

Production of Hollow Polymer Particles by Suspension Polymerizations for Ethylene Glycol Dimethacrylate/Toluene Droplets Dissolving Styrene–Methyl Methacrylate Copolymers

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ABSTRACT: Suspension polymerizations for ethylene glycol dimethacrylate (EGDM)/toluene droplets dissolving styrene–methyl methacrylate copolymers with different compositions were carried out. Hollow particles were obtained independent of the copolymer composition. In suspension copolymerizations for EGDM/divinyl benzene/toluene droplets dissolving poly(methyl methacrylate), hollow particles were produced at high EGDM content, but not at low EGDM content. Preferential adsorption of the polymer

formed by the suspension polymerizations at the interfaces of the droplets over the (co)polymers preliminarily dissolved therein was one of the key factors for the formation of the hollow structure. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1087–1091, 2002

Key words: suspension polymerization; hollow; particle; interfacial tension

INTRODUCTION

In recent years, micron-sized, monodisperse polymer particles have been applied in many fields. Many research groups studying polymer colloids focus their attention on the production of micron-sized, monodisperse polystyrene (PS) particles by dispersion polymerization.^{1–5} However, it has been difficult to produce monodisperse particles greater than 5 μm in size even by dispersion polymerization.

Therefore, to produce such particles, we have suggested a novel swelling method of seed polymer particles with a large amount of monomer, which was named the *dynamic swelling method* (DSM).^{6–8} The seeded polymerizations proceed smoothly therein because almost all of the monomers and initiators exist in the swollen particles. Moreover, we have developed this technique to produce micron-sized, monodisperse, crosslinked polymer particles having one hollow in the inside, where the seeded polymerization was carried out for about 5- μm monodisperse, highly divinylbenzene (DVB)/toluene-swollen PS particles prepared by DSM.^{9,10}

On the basis of the formation mechanism suggested,¹¹ in a previous work,¹² hollow polymer particles were also produced by the suspension polymerization for DVB/toluene droplets dissolving PS, although they were poly-

disperse. Throughout this experiment, it was found that there were minimum concentrations and molecular weights of PS dissolved in the droplets to produce the hollow particles. The kinds of homopolymer and its end groups dissolved in DVB/toluene droplets also affected the formation of a hollow structure.^{13,14} Moreover, the influence of polarity of the polymer dissolved in the droplets using styrene–methyl methacrylate copolymer [P(St–MMA)] with different compositions was clarified.¹⁵ These results suggest that the preferential adsorptions of the homopolymer and the copolymer having high polarities at the interface of the droplets over poly(divinylbenzene) (PDVB) molecules disturb the formation of the hollow structure. In other words, the preferential adsorption of PDVB molecules formed by the suspension polymerization seems to be one of the key factors for the formation of the hollow structure.

In this report, to clarify the point more in detail, suspension polymerizations for ethylene glycol dimethacrylate (EGDM)/toluene droplets dissolving P(St–MMA) having different compositions were carried out. Because EGDM is more hydrophilic than DVB, the formation of the hollow structure must be promoted according to the above concept.

EXPERIMENTAL

Materials

Styrene (St) and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a

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TABLE I
Preparations of P(St-MMA) Having Different Compositions by Solution Polymerizations^a

St content	(mol %)	0	10	30	50	70	90	100
St	(g)	0	0.9	3.9	8.7	13.7	16.9	18
MMA	(g)	13	17.1	14.1	9.3	4.3	1.1	0
AIBN	(mg)	40	108	54	54	54	54	54
Toluene	(g)	19	12	12	12	12	12	12
Polymerization time	(h)	24	1.5	3.0	3.0	3.0	3.5	24
Polymerization temperature	(°C)	70	60	60	60	60	60	60
Conversion ^b	(%)	—	11.8	11.8	9.0	7.7	7.6	—
M_w^c	($\times 10^5$)	1.4	1.5	1.5	1.5	1.2	1.8	1.6
M_w/M_n^d		2.1	1.7	1.8	1.7	1.8	1.7	2.1
St content ^e	(mol %)	0	10	28	49	72	92	100

^a Abbreviations: St, styrene; MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile).

^b Determined by gravimetry.

