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SHORT COMMUNICATION

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Release of toluene from micron-sized, monodispersed, cross-linked, hollow polymer particles

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Abstract The release behavior of toluene from the hollow-inside, micron-sized, monodispersed, cross-linked, polystyrene/polydivinylbenzene composite particles which had various cross-linking densities and shell thicknesses was examined. The hollow particles were produced by seeded polymerization utilizing the dynamic swelling method which we proposed in 1991. In comparison with that from hollow-free particles, there was a clear difference. The cross-linking density and shell thickness of the hollow composite particles did not affect the release rate in the former period, but did it in the latter one.

Key words Hollow · Micron-size · Monodisperse · Seeded polymerization · Dynamic swelling method · Cross-linking · Controlled release

Introduction

Polymer emulsions prepared by emulsion polymerization have been used as films in many industrial fields such as paints, prints, and manufacturing. Moreover, in recent years attention has been focused to apply them directly as particles. Among such emuslions, polymer particles having hollow(s) in the inside have gained much attention as a hiding or opacifying agents in coating and molding compositions [1–4].

On the other hand, recently, many researchers on polymer colloids are concentrating their attention on the production of micron-sized, monodispersed polymer particles [5–9] because they have found used in the biomedical field, microelectronics, and other areas.

In order to produce such particles having more than 5 μm in diameter, we suggested seeded polymerization with a new type of swelling method for seed polymer particles using a large amount of monomer, which was named "the dynamic swelling method (DSM)" [10, 11]. In a previous article [12], this technique was developed to produce micron-sized, monodispersed, cross-linked, polystyrene (PS)/polydivinylbenzene (PDVB) composite polymer particles having one hollow at the center. The size of the hollow was controllable [13] and a mechansim for the formation of the hollow particles was proposed [14]. In addition, we already reported the possibility for their use as reserve and release materials [15].

In this article, the release behavior of toluene from the hollow particles which have various cross-linking densities and shell thicknesses was studied in detail.

Materials and methods

Materials

Vinyltoluene (VT) and divinylbenzene (DVB), which was supplied by Nippon Steel Chemical Co. Ltd. (DVB-960, purity was 96%), were washed with 1 N NaOH and deionized water to remove polymerization inhibitors before use. Regent grade benzoyl peroxide (BPO) was purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Polyvinyl alcohol (PVA) was supplied by Nippon Synthetic Chemical Ind. Co., Ltd. (Gohsenol

GH-17: degree of polymerization, 1700; degree of saponification; 88%). Poly(acrylic acid) (PAA) used as a colloidal stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane. Analytical grade xylene and reagent grade ethanol were used as supplied.

Preparation of PS seed particles

Micron-sized, monodispersed PS seed particles were produced by dispersion polymerization of styrene in an ethanol/water (7/3, w/w) medium in the presence of PAA as colloidal stabilizer with AIBN as initiator at 70 °C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask according to the optimum conditions [7]. The PS seed particles were spherical and monodispersed: the number-average diameter (D_n) and coefficient of variation (C_v) were 1.62 μm and 2.8%, respectively.

Production of single hollow composite particles

Swelling of the PS seed particles produced by dispersion polymerization with DVB and/or VT and xylene was carried out utilizing DSM under the conditions listed in Table 1 according to the previous article [12, 13]. Seeded polymerization for these swollen PS particles was carried out in sealed glass tubes under a nitrogen atmosphere at 70 °C for 24 h. The particles were observed with a JEOL JEM-2010 transmission electron microscope (TEM).

Release of the toluene from the hollow particles

The release rate of toluene from the hollow particles was evaluated by measurement of the weight loss of toluene over time. The same number (about 1×10^8) of dried hollow particles, which was calculated from the volume of a particle, was placed on an ϕ 5 mm aluminum pan and an appropriate amount of toluene was added to immerse them. The weight loss of toluene due to the evaporation was measured by thermogravimetry (Seiko Instrument TG/DTA 220 U) at 20 °C under a nitrogen atmosphere.

