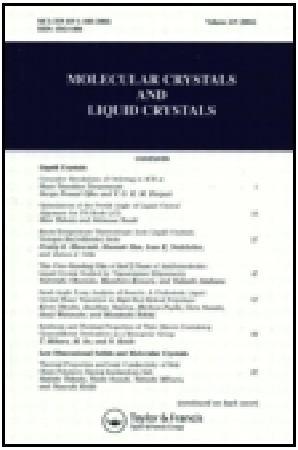


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of Photo-Cross Linking Polymer Beads and Application for Micro Fabrication of Periodic Structure

Masaki Moritsugu [a] , Tomonari Ogata [a] , Seiji Kurihara [a] & Takamasa Nonaka [a]

[a] Department of Applied Chemistry & Biochemistry, Kumamoto University, Kurokami, Kumamoto, Japan

Version of record first published: 31 Jan 2007

To cite this article: Masaki Moritsugu, Tomonari Ogata, Seiji Kurihara & Takamasa Nonaka (2005): Synthesis of Photo-Cross Linking Polymer Beads and Application for Micro Fabrication of Periodic Structure, Molecular Crystals and Liquid Crystals, 443:1, 117-126

To link to this article: http://dx.doi.org/10.1080/15421400500247334

Mol. Cryst. Liq. Cryst., Vol. 443, pp. 117–126, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500247334

Taylor & Francis
Taylor & Francis Group

Synthesis of Photo-Cross Linking Polymer Beads and Application for Micro Fabrication of Periodic Structure

Masaki Moritsugu
Tomonari Ogata
Seiji Kurihara
Takamasa Nonaka
Department of Applied Chemistry & Biochemistry, Kumamoto University, Kurokami, Kumamoto, Japan

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. One of the promising techniques for fabricating three-dimensional (3D) photonic crystal is the preparation of self-assembled colloidal crystal.

In this study, we synthesized monodisperse polymer spheres having photo-cross-linking groups which were synthesized by co-polymerization of styrene and vinyl cinnamate. Then we prepared colloid crystal from photo-cross linking beads, investigated about application for microfabrication of colloidal crystal from the change of solubility from cross linking by UV light.

Keywords: photonic crystal; photo-cross linking polymer beads; polystyrene colloid

1. INTRODUCTION

Films with three-dimensionally ordered macro porous structures called photonic crystals (PC) have recently been studied extensively because of their wide applications for separations, catalysis, optical information processing, and microwave shielding. Photonic crystals have periodic dielectric structures, and possess a unique property on the propagation of the electromagnetic waves within PC. The periodicity and refractive index of the constituents within PC result in an appearance of photonic band gap. The photonic band gap

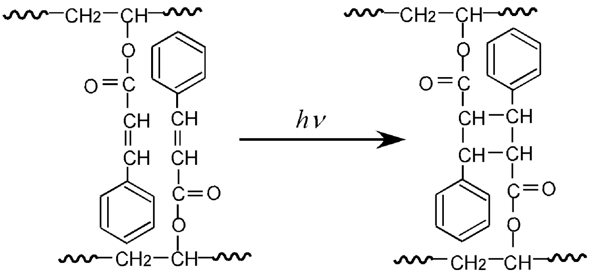
Address correspondence to Seiji Kurihara, Department of Applied Chemistry & Biochemistry, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-855, Japan. E-mail: kurihara@gpo.kumamoto-u.ac.jp

mainly depends on the lattice constants and the refractive indexes of the dielectrics. The propagation of light is forbidden in the photonic band gap. Therefore, if one provide the photonic crystal having photonic band gap as well as the defects, the photonic crystals will provide extremely small optical circuit [1,2]. Photonic crystals can be prepared by self-assembly of latex particles on a substrate [3,4]. In this study, we synthesized sub-micron sized polymer beads having photo-cross liking ability, and investigated preparation of the PC films of the polymer beads assembled as well as the photochemical change in the solubility in order to micro-fabricate the optical circuit.

