Preparation of Monodispersed Polymer Particles Containing Azobenzene Moieties

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Polymer particles containing azobenzene moieties were newly synthesized by a soap-free emulsion copolymerization. The scanning electron micrograph revealed that the polymer particles obtained are round in shape and the size is uniform. The particles spontaneously formed the periodic structure, resulting in Bragg diffraction at a visible region.
Key words: photonic crystal, azobenzene, polymer particles, monodispersed, colloidal crystal

1. INTRODUCTION

Photonic crystal structures have been studied for the purpose of various photonic applications such as waveguide, optical filter, resonant cavities, sensors, and photonic papers.[1-4] The photonic crystal structure contains a periodic change in refractive index, ranging from hundred nanometers to several microns. So far, there have been two approaches to fabricate the periodic structures. One is a top-down process using a semiconductor micromachining technique. This process provides precise structures, while requires costly equipments. The other is a bottom-up process based on self-assembly of colloidal crystals.[5-13] Using appropriate assembly conditions, nanometer-scale monodispersed polymer particles or silica spheres spontaneously form well-ordered fcc periodic 3D structures. Moreover, filling these structures with other materials, and chemically or thermally removing the spheres gives rise to inverse opal replica with high contrast between the air spheres and the remaining material. By infiltrating liquid crystals or dyes into the obtained opal or inverse opal structures, tunable photonic crystals, in which a stop band can be tuned thermally, electrically or optically, have been developed.[3,4] Asher *et al.* prepared environmentally responsive hydrogels including colloidal crystals.[5-7] Takeoka *et al.* reported a template synthesis of the chameleonic gels using self-assembled colloidal crystals.[8,9]

Among them, phototunable photonic crystal structures are significantly attractive in terms of passive and active photonic devices. For instance, Gu *et al.* showed that a photochemical phase transition of an azobenzene liquid crystal infiltrated into an inverse opal structure causes reversible changes in a stop band.[10-12] In researches reported so far, the photoresponsive part was infiltrated into periodic structures. In other words, the photoresponsive part and the periodic structure were separated. In this case, the periodic structures are firstly prepared and then the photoresponsive part is infiltrated. From the

viewpoint of a device fabricatio, the connection of two parts is desirable, which allows a single-step fabrication of phototunable photonic crystal structures. In this paper, we synthesized monodispersed polymer particles including photoresponsive moieties, and prepared photoresponsive photonic crystal structures.

2. EXPERIMENTAL
2.1 Materials

We employed an azobenzene as the photoresponsive part, which is one of the popular dyes with a high photosensitivity. The structures
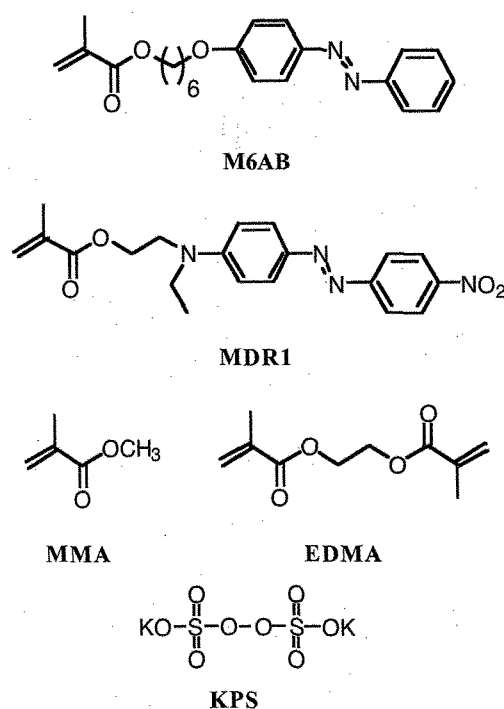

Fig. 1. Chemical structures and their abbreviations of the azobenzene monomers (**M6AB** and **MDR1**), a co-monomer (**MMA**), crosslinker (**EDMA**), and an initiator (**KPS**) used in this study.

of azobenzene monomers, 6-[4-(phenylazo)phenoxy]hexyl methacrylate (**M6AB**) and 2-[4-(4-nitrophenylazo)phenoxy-(*N*-ethyl)amino]ethyl methacrylate (**MDR1**) are shown in Fig. 1. These monomers were synthesized as reported previously with some modifications[14]. Methyl methacrylate (**MMA**) and ethyleneglycol dimethacrylate (**EDMA**) were used as a comonomer and a crosslinker, respectively. Potassium persulfate (**KPS**) was employed as an initiator.

