Colloid Polym Sci (2009) 287:251–257
DOI 10.1007/s00396-008-1983-y

ORIGINAL CONTRIBUTION

Preparation of multihollow polystyrene particles by seeded emulsion polymerization using seed particles with incorporated nonionic emulsifier: effect of temperature

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Received: 9 October 2008 / Accepted: 4 December 2008 / Published online: 19 December 2008

Abstract Seeded emulsion polymerizations of styrene using polystyrene (PS) seed particles with incorporated nonionic emulsifier were carried out at 40 and 70 °C to investigate the influence of temperature during the polymerization process including the swelling step of the seed particles with monomer on the formation of multihollow PS particles. An increase in the temperature during the polymerization process caused an increase in the rate of coalescence (i.e., the degree of coalescence at any given time) of the small water domains in the inside. After the coalescence proceeded excessively, the water domains were eventually discharged from the particles to the medium, resulting in nonhollow particles. The results show that it is important for the preparation of the multihollow PS particles to control the coalescence of a lot of small water domains inside the seed particles with the incorporated nonionic emulsifier, and strongly support the formation mechanism previously proposed.

Keywords Hollow particle · Emulsion polymerization · Incorporation · Nonionic emulsifier

Introduction

In recent years, there has been increasing interest in the preparation of hollow polymer particles due to their wide applications such as weight-saving thermal insulations, hiding and opaquifying agents [1–3] through light scattering, and gloss enhancers [4, 5] for paper coatings. They can also potentially be used as microcapsules for controlled and sustained drug delivery systems [6–8] in the pharmaceutical industry. Various techniques for the preparation of such particles have been proposed [9–17]. One of the earliest approaches to prepare submicron-sized hollow polymer particles is based on osmotic swelling [18, 19]. This method usually starts with emulsion polymerization to prepare a carboxylated polymer core and a thermoplastic polymer-shell particle. Following this, the core is ionized by addition of alkali, and consequently expanded by osmotic swelling. This procedure results in submicron-sized hollow particles with water and ionized polymer inside. A different method consisting of two stages—encapsulation of a water-miscible alcohol and a hydrocarbon nonsolvent by the modified emulsion polymerization and stabilization of morphology with a cross-linker has been reported [20]. Submicron-sized hollow particles were also prepared by miniemulsion polymerization in the presence of larger amounts of a hydrophobe [21].

We have also reported various ways to prepare submicron-sized multihollow polymer particles by post-treatments (the "stepwise alkali/acid method" [22, 23]; the "alkali/cooling method" [24]) for styrene-methacrylic acid copolymer [P(S-MAA)] particles. In both methods, the ionized P(S-MAA) particles absorb water, resulting in numerous small water pools inside the particles in the alkali treatment process. In the stepwise alkali/acid method, ionized carboxyl groups are deionized and the small water pools coalesce to become larger during the acid treatment process, resulting in the hollow structure. Moreover, when the concentration of carboxyl group is above some critical value, the small water pools can coalesce during the alkali treatment (the alkali/cooling method). Throughout these studies, it was surprisingly observed that 75% of polyoxyethylene nonylphenyl

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Part CCCXX of the series "Studies on Suspension and Emulsion".

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ether nonionic emulsifier [Emulgen 911, hydrophilic–lipophilic balance (HLB) 13.7] used in the emulsion copolymerization was incorporated inside P(S-MAA) (MAA, 10 mol%) particles during the polymerization [25]. In further studies, the incorporation was also clearly observed in emulsion polymerization of styrene (S) using two kinds of polyoxyethylene lauryl ether nonionic emulsifiers having different HLB values: Emulgen 109P (HLB 13.6); Emulgen 150 (HLB 18.3), where 30% and 15% of the total mass of Emulgen 109P and Emulgen 150 were, respectively, incorporated inside the PS particles [26]. Moreover, the incorporation of two nonionic emulsifiers (Emulgen 911, Emulgen 109P) having different hydrophobic portions in emulsion polymerizations of methacrylic monomers such as methyl methacrylate, ethyl methacrylate, and *i*-butyl methacrylate was also investigated [27]. The incorporation causes a decrease in the colloidal stability of polymer particles because of a decrease in the amount of emulsifiers used for stabilizing the particles when using normal emulsifier concentrations. Moreover, several problems such as making broad particle size distribution based on byproduct of new particles, which leads to complicated polymerization kinetics, and a decrease in water resistance in film applications are caused by the incorporation. However, inversely, we also found that the nonionic emulsifier incorporated inside the P(S-MAA) particles promotes the formation of multihollow particles by the alkali/cooling method [28].

