap. The photonic band gap mainly depends on the lattice constants and the refractive indices of the dielectrics [1]. In opal structure, the diameter of the spheres, d_{k}, is comparable with the wavelength of visible light so the opal acts as a 3D diffraction lattice for visible light, and the colors of the opal are determined by the diameter of the spheres and the effective refractive index. By analogy with X-ray diffraction, the interaction of light within the photonic crystals is described by following Bragg equation (Eq. (1)) [2],

$$m\lambda = 2d_{(111)}({n_{eff}}^2 - \sin^2\theta)^{1/2} \qquad (n_{\mathrm{eff}} = f_1 n_1 + f_2 n_2) \tag{1}$$

where, n_{eff} is an effective refractive index of the colloidal crystals, n_1 and n_2 are refractive indices of spheres and voids, and f is volume fraction, respectively.

Colloid crystals are formed by drying the suspensions of monodisperse particles, and the consequent iridescent colors can be seen on the substrates. Monodisperse spheres with submicrometer dimensions have interesting applications, some of which are described in a continually increasing number of scientific publications about their use as building blocks for colloidal crystals [3–4].

On the other hand, azobenzene molecules are well known to show photoinduced orientation of the LC molecules by irradiation of polarized light through the photoselection process, causing the change in the birefringence [5]. In addition, the photoisomeization of azo dyes results in massive material movement, providing the surface relief gratings. Therefore, if one can synthesize the polymer beads containing azo dyes, the molecular orientation in the polymer beads as well as the change in their shapes will be controlled by means of the photoisomerization of the azo dye introduced in the polymer beads [6–7]. In this study, we synthesized sub-micron polymer beads containing mesogenic and azobenzene groups, and investigated the effect of the photoisomerization of the azo dyes on the shape of the LC polymer beads as well as the molecular orientation of the mesogenic groups in the LC polymer beads in relating to the tuning of the stop band of the photonic crystals or micro-fabrication for the waveguide in the photonic crystals.

EXPERIMENTAL

Monomers, 3AB6Ac, MAz6Mc and M6PBC, were synthesized according to the methods reported earlier. Homopolymers of 3AB6Ac and MAz6Mc and their copolymers with M6PBC were synthesized by precipitation polymerization. The precipitation polymerization was performed in the presence of AIBN as an initiator in ethanol under a nitrogen atmosphere. PVP and Aerosol were added in the polymerization solutions as surfactants. The polymer beads obtained were purified with centrifugation three times or more. The colloidal crystal films were fabricated on a glass substrate by slow sedimentation of polymer beads during evaporation of solvent. And then the film was irradiated by Ar^+ laser with polarized light of 488 nm. The shape of the polymer beads and the structure of beads assembled films were characterized by scanning electronic microscopy (SEM). In addition, the molecular orientation of the mesogenic groups in the polymer beads was characterized by polarized optical microscopy (POM).

RESULTS AND DISCUSSION

In order to assess the optimal condition for the preparation of monodispersed polymer beads, the precipitation polymerization was carried out by varying temperature, time, molar ratio of monomers in copolymers and agitation speed. It was difficult to achieve polymer beads having spherical shape by homo-polymerization of 3AB6Ac or MAz6Mc. The former homopolymer exhibited no particles and the latter had special shape of particle like flat cylindrical or roundish cube. Contrary to the homo-polymerization, spherical polymer beads were obtained by copolymerization of 3AB6Ac with M6PBC. The structure of monomers and the condition of polymerization are shown in Figure 1 and Table 1, respectively.

In fabricating photonic crystals, the size of the polymer beads is one of important factors influencing on the wavelength of stop band of the photonic crystals. Thus, the effect of the polymerization temperature and the molar ratio of the copolymerization on the size of the polymer beads were explored in detail. The size of the polymer beads as a function of polymerization temperature is shown in Figure 2. It is clear that the size decreased with lowering the polymerization temperature.

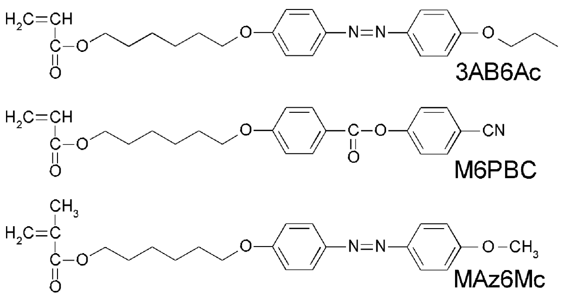


FIGURE 1 Molecular structure of monomer.

