

Size-Controlled Synthesis of Polymer Nanoparticles with Tandem Acoustic Emulsification Followed by Soap-Free Emulsion Polymerization

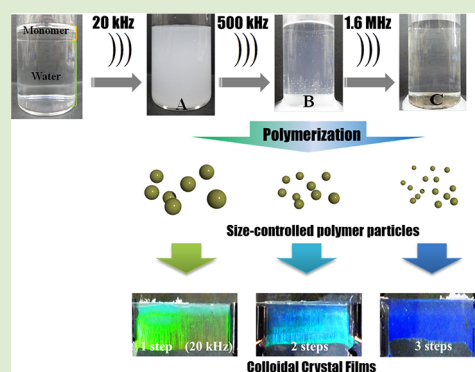
Koji Nakabayashi,[†] Maya Kojima,[†] Shinsuke Inagi,[†] Yuki Hirai,[‡] and Mahito Atobe^{*,†,‡}

[†]Department of Electronic Chemistry, Tokyo Institute of Technology, Yokohama 226-8502, Japan

[‡]Department of Environment and System Sciences, Yokohama National University, Yokohama 240-8501, Japan

S Supporting Information

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 polymer nanoparticles. Furthermore, colloidal crystal films could be easily prepared from the as-polymerized nanoparticle solution using the fluidic-cell method.



Polymer particles are widely used in a variety of coating materials, inks, adhesive additives, and cosmetics. In recent years, there has been great interest in nanosized polymer particles due to their potential applications in electronics, photonics, and biotechnology. For most of these applications, size control is of key importance. To meet this challenge, various approaches have been demonstrated for producing well-controlled polymer spheres in the past decades.^{1–4} Until now, the best-established and most commonly used method is emulsion polymerization. However, this method requires the use of a relatively large amount of surfactant. The presence of the surfactant increases cost and difficulty of purification. Thus, the development of a new method for surfactant-free (soap-free) emulsion polymerization has been strongly desired from both industrial and academic points of view.

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.^{5–7} This has been termed “acoustic emulsification” and is regarded as one of the powerful tools for rapid and environmentally 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.⁸ We observed that the droplet size was clearly reduced by using sequential ultrasonic processing. This 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. We report here the realization of this concept.

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 (Figure 1). A milky white solution was obtained immediately after 20 kHz ultrasonic treatment, and this appearance was not changed by elongation of the sonication time (Figure 1b). In our experiments, an

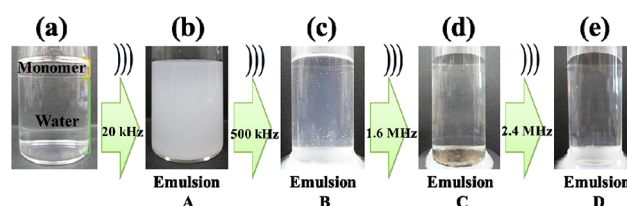


Figure 1. Photographic observations of tandem acoustic emulsification of MMA in aqueous solution. Photograph (a) represents the original MMA in aqueous solution mixture. Emulsification conditions were (b) 20 kHz, 8 min; (c) 20 kHz, 8 min → 500 kHz, 10 min; (d) 20 kHz, 8 min → 500 kHz, 10 min → 1.6 MHz, 10 min; and (e) 20 kHz, 8 min → 500 kHz, 10 min → 1.6 MHz, 10 min → 2.4 MHz, 10 min.

Received: April 12, 2013

Accepted: May 16, 2013

Published: May 20, 2013

ultrasonic horn was used for the 20 kHz treatment to create such a milky white solution. However, ultrasonication with more common sonicators such as ultrasonic baths could not emulsify the original MMA/aqueous solution mixture, due to their low mechanical effects. On the other hand, sequential ultrasonication with 500 kHz treatment after the 20 kHz treatment gave a clearer emulsified solution (Figure 1c), and finally, a perfectly clear and transparent solution was obtained by further sequential ultrasonication with 2.4 MHz treatment after the 20 kHz, 500 kHz, and 1.6 MHz treatments (Figure 1e). This emulsified solution was so stable that the clear and transparent appearance was maintained for at least 6 months, even under surfactant-free conditions. The actual reason why the tandem acoustic emulsified solution was so stable, even without the addition of surfactants, has not been clarified at present. However, it has been proposed by Fogler et al. that the acoustic emulsions are stabilized as a result of the preferential adsorption of OH ions that are always present in the aqueous media.⁹ Therefore, we can speculate this phenomenon on the basis of preferential adsorption of OH ions at the MMA–water interface.