Table 1 Recipes for the production of PS/P(DVB-VT) and PS/PDVB composite particles by seeded polymerizations[a] for the dispersions of (DVB/VT/xylene)-, (DVB/xylene)- and DVB-swollen PS particles prepared by utilizing the dynamic swelling method

Ingredients	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
PS particles[b] (mg)	30	30	30	30	30	30
DVB[c] (mg)	120	210	300	400	500	450
VT (mg)	180	90	–	–	–	–
Xylene (mg)	150	150	150	150	150	–
BPO (mg)	6	6	6	8	10	9
PVA (mg)	15	15	15	15	15	15
Ethanol (g)	7	7	7	7	7	7
Water[d] (g)	43	43	43	43	43	43
$D_n^{[e]}$ (μm)	4.18	4.25	4.27	4.46	4.60	4.24
$D_h^{[e]}$ (μm)	1.88	1.95	1.99	1.66	1.40	–

[a] N_2, 70 °C, 24 h

[b] 1.62 μm; Cv, 2.8%

[c] Purity, 96% (from catalog).

[d] 40.0 g of water were post-added at the rate of 2.88 mL/h at room temperature

[e] D_n, number-average particle diameter; D_h, number-average hollow diameter

Abbreviations: PS = polystyrene, VT = vinyltoluene, DVB = divinylbenzene, BPO = benzyl peroxide, PVA = polyvinyl alcohol

Results and discussion

Fig. 1 shows a TEM photograph of typical hollow composite particles produced by seeded polymerization for the dispersion of (DVB/xylene)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 3 listed in Table 1. The D_n, C_v, and number-average hollow diameter (D_h) were determined from the particle observation on a TEM photo-

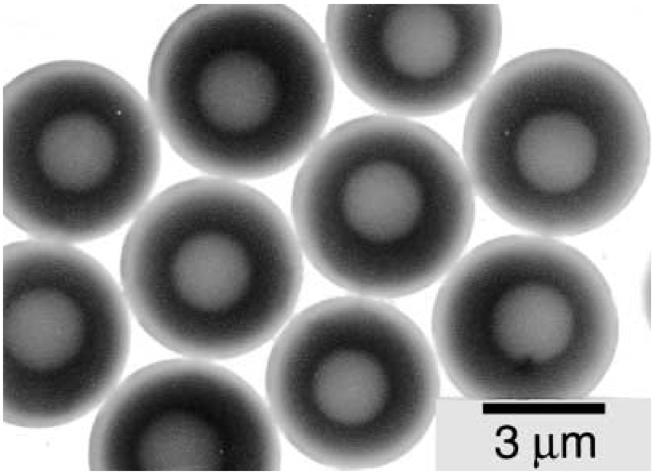

Fig. 1 A TEM photograph of PS/PDVB (1/9.6 w/w) composite particles produced by seeded polymerization for the dispersion of (DVB/xylene)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 3 listed in Table 1

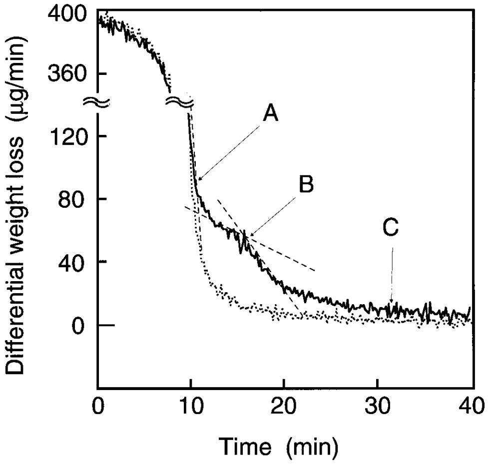

Fig. 2 Differential weight loss curves due to the evaporation of toluene at 20 °C from the dispersions in which hollow-present (No. 3, ——) and hollow-free (No. 6, - - - -) PS/PDVB composite particles were dispersed

graph with a Personal Image Analysis System (PIAS Co. Ltd., LA-525, Osaka, Japan). The particles had a low C_v, which means high monodispersity, and each particle had a single hollow structure: D_n, C_v and D_h were 4.27 μm, 3.1% and 1.99 μm, respectively. The other monodispersed, hollow particles having similar diameters, low C_v and various cross-linking densities or shell thicknesses were also prepared by seeded polymerizations under the conditions listed in Table 1. Each D_n and D_h is shown in Table 1. When each hollow particle absorbed toluene, there were only small changes in the diameter and shell thickness of these hollow particles because of the high cross-linking.

