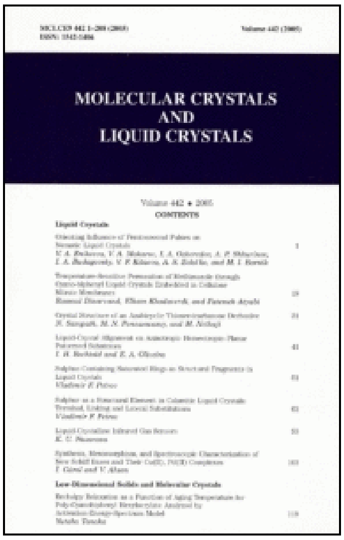

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Preparation of Monodisperse Dye-Doped Copolymer Spheres for Photonic Crystals

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Monodisperse dye-doped copolymer spheres were prepared via a soap-free emulsion polymerization and swelling method. To study the relationship between the particle diameters and the optical properties of the dye-doped photonic crystals, monodisperse copolymer spheres with particle diameters varying from 581 to 98 nm were prepared. When melanin dye was doped into the spheres, it efficiently reduced the light scattering inside the crystals and eliminated the iridescent effect in the photonic crystal images. The results of this study are expected to provide useful information for the synthesis of monodisperse dye-doped copolymer spheres and applications involving photonic papers.

Keywords Dye-doped sphere; monodisperse sphere; photonic crystal; soap-free emulsion polymerization

Introduction

Monodisperse particles have potential applications in various fields and have been used to prepare advanced materials such as photonic crystals [1–7]. Photonic crystals exhibit brilliant colors by preventing the propagation of electromagnetic waves through the crystal structure for a particular frequency range in the visible spectrum [8]. The structural color of the crystal depends on the photonic bandgap (PBG), which is determined using the crystal lattice and period. Photonic crystal materials are fabricated using self-assembled monodisperse polymer particles and the structural color is controlled by changing the size of the particles [9].

Monodisperse polymer particles have been synthesized using different polymerization methods such as emulsion polymerization [10], dispersion polymerization [11,12], suspension polymerization [13], and soap-free emulsion polymerization [14–17]. Among these methods, soap-free emulsion polymerization is the simplest method for synthesizing monodisperse polymer particles with a self-assembling properties, which can then be used for fabricating photonic crystals. Typically, in soap-free emulsion polymerization, synthesis parameters such as monomer, initiator concentration, agitation rate, and temperature are key factors that influence the particle diameter, coefficient of variation of particle size distribution (C_v), and

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polymerization rate. Ou *et al.* synthesized monodisperse polymer submicrospheres with different particle diameters and proposed a mechanism for the nucleation process that occurs during the polymerization reaction [18]. They obtained microspheres (sizes: 270–750 nm) using soap-free emulsion polymerization with a solvent (polar or nonpolar) or a hydrophilic comonomer in a styrene/potassium persulfate/H_2O system. Gu *et al.* [19] proposed a rapid soap-free emulsion polymerization process, in which the monomers were polymerized at the boiling point, for synthesizing monodisperse copolymer submicrospheres. These submicrospheres were used to fabricate photonic crystals exhibiting brilliant colors [19]. It is necessary to achieve precise control of the particle diameter in the soap-free emulsion polymerization technique to synthesize polymer particles with lower C_v, which, can in-turn be used to fabricate photonic crystals exhibiting brilliant colors.

During the study of photonic crystals conducted by Moon *et al.*, it was observed that the spherical surface of the crystals led to iridescence due to the variation of the incident angle relative to the (111) plane on the surface [20]. This phenomenon was limited to applications involving paint, photonic paper, and bioassays. Zhang *et al.* found that melanin dye has the ability to absorb light over the entire visible spectrum. It absorbs the diffusion light and makes the interference color brilliant (it displays the true color of the particle) [21].

