Colloid Polym Sci (2003) 282: 193–197
DOI 10.1007/s00396-003-0995-x

SHORT COMMUNICATION

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Influence of nonionic emulsifier included inside carboxylated polymer particles on the formation of multihollow structure by the alkali/cooling method

Received: 28 April 2003
Accepted: 27 August 2003
Published online: 21 October 2003

Part CCL of the series "studies on suspension and emulsion"

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Abstract The influence of nonionic emulsifier, included inside styrene-methacrylic acid copolymer [P(S-MAA)] particles during emulsion copolymerization, on the formation of multihollow structure inside the particles via the alkali/cooling method (proposed by the authors) was examined in comparison to emulsifier-free particles. It was clarified that the nonionic emulsifier included inside the P(S-MAA) particles eased the formation of multihollow structure.

Keywords Particle · Multihollow · Nonionic emulsifier · Inclusion · Emulsion polymerization

Introduction

Submicron-sized polymer emulsions prepared by emulsion polymerization have been used as films in many industrial fields; for example, painting, printing, and manufacturing. Recently, attention has focused on using the particles themselves. For example, thermoplastic styrene/acrylic polymer particles containing one hollow at the center, which are prepared by alkali-swelling of a structured particle with a carboxylated core polymer and an outer thermoplastic shell [1], have received much attention. The hollow is filled with water in the emulsion state, but with air in the dry state. Such particles are commercially supplied as a hiding or opacifying agent in coating and molding compositions [2].

We reported some ways to prepare submicron-sized polymer particles having one or more hollows inside by post-treatments, which were named the "stepwise alkali/acid method" [3, 4] and the "alkali/cooling method" [5, 6] for carboxylated polymer particles, and the "stepwise acid/alkali method" [7, 8] for polymer particles having dimethylamino groups. Throughout these studies, when the swelling state of styrene-methacrylic acid copolymer [P(S-MAA)] particles in the alkali treatment process was examined using ^{1}H NMR, it was also observed that nonionic emulsifier, which was used in the emulsion polymerization for the preparation of the P(S-MAA) particles, was eluted from the inside of the particle into alkali aqueous medium. For example, in a previous article [9], about 75% of the nonionic emulsifier used in the emulsion polymerization was included inside the P(S-MAA) particles during the emulsion polymerization process. To our knowledge, there is no detailed information on the inclusion of nonionic emulsifier inside particles produced by emulsion polymerization, although some effects of nonionic emulsifier distributed in monomer phase, on the behavior of emulsion polymerization have been studied [10, 11, 12, 13]. This inclusion inside the particle should be a disadvantage for stabilizing the particle in an aqueous medium, but may be an advantage to the formation of the multihollow structure by the above methods,

because the nonionic emulsifier added during the swelling process of the above method greatly influenced the formation of the multihollow structure [8].

In this article, the effect of emulsifier (included inside the particles) on the formation of multihollow particles by the alkali/cooling method will be clarified, by comparing to emulsifier-free particles produced by emulsifier-free emulsion copolymerization.

Experimental

Materials

Styrene and methacrylic acid (MAA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical grade potassium persulfate (Nacalai Tesque Inc., Kyoto, Japan) was purified by recrystallization. Analytical grade KOH and guaranteed reagent grade tetrahydrofuran (THF) were used as received from Nacalai Tesque Inc. Commercial grade polyoxyethylene nonylphenylether nonionic emulsifier (Emulgen 911, Kao Co., Tokyo, Japan), with formula C_9H_{19}-C_6H_4-$O(CH_2CH_2O)_{10.9}H$ (HLB, 13.7), was used as received. Deionized water with a specific resistance of 5×10^6 Ωcm was distilled.