Fig. 2 shows differential weight loss (release rate) curves due to the evaporation of toluene at 20 °C from the dispersion in which hollow-present (No. 3) and hollow-free (No. 6) PS/PDVB composite particles were dispersed. Both release rates were initially constant and drastically dropped after about 10 minutes. This indicates that toluene initially existing outside the particles evaporates and the weight loss after 10 minutes is due to the evaporation of the toluene existing inside the particles [15]. It is noted that on comparison of the two curves, there was a clear difference. In the case of the hollow-free particles, the release rate dropped to zero soon after 10 minute. On the other hand, in the case of the hollow-present particles, toluene was released gradually over a certain period (A–B) and after that (period B–C) the release rate decreased markedly. The points A and B are the positions of the inflection points on the release rate curve and point C is defined as the position at which 0.3 mg of toluene remained inside the particles. The same phenomenon was observed in the release rate curves from the other hollow-present particles shown in Figs. 3 and 4.

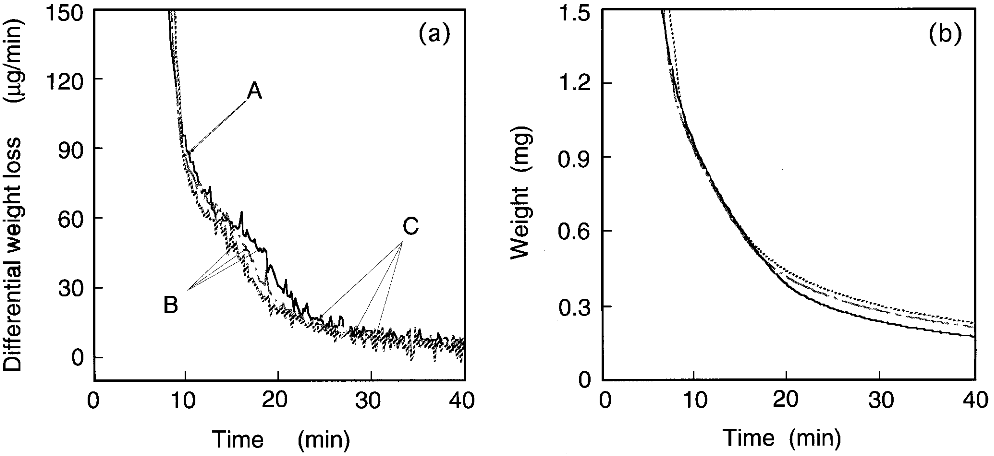

Fig. 3 Differential weight loss curves (*a*) and weight loss curves (*b*) due to the evaporation of toluene at 20 °C from the dispersions in which hollow PS/P(DVB-VT) or PS/PDVB composite particles having different compositions were dispersed. (——), No. 1; (– – –), No. 2; (- - - - -), No. 3 listed in Table 1

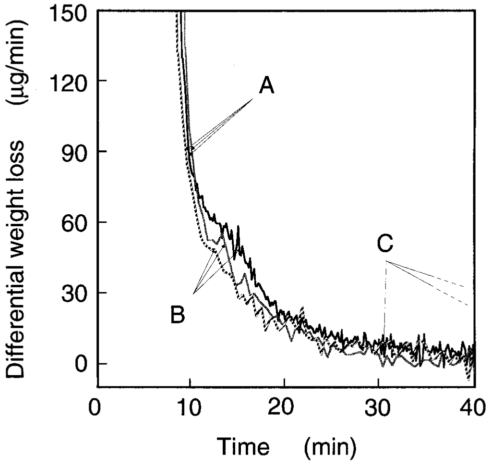

Fig. 4 Differential weight loss curves due to the evaporation of toluene at 20 °C from the dispersions in which hollow PS/PDVB composite particles having different shell thicknesses were dispersed. (——), No. 3; (– – –), No. 4; (- - - - -), No. 5 listed in Table 1