2. EXPERIMENTAL

Polymer beads having photo-crosslinkable groups were prepared by polymerization of styrene with vinyl cinnamate. Photo-crosslinking reaction of vinyl cinnamate was shown in Scheme 1 [5]. The fed molar ratios were varied at 100:0 and 70:30 in mol% of styrene and vinyl cinnamate. Polymerization was carried out by emulsifier-free polymerization in distilled water in the presence of potassium peroxodisulfate (KPS) as a radical initiator [6]. The polymer beads obtained were purified by centrifugation several times. The size and its distribution were revealed by scanning electron microscopy (SEM) and dynamic light scattering (DLS), respectively. Photochemical properties of the polymer beads were explored by comparing UV-VIS absorption spectra and FT-IR spectra before and after UV irradiation with high pressure mercury lamp.

Films of polymer bead assembled was prepared by extremely slow sedimentation of the polymer beads on a glass substrate from suspension liquid. Prior to use a glass substrate, it was hydrophilized by



SCHEME 1 Photo-cross linking of cinnamic acid.

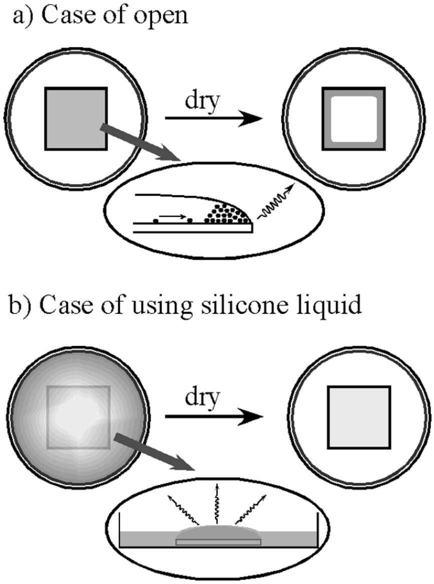


FIGURE 1 Two methods for colloidal crystallization: a) Crystallization method in air without silicone liquid, b) Crystallization method under silicone liquid.

treating with 70% of sulfuric acid and 30% of hydrogen peroxide aqueous solution subsequently. The hydrophilized glass substrate was placed in a petri dish. Colloidal suspension containing polymer beads was put on the glass substrate, and was covered with silicone liquid as can be seen in Figure 1 [7]. In a case of drying without silicone liquid, a contact line of the suspension during drying was produced, because the evaporation of solvent from edge of the suspension is higher than that from center. Consequently, the colloidal films with uniform thickness was hardly obtained by drying without silicone liquid. Contrary without silicone liquid, drying under silicon covering gave films with uniform thickness due to retardation of evaporation of solvent mainly from the edge.

Films of the polymer beads having styrene and cinnamate groups were prepared by casting the suspension on the hydrophilized glass substrate and drying water with silicone liquid. The absorption spectra of the film prepared were examined in order to clarify the formation of PC. Then, the film was irradiated with UV light and dipped in dimethylsulfoxide (DMSO) for development.

3. RESULT AND DISCUSSION

3.1. Estimation of Prepared Colloid Crystal Film with PS Beads

SEM image and size distribution of PS beads used to prepare colloid crystal was shown in Figures 2 and 3, respectively. Consequently, beads showed relatively monodisperse. Figure 4a, b show colloid crystal films crystallized with PS beads (d = 213 nm) by two methods. Colloid crystal film in Figure 4a was crystallized in an oven at 55°C for an hour without silicone liquid, and in Figure 4b was crystallized in an oven at 55°C for 12 h under silicone liquid. The sample in Figure 4a thick contact line arose at the edge of substrate. The line exhibited a structure color like a natural opal, furthermore, thin colloid crystal film formed inside the ring. In contrast, a contact line of sample in Figure 4b was decreased; the line was relatively thin and had homogeneous broadening. And then this colloid crystal film was gave a rinse by low-molecular-weight silicone liquid to remove silicone liquid from voids between beads.

