Colloid Polym Sci 276:103–108 (1998)

ORIGINAL CONTRIBUTION

M. Okubo
T. Yamashita

Morphology of micron-sized monodispersed composite polymer particles produced by seeded polymerization for the dispersion of highly monomer-swollen polymer particles

Received: 04 June 1997
Accepted: 27 August 1997

Part CLXXII of the series
"Studies on Suspension and Emulsion"

Prof. M. Okubo (✉) · T. Yamashita
Department of Chemical Science and
Engineering
Faculty of Engineering
Kobe University
Rokko, Nada,
Kobe 657,
Japan

Abstract Monodispersed polystyrene (PS)/poly(*n*-butyl methacrylate) (PBMA) composite particles having 9.4 μm in diameter were produced by seeded polymerization for the dispersion of highly *n*-butyl methacrylate (BMA)-swollen PS particles, and their morphologies were examined. The highly BMA-swollen PS particles (about 150 times the weight of the PS seed particles) were prepared by mixing monodispersed 1.8 μm-sized PS seed particles and 0.7 μm sized BMA droplets prepared with an ultrasonic homogenizer in ethanol/water (1/2, w/w) medium at room temperature. After $NaNO_2$ aqueous solution as inhibitor was added in the dispersion, the seeded polymerization was carried out at 70 °C. In an optical microscopic observation, one or two spherical high contrast regions which consisted mainly of PS were observed inside PS/PBMA composite particles. In the PS domain, there were many fine spherical PBMA domains. Such morphologies were based on the phase separation of PS and PBMA within the homogeneous swollen particles during the seeded polymerization.

Key words Morphology – phase separation – micron-sized – monodispersed – swelling – seeded polymerization

Introduction

Recently, micron-sized monodispersed polymer particles have been applied in the biomedical field, microelectronics, etc. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized monodispersed polymer particles. Almog et al. [1] suggested that dispersion polymerization technique is useful for their production. Later, Ober et al. [2], Tseng et al. [3], and the present authors [4] have recognized the usefulness of this technique.

Nevertheless, the technique seems to be restricted to a variety of monomers for producing such particles having functional groups thereon, which would be required in the above applications. Therefore we have been producing about 2 μm-sized monodispersed functional polymer particles by seeded polymerizations in the presence of 1.8 μm-sized monodispersed polystyrene (PS) seed particles produced by dispersion polymerization [4–7].

In order to produce monodispersed polymer particles having more than 5 μm diameter, we proposed that seeded polymerization utilizing a new type of swelling method of seed polymer particles with a large amount of monomer which was named "dynamic swelling method (DSM)" [8–11]. We clarified that the high swelling by DSM is based on the size difference between micron-sized polymer seed particles and submicron-sized monomer droplets and on the high saturated monomer concentration in the medium [12]. Moreover, in similar experimental conditions as DSM, about 10 μm-sized monodispersed *n*-butyl methacrylate (BMA)-swollen PS particles were prepared by mixing 0.70 μm-sized BMA droplets prepared with an ultrasonic homogenizer and 1.77 μm-sized PS particles in ethanol/water (1/2, w/w) medium [13] on the basis of the idea of thermodynamic treatment of DSM.

Morphology of micron-sized monodispersed composite polymer particles consisting of two kinds of polymers, which are not compatible, produced by seeded polymerization for the dispersion of "highly" monomer-swollen polymer particles seems to be attractive, because viscosity within the monomer-swollen polymer particles is extremely low as for monomer droplets. In a series of investigations on the morphologies of submicron-sized [14] and micron-sized [15–18] composite polymer particles produced, respectively, by seeded emulsion polymerization and seeded dispersion polymerization, it is clear that the viscosity within particles during the seeded polymerizations is one of the key factors which give a great influence on the morphology.

In this article, in order to characterize the morphology of composite particles produced by seeded polymerization for the dispersion of "highly" monomer-swollen polymer particles, the micron-sized monodispersed PS/poly(*n*-butyl methacrylate) (PBMA) composite particles will be produced under such a condition.