2.2 Synthesis of polymer particles

To obtain monodispersed polymer particles, a soap-free emulsion copolymerization was carried out. The monomers, **M6AB** and **MMA** (mol/mol: 5/95) containing 0.6 mol% of the crosslinker were put into 4 ml of water then added with 1-ml water including an initiator, **KPS**, at a concentration of 1.5×10^{-3} mol/l for the total solution. The solution was stirred and heated at 90 °C for 80 min under nitrogen atmosphere. After polymerization, residues and sediments were removed by filtration and centrifugation at 5,000 rpm to yield the latex of polymer particles, **PMAB6**. The **MDR1**-containing polymer particles, **PMDR1**, were prepared in the same manner. The solution was cast onto a clean glass substrate and slowly dried under humid conditions to obtain the film of the polymer particles.

2.3 Characterization of polymer particles

Glass transition temperatures (Tg) of the particles were determined by differential scanning calorimetry (Seiko I&E, SSC-5200 and DSC220C). Molar ratio of the azobenzene moiety was estimated by elemental analysis. The particles were observed by scanning electron microscopy (SEM, Hitachi, S-4700). Transmission spectrum was measured on a UV/Vis absorption spectrometer (JASCO, V-550).

3. RESULTS AND DISCUSSIONS

3.1 Observation of polymer particles

By elemental analysis, the molar ratio of azobenzene moieties introduced to polymer particles was found to be 1.4 mol% and 1.8 mol% for **PM6AB** and **PMDR1**, respectively. Even though the azomonomers were fed for 5 mol%, the ratio of azobenzene moieties incorporated to polymer particles decreased. This may be caused by a low solubility of the azobenzene monomers to MMA and water. Fig. 2 shows the scanning electron micrograph of the **PM6AB** film. It was revealed that the obtained particles are round in shape and spontaneously form the periodic structure. The mean diameter of the particles was estimated as ~250 nm. In **PMDR1**, the same structure formed by monodispersed particles with ~230-nm diameter was obtained. To express the relative uniformity of particles, standard deviation and coefficient of variation (CV) are widely used, where CV is the standard deviation of the size distribution divided by the mean

diameter. From the scanning micrographs of **PM6AB** and **PMDR1**, the diameter distribution was estimated as shown in Fig. 3. The values of standard deviation and CV calculated from the diameter distribution were 10.4 nm and 4.2 % for the **PM6AB** particles and 6.7 nm and 2.8 % for the **PMDR1** particles, respectively. These values are similar to those in commercially available standard particles, concluding that the particles prepared here are quite monodispersed.

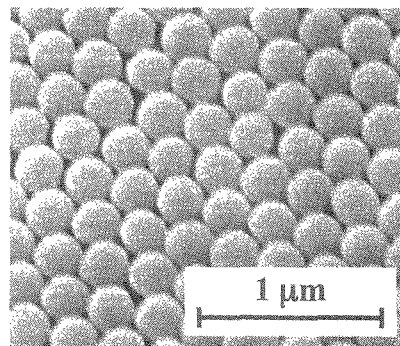Tg of the particles was 112 °C and 114 °C for **PM6AB** and **PMDR1**, respectively. These values

Fig. 2. A scanning electron micrograph of the polymer particles, **PMAB6**.

