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Size-controlled spherical polymer nanoparticles: Synthesis with tandem acoustic emulsification followed by soap-free emulsion polymerization and one-step fabrication of colloidal crystal films of various colors

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ABSTRACT

We have developed a novel synthesis method for size-controlled polymer nanoparticles using soap-free emulsion polymerization. This new synthetic method involves sequential ultrasonic irradiation (20 kHz → 500 kHz → 1.6 MHz → 2.4 MHz) for acoustic emulsification of a water-insoluble monomer such as methylmethacrylate (MMA) in an aqueous medium, followed by emulsion polymerization in the obtained solution without using any surfactants. The sequential ultrasonication (tandem acoustic emulsification) could provide a clear and stable emulsified solution containing monomer droplets with relatively narrow size distribution in the nanometer range. The subsequent polymerization in this solution yielded size-controlled polymethylmethacrylate (PMMA) nanoparticles and monodisperse PMMA nanoparticles of different sizes. Furthermore, colloidal crystal films could be easily prepared from the as-polymerized nanoparticle solution using the fluidic-cell method. Moreover, we succeeded to modify the structural color of colloidal crystal films by the addition of a small amount of organic solvent to the as-polymerized nanoparticle solution for the fluidic-cell method.

1. Introduction

In recent years, structural colors have attracted much attention in a wide variety of research fields. Structural colors are quite widespread in nature, such as in opals and some animals. On the other hand, they are deeply connected with recent rapidly growing fields as photonics and have been extensively studied to clarify their peculiar optical properties. In principle, their mechanisms are of a purely physical origin, which differs completely from the ordinary coloration mechanisms such as in pigments and dyes, where the colors are produced by virtue of the interaction with light.

It is recognized that structural colors are mainly based on several elementary optical processes, including thin-layer interference, diffraction, light scattering. Therefore, in general, the structural color is maintained for a long period of time, unlike the color of pigments or dyes [1–4].

A colloidal crystal is an ordered array of colloid particles and one of the most promising structural color materials. Colloidal crystal can be prepared as a film structure by simple methods such as gravity sedimentation [5,6], dipping [7,8], solvent evaporation [9], spin coating [10] and microfluidic cell method [11].

On the other hand, the use of monodisperse fine particles is strongly required for the brilliant coloration of colloidal crystals [12–18]. Until now, the best-established and most commonly used method for the production of monodisperse fine particles is emulsion polymerization. However, this method requires the use of a relatively large amount of surfactant. The presence of the surfactants increases cost and difficulty of purification of the obtained particles. Therefore, the development of a new method for surfactant-free (soap-free) emulsion polymerization has been strongly desired not only for the colloidal crystal synthesis but also for the industrial synthesis of monodisperse polymer particles.

On the other hand, ultrasonic irradiation provides stable emulsions without using surfactants by means of mechanical forces generated from acoustic cavitation at the liquid/liquid interphase boundaries [19–21]. This has been termed 'acoustic emulsification' and is regarded as one of the powerful tools for rapid and environmental-friendly emulsion production. Recently, our group reported a new technique for the preparation of a highly clear and transparent emulsified aqueous solution containing water immiscible organic droplets with diameters of a few tens of nanometers under surfactant-free conditions using several ultrasonic devices having different frequencies [22]. We observed that the droplet size was clearly reduced by using sequential ultrasonic processing. This

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Table 1
Details of each ultrasonication step in the sequential ultrasonications.

Frequency	Power/ W cm^{-2}	Sonication time/ min	Devise used
20 kHz	44	8	Ultrasonic stepped horn (13 mm diameter, titanium alloy) connected with a 20 kHz oscillator (SONIFIER-250D, Branson Ultrasonics Co.)
500 kHz	4	10	Ultrasonic transducer (Honda Electric Co.) connected with a Pyrex glass cylindrical tube (diameter, 24 mm; length, 75 mm)
1.6 MHz	16	10	Ultrasonic transducer (Honda Electric Co.) connected with a Pyrex glass cylindrical tube (diameter, 24 mm; length, 75 mm)
2.4 MHz	7	10	Ultrasonic transducer (Honda Electric Co.) connected with a Pyrex glass cylindrical tube (diameter, 24 mm; length, 75 mm)

novel technique, tandem acoustic emulsification, was found to be adequate for producing emulsion nanodroplets with desired size in the absence of any surfactant. Hence, we envisioned that size-controlled polymer nanoparticles could be synthesized by soap-free polymerization with a tandem acoustically emulsified monomer solution. In fact, we have already reported that this approach works in the preparation of size-controlled polymer particles. Furthermore, colloidal crystal films were found to be easily prepared from such size-controlled polymer particles. The successful results promoted us to perform a systematic study on the fabrication of colloidal crystal films with a variety of structural colors using size-controlled polymer particles.