This article presents the preparation of monodisperse dye-doped copolymer spheres that are used to fabricate self-assembled photonic crystals. The morphologies, particle diameters, C_v, and optical properties of the copolymer spheres prepared under various synthesis conditions were characterized. Next, the distinct relationship between particle diameter and incident angle variations, which is important for the proper design of the photonic bandgap, was recorded. Additionally, melanin dye was used to dope the spheres to efficiently reduce the light scattering inside the photonic crystals, thus causing the particles to display monochromatic color. Next, the effect of the dye contents on the optical properties of photonic crystals was studied. The results of this study are expected to provide useful information for the synthesis of monodisperse dye-doped copolymer spheres, which can be employed in the fabrication of photonic crystals.

Experimental

Materials

Methyl methacrylate monomer (MMA, Showa, Okinawa, Japan) and styrene monomer (St, Showa) were purified by vacuum distillation and stored at 4°C until use. Sodium *p*-styrenesulfonate comonomer (NaSS) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Potassium persulfate (KPS, Showa) was used as an initiator for the polymerization without purification. Melanin dye (Solvent Black 34) was purchased from Up-Lift (Taipei, Taiwan). Acetone was purchased from Echo (Miaoli, Taiwan). Water was through reverse osmosis and deionized (DI) to have an electric resistance higher than 18 MΩ cm.

Synthesis of Monodisperse Copolymer Spheres

The monodisperse copolymer spheres were synthesized via soap-free emulsion polymerization. A typical polymerization procedure was as follows: 90 mL DI water was added into a three-necked flask equipped with a reflux condenser and a mechanical stirrer. After deoxygenated (bubbling with nitrogen for 30 min), 0.087 g KPS and 10 mL monomer (MMA or St) with various weight percentages of NaSS comonomer were added to the flask. Subsequently, the temperature of the mixture was increased to 70°C for 24 h under continuous nitrogen purge at an impeller speed of 400 rpm. After the synthesis process was completed, the latexes were washed with DI water to remove impurities using a centrifugal technique.

Preparation of Dye-Doped Copolymer Spheres

The dye-doped copolymer spheres were prepared by a swelling method. Various weight percentages of Solvent Black 34 were dissolved in acetone (1 mL) and the latexes (10 mL) were added into the solution. The temperature of the solution was maintained at 25°C for 24 h while stirring. After these processes, acetone was removed by vaporizing at 60°C for 1 h. All of the spheres were washed three times to remove unloaded dye using a centrifugal technique and adjusted to the right concentration for fabrication of photonic crystals.

Fabrication of Photonic Crystals

The dye-doped copolymer spheres were fabricated for construction of photonic crystals. One hundred-microliter suspensions containing 10 wt% dye-doped copolymer spheres were dropped on the glass substrates to form an image and then dried at 25°C for 24 h, 60°C for 30 min, and 100°C for 5 min, respectively. After evaporating water in the images, spheres were assembled into ordered lattices on the glass substrates.

Measurements

More than 100 particle diameters were measured for each latex using field emission scanning electron microscopy (FE-SEM, Hitachi, model S80, Tokyo, Japan) to determine morphology, number-averaged diameter (d_n), center distance of two neighbor spheres (d_c), standard deviation (σ), and coefficient of variation of particle size distribution (C_v), defined as follows:

$$\overline{d_n} = \left(\sum n_i d_i \Big/ \sum n_i\right) \tag{1}$$

$$\sigma = \left(\sum (d_i - \overline{d_n})^2 \Big/ \sum n_i\right)^{1/2} \tag{2}$$

$$C_v = \frac{\sigma}{\overline{d_n}} \times 100 \tag{3}$$

Here, n_i is the number of particles with diameter d_i. In addition, the hydrodynamic diameter (d_h) was measured by dynamic light scattering (DLS, Malvern, Zetasizer Nano ZS, Worcestershire, U.K.) for each latex in DI water at 25°C (633 nm laser, 173° scattering angle).