TABLE 1 Copolymerization of M6PBC and 3AB6Ac with Different Ratio of Composed Monomer and Temperature. The Reaction is Performed with AIBN as Initiator in Ethanol for 24 hrs. Polyvinylpyrrolidone (PVP) and Aerosol-OT are Used as Stabilizer

3AB6Ac [mg]	M6PBC [mg]	PVP [mg]	A-OT [mg]	T [°C]	*t* [*h*]
20	80	180	40	70	24
20	80	180	40	60	24
30	70	180	40	70	24
30	70	180	40	60	24
30	70	180	40	50	24
50	50	180	40	70	24

In addition, the higher the molar ratio of 3AB6Ac in the copolymer, the smaller the size of the polymer beads at the same polymerization temperature. On the other hand, excessive agitation speed suppressed the formation of the spherical polymer beads. Prior to fabricate the films of the polymer beads assembled, the dispersion condition of the polymer beads was clarified by changing the dispersion solvent. The polymer

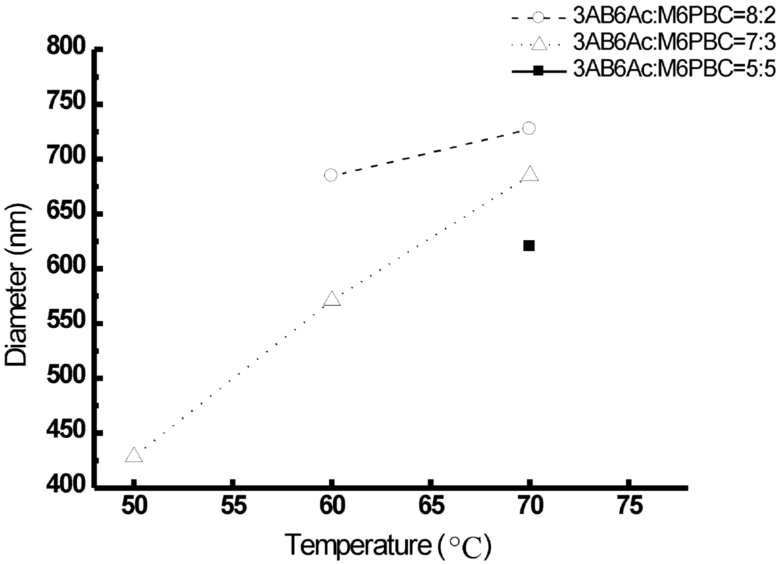
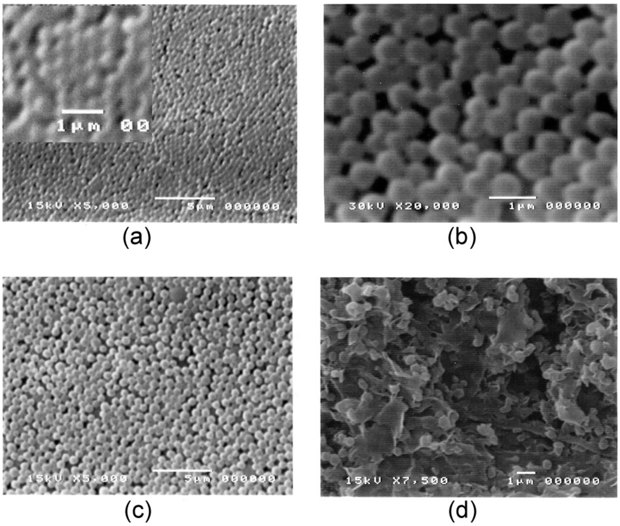


FIGURE 2 Dependence of sphere size on temperature and copolymerization (M6PBC:3AB6Ac) ratio. The diameter of polymer beads is measured by ELS (electrophoretic light scattering spectrophotometer).

beads were not dispersed in water, because of lack of ionic moieties on the surface of the polymer beads. The partially arrayed colloidal crystals were obtained by dropping of polymer bead dispersed in 2-propanol on the glass substrate or dipping the glass in the same dispersion liquid as can be seen in Figure 3.

An iridescent light of the films could not be observed, because the control of the size distribution as well as the order of the packing was not enough. Consequently, the resulting films scattered light strongly. Prior to explore the effect of the photoisomerization of azo groups introduced in the polymer beads, the photoisomerization of the azo dyes in the film was clarified by UV and visible light irradiation.