^c Weight-average molecular weight, measured by GPC.

^d Number-average molecular weight, measured by GPC.

^e Measured by ¹H-NMR.

nitrogen atmosphere. DVB (purity, 96%; Nippon Steel Chemical, Tokyo, Japan) and EGDM were washed with 1N NaOH and distilled water to remove polymerization inhibitors before use. Poly(vinyl alcohol) (PVA; Gohsenol GH-17; degree of polymerization, 1700; degree of saponification, 88%) was supplied by Nippon Synthetic Chemical (Osaka, Japan). Reagent grade 2,2'-azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO) were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Reagent-grade toluene was used as received.

P(St-MMA) copolymers having different compositions were prepared by solution copolymerizations and characterized according to a previous work.¹⁵ The conditions and results are listed in Table I. Soluble PDVB and PEGDM were prepared by solution polymerizations under the conditions listed in Table II. The polymerizations were stopped by addition of hydroquinone at low conversion and both polymers were purified by reprecipitation into methanol or water/methanol mixed solvent and dried under reduced pressure.

TABLE II
Preparations of Soluble PDVB and PEGDM by Solution Polymerizations Under N₂ Atmosphere^a

Ingredient	PDVB	PEGDM
DVB ^b (g)	3.0	—
EGDM (g)	—	3.0
AIBN (mg)	120	300
Toluene (g)	27	—
DMF (g)	—	27
Polymerization time (min)	30	20
Polymerization temperature (°C)	60	50

^a Abbreviations: DVB, divinylbenzene; EGDM, ethylene glycol dimethacrylate; DMF, *N,N*-dimethylformamide.

^b Purity, 96% (by catalog).

Suspension polymerizations

Homogeneous solutions of EGDM (250 mg), toluene (250 mg), BPO (5 mg), and copolymers (5–50 mg) were mixed with 0.33 wt % PVA aqueous solution (15 g), and stirred vigorously by a Nissei ABM-2 homogenizer (Japan) at 1000 rpm for 2 min in glass cylindrical reactors. Suspension polymerizations for the dispersions were carried out at 70°C for 24 h under a nitrogen atmosphere in sealed glass tubes under the conditions listed in Table III. The tubes were horizontally shaken at 80 cycles/min (3-cm strokes). Particles were observed with a Nikon Microphot-FXA optical microscope (Nikon, Tokyo, Japan) and a Hitachi S-2500 scanning electron microscope (Hitachi, Tokyo, Japan).

Observation of ultrathin cross sections of particles

Composite particles were exposed to RuO₄ vapor at room temperature for 30 min in the presence of 1% RuO₄ solution, and then dispersed in epoxy matrix,

TABLE III
Suspension Polymerizations for EGDM/Toluene droplets Dissolving P(St-MMA) Having Different Compositions at 70°C for 24 h Under N₂ Atmosphere^a

Ingredient	No. 1	No. 2	No. 3	No. 4
P(St-MMA) ^b (mg)	5	12.5	25	50
EGDM (mg)	250	250	250	250
Toluene (mg)	250	250	250	250
BPO (mg)	5.0	5.0	5.0	5.0
PVA (mg)	50	50	50	50
Water (g)	15.0	15.0	15.0	15.0

^a Abbreviations: BPO, benzoyl peroxide; P(St-MMA), styrene-methyl methacrylate copolymer; PVA, poly(vinyl alcohol).

^b Prepared by solution copolymerizations under the conditions listed in Table I.

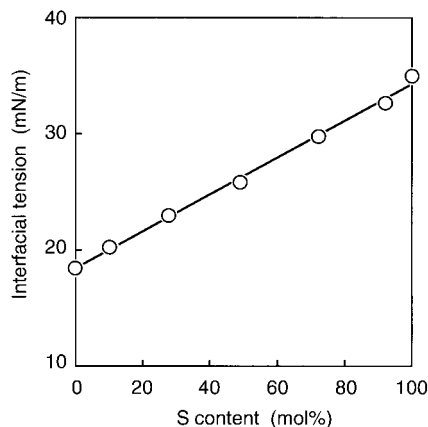


Figure 1 Interfacial tensions between water and xylene/toluene (1/1, w/w) solutions with 0.01 wt % of styrene-methyl methacrylate copolymer [P(St-MMA)] having different compositions at $23 \pm 2^\circ\text{C}$.

cured at room temperature for 24 h, and microtomed. The ultrathin cross sections were observed with a Hitachi H-7100 TEM transmission electron microscope.

