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SHORT COMMUNICATION

M. Okubo
Y. Konishi
H. Minami

Production of hollow polymer particles by suspension polymerization

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Prof Dr. M. Okubo (✉) · Y. Konishi
H. Minami
Department of Chemical Science
and Engineering
Faculty of Engineering
Kobe University
Rokko, Nada
Kobe 657-8501
Japan
E-mail: okubo@cx.kobe-u.ac.jp

Abstract Polymer particles having single hollow in the inside were successfully prepared by suspension polymerization for divinylbenzene/toluene droplets dissolving polystyrene (PS) in an aqueous solution of poly(vinyl alcohol). Such a hollow polymer particle was not obtained without PS. The hollow structure was affected by the molecular weight and the concentration of PS.

Key words Suspension polymerization – hollow – porous – polystyrene – particle

Introduction

Recently, micron-sized monodispersed polymer particles have been applied in the biomedical field, microelectronics, etc. Many research groups studying polymer colloids concentrate their attention on the production of micron-sized monodispersed polystyrene (PS) particles by dispersion polymerizations [1–5]. Using such PS particles as seed, about 2 μm-sized PS particles having chloromethyl [5] and vinyl groups [6, 7] at the surfaces were produced by seeded dispersion polymerizations of styrene (S) and chloromethylstyrene and of S and divinylbenzene (DVB) in ethanol/water media in which almost all of the corresponding monomers and initiators dissolve. However, it was difficult to produce monodispersed particles having more than 5 μm-size even by the dispersion polymerization and the seeded dispersion polymerization.

Therefore, in order to produce such particles, we suggested a novel swelling method of seed polymer particles with a large amount of monomer, which was named "dynamic swelling method (DSM)" [8–10]. Actually, seeded polymerization for highly monomer-swollen particles prepared by DSM using about 2 μm-sized monodispersed PS particles gave 9.4 μm-sized monodispersed PS/polybutyl methacrylate (1/148, w/w) composite particles [11], and about 5 μm-sized monodispersed PS/polydivinylbenzene (PDVB) (1/10, w/w) composite particles having tightly cross-linked structure and high concentration of vinyl groups at surface [12]. Such successes are based on the strong point of the technique that since almost all of monomers and initiators exist in the swollen particles, the seeded polymerizations proceeded smoothly therein. Moreover, we developed this technique to produce micron-sized monodispersed cross-linked polymer particles having one hollow in the inside, where the seeded polymerization for about 5 μm-sized monodispersed highly (DVB/toluene) swollen PS particles prepared by the DSM [13, 14], and discussed the formation mechanism of such hollow particles [15].

In this study, in order to clarify the formation mechanism more in detail, especially, the function of PS in the highly (DVB/toluene) swollen particles and to develop the idea in suspension polymerization, suspension polymerization for DVB/toluene droplets dissolving/undissolving of PS will be carried out.

Experimental

Materials

S was purified by distillation under reduced pressure in a nitrogen atmosphere. DVB was washed with 1 N NaOH and deionized water to remove polymerization inhibitors before use. DVB was supplied by Nippon Steel Chemical. Co. Ltd and the purity was 96%. Polyvinyl alcohol (PVA) (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%) were supplied by Nippon Synthetic Chemical Ind. Co. Ltd. Benzoyl peroxide (BPO) and 2, 2′-azobisisobutyronitrile (AIBN) of reagent grade were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Reagent grade of toluene was used as received.

PS molecules having different molecular weights were prepared by solution polymerization and suspension polymerization in sealed glass tubes under the conditions listed in Table 1. The tubes were horizontally shaken at 80 cycles/min (3 cm strokes). Each PS was purified by reprecipitation, washed with methanol and dried under reduced pressure. Weight-average molecular weight (M_w) was measured by gel permeation chromatography with calibration obtained using PS standards with tetrahydrofuran as the eluent.

Suspension polymerizations

A solution of DVB (250 mg) and toluene (250 mg) dissolving BPO (5 mg) and PS (0–150 mg) was mixed with an aqueous solution (15 g) of 0.33 wt% PVA and stirred by NISSEI ABM-2 homogenizer at 1000 rpm for 2 min in a glass cylindrical reactor. The suspension polymerizations were carried out at 70 °C for 24 h under a nitrogen atmosphere in sealed glass tubes under the conditions listed in Table 2. The tubes were horizontally shaken at 80 cycles/min (3 cm strokes). Droplets and each particles were observed with Nikon MICROPHOT-FXA optical microscope and a Hitachi S-2500 scanning electron microscope (SEM).