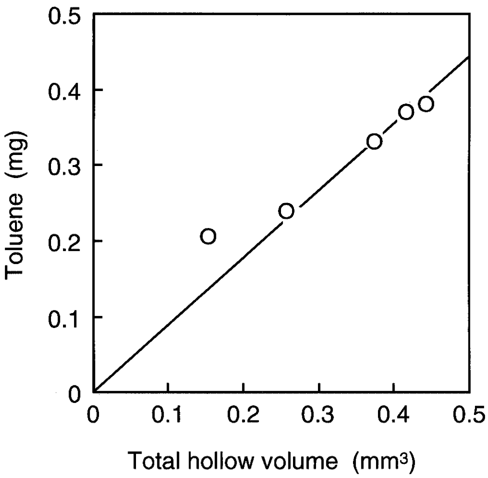

Fig. 5 Relationship between total hollow volume (○) of the PS/P(DVB-VT) and PS/PDVB composite particles and the amounts of toluene released between points A and B on the weight loss curves. Full line indicates the calculated amounts of toluene to fill the hollows

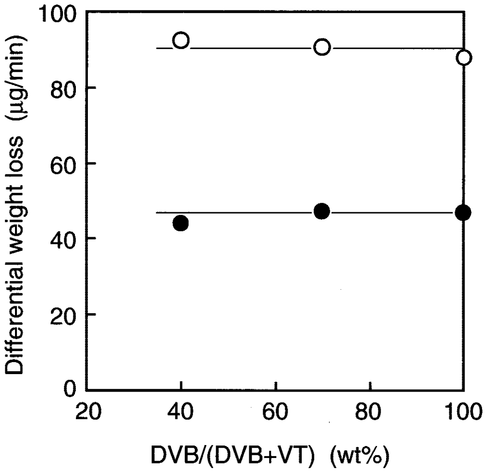

Fig. 6 Relationships between DVB content in the shell of the hollow PS/P(DVB-VT) or PS/PDVB composite particles and the release rates of toluene due to their evaporation at the points A (○) and B (●) on the curve shown in Fig. 3(a)

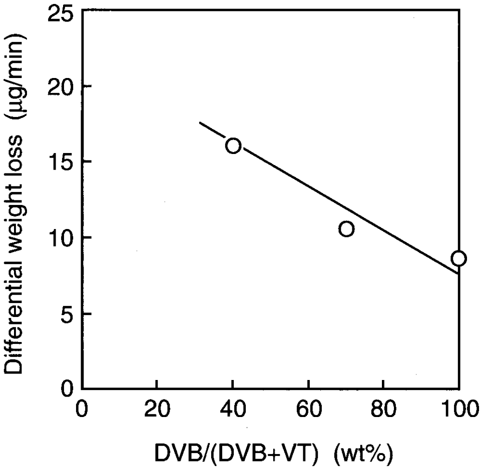

Fig. 8 Relationship between DVB content in the shell of the hollow PS/P(DVB-VT) or PS/PDVB composite particles and the release rates of toluene due to their evaporation at the point C on the curve shown in Fig. 3(a)

Fig. 3 shows release rate curves (*a*) and weight loss curves (*b*) due to the evaporation of toluene at 20 °C from the dispersions in which hollow polystyrene/polydivinylbenzene (PS/PDVB) or polystyrene/poly(divinylbenzene-vinyltoluene) [PS/P(DVB-VT)] composite particles having different cross-linking densities. In Fig. 3a, the whole release rate decreased with increases in the DVB content of the shell. The weight loss of toluene became slower in order of increasing DVB content as shown in Fig. 3b. This indicates that the toluene was retained for a longer time as the cross-linking density increased.

Fig. 4 shows release rate curves due to the evaporation of toluene at 20 °C from the dispersions in which hollow polystyrene/polydivinylbenzene (PS/PDVB) particles having different shell thicknesses were used. In Fig. 4, the release rate decreased with increases in the PDVB shell thickness, and toluene was retained for a longer time as the shell thickness increased.

Fig. 5 shows a relationship between the hollow volumes and amounts of toluene evaporated from the hollow PS/PDVB composite particles (Nos. 1–5) during the period from point A to B. They gave good agreement with the amounts of toluene calculated by assuming that all of the hollow was completely filled with toluene.