Optical properties of the photonic crystals were evaluated by measuring reflection spectra to determine λ_{max} (wavelength of maximum reflected intensity), using an ultraviolet-visible spectrophotometer (UV-Vis, Jasco, V-670, Essex, U.K.) with an ARSN-733 absolute reflectance measurement accessory. The usual method of describing the bandgap position with a (1 1 1) face of a face-centered cubic (FCC) lattice involves a modified Bragg's law [22,23],

$$\lambda = 2d_{111}\sqrt{n_{eff}^2 - \sin^2\theta} \tag{4}$$

where λ is the wavelength, d_{111} is the grating constant that is related to the particle diameter (D) by $(2/3)^{1/2}D$ for FCC, θ is the angle between the incident light and the normal to the diffraction planes, n_{eff} is an effective refractive index of the photonic crystals determined as $n_{eff} = n_{polymer}\varphi + n_{air}(1-\varphi)$. Here n is the refractive index of the polymer and air (polystyrene:1.59, poly(methyl methacrylate):1.49, air:1). φ is the volumetric proportion. Assume that the photonic crystals are close-packed with an ideal particle volume fraction (φ:0.74) in the image.

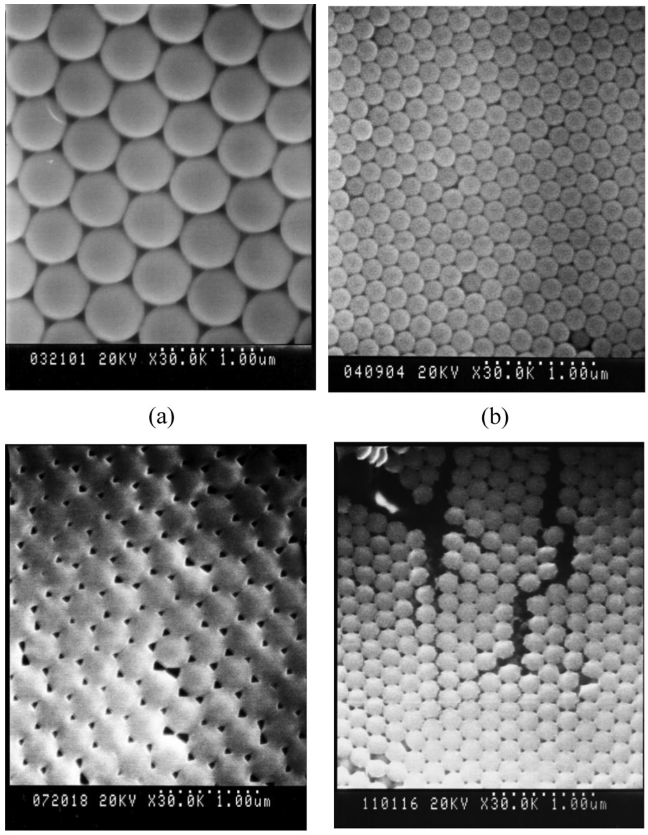
Results and Discussion

Characterization of Copolymer Spheres

Two kinds of copolymer spheres, P(St-co-NaSS) and P(MMA-co-NaSS), were characterized. The morphologies, number-averaged diameter (d_n), variation of particle-size distribution (C_v), distance between the centers of two neighboring spheres (d_c), and the hydrodynamic diameter (d_h) were determined using FE-SEM and DLS. The FE-SEM micrographs in Fig. 1 show the morphologies of copolymer spheres with various NaSS weight percentages. From the images, it was observed that the spheres were uniform and spherical; the particle diameters of the copolymer spheres were of the order of several hundred nanometers and they decreased with an increase in the NaSS weight percentages. Figure 2 shows the relationship between the particle diameters and weight percentages of the NaSS for P(St-co-NaSS) spheres. It can be seen that with an increase in NaSS weight percentages, d_n and d_h change from 581 to 98 nm and 728 to 121 nm, respectively. The d_h values are greater than the d_n values because the d_h particles can produce an extended double layer of ions in latex. Because NaSS monomers easily dissolve to an aqueous phase, the number of nucleation sites of the reaction mixture containing St and NaSS increased with the NaSS weight percentage. The large number of nucleation sites in the initial stages of polymerization led to a decrease in particle diameters. Thus, the particle diameters of the resulting polymers could be controlled by adjusting the quantity of the hydrophilic monomer in the aqueous phase [18]. In addition, all the C_v values recorded for these two kinds of copolymer spheres, which were prepared at different NaSS weight percentages, were less than 5.0%. These results indicated that the monodisperse copolymer spheres with different particle diameters were successfully prepared using the soap-free emulsion polymerization technique.