Table 1 Preparations of PS by solution polymerizations and suspension polymerizations

Ingredient	Solution polymerizations				Suspension polymerizations		
	I[a]	II[b]	III[b]	IV[c]	V[a]	VI[a]	VII[a]
Styrene (g)	18	18	18	18	15	11	10
Toluene (g)	12	12	12	12	0	0	0
AIBN (mg)	126	126	54	54	150	90	50
PVA (mg)	0	0	0	0	370	500	550
Water (g)	0	0	0	0	15	15	25
M_w[d] of PS ($\times 10^5$)	0.5	0.9	1.6	2.5	3.8	9.1	11.2
M_w/M_n	2.0	1.9	2.1	2.0	8.9	7.2	6.1

[a] N_2, 70 °C, 24 h.
[b] N_2, 60 °C, 24 h.
[c] N_2, 50 °C, 48 h.
[d] Weight-average molecular weight measured by gel permeation chromatography.
Abbreviations: PS, polystyrene; AIBN, 2,2′-azobisisobutyronitrile; PVA, polyvinyl alcohol.

Table 2 Recipes for the productions of PDVB particles and PS/PDVB composite particles by suspension polymerizations[a]

Ingredient	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
PS[b] (mg)	0	12.5	50	72.5	12.5	12.5
DVB[c] (mg)	250	250	250	250	250	250
Toluene (mg)	250	250	250	250	250	250
BPO (mg)	5.0	5.0	5.0	5.0	5.0	5.0
PVA (mg)	50	50	50	50	50	50
Water (g)	15.0	15.0	15.0	15.0	15.0	15.0
M_w[d] of PS ($\times 10^5$)	—	1.6	1.6	1.6	9.1	11.0

[a] N_2, 70 °C, 24 h.
[b] Prepared by solution or suspension polymerizations.
[c] Purity, 96 % (by catalog).
[d] Weight-average molecular weight measured by gel permeation chromatography.
Abbreviations: PS, polystyrene; DVB, divinylbenzene; BPO, benzoyl peroxide; PVA, polyvinyl alcohol.

Observations of the ultrathin cross sections of particles

PS/PDVB 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 24 h and microtomed. The ultrathin cross sections were observed with a Hitachi H-7100 TEM transmission electron microscope (TEM).

Results and discussion

Figure 1 shows optical micrographs of DVB/toluene (a) and DVB/toluene/PS droplets (PS: 9.1 wt%) (b) and of their particles (c, d) after suspension polymerizations under the conditions of Nos. 1 (a, c) and 3 (b, d), respectively, listed in Table 2. The PS of which M_w was 1.6×10^5 synthesized under the conditions of III listed in Table 1 was used. As clear in comparison with Figs. 1a and c, the produced PDVB particles had a similar size range as the DVB/toluene droplets of which size was in the range from submicron to a few ten micron. This suggests that the suspension polymerization proceeded mainly in the droplets. In Fig. 1c the PDVB particles were observed to be homogeneous, on the other hand, in Fig. 1d the PS/PDVB particles had a hollow structure on the basis of in the previous results [13–15]. These suggest that the existence of PS dissolving in the droplets is important for the formation of hollow structure.

Figure 2 shows optical micrographs of the particles produced by the suspension polymerizations for DVB/toluene droplets dissolving different amounts of PS (M_w, 1.6×10^5) under the conditions of Nos. 1(a), 2(b), 3(c), and 4(d) listed in Table 2: PS content in the droplets (wt%): (a), 0; (b), 2.4; (c), 9.1; (d), 13.0. In Fig. 2a, the inside of PDVB particles was observed to be homogeneous. In Fig. 2b, PS/PDVB (1/20, w/w) composite particles did not have the hollow strucutre, but heterogeneous structure. In Figs. 2c and d, PS/PDVB ((c), 4/20; (d), 6/20, w/w) composite particles had the hollow structure. These suggest that there is a minimum PS concentration in the droplets to form the hollow structure.

Figures 3 and 4 show, respectively, SEM photographs of the particles shown in Fig. 2a, b, and c and TEM photographs of their ultrathin cross sections. In Fig. 3a and 4a, the PDVB particles had smooth surfaces, and pore and hollow structures were not observed in the inside. In Fig. 3b and 4b, the PS/PDVB (1/20, w/w) composite particles had a porous structure at the surfaces and in the inside. In Fig. 3c and 4c, the PS/PDVB (4/20, w/w) composite particles had the smooth surfaces and the hollow structures.