Figure 4 shows changes in absorption spectra of the film of the poly(3AB6Ac) with the thickness of 200 nm. The absorption maximum is located at around 350 nm corresponding to $\pi - \pi^*$ transition of the azobenzene group. There also exists a weak absorption band at around 450 nm in the visible region due to $n - \pi^*$ transition. Upon irradiation of UV light at 366 nm, the absorbance at 350 nm decreased while the other band at 450 nm increased slightly, corresponding to the photoisomerization from trans-azobenzene to cis-azobenzene. The photoisomerization became the photostationary state within 60 s.



(a) (b)

(c) (d)

FIGURE 3 SEM images of films assembled with copolymer beads. Copolymer of M6PBC:3AB6Ac = 7:3, at 60°C (a) and 70°C (b), M6PBC:3AB6Ac = 8:2, at 70°C (c), and 3AB6Ac homopolymer (d).

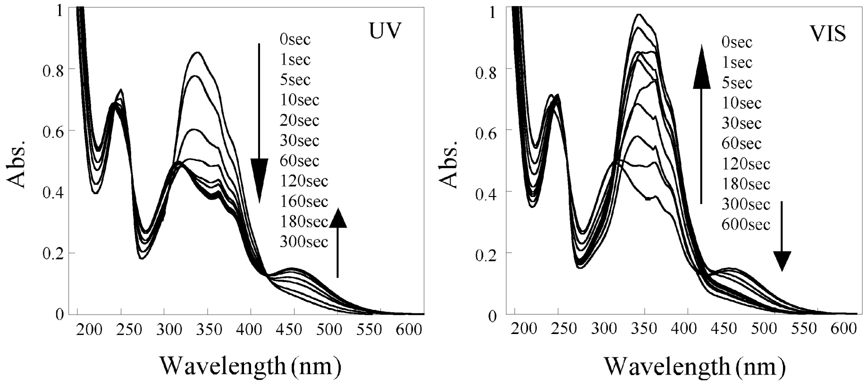


FIGURE 4 Photoisomerization of 3AB6Ac polymer film.

Then, subsequent visible light irradiation restored the initial state from the photostationary state, indicating a rapid back-isomerization from cis- to trans-azobenzene. Namely, a reversible photoisomerization of the azo dye was carried out by UV and visible light irradiation. Next, the polarized light irradiation at 488 nm through a photomask resulted in the formation of the surface relief gratings. The formation of the surface relief gratings may be interpreted in terms of a repeating trans-cis photoisomerization cycle. At 488 nm, the absorption coefficient of the cis-form produced photochemically is higher than that of the trans-form as can be seen in Figure 4. Therefore, the cis-form returns readily to the trans-form by absorbing the visible light. Consequently, the visible light irradiation at 488 nm brings about the repeating cycle of the photoisomerization between trans-form and cis-form, resulting in the massive movement of the polymer materials.

On the basis of these results, it can be expected that the polarized visible light irradiation results in an orientation of the molecules in the polymer beads as well as the massive material movement in the polymer bead assembly. First, a change in the molecular orientation of the mesogenic groups in the polymer beads was explored by an irradiation of Ar^+ laser with polarized light at 488 nm. Figure 5 shows the changes in transmitted light intensity through the irradiated films as a function of rotation angle with a He-Ne laser as a monitor light. The transmitted light intensity (I) through the films having a uniaxial molecular orientation between crossed polarizers is expressed as follows,

$$I = \sin^2(\pi \Delta n\, d/\lambda) \tag{2}$$

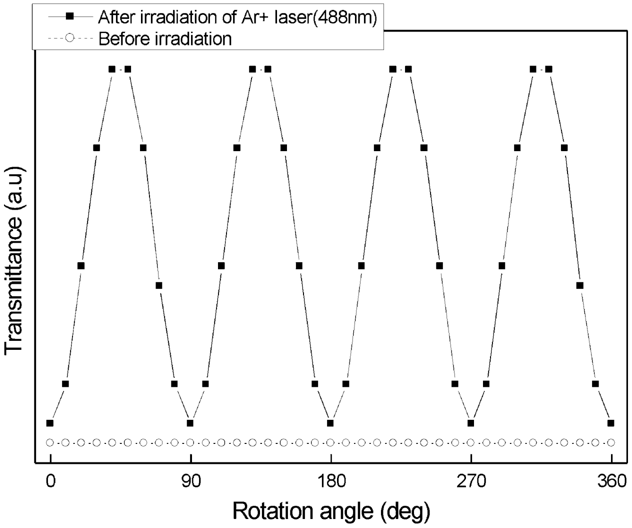
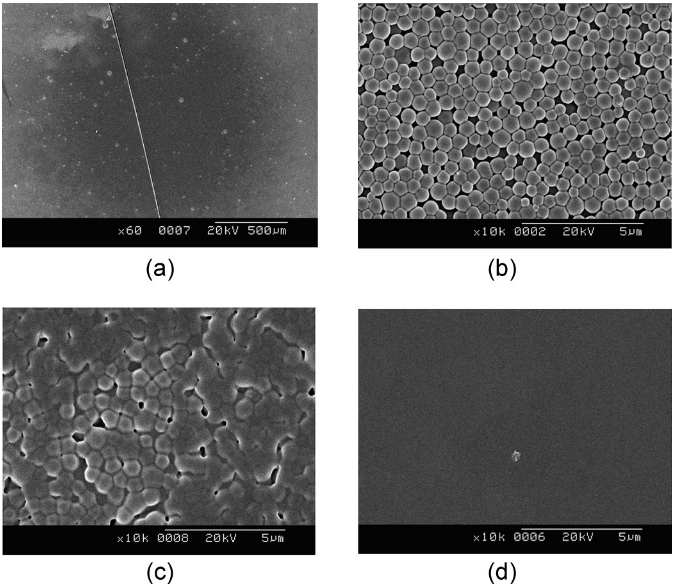