Measurement of interfacial tension

The interfacial tensions between water and xylene/toluene (1/1, w/w) solutions with 0.01 wt % of polymers were measured by the du Noüy ring method at room temperature with a Shimadzu DN surface tensiometer (Shimadzu, Kyoto, Japan). Each polymer solution (40 g) was gently poured into water (50 g), and after 3 h the measurement was carried out with a platinum ring (diameter, 19 mm).

RESULTS AND DISCUSSION

Figure 1 shows the interfacial tensions between water and xylene/toluene (1/1, w/w) solutions with 0.01 wt % of the copolymers that were prepared under the conditions listed in Table I. The interfacial tension decreased linearly with a decrease of St content in the copolymer.

Figure 2 shows optical micrographs of P(St-MMA)/PEGDM composite particles produced by suspension polymerizations for EGDM/toluene (1/1, w/w) droplets under the conditions of nos. 1 [Fig. 2(a)–(c)] and 4 [Fig. 2(d)–(f)] listed in Table III. St contents in P(St-MMA) dissolved in the droplets were 10 mol % [Fig. 2(a), (d)], 28 mol % [Fig. 2(b), (e)], and 49 mol % [Fig. 2(c), (f)]. At a low concentration of P(St-MMA), the composite particles had no hollow structure [Fig. 2(a)–(c)]. On the other hand, at a high concentration of P(St-MMA), they had a hollow structure in the inside [Fig. 2(d)–(f)]. The tendency that the hollow particles were obtained at the high concentration of polymer in the droplets was similar to that obtained with DVB in the previous studies.^{12–15} However, the formation of the hollow structure in P(St-MMA)/PDVB composite particles depended on the composition of the P(St-MMA). For example, at St content of 28 mol %, the composite particles had an incomplete hollow structure with a rough inner surface of the PDVB shell, and at 10 mol % they had a nonhollow structure. On the other hand, P(St-MMA)/PEGDM composite particles always had the hollow structure independent of composition.

Figure 3 shows SEM micrographs of the P(St-MMA)/PEGDM composite particles (St content, 10 mol %) shown in Figure 2(a), (d) and TEM micrographs of their ultrathin cross sections. A porous

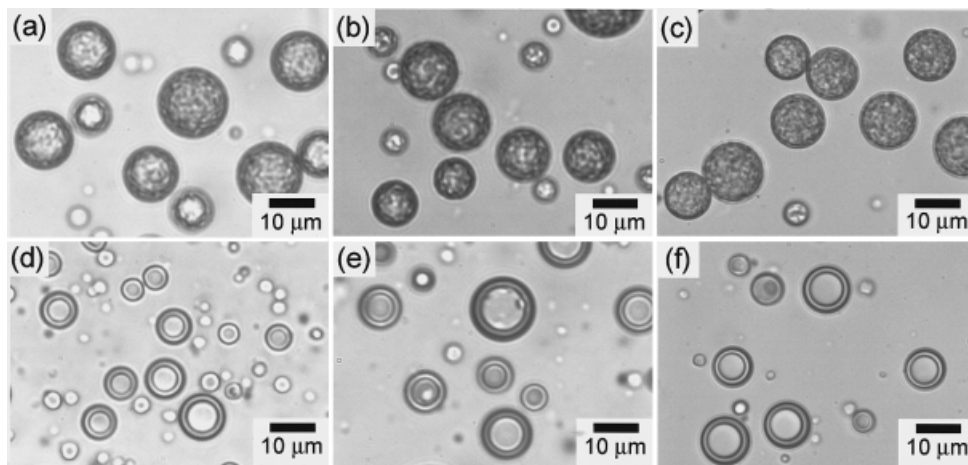


Figure 2 Optical micrographs of P(St-MMA)/poly(ethylene glycol dimethacrylate) (PEGDM) composite particles produced by suspension polymerizations for EGDM/toluene (1/1, w/w) droplets dissolving P(St-MMA) under the conditions of nos. 1 and 4 listed in Table III. St contents (mol %) in P(St-MMA): (a, d) 10; (b, e) 28; (c, f) 49. BPO, 2 wt % based on EGDM. P(St-MMA)/PEGDM (w/w): (a, b, c) 1/50, (d, e, f) 4/20.