Recently, we reported the preparation of submicron-sized, multihollow PS particles by seeded emulsion polymerization of S using PS seed particles with incorporated nonionic emulsifier [29]. This method potentially enables preparation of hollow particles with fewer requirements on the kind of base-polymer (carboxyl groups not required) and no use of ingredients having an adverse effect on the environment. Moreover, it was clarified that the nonionic emulsifier incorporated inside particles was necessary for the formation of hollow structure resulting from absorption of water into the particles. Generally, hydrophilicity of nonionic emulsifier decreases with increasing temperature because the degree of hydration of the polyethylene oxide chains decreases. Consequently, the emulsifiers phase separate from their aqueous solutions on heating at certain temperature (the so-called cloud point, CP). Therefore, it is speculated that the formation of hollow structure depends on the differences in the hydrophilicity and interfacial active ability of emulsifier at different temperatures. In this article, in order to clarify the influence of temperature during polymerization process including the swelling step of the PS seed particles with S on formation of multihollow PS particles, seeded emulsion polymerizations were carried out at 40 and 70 °C, which are much lower than and near to the CP of Emulgen 911 (73.6 °C, according to the manufacturer), respectively.

Experimental

Materials

S was purified by distillation under reduced pressure. Potassium persulfate (KPS) of analytical grade (Nacalai Tesque Inc., Kyoto, Japan) was purified by recrystallization. Commercial grade polyoxyethylene nonylphenyl ether nonionic emulsifiers (Emulgen 911, HLB 13.7) with averages of 10.9 ethylene oxides per molecule were used as received (Kao Co., Tokyo, Japan). Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), 2-propanol and tetrahydrofuran (THF) of guaranteed reagent grade were used as received (Nacalai Tesque Inc., Kyoto, Japan). Deionized water with a specific resistance of 5×10^6 Ω cm was distilled before use.

Preparation of PS seed particles

PS seed particles were prepared by emulsion polymerization at 70 °C for 24 h under a nitrogen atmosphere in a four-necked 1-L round-bottom flask equipped with an inlet of nitrogen gas and a reflux condenser. Water (120 g) and Emulgen 911 (0.4 g) was added to the reactor, and the solution was stirred with a half-moon type stirrer at 240 rpm under a nitrogen atmosphere. The distance between the lower edge of the blade of the stirrer and the bottom of the flask was set to be approximately 1 cm. After the solution was heated to 70 °C, S (4 g) was poured into the reactor. The mixture was deoxygenated with a stream of nitrogen gas for 30 min and then a KPS aqueous solution (0.32 g of KPS were dissolved in 20 g of water) was added to the reactor to initiate polymerization. The conversion was 98% by gravimetry.

Seeded emulsion polymerization

The PS seed emulsion was centrifugally purified with distilled water to remove undecomposed initiator. The purified PS emulsion (7.2 g; solid content, 2.8%) was put into a two-necked 30-mL reactor. The seed particles were swollen with S (PS seed/S, 1/0.5, w/w) at 40 °C for 24 h before starting polymerization. After the swelling, a KPS/$CuCl_2$ aqueous solution (10 mg of KPS and 2 mg of $CuCl_2$ were dissolved in 0.75 g of water) and a $Na_2S_2O_3$ aqueous solution (4 mg of $Na_2S_2O_3$ dissolved in 1.25 g of water) as a redox initiator were added to the reactor. Seeded emulsion polymerization was carried out at 40 °C for 24 h under a nitrogen atmosphere. The same amounts of the redox initiator solutions described above were added to the reactor every 6 h. The same PS seed