Experimental

Materials

Styrene and BMA were purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) of reagent grade were purified by recrystallization. Poly(vinyl alcohol) (PVA) as a stabilizer was supplied by Nippon Synthetic Chemical (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%). Reagent grade of sodium dodecyl sulfate (SDS), sodium nitrite ($NaNO_2$), toluene and ethanol were used as received.

Production of PS seed particles

Monodispersed PS seed particles were produced under the optimum dispersion polymerization conditions determined in the previous work [4]. The PS seed particles were observed with a JEOL JEM-200CX transmission electron microscope (TEM). The number-average diameter (D_n) and the coefficient of variation (C_v) measured with the Personal Image Analysis System (PIAS Co., Ltd., LA-525, Japan) were, respectively, 1.77 μm and 3.9%.

Swelling of PS seed particles with BMA and seeded polymerization

Swelling of PS seed particles with a large amount of BMA was carried out under the conditions listed in Table 1 according to the previous articles [13] as follows. BMA dissolving BPO was emulsified in ethanol/water medium dissolving SDS using an ultrasonic homogenizer at 0 °C for 10 min. The size of BMA droplets determined by dynamic light scattering was 0.7 μm. The prepared monomer emulsion was mixed with the PS seed emulsion which consisted of PS particles, PVA, ethanol and water. The mixture was stirred at room temperature in a 50 ml glass cylindrical reactor (inside diameter: 31 mm) with a magnetic stirrer at 250 rpm for 2 h. After the absorption of BMA into the PS seed particles for 2 h, 60 g of water dissolving $NaNO_2$ (8.7 mg) as a water soluble inhibitor was added to the mixture at a rate of 14.4 ml/h to depress the redissolving of BMA from the swollen particles into the medium and the by-produced PBMA particles in the medium by raising the temperature to the polymerization temperature of 70 °C. The seeded polymerization was carried out at 70 °C for 24 h under a nitrogen atmosphere.

In the polymerization system, conversion measured by gas chromatography (Yanagimoto MFG. Co., Ltd., G-2800, Japan) was higher than 98%.

The dispersions of swollen particles and composite particles were dropped onto slide glass, and observed with a Nikon MICROPHOTO FXA optical microscope. The produced composite particles were also observed with a Hitachi S-2500 scanning electron microscope (SEM).

Table 1 Preparation for monodispersed "highly" BMA-swollen PS particles by mixing BMA monomer emulsion and PS seed emulsion

Ingredients		
Monomer emulsion[a]		
BMA	(g)	3.0
BPO	(mg)	30.0
SDS	(mg)	16.0
Ethanol	(g)	4.0
Water	(g)	8.0
Seed emulsion		
PS seed particles[b]	(mg)	20.0
PVA	(mg)	50.0
Ethanol	(g)	1.65
Water	(g)	3.35

[a] Monomer emulsion was prepared with ultrasonic homogenizer at 0 °C for 10 min

[b] PS seed particles were produced by dispersion polymerization: Dn, 1.77 μm; Cv, 3.9 %

Abbreviations: BMA, *n*-butyl methacrylate; BPO, benzoyl peroxide; SDS, sodium dodecyl sulfate; PS, polystyrene; PVA, poly(vinyl alcohol)

Observation of ultrathin cross sections of PS/PBMA composite particles

Dried PS/PBMA composite particles were exposed to RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution, and then dispersed in epoxy matrix, cured at room temperature for 48 h, and microtomed. The ultrathin cross sections were observed with TEM.

Diameter measurements

D_n, the weight-average diameter (D_w), and C_v were determined by measuring the diameters of 50–150 droplets and particles on optical micrographs taken at room temperature with the Personal Image Analysis System. The swelling ratio (V_m/V_p) was calculated from D_n values of PS seed particles and BMA-swollen PS particles. V_m and V_p are, respectively, the volumes of monomer and polymer in the swollen particle.

Plasticization of the PS/PBMA composite particles

Toluene was emulsified in ethanol/water (1/2, w/w) medium dissolving SDS using the ultrasonic homogenizer at 0 °C for 5 min. The prepared toluene emulsion was mixed with the PS/PBMA emulsion and the mixture was stirred at room temperature in a 50 ml glass cylindrical reactor (inside diameter: 31 mm) with a magnetic stirrer at 250 rpm for 30 min. The weight ratio of toluene to polymer particles was 8/1. After swelling for 30 min, toluene was removed from the swollen particles in two ways: (1) adding ethanol to ethanol/water (1/1, w/w) medium to remove toulene from the swollen particles quickly and (2) the medium was stirred at room temperature for 48 h to evaporate toluene from the system slowly.