Figure 5 shows transmittance spectrum of colloid crystal film with PS beads (d = 213 nm), and could be confirmed PBG due to Bragg diffraction. This dip center position was located at about 500 nm, which generally corresponded with calculated wavelength (518 nm) given

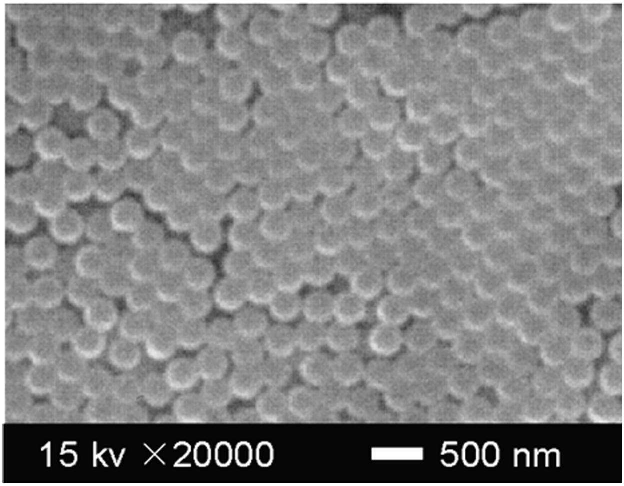


FIGURE 2 SEM image of PS beads.

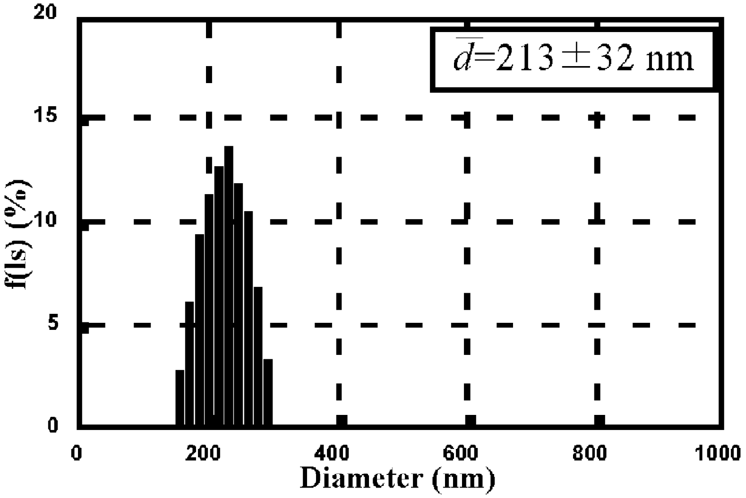


FIGURE 3 Size distribution of PS beads.

by the equation [8]:

$$\lambda = 2\sqrt{\frac{2}{3}}\,d\sqrt{n_a^2 - \sin^2\theta} \tag{1}$$

$$n_a = \sqrt{n_{\text{sphere}}^2 f + n_{\text{void}}^2 (1 - f)} \tag{2}$$

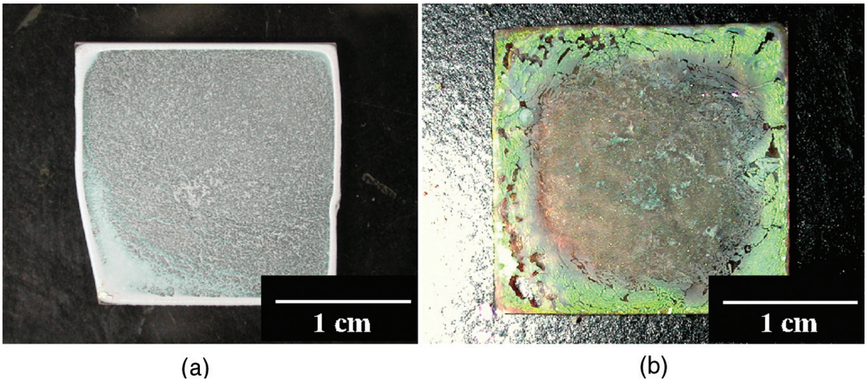


FIGURE 4 Colloidal crystals prepared by two methods: a) is crystallized by drying in oven at 55°C for 1 h without silicone liquid, b) is crystallized by drying in oven at 55°C for 12 h under silicone liquid.