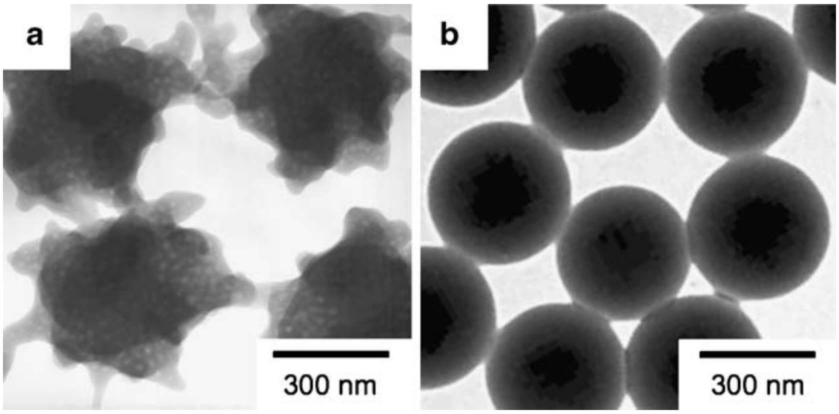


Fig. 1 TEM photographs of PS particles prepared by emulsion polymerization with (**a**) and without (**b**) Emulgen 911 at 70 °C

particles were swollen with S at 70 °C for 1 h and 24 h before starting polymerization. After the swelling, the seeded emulsion polymerizations were carried out with a KPS aqueous solution (10 mg of KPS were dissolved in 2 g of water) at 70 °C for 24 h under a nitrogen atmosphere.

The obtained particles were observed with a transmission electron microscope (TEM, JEM-1230, JEOL Datum Ltd., Tokyo, Japan). Each PS emulsion was diluted to about 50 ppm, and a drop was placed onto a carbon-coated copper grid and allowed to dry at room temperature in a desiccator. Quantitative analysis of nonionic emulsifier inside particles by gel permeation chromatography (GPC) was conducted according to a previous work [29].

Quantitative analysis of water inside particle

The evaporation behavior of water from the PS emulsion was examined by measuring the weight loss of the sample with a thermo gravimetry/differential thermal analyzer (TG/DTA, TG/DTA 6200, Seiko Instruments Inc., Chiba, Japan). The amount of water inside particles was determined according to a previous work [30]. The TG/DTA measurement was carried out for 30 mg of PS emulsion (the solid content was approx. 10 wt.%) after centrifugal washing with water five times on an aluminum pan (5-mm diameter) at 30 °C under nitrogen atmosphere (the flow rate: 250 ml/min). The instantaneous evaporation rate of water was determined by differentiation of the weight-loss curve.

Quantitative analysis of water in monomer phase

S was added to emulsifier aqueous solution (S/Emulgen 911/water=1/0.1/9, weight ratio). This mixture was left for 1 h at 40 or 70 °C. About 1.0 g of monomer was carefully taken from the monomer phase by a syringe, and then the amount of water in the monomer phase was determined with a Karl–Fischer moisture meter (CA-100, Dia Instruments Co., Ltd., Kanagawa, Japan).

Results and discussion

Preparation of PS seed particles with incorporated nonionic emulsifier

Nonspherical PS seed particles with incorporated nonionic emulsifier were obtained by emulsion polymerization with

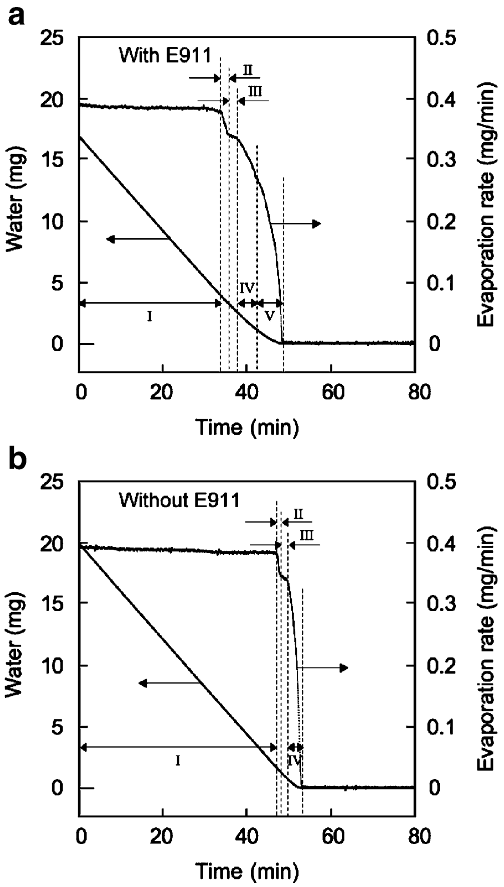


Fig. 2 Weight-loss curves and differential weight-loss curves due to the evaporation of water at 30 °C from 10 wt.% of PS seed emulsions prepared by emulsion polymerizations with (**a**) and without (**b**) Emulgen 911