FIGURE 5 Angular-dependent transmittance of M6PBC:3AB6Ac film evaluated by polarized microscopy after irradiation with linear polarized light of 488 nm at power density of 5 mW/cm^2 and 0.01 mW/cm^2.

where, d/λ express the sample thickness, and the wavelength of the monitor light (633 nm, He-Ne laser). Before the irradiation of the polarized light, the transmitted intensity was independent on the rotation angle. On the contrary, the maximum transmittance of the film irradiated was clearly observed at every 45°. The results indicate that the azo and mesogenic groups in the polymer beads assembled were oriented in the uniaxial direction by irradiation with polarized visible light. Therefore, the refractive index change in the colloidal crystal will be induced by irradiation with polarized light at 488 nm.

Next, the effect of the light intensity of the laser irradiation on the bead assembly was explored by POM and SEM measurements. Although the orientation was quite rapid by irradiation with strong power of density of 5 mW/cm^2 laser, the colloidal crystal consisting of spheres seemed to be destroyed as can be seen in Figure 6. Figure 6 shows SEM image of spheres of the irradiated site, and no spherical shape was observed. On the other hand, the photochemical control of the molecular orientation in the polymer beads was achieve without the destruction of structure by Ar$^+$ irradiation with a weak intensity of 0.01 mW/cm^2.



(a) (b)

(c) (d)

FIGURE 6 (a) SEM image of M6PBC:3AB6Ac copolymer film after Ar^+ laser irradiation of polarized light (488 nm) with 5 mW, (b) no irradiated part, (c) border of irradiated part, (d) irradiated part. After irradiation, the shape of bead polymer on film destroyed. Scale bars are 500 μm (a) and 5 μm (b–d), respectively.

CONCLUSION

Sub-micron polymer beads containing azo and mesogenic groups were synthesized by the precipitation polymerization in ethanol. The size of the polymer beads was dependent on the polymerization temperature and molar ratio of the azo and mesogenic groups. The molecular orientation of the polymer beads could be controlled photochemically by irradiation with polarized at 488 nm with or without destruction of the polymer beads. The polymer beads containing of the azo and mesogenic groups will be candidate for fabrication of the photonic crystals showing photochemical tuning of the band gap as well as the waveguide in the photonic crystals.

REFERENCES

[1] Johnson, S. G. & Joannopoulos, J. D. (2003). *Acta Materialia*, *51*, 5823.
[2] Xia, Y., Gates, B., Yin, Y., & Lu, Y. (2000). *Adv. Mater.*, *12*, 693.
[3] Anselmann, R. & Winkler, H. (2003). *Adv. Eng. Mater.*, *5*.

[4] Fudouzi, H. & Xia, Y. (2003). *Langmuir*, *19*, 9653.

[5] Ozaki, M., Shimoda, Y., Kasano, M., & Yoshino, K. (2002). *Adv. Mater.*, *14*, 514.

[6] Viswanathan, N. K., Kim Dong Yu, Bian Shaoping, Williams John, Liu Wei, Li Lian, Samuelson Lynne, Kumar Jayant, & Tripathy Sukant, K. (1999). *J. Mater. Chem.*, *9*, 1941.

[7] Hubert, C., Malcor, E., Maurin, I., Nunzi, J. M., Raimond, P., & Fiorini, C., (2002). *Applied Surface Science*, *186*, 26.