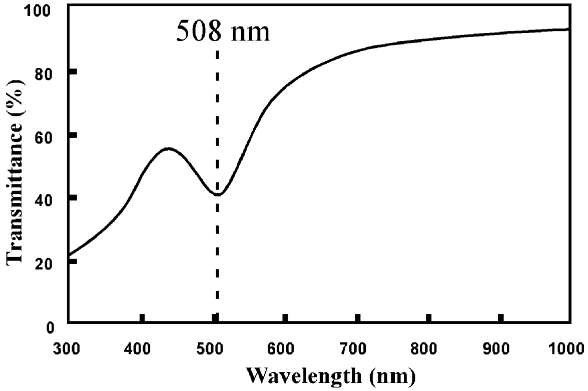


FIGURE 5 UV-VIS spectrum of PS beads (d = 213 nm) assembled on a glass substrate.

where λ is Bragg diffraction wavelength (nm), d is diameter of beads (nm), θ is angle of incident light, f is volume fraction, and n_{sphere} and n_{void} are refractive index of PS and air, respectively. In this expression, θ is 0°, f is 0.74 on the assumption that PS beads filled up at close-packed structure, and n_{sphere}, n_{void} is 1.5916, 1, respectively.

3.2. Confirmation of Photo Reactivity in Synthesized Photo-cross-linking Polymer Beads

Figures 6 and 7 show SEM image and size distribution of synthesized photo-crosslinkable polymer beads. From the results of these measurements, it was determined that synthesized photo-crosslinkable polymer beads were superior in monodispersibility. Figures 8 and 9 show changes in UV-VIS absorption spectrum and changes in FT-IR spectrum of photo-crosslinkable polymer between before and after UV irradiation. From both Figures 8 and 9, it was confirmed that cleavage of double bond in C=C was arose by UV irradiation, furthermore, cinnamic acid groups was crosslinked.

3.3. Patterning of Photo Reactive Colloid Crystal Film by UV Light

We prepared colloid crystal with synthesized photo-crosslinkable polymer beads on glass substrate as described above. Prepared photo reactive colloid crystal film was irradiated by UV light on only right

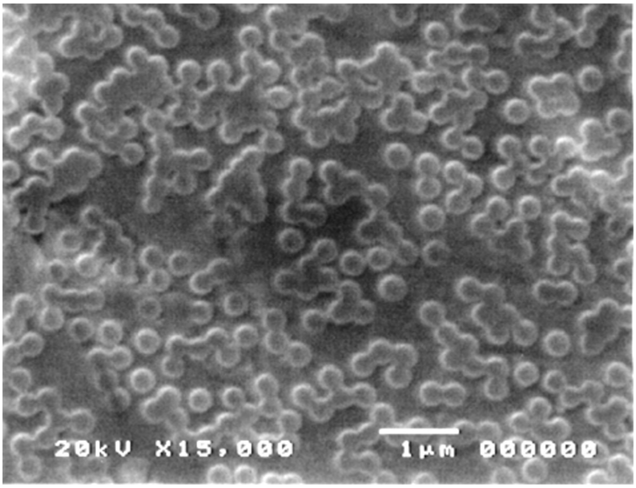


FIGURE 6 SEM image of photo-cross linkable beads.

side, and dipped in development solution (DMSO) as Figure 10. Figure 10a, b shows photo reactive colloid crystal film before and after development. The result of Figure 10b was suggested the possibility of patterning of the colloidal crystal by UV light. We observed border