Emulgen 911 (Fig. 1a). According to the measurement by GPC [27, 29], 3.2 wt% of Emulgen 911 (relative to the weight of PS) was incorporated inside the seed particles, which was equivalent to 32% of the total added Emulgen 911. Emulsifier-free emulsion polymerization was conducted under the same recipe as the emulsion polymerization for comparison, resulting in monodisperse spherical particles (Fig. 1b). The difference in the shape between the particles will be discussed in elsewhere. The nonspherical PS seed particles with the incorporated emulsifier had a large number of less contrast small domains (Fig. 1a), which are considered to be filled with water before drying [29]. On the other hand, emulsifier-free spherical PS particles had no domain in the inside. The amount of water inside the seed particles was determined based on the evaporation behavior of water from the PS emulsion by measuring a weight loss of the sample with TG/DTA [30].

Figure 2a shows the weight-loss curves and the differential weight-loss curves due to the evaporation of water at 30 °C from 10 wt.% of the PS seed emulsion (Fig. 1a). For the comparison, the result obtained for emulsifier-free PS particles (Fig. 1b) is also shown in Fig. 2b. Both evaporation rates of water were almost constant in period I, where free water evaporated from the aqueous media. In period II, some particles near air/water surface began to be exposed to air, and consequently the evaporation area of water decreased, resulting in a decrease in the evaporation rates. Subsequently, the free water among the particles evaporated in period III. Finally, in the case of the emulsifier-free particles, a small amount of water adsorbed at the particle surface evaporated and the rate rapidly decreased to zero in period IV (Fig. 2b). On the other hand, in the case of the particles with the incorporated emulsifier (having the small domains), the evaporation rate decreased in two steps (period IV and V). The periods IV and V were attributed to the evaporations of water from the surface and the inside of the particles, respectively. The water inside the particles must diffuse through a hydrophobic polymer phase to evaporate in the period V. From the above results, it was concluded that the PS seed particles with the incorporated emulsifier contained water as a lot of small water domains. The volume percentage of the water domains inside the particles was approx. 23 vol.%.

Influence of temperature during seeded emulsion polymerization process on formation of multihollow structure

Figure 3 shows TEM (a, b) and SEM (a′, b′) photographs of PS particles prepared by seeded emulsion polymerization at

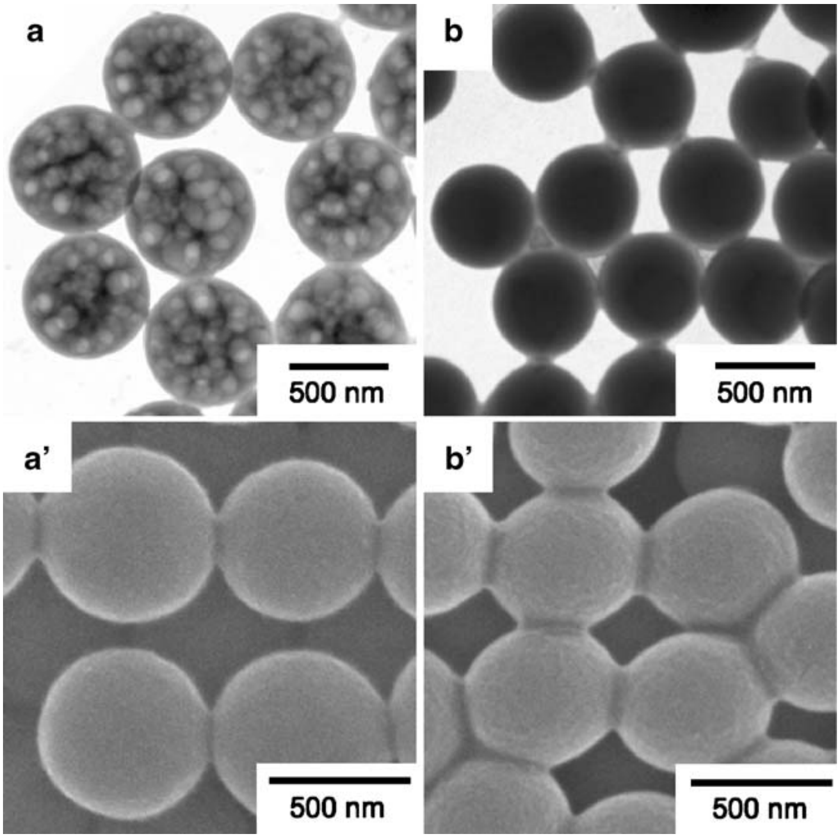


Fig. 3 TEM (**a**, **b**) and SEM (**a′**, **b′**) photographs of PS particles prepared by seeded emulsion polymerization at 40 (**a**, **a′**) and 70 °C (**b**, **b′**) using PS seed particles with incorporated Emulgen 911 (Fig. 1a). Initiator was added 24 h after addition of monomer to the purified PS seed emulsion