P(S-MAA) particles

The emulsifier-free and the emulsifier-including P(S-MAA) particles were produced by emulsifier-free and emulsifier-present emulsion copolymerizations respectively under the conditions listed in Table 1. The particles were centrifugally washed five times at 12000 rpm with distilled water. In the following experiments, the centrifugally washed particles were used. Weight-average hydrodynamic diameters (D_w) of the particles were measured at 10 ppm concentration by dynamic light scattering (DLS) (DLS-700, Otsuka Electronics, Kyoto, Japan) with the data taken at a light-scattering angle of 90° at room temperature. Weight-average molecular weight (M_w) of the particles was measured by gel permeation chromatography (GPC). Calibration was performed with polystyrene standards using THF as the eluent. Amount of Emulgen 911 included in the P(S-MAA) particle produced by the emulsifier-present emulsion polymerization was quantitatively measured according to our previous article [9].

Table 1 Styrene-methacrylic acid copolymer [P(S-MAA)] (MAA, 10 mol%) particles produced by emulsifier-free and emulsifier-present emulsion copolymerizations[a]

Ingredients	Emulsifier-free	Emulsifier-present
Styrene (g)	10.1	55.0
Methacrylic acid (g)	1.01	5.0
Potassium persulfate (mg)	5.5	32.0
Emulgen 911[b] (g)	–	4.0
Water (g)	288	540
D_w[c] (nm)	415	429
D_w/D_n[d]	1.01	1.01
M_w[e] ($\times10^5$ g/mol)	12	13
M_wM_n[f]	1.3	1.5
Copolymer dissolved[g] (wt%)	0.2	~0

[a] N_2; 24 h; 80 °C; stirring rate, 120 rpm
[b] Nonionic emulsifier, with formula C_9H_{19}-C_6H_4-$O(CH_2CH_2O)_{10.9}H$ (HLB, 13.7)
[c] Weight-average hydrodynamic diameter measured by dynamic light scattering (DLS)
[d] Number-average hydrodynamic diameter measured by DLS
[e] Weight-average molecular weight measured by gel permeation chromatography (GPC)
[f] Number-average molecular weight measured by GPC
[g] Amount of copolymer dissolved in aqueous medium after copolymerization, based on the weight of monomer mixture, measured via gravimetry

Compatibility of Emulgen 911 with P(S-MAA)

P(S-MAA) films containing Emulgen 911 were prepared at room temperature by casting THF solutions for one day in which centrifugally-washed P(S-MAA) particles produced by emulsifier-free emulsion polymerization and Emulgen 911 were dissolved. The films were further dried under vacuum for two days at room temperature. The thickness of each film was about 300 μm. The compatibility of Emulgen 911 with P(S-MAA) was estimated by measuring the turbidity of the film at a wavelength of 350 nm with a spectrophotometer according to the Beer-Lambert law:

$$T=-\log_{10}\left(\frac{I}{I_0}\right)\Big/d \quad (1)$$

where τ is the turbidity; I_0 is the intensity of incident light; I is the intensity of transmitted light; d is the thickness of the film.

Alkali/cooling treatment

The emulsifier-free and the emulsifier-including P(S-MAA) particles were treated with alkali as follows. They were diluted to 0.5 g/L, and adjusted to pH 12.0 with 1 N KOH aqueous solution. The emulsions were placed in 50 mL-capacity stainless steel pressure-resistant vessels having a polytetrafluoroethylene inner container, and the vessels were dipped in an oil bath at 150 °C for 3 h. After the treatment, they were cooled in air to room temperature.

Glass transition temperature (T_g) in emulsion state

T_g of the P(S-MAA) particles in the emulsion state were measured using a power compensative differential scanning calorimeter (PC-DSC) (Nano-DSC II 6100, Calorimetry Sciences Corp., Utah, USA) according to a previous article [14]. The solid content and pH of the emulsion was adjusted to 40 g/L and 12.0 with 1 N KOH aqueous solution, respectively.

Electron microscopy

A JEOL JEM-2010 electron microscope was used for transmission electron microscope (TEM) observation. Each P(S-MAA) emulsion was diluted to about 50 ppm, and a drop was placed onto a carbon-coated grid and allowed to dry at room temperature in a desiccator.