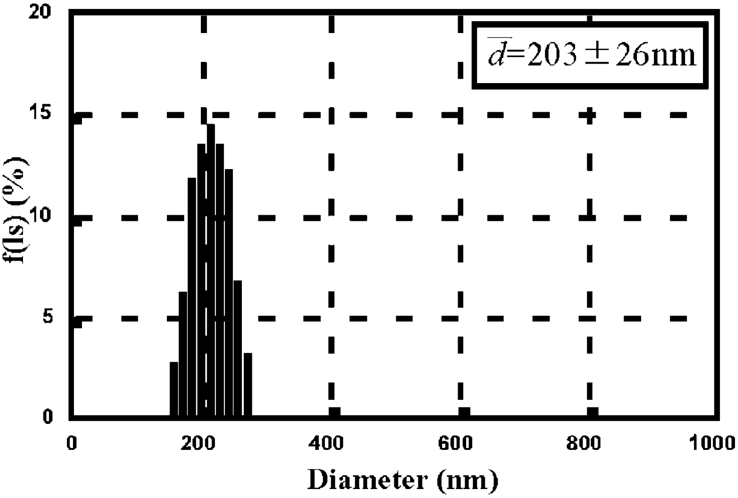


FIGURE 7 Size distribution of photo-cross linkable beads.

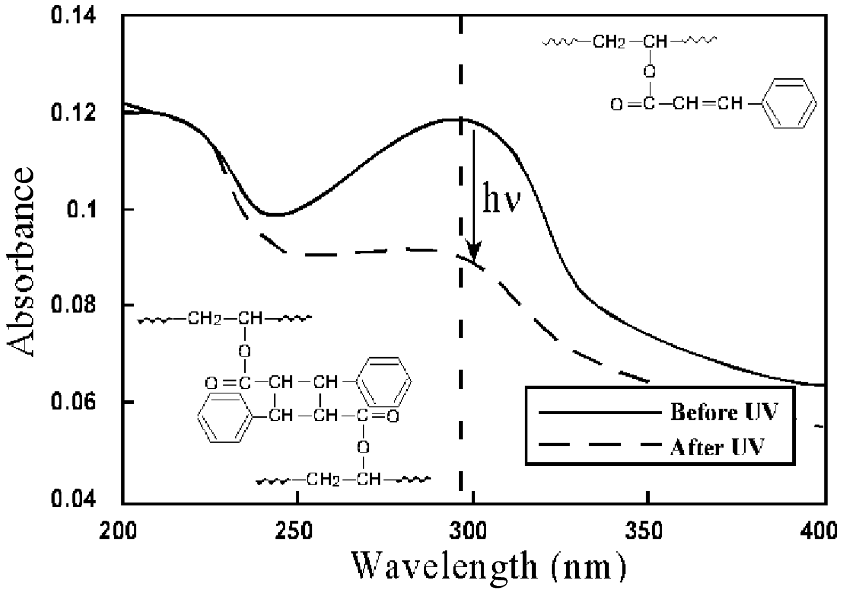


FIGURE 8 UV absorption spectra of photo-cross linkable polymer film.

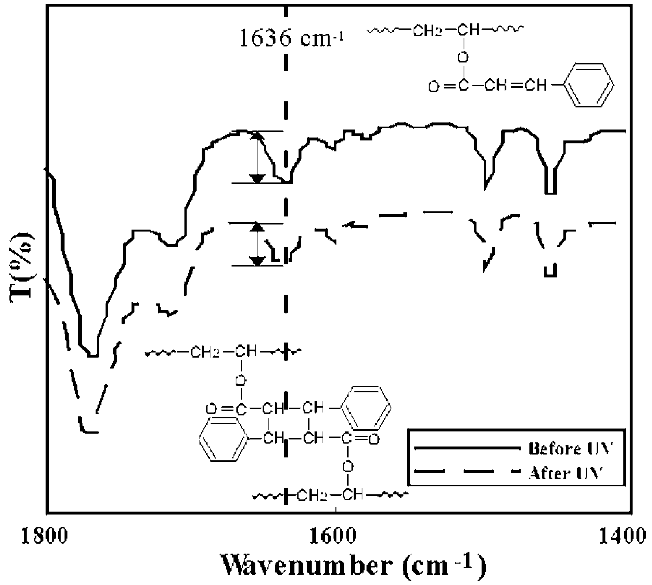


FIGURE 9 Change in FT-IR spectrum by UV irradiation.