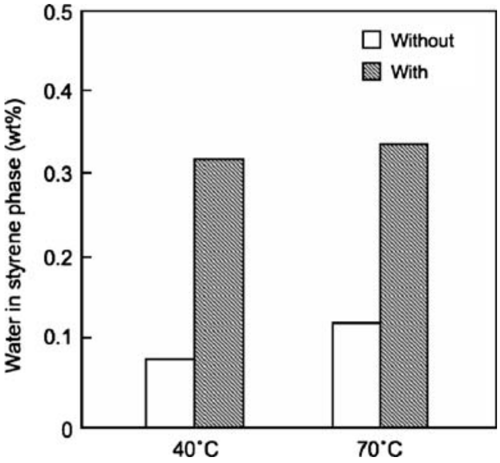


Fig. 4 Weight percentages of water in the S phase without [S/water=1/9, *w/w*] and with Emulgen 911 [S/Emulgen 911/water=1/0.1/9, *w/w/w*] at 40 and 70 °C

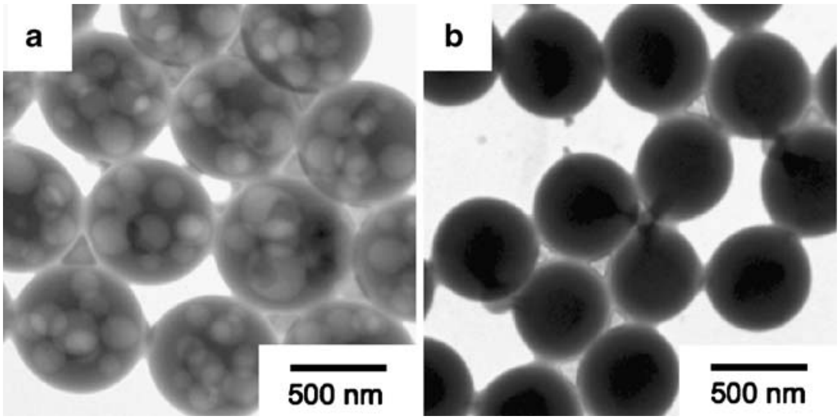
40 (a, a′) and 70 °C (b, b′) using the PS seed particles with incorporated Emulgen 911 (Fig. 1a). A lot of lower contrast regions in the TEM photograph (Fig. 3a) were observed in the particles prepared at 40 °C. From the SEM photograph (Fig. 3a′), the surface of the spherical particles was smooth. Therefore, the lower contrast regions in the particles were attributed to a multihollow structure inside the particles. The volume percentage of hollows estimated by the TG/DTA measurement was approx. 35 vol.%, which was close to that calculated from the TEM photograph (approx. 32 vol.%). Considering the increase in the volume percentage of hollows from 23 vol.% for the PS seed particles (Fig. 1a) to 35 vol.%, further absorption of water into the particles occurred during the seeded emulsion polymerization. On the other hand, spherical particles with homogeneous contrast were obtained at 70 °C (Fig. 3b). This indicates no multihollow structure in the particles. There are two possible reasons for this difference between the temperatures.

The first reason is that there may be difference in the ability of the particles to absorb water between the temperatures considering that the hollows were filled with water before drying. From the fact that an incorporated emulsifier is important for the formation of multihollow particles [28, 29], it is speculated that the hydrophilicity of emulsifier at the temperatures affects the amount of water absorbed into the particle. That is, the higher the temperature in the seeded emulsion polymerization, the smaller the amount of water that will be absorbed inside particles, because the hydrophilicity of emulsifier decreases with increasing temperature. In order to examine this idea, a model experiment was carried out.