Figure 5 shows optical micrographs of three kinds of PS/PDVB (1/20, w/w) composite particles produced by the suspension polymerizations for DVB/toluene droplets in which different M_w values of PS were dissolved at the same PS content of 2.4 wt%. At the lowest M_w of PS (1.6×10^5) (a), the produced particles had a porous structure. On the

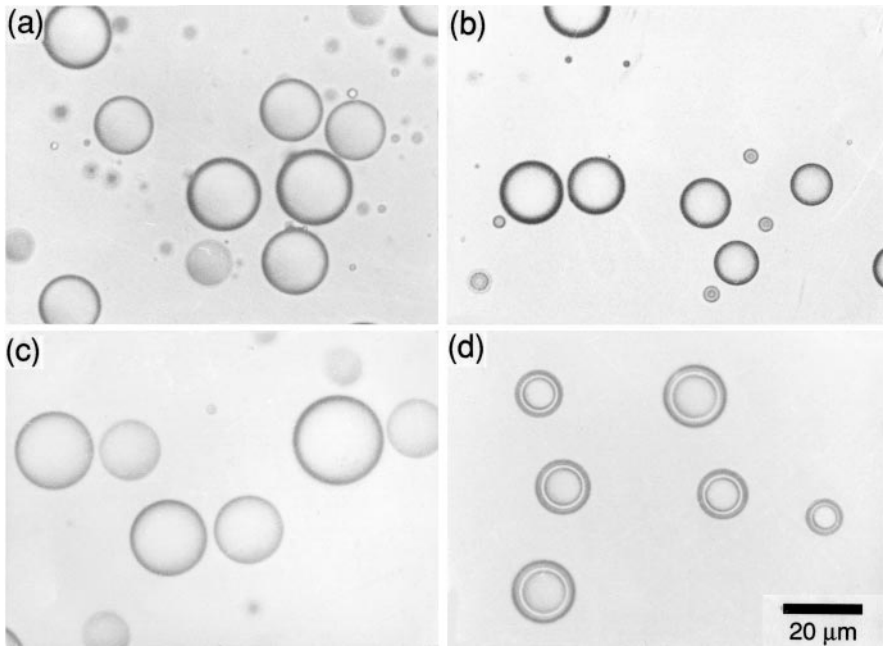

Fig. 1 Optical micrographs of DVB/toluene (a), PS/DVB/toluene droplets (b), and produced particles (c, d) after polymerizations with BPO under the conditions of Nos. 1 (a, c) and 3 (b, d), respectively, listed in Table 2: PS (wt%): (a, c) 0; (b, d) 9.1. M_w of PS: 1.6×10^5. DVB/toluene (w/w), 1/1; BPO, 2 wt% per DVB

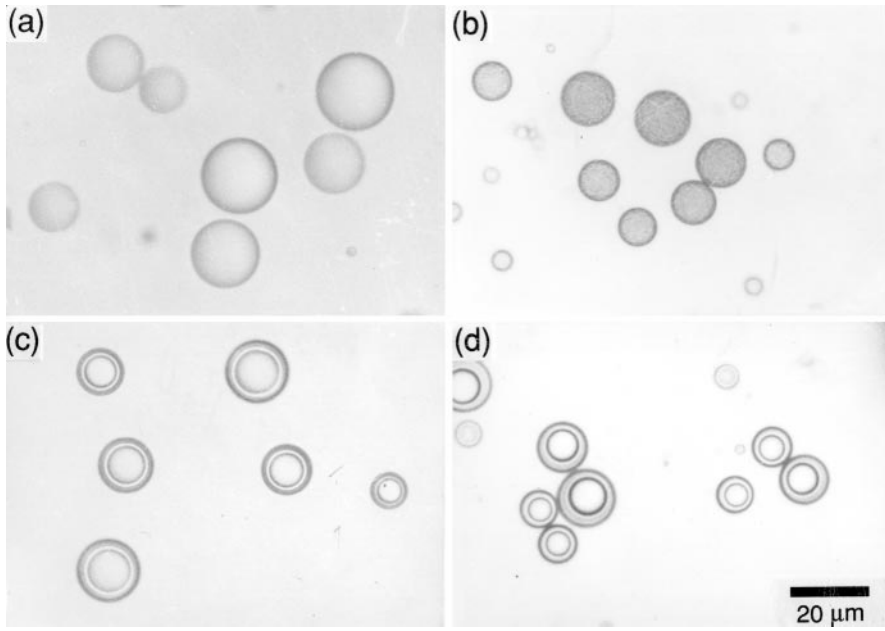

Fig. 2 Optical micrographs of PS/PDVB composite particles having different PS content in droplets produced by suspension polymerizations for PS/DVB/toluene droplets with BPO under the conditions of Nos. 1 (a), 2 (b), 3 (c) and 4 (d), respectively, listed in Table 2: PS (wt%): (a) 0; (b) 2.4; (c) 9.1; (d) 13.0. M_w of PS: 1.6×10^5. DVB/toluene (w/w), 1/1; BPO, 2 wt% per DVB