Results and discussion

Fig. 1 shows TEM photographs of the P(S-MAA) (MAA, 10 mol%) particles produced by the emulsifier-free and

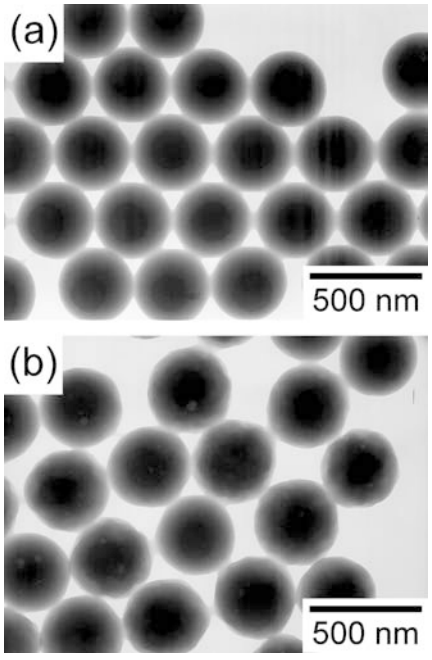

Fig. 1 TEM photographs of the styrene-methacrylic acid copolymer [P(S-MAA)] (MAA, 10 mol%) particles produced by emulsifier-free (**a**) and emulsifier-present (**b**) emulsion copolymerizations under the conditions listed in Table 1

the emulsifier-present emulsion copolymerizations under the conditions listed in Table 1. Both D_w and M_w of the particles produced by the emulsifier-free emulsion copolymerization were almost equal to those produced by the emulsifier-present one, as shown in Table 1. The amounts of water-soluble polymer dissolved in aqueous media after both copolymerizations were almost negligible, and residual monomers were also almost negligible by gas chromatography. These results indicate that the MAA content in the P(S-MAA) particles after both copolymerizations were the same as those calculated from the polymerization recipes. Although the D_w, M_w, and MAA content of P(S-MAA) particles influenced the formation of multihollow structure as reported in the previous articles [5, 6], these influences could be neglected in the comparison between both particles in this study.

Fig. 2 shows the partition of Emulgen 911 among the medium, the particle surfaces, and the particle insides of the P(S-MAA) (MAA, 10 mol%) emulsion produced by the emulsifier-present emulsion copolymerization under the conditions listed in Table 1. 75% of the Emulgen 911 charged in the polymerization was included inside the P(S-MAA) particles, and only 20% existed at the particle surfaces. The amount of Emulgen 911 included corresponded to 5 wt% based on the weight of the particles.

Fig. 3 shows the turbidities of the P(S-MAA) (MAA, 10 mol%) films having different Emulgen 911 contents,

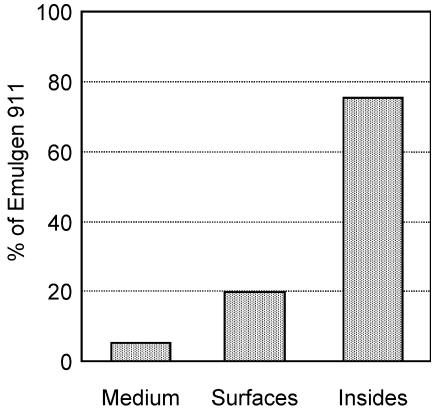

Fig. 2 Partition of Emulgen 911 among the medium, the particle surfaces, and the particle insides of P(S-MAA)(MAA, 10 mol%) emulsion produced by emulsifier-present emulsion copolymerization under the conditions listed in Table 1

prepared by casting THF solutions, in which the centrifugally-washed P(S-MAA) (MAA, 10 mol%) particles produced by the emulsifier-free emulsion polymerization and Emulgen 911 were dissolved. The turbidity of the film was measured with a spectrophotometer at 350 nm, at which almost no absorption was detected for both P(S-MAA) and Emulgen 911. For Emulgen 911 content below 5 wt%, the film was transparent. On the other hand, for Emulgen 911 content above 5 wt%, the film became cloudy, and the turbidity linearly increased with increasing Emulgen 911 content. These results suggest that Emulgen 911, which was included inside the P(S-MAA) particles, existed homogeneously in the particles, because the amount of