Results and Discussion

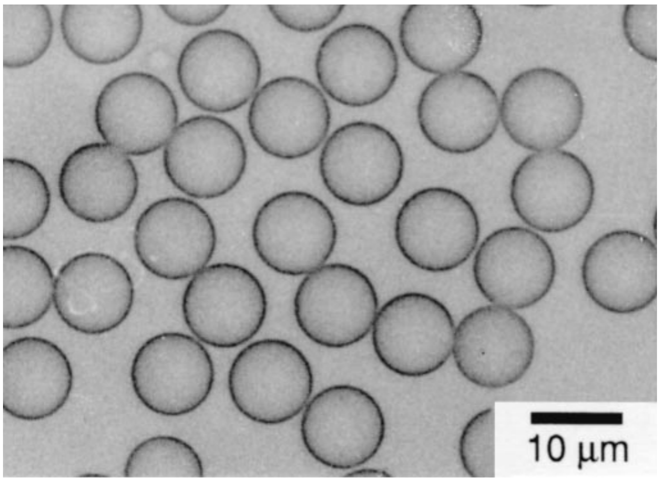


Fig. 1 An optical micrograph of BMA-swollen PS particles prepared under the conditions listed in Table 1

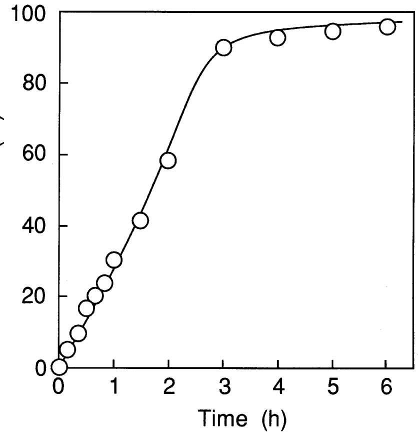


Fig. 2 Time-conversion curve of BMA in seeded polymerization for the dispersion of BMA-swollen PS particles prepared under the conditions listed in Table 1

Figure 1 shows an optical micrograph of BMA-swollen PS particles prepared under the conditions listed in Table 1, after the swelling for 2 h. Monodispersed "highly" BMA-swollen PS particles were prepared: D_n, 9.68 μm; D_w/D_n, 1.004; C_v, 3.5%. It is obvious that the monodispersed swollen particles were derived from PS seed particles, based on the fact that unswollen 1.77 μm-sized PS seed particles and 0.7 μm-sized BMA droplets disappeared, and D_n value of the swollen particles agreed well with the diameter (= 9.75 μm) calculated from the recipe assuming that all monomers are absorbed evenly by the PS seed particles. From the results that the inside of the swollen particles were observed as homogeneous in Fig. 1 and 0.025 g of the PS seed particles completely dissolved in 3.75 g of BMA monomer at room temperature for 10 min, PS seed particle should dissolve completely in the swollen particle before seeded polymerization.

Figure 2 shows a time-conversion curve of the seeded polymerization at 70 °C for the dispersion of BMA-swollen PS particles shown in Fig. 1. Seeded polymerization proceeded smoothly and the conversion attained more than 90% after 3 h.

Figure 3 shows optical microscopic (a) and SEM (b) photographs of PS/PBMA composite particles produced by seeded polymerization. In both photographs, the produced PS/PBMA composite particles had high monodispersity: D_n, 9.43 μm; D_w/D_n, 1.008; C_v, 5.8%. The D_n value of the composite particles agreed well with the presumed diameter (= 9.40 μm) based on the recipe (PS/PBMA = 1/150, w/w). All composite particles had smooth surfaces and one or two spherical heterogeneous domains inside. The domains seem to be composed of a PS-rich component because of the size of about 2 μm which nearly equals that of the PS seed particle.