230 240 250 260 270 280
Diameter (nm)
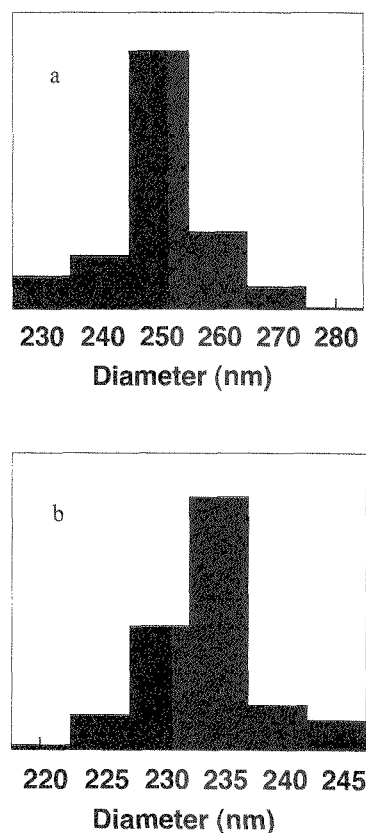
220 225 230 235 240 245
Diameter (nm)

Fig. 3. Distribution of diameter of the polymer particles. a) **PM6AB** and b) **PMDR1**.

are approximately equal to that of PMMA having no azobenzene moiety. As long as the films were thermostated below Tg, the shape of the particles remained unchanged.

3.2 Bragg diffraction from the periodic structures

It is known that regular periodic structures give rise to an optical stop band at a specific wavelength due to Bragg diffraction. Therefore, the transmission spectrum of the PM6AB film was measured to characterize the optical property of the periodic structure as shown in Fig. 4. A small peak around 450 nm and a large peak at 578 nm were observed. The azobenzene monomer, M6AB, exhibits strong absorption around 350 nm according to π-π^* transition and weak absorption around 450 nm due to n-π^* transition, indicating that the shallow 450-nm peak corresponds to the absorption of the azobenzene incorporated to the polymer particles. On the other hand, the other deep peak that is not assigned to the absorption also emerged at 578 nm only in the PM6AB film. It is explained by the Bragg diffraction of periodic polymer particles. The maximum peak position (λ_{max}) in Bragg diffraction is described by:

$$\lambda_{max} = 2\sqrt{\frac{2}{3}}d\sqrt{n_a^2 - \sin^2\theta} \qquad \text{(Eq. 1)}$$

where d is particle diameter, θ is incident angle, and n_a is effective refractive index expressed by:

$$n_a = \sqrt{\left(1 - V_f\right)n^2_{void} + V_f \cdot n^2_{particle}} \qquad \text{(Eq. 2)}$$

where V_f is filling factor, which is 0.74 for fcc structure, and n_{void} and $n_{particle}$ are refractive indices for void and particle, respectively. When the values of the refractive index, 1 for air and 1.49 for PMMA are substituted in n_{void} and $n_{particle}$, respectively and the measured particle diameter of 250 nm is used as d, λ_{max} can be estimated as 550 nm. The rough coincidence of this value with the peak (575 nm) in Fig. 2 indicates that the diffraction peak arises from the periodic structure formed by the polymer particles. In fact, the flat film with no periodic structure did not exhibit any peak except the absorption of azobenzene moieties. The diffraction peak corresponding to the diameter of particles appeared also in the PMDR1 film.

4. CONCLUSIONS

Photonic crystal structures formed by monodispersed polymer particles containing azobenzene moieties were prepared and their optical property was investigated. The polymer particles with 250 nm in diameter were successfully obtained by a soap-free emulsion copolymerization for MAB6, and it was revealed that the particles self-assemble the periodic structure just by casting the latex on a glass

substrate. The films exhibited Bragg reflection peaks at 575 nm, confirming the formation of the periodic structure.
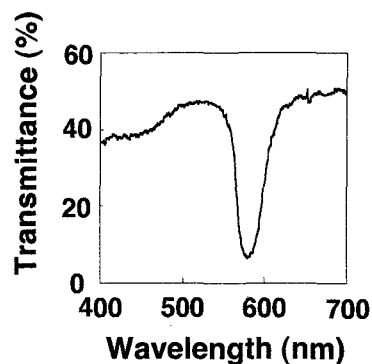

Fig. 4. Transmission spectrum of the PM6AB film.

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