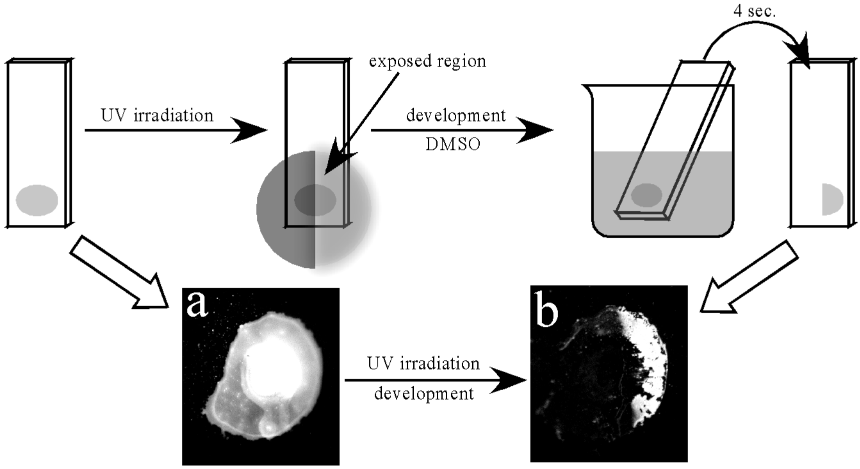


FIGURE 10 Scheme of process for development and colloidal crystal film made from photo-cross linkable beads: (a) before UV irradiation and development, (b) after UV irradiation (on right side) and development.

between UV irradiation area and no irradiation area by SEM, however distinct border line could not be found (there are not in this paper). Thus result is attributed to the fact that organic solvent must be used for development.

4. CONCLUSION

By the use of silicone liquid, colloid crystal made with beads could be fabricated with simply and relative larger area. And monodisperse photo-cross-linking polymer beads could be synthesized by copolymerization of styrene (70 mol%) and vinyl cinnamate (30 mol%). These beads were cross-linked by UV irradiation and indicated insolubility toward organic solvent. We could put contrast of dissoluble in photo reactive colloid crystal fabricated from these beads by UV irradiation and development by DMSO, however it was far from microfabrication of colloid crystal. We attribute thus results to the fact that organic solvent must be used for development. In this study, organic solvent (DMSO) was used for development, however we have considered ways and means that development by organic solvent and even development process are unnecessary, right now.

REFERENCES

[1] Romanov, S. G., Ferrand, P., Egen, M., Zentel, R., Ahopelto, J., Gaponik, N., Eychmüller, A., Rogach, A. L., & Sotomayor Torres, C. M. (2003). *Synthetic Metals*, *139*, 701.

[2] Bresson, F., Chen, C.-C., Chi, G.-C., & Chen, Y.-W. (2003). *Appl. Surf. Sci.*, *217*, 281.

[3] Xia, Y., Gates, B., Yin, Y., & Lu, Y. (2000). *Adv. Mater.*, *12*, 693.

[4] Kopnov, F., Lirtsman, V., & Davidov, D. (2003). *Synthetic Metals*, *137*, 993.

[5] Furumi, S., Ichimura, K., Sato, H., & Nishiura, Y. (2000). *Appl. Phys. Lett.*, *77*, 2689.

[6] Goodwin, J. W., Hearn, J., Ho, C. C., & Ottewill, R. H. (1974). *Colloid & Polymer Sci.*, *252*, 464.

[7] Fudouzi, H. (2004). *J. Colloid and Interface Sci.*, *275*, 277.

[8] Gu, Z.-Z., Hayami, S., Kubo, S., Meng, Q.-B., Einaga, Y., Tryk, D. A., Fujishima, A., & Sato, O. (2001). *J. Am. Chem. Soc.*, *123*, 175.