To estimate the droplet size quantitatively, we then measured the size distributions of the MMA droplets after the acoustic emulsification treatments by dynamic light scattering (DLS; Figure 2). After 20 kHz ultrasonication, a single peak in the

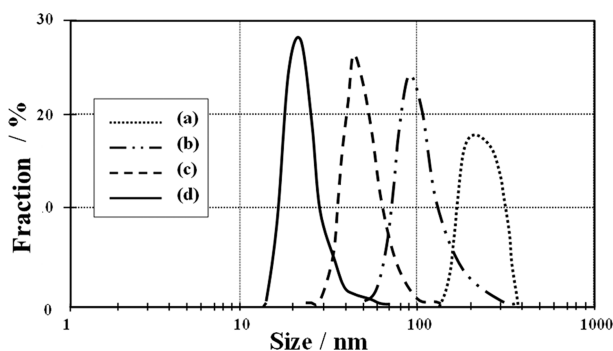


Figure 2. Size distributions of MMA droplets in acoustically emulsified aqueous solutions. Emulsification conditions used were (a) 20 kHz, 8 min (average droplet size: 220 nm); (b) 20 kHz, 8 min → 500 kHz, 10 min (average droplet size: 112 nm); (c) 20 kHz, 8 min → 500 kHz, 10 min → 1.6 MHz, 10 min (average droplet size: 51 nm); and (d) 20 kHz, 8 min → 500 kHz, 10 min → 1.6 MHz, 10 min → 2.4 MHz, 10 min (average droplet size: 23 nm).

number-mode was observed at 220 nm. Sequential ultrasonication at a higher frequency could break up the larger droplets to form smaller droplets, and finally, ultrasonication with 2.4 MHz after 20 kHz, 500 kHz, and 1.6 MHz led to a peak shift to 23 nm. Therefore, it can be stated that the size of the MMA nanodroplets was controlled intentionally by selecting the number of ultrasonication steps in the tandem operation.

To obtain size-controlled polymethylmethacrylate (PMMA) nanoparticles, we then carried out soap-free emulsion polymerization using these emulsified solutions (emulsions A–D in Figure 1). Polymerization was started by the addition of ammonium peroxodisulfate (APS) as an initiator at 78 °C for 15 min, and the reaction vessel was then cooled to 25 °C to stop the polymerization. Figure 3 shows the size distribution of the PMMA nanoparticles polymerized from emulsions A–D. Although the average size of the PMMA prepared from the 20

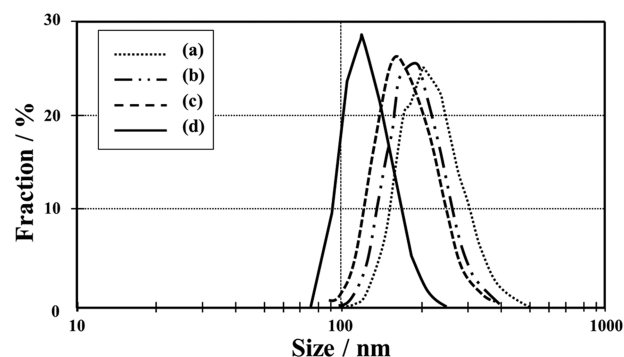


Figure 3. Size distributions of PMMA particles prepared from acoustically emulsified aqueous solutions. PMMA samples were synthesized from (a) emulsion A (average particle size: 241 nm), (b) B (average particle size: 191 nm), (c) C (average particle size: 164 nm), and (d) D (average particle size: 129 nm) of Figure 1.

kHz sonicated solution (emulsion A) was almost equal to the corresponding MMA droplet size, it was not in accord with the corresponding MMA droplet size when using the tandem sonicated solutions (emulsions B–D). Because the Ostwald ripening would be greatly enhanced at higher temperatures,¹⁰ this fact would indicate that the elevated temperature for the polymerization lead to the Ostwald ripening, and thus, the increase in MMA droplets size occurred during the polymerization. However, the size order between PMMA samples tightly reflected that between the corresponding MMA droplets. Moreover, the size distribution of all PMMA samples obtained by this synthesis method was found to be relatively narrow.

Colloidal crystals consist of monodispersed submicrometer spheres, and they exhibit structural colors due to Bragg's law of diffraction of visible light. Therefore, colloidal crystals have attracted much interest owing to their potential in applications such as optoelectronics and photonics.¹¹ Surfactant-free polymer latexes are suitable for the preparation of colloidal crystals because pretreatments for removing impurities such as surfactants are not needed.

Using the fluidic-cell method,¹² we fabricated colloidal crystal films composed of size-controlled PMMA nanoparticles prepared by the present synthesis method. In this demonstration, an as-polymerized nanoparticle solution was simply used for the fabrication.

Different optical properties were observed for the film samples. Figure 4 shows photograph of PMMA colloidal crystal films formed within a fluidic cell. Figure 5 shows their transmission spectra. In general, the transmission peak wavelength (λ_{peak}) is strongly related to the sphere diameter, that is, λ_{peak} of the colloidal crystal film composed of bigger spheres is longer because of the longer interparticle distance. In fact, as shown in Figure 5, λ_{peak} of film A composed of bigger PMMA spheres was longer than that of other film samples at 551 nm. On the other hand, λ_{peak} of films B and C was found to be 509 and 417 nm, respectively. λ_{peak} of film D was not detected in the visible-light region. This may be ascribed to the fact that visible light was not diffracted in film D that was composed of smaller PMMA particles.