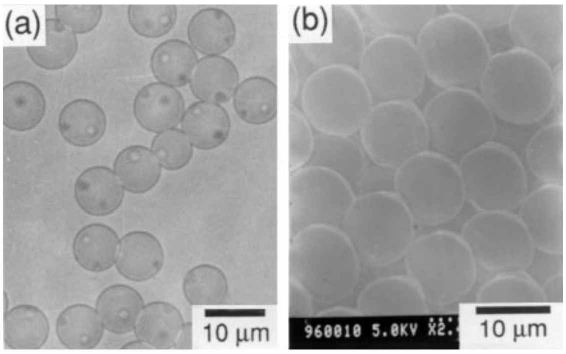
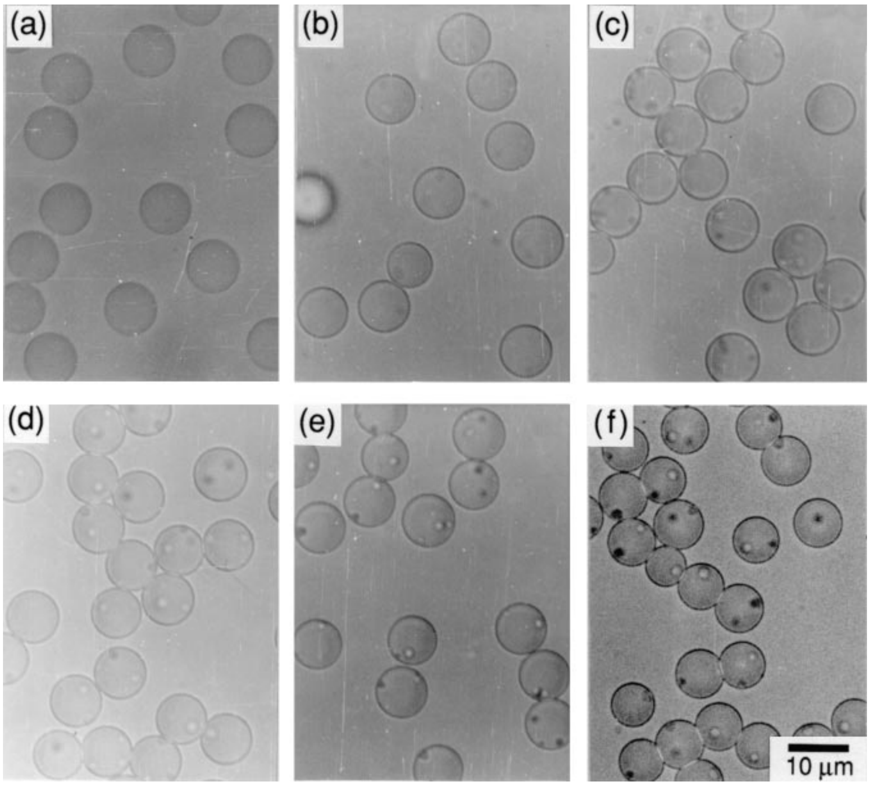


Fig. 3 Optical microscopic and SEM photographs of the PS/PBMA composite particles produced by seeded polymerization for the dispersion of BMA-swollen PS particles prepared under the conditions listed in Table 1

Figure 4 shows optical micrographs of PS/PBMA composite particles at various conversions, in which unpolymerized BMA remained. At 0% conversion (a), the inside of the swollen particles was observed to be homogeneous. This indicates that PS seed particles dissolved completely in the swollen particles. However, at 10% conversion (b) some spherical domains appear dimly in each particle, and at 17% conversion (c) they were clearly observed. The domains aggregate with the conversion and at 98% conversion (f) the number in the composite particle decreased to one or two. In order to clarify that the existence of the two domains in the particle is still unstable thermodynamically, the dispersion obtained at the conversion of 17% was kept at 0 °C for 6 h to give enough time for aggregation among the domains in the particles, and the seeded polymerization was restarted at 70 °C again.