Figs. 6 and 7 show, respectively, the relationships between DVB content and shell thickness and the release rate of toluene retained in the hollow PS/P(DVB-VT) or

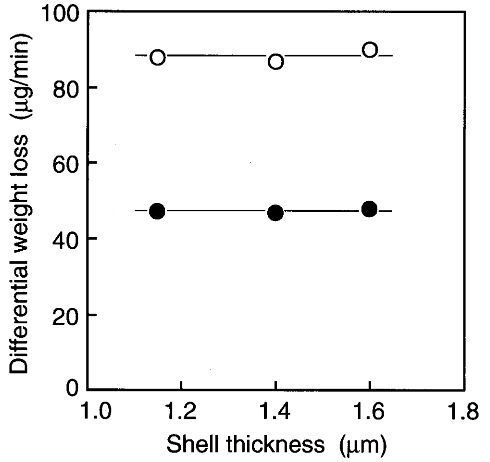

Fig. 7 Relationships between the shell thickness of the hollow PS/PDVB composite particles and the release rates of toluene due to their evaporation at the points A (○) and B (●) on the curve shown in Fig. 4

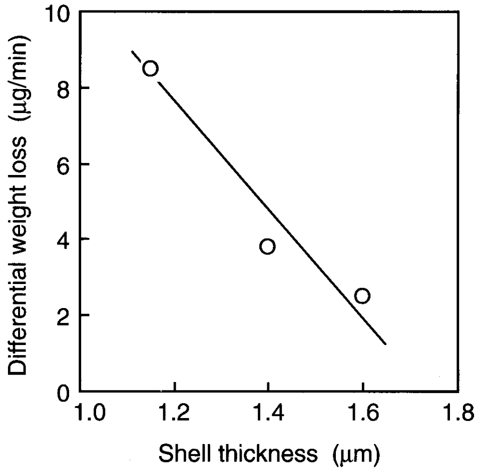

Fig. 9 Relationship between the shell thickness of the hollow PS/PDVB composite particles and the release rates of toluene due to evaporation at the point C on the curves shown in Fig. 4

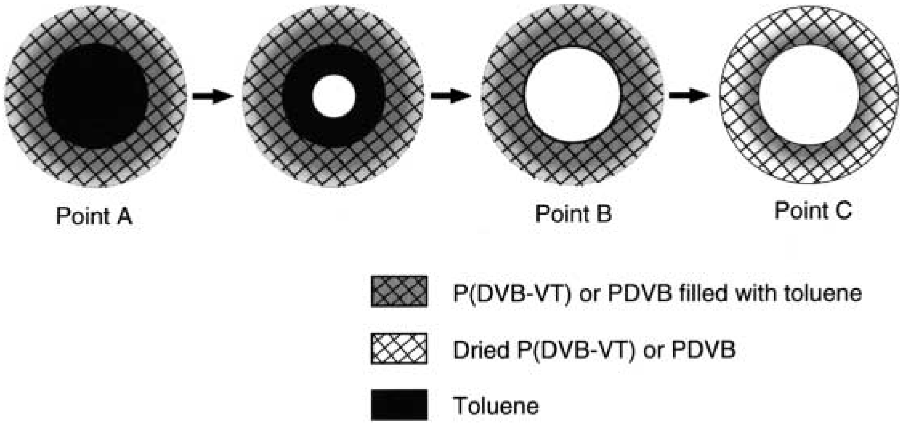

Fig. 10 Schematic diagram for release of toluene retained in the hollow PS/P(DVB-VT) and PS/PDVB composite particles

PS/PDVB composite particles at the points A and B measured from the curves. The release rate at each point was the same and not affected by the cross-linking density and shell thickness of the hollow particles.

Figs. 8 and 9 show, respectively, the relationships between the DVB contents and the shell thickness and the release rate of toluene retained in the hollow PS/P(DVB-VT) or PS/PDVB composite particles at the point C. The release rate at the point C was affected by the shell properties. The higher the cross-linking density or the thicker the shell thickness of the hollow particles, the more slowly was toluene released. This suggests that the release in this period (after point B) was controlled by the cross-linking density and shell thickness.

From these results, the release of toluene from the hollow PS/PDVB composite particles seems to proceed as shown schematically in Fig. 10. During the release of toluene from the particles in which toluene exists in the polymer shell and the hollow (points A to B in Figs. 2–4), toluene is delivered to the shell from the hollow as soon as it evaporates from the particle, where the hollow is working as a reservoir. In the evaporation stage from A to B, a steady state was attained between evaporation from the outer shell surface and supply of toluene from the hollow to the inner shell surface. After toluene has disappeared in the hollow (B–C), the evaporation rate seem to be affected by the diffusion of toluene in the shell which depends on the cross-linking density and the shell thickness.

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