Figure 4 shows the weight percentages of water in the S phase of S/water mixture without/with Emulgen 911 (see the experimental section for details) at 40 and 70 °C. In the absence of the emulsifier, the weight percentage of water was higher at 70 °C than at 40 °C. This is because the solubility of water in S increases with increasing temperature. In the presence of the emulsifier, unexpectedly, the percentage of water was also somewhat higher at 70 °C than at 40 °C. This suggests that the ability of the particles to absorb water would not be directly related to the hydrophilicity of emulsifier. That is, the first reason described above is not the main reason that multihollow particles were not prepared by the seeded emulsion polymerization at 70 °C after the swelling step for 24 h.

In both temperatures, the larger amount of water existed in the S phase with the emulsifier than without the emulsifier. This supports the idea that emulsifiers incorporated inside particles promote absorption of water into the particles (i.e., formation of multihollow structure). However, the weight percentage of water in the S phase was in disagreement with the volume percentage of hollows even though the emulsifier existed. This is because other factors would also be involved in the absorption of water into the particles. In the actual polymerization, not only monomer

Fig. 5 TEM photographs of PS particles prepared by seeded emulsion polymerization at 70 °C using PS seed particles with incorporated Emulgen 911. Initiator was added 1 h (**a**) or 24 h (**b**) after the addition of monomer to the purified PS seed emulsion at 70 °C



but also polymer exists, moreover, the total interface area between water and S-swollen particles is much larger than that between water and S phase in the model experiment. The reason why the absorption of water occurs during an ab initio and a seeded emulsion polymerizations will be discussed in a future.

The second reason is that the coalescence of the water domains proceeds excessively, and finally coalesced domains are discharged from the particles to minimize total interfacial free energy, resulting in nonhollow particles. The multihollow structure is based on the coalescence of a lot of water domains inside particles [29, 30] to decrease the total interfacial free energy [31] during the swelling step (the period from the monomer addition until the initiator addition) and the seeded emulsion polymerization, where the glass transition temperature of the monomer-swollen particles must be below the temperatures at the swelling and the polymerization process. The coalescence level of water domains (i.e., the number and size of hollows) is determined by the coalescence rate and the time. The coalescence rate mainly depends on the interfacial tension between the water domain and the polymer phase and the viscosity inside the particles. On the other hand, the coalescence time mainly depends on swelling time and polymerization rate. In order to confirm whether the second reason is proper, the swelling time prior to the polymerization at 70 °C was shortened from 24 h to 1 h.

As expected, multihollow structure was clearly observed even at 70 °C by shortening the swelling time from 24 h (Fig. 5b) to 1 h (Fig. 5a). This result clearly indicates that the second reason is the main reason that a multihollow structure was not obtained by the seeded emulsion polymerization at 70 °C when the swelling time was 24 h, and strongly supports the formation mechanism of multihollow polymer particles previously proposed [29, 30]. It can thus be concluded that the temperature during the polymerization process does not have significant influence on the absorption of water into the particles, but influences the degree of coalescence of the small water domains inside the particles and the discharge of the coalesced domains from the particles to the medium.

Conclusions

The influence of temperature during polymerization process on the preparation of multihollow polymer particles was investigated. PS seed particles with incorporated nonionic emulsifier were prepared by emulsion polymerization at 70 °C. The seed particles contained a lot of small water domains, which was directly confirmed by quantitative analysis of water with TG/DTA. Seeded emulsion polymerizations of S using the seed particles with the incorporated nonionic emulsifier were carried out at 40 and 70 °C. When the swelling time of PS seed particles with S was 24 h, multihollow and nonmultihollow were obtained at 40 and 70 °C, respectively. However, multihollow particles were also obtained even at 70 °C by shortening the swelling time to 1 h. These results indicate that it is important for the preparation of multihollow polymer particles to control the coalescence of a lot of water domains. The findings in the quantitative analysis of water in S phase without/with emulsifier show that the emulsifiers incorporated inside particles can promote absorption of water into the particles. However, the weight percentages of water in the S phase were in disagreement with the volume percentage of hollows even though emulsifier existed, and it appears that the temperature scarcely affect the absorption of water into the particles. The relationship between the absorption of water into the particles and the incorporated emulsifier is presently unclear, but forms the subject of ongoing work in our laboratory.

Acknowledgement This work was supported by Grant-Aid for Scientific Research (No. 17201025) from the Japan Society for the Promotion of Science (JSPS) and by Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists (given to H. K.).

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