Figure 5 shows optical micrographs of BMA-swollen PS/PBMA particles (a) at 17% conversion after keeping for 6 h at 0 °C and of PS/PBMA composite particles (b) produced by restarting the seeded polymerization. In both photographs, single PS domain was observed in almost all particles. From a comparison of Fig. 5a with Fig. 4c it is

Fig. 4 Optical micrographs of PS/PBMA composite particles in which unpolymerized BMA remained at various conversions (%): (a) 0, (b) 10, (c) 17, (d) 24, (e) 58, (f) 98



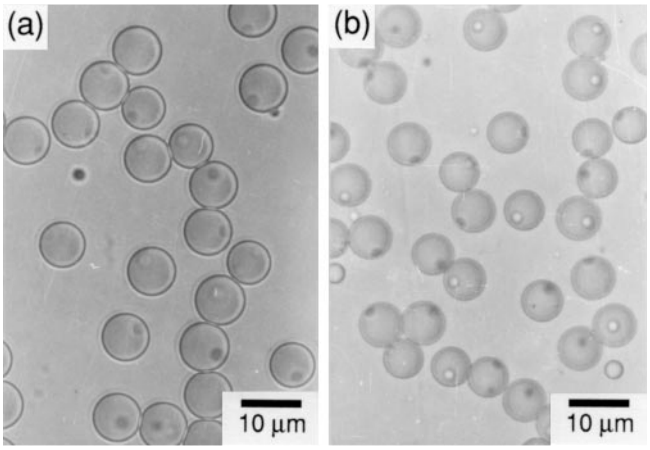


Fig. 5 Optical micrographs of BMA-swollen PS/PBMA particles (a) at 17% conversion after keeping for 6 h at 0 °C and of PS/PBMA composite particles (b) produced by restarting the seeded polymerization

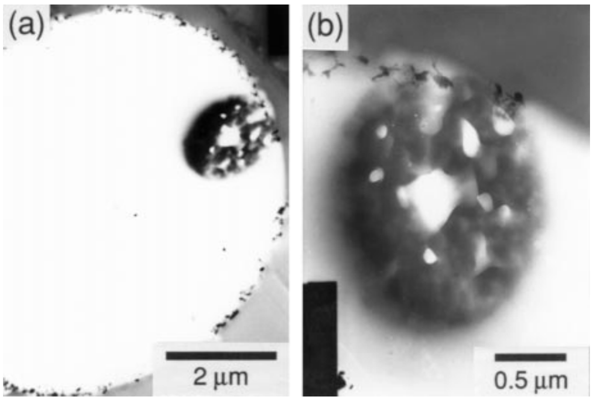


Fig. 6 TEM photographs of ultrathin cross sections of the PS/PBMA composite particles exposed with RuO_4

clear that single PS domain is thermodynamically the most stable.

Subsequently, for the purpose of producing the composite particles having single PS domain, the seeded polymerization was carried out at 70 °C for 48 h under the conditions in which only BPO initiator concentration was decreased to 10 mg in the recipe shown in Table 1. In the system, seeded polymerization proceeded smoothly and the conversion was attained at 98 %. All particles had a single domain (photograph was omitted).

Figure 6 shows TEM photographs of ultrathin cross section of the PS/PBMA composite particles shown in Fig. 3 exposed with RuO_4 which stains not PBMA, but PS [16]. In Fig. 6a, one 1.8 μm-sized PS domain was observed in the particle. In Fig. 6b which shows the magnified PS domain, many fine PBMA domains were observed in the PS domain. The formation of PBMA domains seems to be based on the incomplete phase separation of PBMA formed at high conversion in PS domain because of high viscosity.