Fabrication of Photonic Crystals and Optical Properties

The P(St-co-NaSS) (198 nm) and P(MMA-co-NaSS) (192 nm) were used for the fabrication of photonic crystals. The PBG (λ_{max}) of the photonic crystals, measured at a normal incidence angle (0°) using a UV-Vis spectrophotometer (with an absolute



(a) (b) (c) (d)

Figure 1. FE-SEM images of two kinds of copolymer spheres with various weight percentages of NaSS: (a) 0 wt% and (b) 0.2 wt% of P(St-co-NaSS); (c) 0 wt% and (d) 0.2 wt% of P(MMA-co-NaSS).

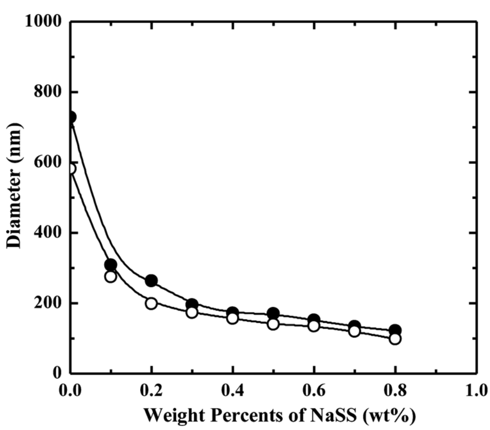


Figure 2. Relationship between the particle diameter and weight percentages of NaSS for P(St-co-NaSS) spheres. (●) Hydrodynamic diameter and (○) number-averaged diameter.

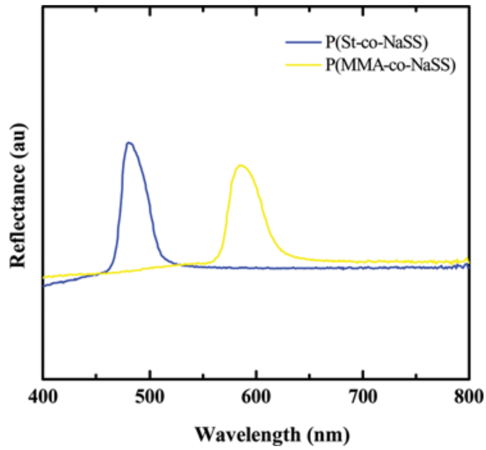


Figure 3. Reflection spectra of two types of photonic crystals: P(St-co-NaSS) photonic crystal (particle diameter: 198 nm) and P(MMA-co-NaSS) photonic crystal (particle diameter: 192 nm).

reflectance measurement accessory), is shown in Fig. 3 and Table 1. Next, the PBG (λ_n and λ_c) of the photonic crystals was calculated using the modified Bragg's law. From Table 1, we can see that λ_n in the P(St-co-NaSS) series is consistent with λ_{max}. ever, λ_n in the P(MMA-co-NaSS) series does not correspond with λ_{max} because the PMMA series spheres exhibit a necking phenomenon (Figs. 1c and 1d). The necking phenomenon leads to an increase in the distance between spheres where the λ_n value can be smaller than λ_{max}. The distances between the centers of two neighboring spheres (d_c) are defined as shown in Table 1. The λ_c values calculated for the P(St-co-NaSS) and P(MMA-co-NaSS) series (calculated using d_c) are both consistent with λ_{max}. Figure 4 shows the effect of temperature on the fabrication of photonic crystals. When the lattice was dried at various temperatures, higher reflectance intensities were obtained at the appropriate temperature (60°C dry condition).