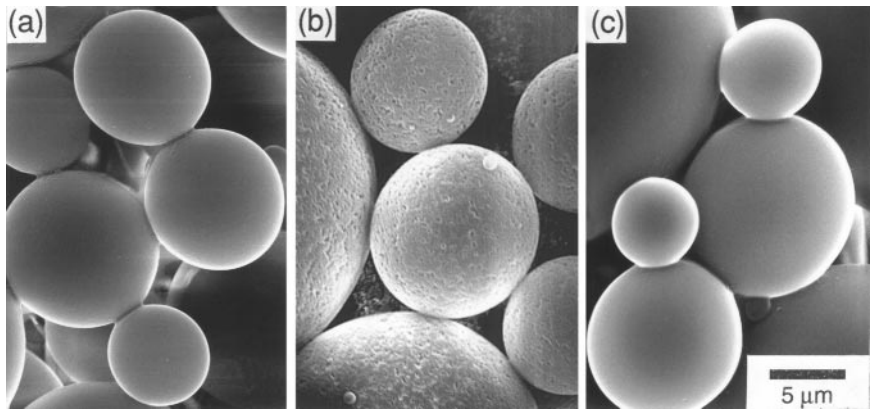

Fig. 3 SEM photographs of PS/PDVB composite particles having different PS content in droplets produced by suspension polymerizations for PS/DVB/toluene droplets with BPO under the conditions of Nos. 1 (a), 2 (b), 3 (c) respectively, listed in Table 2: PS (wt%): (a) 0; (b) 2.4; (c) 9.1. M_w of PS: 1.6×10^5. DVB/toluene (w/w), 1/1; BPO, 2 wt% per DVB

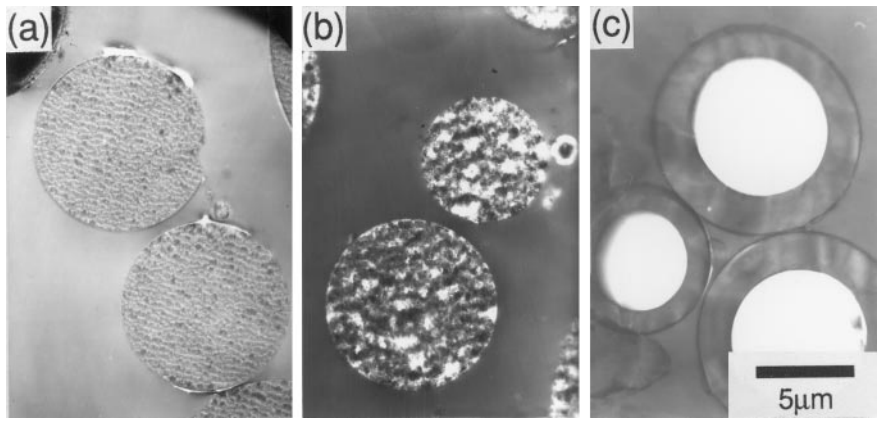

Fig. 4 TEM photographs of ultrathin cross sections of PDVB partricles and PS/PDVB composite particles exposed to RuO_4 vapor for 30 min which had been produced by suspension polymerizations for PS/DVB/toluene droplets with BPO under the conditions of Nos. 1 (a), 2 (b) and 3 (c), respectively, listed in Table 2: PS (wt%): (a) 0; (b) 2.4; (c) 9.1. M_w of PS: 1.6×10^5. DVB/toluene (w/w), 1/1; BPO, 2 wt% per DVB