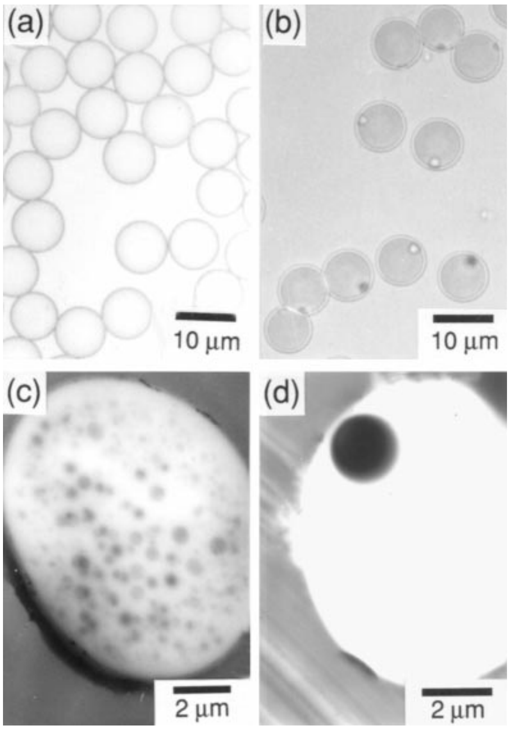


Fig. 7 Optical micrographs (a, b) of PS/PBMA composite particles and TEM photographs (c, d) of the ultrathin cross sections, exposed to RuO_4 vapor, after the fast (a, c) and slow (b, d) removals of toluene, respectively, by the addition of ethanol in the medium and by the evaporation of toluene at room temperature

In order to examine it, 8 times weight of toluene was absorbed into the PS/PBMA composite particles shown in Fig. 3 and was removed by ethanol addition (fast removal) and by evaporation (slow removal) from the homogeneous swollen particles in which the PS and PBMA dissolve in toluene.

Figure 7 shows optical micrographs (a, b) of PS/PBMA composite particles and TEM photographs (c, d) of the ultrathin cross sections, exposed to RuO_4 vapor, after the fast (a, c) and slow (b, d) removals of toluene. In the case of the fast removal, many fine PS domains dispersed homogeneously in the particles as shown in the TEM photograph (c), though such domains were not observed in the optical micrograph (a). This indicates that the phase separation between PS and PBMA was incomplete inside the composite particle. On the other hand, in the case of the slow removal, a single PS domain was observed inside each particle in the optical micrograph (b) and no fine

PBMA domain in the PS domain was observed in the TEM photograph (d). This indicates that the phase separation proceeded completely inside the particle.

From these results, it is concluded that seeded polymerization for the dispersion of highly monomer-swollen polymer particles has a characteristic that produced composite polymer particles having comparatively thermodynamically stable morphology, based on extremely low viscosity within polymerizing particles except for the final stage.

Acknowledgements This work was supported by Grant-in-Aids for the Japan Society for the Promotion of Science (JSPS) Fellows (given to T. Yamashita) from the Ministry of Education, Science, Sports and Culture of Japan.

References

1. Almog Y, Reich S, Levy M (1982) Br Polym J 14:131
2. Ober CK, Lok KP, Hair ML (1985) J Polym Sci Polym Lett Ed 23:103
3. Tseng CM, Lu YY, El-Aasser MS, Vanderhoff JW (1986) J Polym Sci Polym Chem Ed 24:2995
4. Okubo M, Ikegami K, Yamamoto Y (1989) Colloid Polym Sci 267:193
5. Okubo M, Katayama Y, Yamamoto Y (1991) Colloid Polym Sci 269:217
6. Okubo M, Yamamoto Y, Iwasaki Y (1991) Colloid Polym Sci 267:1126
7. Okubo M, Nakagawa T (1992) Colloid Polym Sci 270:853
8. Okubo M, Nakagawa T (1994) Colloid Polym Sci 272:530
9. Okubo M, Shiozaki M (1993) Polymer International 30:469
10. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) Colloid Polym Sci 269:222
11. Okubo M, Yamashita T, Suzuki T, Shimizu T (1997) Colloid Polym Sci 275:288
12. Okubo M, Yamashita T, Shiozaki M (1996) J Polym Sci 60:1025
13. Yamashita T, Okubo M, Colloid Polym Sci, in press
14. For Example, Matsumoto T, Okubo M, Imai T (1974) Kobunshi Ronbunshu 31:576
15. Okubo M, Nakagawa T, Yamashita T, Tsuji M (1995) Macromol Chem Macromol Symp 92:83
16. Okubo M, Hosotani T, Yamashita T (1996) Colloid Polym Sci 247:279
17. Okubo M, Hosotani T, Yamashita T, Izumi J, Colloid Polym Sci, in press
18. Okubo M, Izumi J, Hosotani T, Yamashita T (1997) Colloid Polym Sci 275:797