Table 1. Optical properties of self-assembled photonic crystals

Samples	Dye (wt%)	d_n[a] (nm)	d_c[b] (nm)	λ_n[c] (nm)	λ_c[d] (nm)	λ_{max}[e] (nm)	Color
P(St-co-NaSS)	0	198	204	465	479	481	Blue
	1	196	202	460	474	482	
P(MMA-co-NaSS)	0	192	266	427	592	588	Yellow
	1	204	265	454	590	594	

[a] d_n was determined by a survey of 100 particles from FE-SEM photographs.
[b] d_c was determined by distances between the centers of two neighboring spheres from FE-SEM photographs.
[c] λ_n was calculated from Bragg's law using d_n.
[d] λ_c was calculated from Bragg's law using d_c.
[e] λ_{max} was determined from the reflection spectra of maximum reflected intensity.

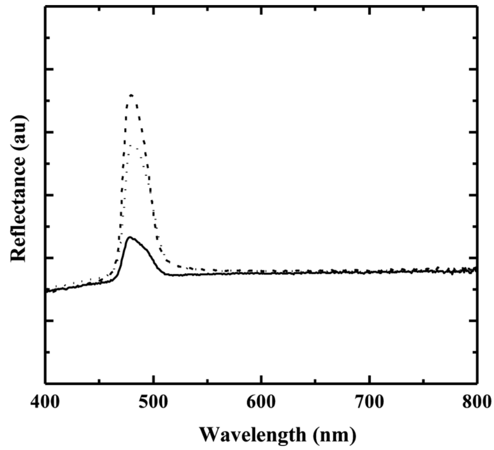


Figure 4. Effect of temperature on the fabrication of photonic crystals: (–) 25°C, (– – –) 60°C, and (. . .) 100°C.

Optical Properties of Dye-Doped Photonic Crystal Images

In this section, the optical properties of photonic crystals prepared using different dye contents are discussed. The dye was doped into the P(St-co-NaSS) (198 nm) and P(MMA-co-NaSS) (192 nm) spheres by using the swelling method. Photonic crystals of dye-doped or undoped copolymer spheres were fabricated by the evaporation method to form photonic crystal images. Figure 5 shows the photographs of the photonic crystals for different dye contents. In the case of the undoped photonic crystals, the image exhibits pearly coloration due to the influence of defects such as cracks, point defects, and dislocations. These defects decrease the optical quality of the images, making them appear whitish. The whitish tone of the photonic crystals composed of undoped spheres originates mainly from the light scattering within the crystals and at the boundaries between the spheres and air. While observing dye-doped photonic crystals (0.5 and 1 wt% dye), monochromatic colors are clearly

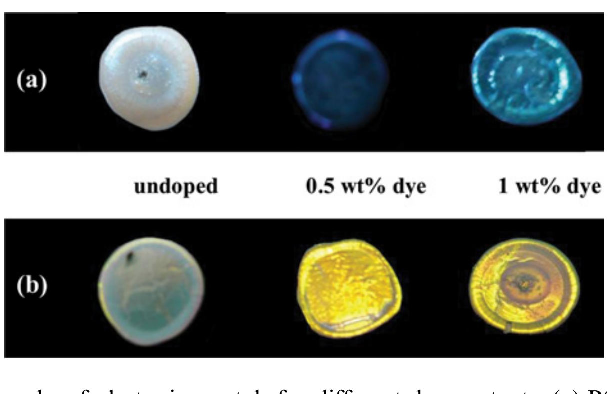


Figure 5. Photographs of photonic crystals for different dye contents: (a) P(St-co-NaSS) and (b) P(MMA-co-NaSS).