2. Experimental

2.1. Abbreviation

In the present paper, MMA, PMMA, APS, DLS, and SEM are used to indicate methylmethacrylate, polymethylmethacrylate, ammonium peroxodisulfate, dynamic light scattering, and scanning electron microscopy, respectively.

2.2. Chemicals and materials

MMA (analytical grade) was purchased from Tokyo Chemical Industry Co., Ltd. and passed through a basic alumina column for the removal of polymerization inhibitor (6-tert-butyl-2,4-xylenol). Aluminum oxide 90 active basic (0.063–0.200 mm) (activity stage I) for column chromatography was purchased from MERCK. APS (analytical grade) was purchased from Wako Pure Chemical Industries, Ltd. and used as received. Methanol, 2-propanol, and ethylene glycol were purchased from Kanto Chemical Co., Inc. Water for emulsification and polymerization was deionized to a resistivity of 18.2 MΩ cm using a Barnstead DI water system.

2.3. Acoustic emulsification

2.134 g of MMA was added to 22.7 ml of deionized water in glass beaker cell (1:10 volume ratio of MMA to water). Then, the sequential ultrasonications (20 kHz → 500 kHz → 1.6 MHz → 2.4 MHz) were conducted to the water/MMA mixture. Details of each ultrasonication step are summarized in Table 1.

The ultrasound intensity (power level) in indicated by the electrical input power to the oscillator in this paper.

2.4. Photographic recording of MMA emulsion

The appearance of the MMA emulsion was monitored with photographic recording. The photographs were taken with a digital camera (IXY 300, Cannon Co.).

2.5. Measurement of droplet size and distribution

Droplet size distribution was determined by DLS at 25 °C with light scattering photometer (nano-ZS ZEN 3600, Sysmex Co.) without diluting the mixture. The minimal measurement time of 10 min was required for setting and stabilizing the sample before the first data point was taken.

2.6. Preparation of PMMA nanoparticles

The PMMA particles were synthesized from the emulsified solution using radical polymerization method [23]. Polymerization was started by the addition of 0.025 g of APS as an initiator at 78 °C for 15 min and then the reaction vessel was cooled to 25 °C to stop the polymerization. By this procedure, polymerization of MMA droplets was completed (the conversion of MMA monomer was 100%).

2.7. Fabrication of fluidic cells

The fluidic cell used in this study is composed of two flat glass substrates (Matsunami, S-1226, 76 × 26 × 1 mm) and two spacers sandwiched between them. Two stick tapes (Nitto Denko Corporation, No. 5601, 10 μm in thickness) were used as spacer. The cell has two openings with the same thickness as the spacers. A fluid reservoir is connected with one side of the opening (Fig. 1).

2.8. Preparation of colloidal crystal films

As-polymerized nanoparticle solutions were simply used for preparation of colloidal crystal films. The dispersion of PMMA spheres penetrated into the space of the fluidic cell caused under capillary forces (Fig. 2). The fluidic cell was held to supply the dispersion from the reservoir, and then the colloidal crystal film constructed across the inside of the fluidic cell. The colloidal crystal grew gradually from the edge of another opening and reached over several square centimeters after several days (Fig. 3).

2.9. Scanning electron microscopy (SEM)

After the polymerization, the PMMA colloidal crystal films were prepared by fluidic cell method and then dried under reduced pressure. After this process, the surface morphology of the films was observed by SEM (VE-7800, Keyence Co.). The accelerating voltage of SEM was 15 kV.

2.10. Modification of structural color

1.0 ml of organic solvent (methanol, 2-propanol, or ethylene glycol) was added to 10 ml of an as-polymerized nanoparticle solution in order to expand the size of PMMA nanoparticle. Then, the solution of nanoparticles swelled for 30 min was used for the fabrication of colloidal crystal films by the fluidic cell method.

2.11. Measurement of transmittance spectra

Optical properties of PMMA colloidal crystal films are evaluated by measuring their transmittance spectra, using a UV–Vis spectrometer (UV-1800, Shimadzu Co.). The spectra were measured over a range from 400 to 700 nm.