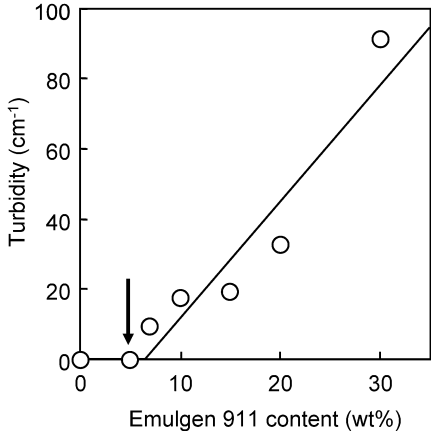

Fig. 3 Relationships between Emulgen 911 content in P(S-MAA) (MAA, 10 mol%) film prepared by casting THF solution, in which centrifugally-washed P(S-MAA) particles produced by emulsifier-free emulsion coplymerization and Emulgen 911 were dissolved, and turbidity of the film measured with a spectrophotometer (350 nm). The arrow shows the content of Emulgen 911 included inside the P(S-MAA) particles produced by emulsifier-present emulsion copolymerization

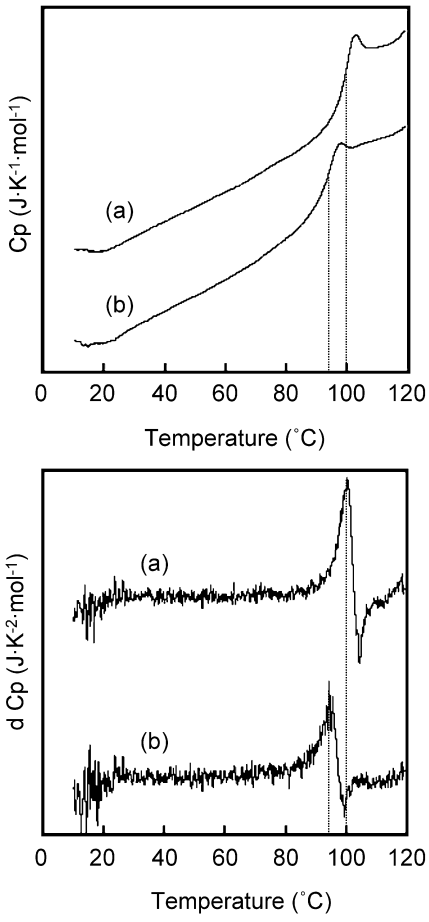

Fig. 4 PC-DSC second heating curves (top) and their differential curves (bottom) of emulsifier-free (**a**) and emulsifier-included (**b**) P(S-MAA) particles in emulsion states at initial pH 12.0

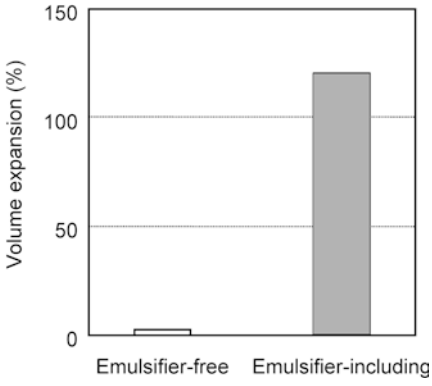

Fig. 5 Volume expansions of emulsifier-free (left column) and emulsifier-including (right column) P(S-MAA) (MAA, 10 mol%) particles after alkali/cooling treatment (initial pH 12.0; 150 °C; 3 h)