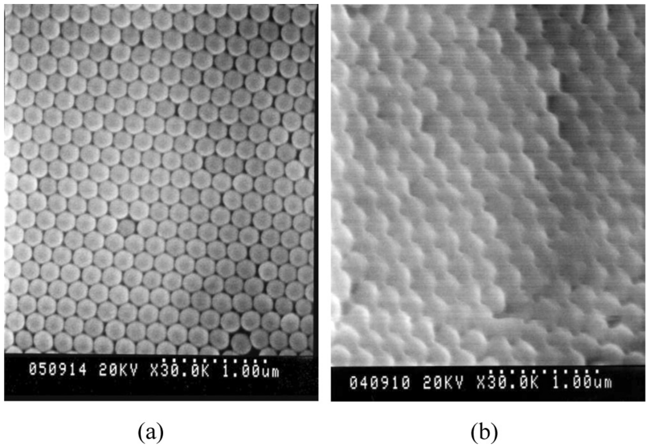


Figure 6. Fe-SEM images of dye-doped photonic crystals: (a) P(St-co-NaSS) and (b) P(MMA-co-NaSS).

visible to the naked eye. The results indicated that the melanin dye has the ability to absorb light over the entire visible spectrum, which is effective in reducing the light scattering and enhancing the structural color [21].

The morphologies and d_n of the dye-doped photonic crystals are shown in Fig. 6 and Table 1, respectively. The photonic crystal structure and d_n remain unchanged, which implies that the melanin dye does not affect the structural arrangement of the photonic crystal. These results indicate that the melanin dye doped into the photonic crystals can efficiently reduce the light scattering inside the photonic crystals and eliminate the iridescent effect in the photonic crystal images, while leaving other optical properties unaffected. In addition, for the most part the two parameters (the particle diameter and the incident angle) can be controlled to vary the λ_{max} value

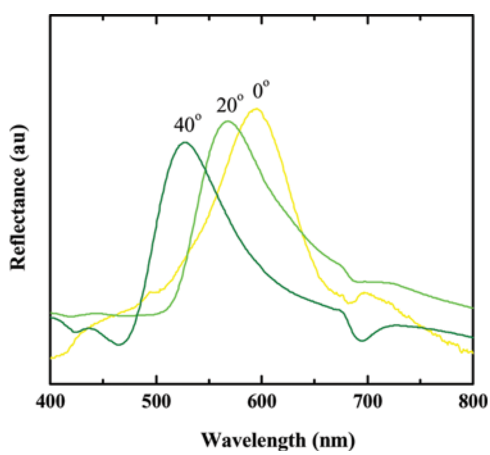


Figure 7. Reflection spectra of dye-doped P(MMA-co-NaSS) photonic crystals (1 wt% dye) with varying incident angle values.

using the modified Bragg's law. The reflection spectra of dye-doped P(MMA-co-NaSS) photonic crystals with varying incident angles were evaluated as shown in Figure 7. The λ_{max} value at different incident angles of 0, 20, and 40° were 595 (yellow), 567 (green), and 527 nm (green), respectively. The λ_{max} clearly led to a blue-shift with an increase in the incident angle values.

Conclusions

Monodisperse copolymer spheres with different particle diameters were successfully prepared by soap-free emulsion polymerization. The NaSS contents played an important role in controlling the particle diameters of the spheres. The particle diameters of the copolymer spheres decreased from 581 to 98 nm with an increase in the NaSS contents, and the C_v values were all less than 5.0%. As a result of the necking phenomenon of the P(MMA-co-NaSS) spheres, the λ_n values were smaller than λ_{max}. Therefore, the distances between the centers of two neighboring spheres (d_c) were defined, and the calculated λ_c values were then consistent with λ_{max}. Photonic crystals were obtained using self-assembled dye-doped or undoped copolymer spheres. Monochromatic colors of dye-doped photonic crystals can be clearly observed by the naked eye. It can thus be concluded that melanin dye has the ability to absorb light over the entire visible spectrum, thereby making the monochromatic colors of the crystal brilliant. The observed λ_{max} values were in good agreement with the values calculated using the modified Bragg's law. The results of this study provide useful information about the optical properties of dye-doped photonic crystals.

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