Finally, in order to evaluate the crystallinity (i.e., the ordering of the PMMA spheres), the surface of the films was observed by SEM (Figure 6). The SEM images clearly revealed that both sample films (films A and D of Figure 4) have a densely packed

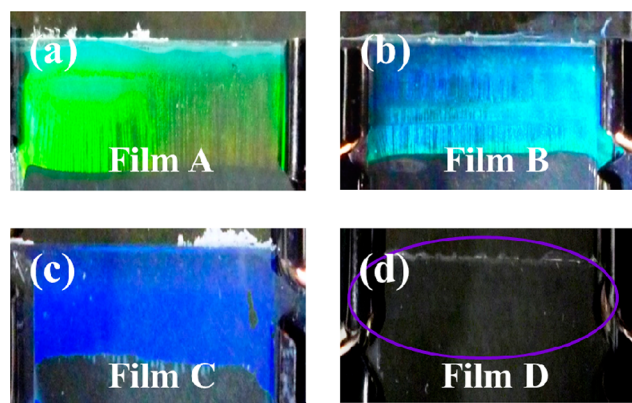


Figure 4. Photographic images of colloidal crystal films composed of size-controlled PMMA particles prepared from (a) emulsions A, (b) B, (c) C, and (d) D of Figure 1.

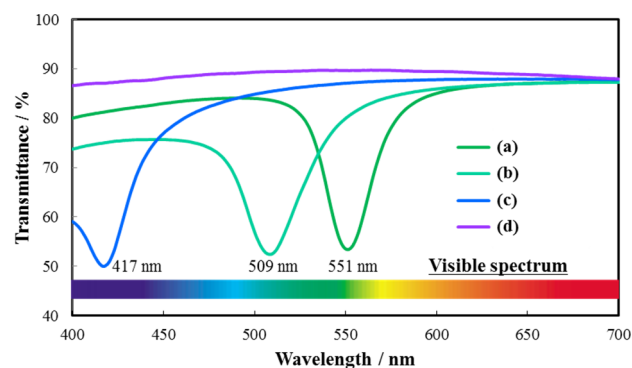


Figure 5. Transmission spectra of colloidal crystal films composed of size-controlled PMMA nanoparticles prepared from (a) emulsion A, (b) B, (c) C, and (d) D of Figure 1.

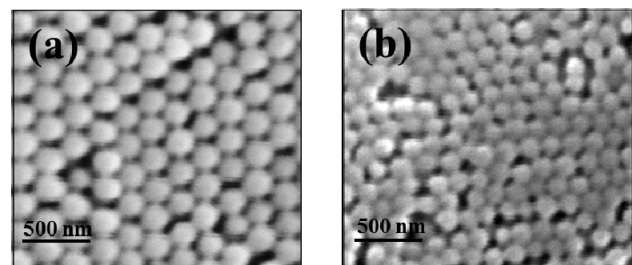


Figure 6. SEM micrographs of colloidal crystal films: (a) film A, (b) film D.

structure with a periodic array of size-controlled PMMA polymer particles.

In conclusion, we successfully prepared size-controlled polymer nanoparticles under a surfactant-free condition using tandem acoustic emulsification. Tandem acoustic emulsification is clearly a powerful tool for the synthesis of size-controlled polymer nanoparticles. In addition, structural color materials were successfully made from such size-controlled polymer nanoparticles prepared by tandem acoustic emulsification.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: atobe@ynu.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by the Global COE Program (Tokyo Institute of Technology) and a Grant-in-Aid for Scientific Research on Innovative Areas “Organic Synthesis Based on Reaction Integration. Development of New Methods and Creation of New Substances” (No. 2105).

■ REFERENCES

- (1) Chai, G. S.; Shin, I. S.; Yu, J. S. *Adv. Mater.* **2004**, *16*, 2057.
- (2) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693.
- (3) Ugelstad, J.; Berge, A.; Elingsen, T.; Smid, R.; Nielsen, T. N. *Prog. Polym. Sci.* **1992**, *17*, 87.
- (4) Song, J.-S.; Tronc, F.; Winnik, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 6562.
- (5) Li, M. K.; Fogler, H. S. *J. Fluid Mech.* **1978**, *88*, 499.
- (6) Li, M. K.; Fogler, H. S. *J. Fluid Mech.* **1978**, *88*, 513.
- (7) Reddy, S. R.; Fogler, H. S. *J. Phys. Chem.* **1980**, *84*, 1570.
- (8) Nakabayashi, K.; Amemiya, F.; Fuchigami, T.; Machida, K.; Takeda, S.; Tamamitsu, K.; Atobe, M. *Chem. Commun.* **2011**, *47*, 5765.
- (9) Reddy, S. R.; Fogler, H. S. *J. Phys. Chem.* **1980**, *84*, 1570.
- (10) Madras, G.; McCoy, B. J. *Chem. Eng. Sci.* **2004**, *59*, 2753.
- (11) Lopez, C. *Adv. Mater.* **2003**, *15*, 1679.
- (12) Ishii, M.; Nakamura, H.; Nakano, H.; Tsukigase, A.; Harada, M. *Langmuir* **2005**, *21*, 5367.