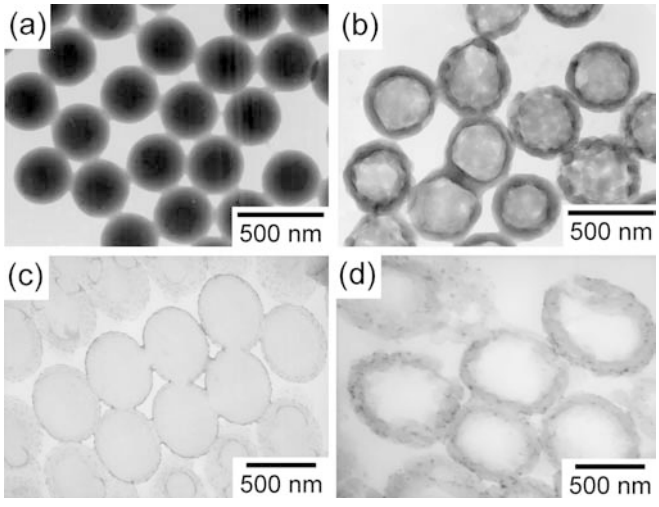

Fig. 6 TEM photographs (**a**, **b**) and ultrathin cross sections (**c**, **d**) of emulsifier-free (**a**, **c**) and emulsifier-including (**b**, **d**) P(S-MAA) (MAA, 10 mol%) particles after alkali/cooling treatment (initial pH 12.0; 150 °C; 3 h)

Emulgen 911 included was 5 wt% based on the amount of the particles as described above.

Fig. 4 shows PC-DSC second heating curves and their differential curves for the emulsifier-free and the emulsifier-including P(S-MAA) particles in emulsion states at initial pH 12.0. The T_g values in the emulsion states were obtained at temperatures (T_{gE}^{d}) at which the differential specific heats were maximums. T_{gE}^{d} (94 °C) of the emulsifier-including particles was smaller than that (100 °C) of the emulsifier-free particles. These results indicate that Emulgen 911 included (dissolved) in the particles acted as a plasticizer.

Fig. 5 shows the volume expansions of the emulsifier-free and the emulsifier-including P(S-MAA) (MAA, 10 mol%) particles after the alkali/cooling treatment (initial pH 12.0; 150 °C; 3 h). The emulsifier-free particles showed almost no expansion after the alkali/cooling treatment. On the other hand, the emulsifier-including particles showed a considerable expansion. These results indicate that the existence of the nonionic emulsifier inside the P(S-MAA) particles increases the amount of water absorbed into the particles.

Fig. 6 shows TEM photographs of the emulsifier-free and the emulsifier-including P(S-MAA) particles after the alkali/cooling treatment (initial pH 12.0; 150 °C; 3 h), and of the ultrathin cross sections of their particles. Hollow structure was not observed inside the alkali/cooling-treated emulsifier-free particles. On the other hand, hollow structure was clearly observed inside the alkali/cooling-treated emulsifier-including particles.

Conclusions

From the above results, it is concluded that the nonionic emulsifier included inside the P(S-MAA) (MAA,

10 mol%) particles during the emulsion copolymerization operates effectively to form multihollow structure inside the particles by the alkali/cooling method. This conclusion supports the formation mechanism of the multihollow structure by the alkali/cooling method described in [4, 6], because the nonionic emulsifier included inside the particles increased the amount of water absorbed and acted as a plasticizer. First, the carboxyl groups inside the particle are neutralized by the alkali treatment at higher temperature than the T_g. Because of osmotic pressure due to the ionized carboxyl groups and the included nonionic emulsifier molecules, H_2O molecules penetrate inside, and the H_2O molecules around the carboxyl group and the hydrophilic ethylene oxide unit of the emulsifier molecule become a small-sized water pool, which drastically increases the interfacial area between ionized P(S-MAA) and water. In order to obtain a more thermodynamically stable state, the water pools coagulate into larger pools to decrease the interfacial area. In the case that the amount of H_2O molecules inside the particles is small, it is difficult to form the multihollow structure in a short time because the rate of the coagulation is too slow [4]. On the other hand, in the case that the amount of the H_2O molecules inside the particles is large enough, since the rate of coagulation is fast, the multihollow structure is formed in a short time [6]. Finally, in the cooling process, the multihollow structure is fixed because the molecular movement is frozen.

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