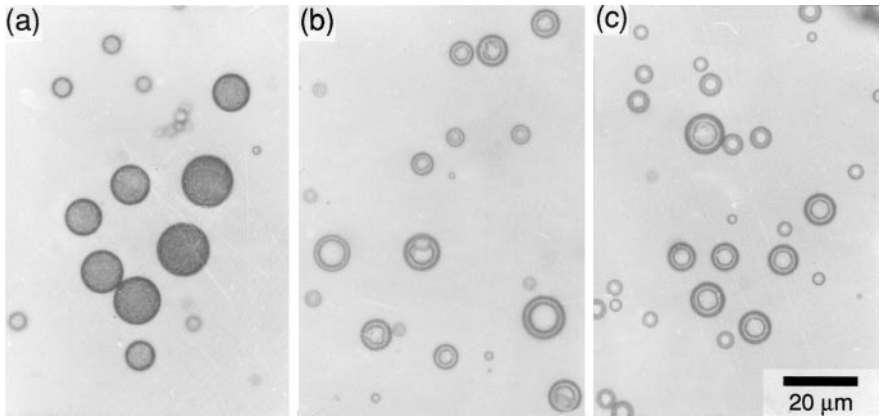

Fig. 5 Optical micrographs of PS/PDVB composite particles containing different M_w of PS produced by suspension polymerizations for PS/DVB/toluene droplets (PS: 2.4 wt%) with BPO under the conditions of Nos. 2 (a), 5 (b) and 6 (c), respectively, listed in Table 2: M_w of PS ($\times 10^5$): (a) 1.6; (b) 9.1; (c) 11.0. DVB/toluene (w/w), 1/1 BPO, 2 wt% per DVB

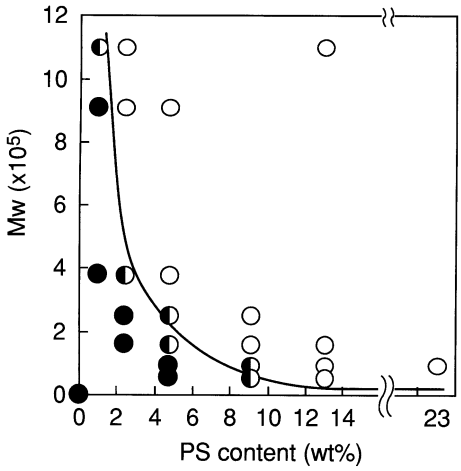

Fig. 6 Effects of PS content in DVB/toluene droplets and its M_w on the formation of hollow structure: ○, hollow; ●, non-hollow; ◐, hollow + non-hollow

other hand, the other particles produced with higher M_w values of PS ((b), 9.1×10^5; (c), 11.0×10^5) had hollow structures. These indicate that there is a minimum M_w of PS in the droplets to form the hollow structure.

Figure 6 shows effects of PS content in DVB/toluene droplets and its M_w on the formation of hollow structure. The curve shows a rough bound of the two parameters indicating whether the hollow structure is formed or not. This indicates that the higher content and M_w of PS in droplets are, the easier the hollow structure is formed.

From these results, it is concluded that PS dissolving in the DVB/toluene droplets is one of key factors for the formation of the hollow structure by seeded polymerization utilizing the DSM reported in the previous articles [13–15] and suspension polymerization technique can be also applied to get hollow polymer particles though they are polydisperse. The reason why PS is needed to form the hollow structure will be discussed in a following article.

References

1. Corner T (1981) Colloids Surf 3:119
2. Almog Y, Reich S, Levy M (1982) Br Polym J 14:131
3. Ober CK, Lok KP, Hair ML (1985) J Polym Sci, Polym Lett Ed 23:103
4. Tseng CM, Lu YY, El-Aasser, Vanderhoff JW (1986) J Polym Sci, Poly Chem Ed 24:2995
5. Okubo M, Ikegami K, Yamamoto Y (1989) Colloid Polym Sci 267:193
6. Okubo M, Katayama Y, Yamamoto Y (1991) Colloid Polym Sci 269:217
7. Okubo M, Iwasaki Y, Yamamoto Y (1992) Colloid Polym Sci 270:733
8. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) Colloid Polym Sci 269:222
9. Okubo M, Shiozaki M (1993) Polymer International 30:469
10. Okubo M, Yamashita T, Suzuki T, Shimizu T (1997) Colloid Polym Sci 275:288
11. Okubo M, Yamashita T Colloid Polym Sci, in press
12. Okubo M, Nakagawa T (1992) Colloid Polym Sci 270:853
13. Okubo M, Minami H, Yamashita T (1996) Die Makromol Chem Macromol Symp 101:509
14. Okubo M, Minami H (1996) Colloid Polym Sci 274(5):433
15. Okubo M, Minami H (1997) Colloid Polym Sci 275:992