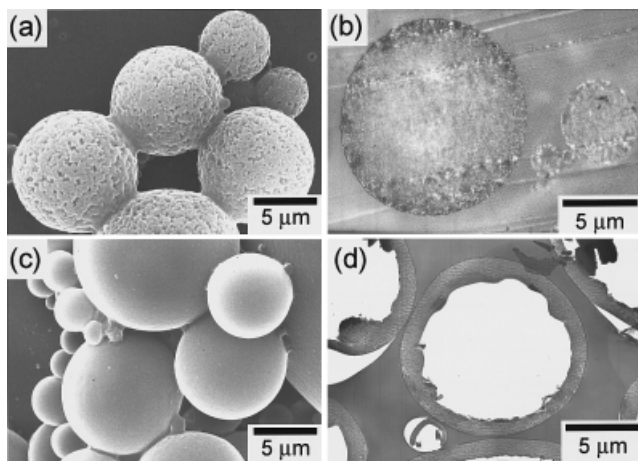


Figure 3 SEM micrographs (a, c) of P(St-MMA)/PEGDM composite particles produced by suspension polymerizations for EGDM/toluene (1/1, w/w) droplets dissolving P(St-MMA) (St content, 10 mol %) under the conditions of nos. 1 and 4 listed in Table III, and TEM micrographs (b, d) of ultrathin cross sections of composite particles exposed to RuO_4 vapor for 30 min. BPO, 2 wt % based on EGDM. P(St-MMA)/PEGDM (w/w): (a, b) 1/50 (no. 2); (c, d) 4/20 (no. 4).

structure was observed at the low P(St-MMA) concentration [Fig. 3(a), (b)]. At the high P(St-MMA) concentration, the composite particles had smooth surfaces and a hollow structure in the inside [Fig. 3(c), (d)]. The porous and hollow structures were similar to those of P(St-MMA)/PDVB composite particles obtained in the previous study.¹⁵

Figure 4 shows optical micrographs of PMMA/P(DVB-EGDM) (4/20, w/w) composite particles produced by suspension polymerizations for DVB/EGDM/toluene droplets dissolving PMMA under the conditions of no. 4 listed in Table IV and TEM micro-

TABLE IV
Suspension Polymerizations for DVB/EGDM/Toluene Droplets Dissolving PMMA at 70°C for 24 h Under N_2 Atmosphere^a

Ingredient	No. 1	No. 2	No. 3	No. 4
PMMA ^b (mg)	5	12.5	25	50
DVB ^c + EGDM (mg)	250	250	250	250
Toluene (mg)	250	250	250	250
BPO (mg)	5.0	5.0	5.0	5.0
PVA (mg)	50	50	50	50
Water (g)	15.0	15.0	15.0	15.0

^a Abbreviation: PMMA, poly(methyl methacrylate).

^b Prepared by solution polymerization listed in Table I.

^c Purity, 96% (by catalog).

graphs of their ultrathin cross sections. DVB contents in the monomers of DVB and EGDM were 50 mol % [Fig. 4(a), (d)], 30 mol % [Fig. 4(b), (e)], and 10 mol % [Fig. 4(c), (f)]. At the DVB content of 50 mol % [Fig. 4(a), (d)], the composite particles did not have a hollow structure but, rather, a heterogeneous multihollow structure, which was similar to that of P(St-MMA)/PDVB composite particles at high St content in the copolymer. At 30 mol % [Fig. 4(b), (e)], incomplete hollow particles were obtained, although the inner surface was rough. At 10 mol % [Fig. 4(c), (f)], the composite particles also had the incomplete hollow structure, but the inner surface became smoother. These indicate that the monomer composition affects the formation of the hollow structure.

Table V shows the relationship between the monomer composition and the structure of the PMMA/P(DVB-EGDM) composite particles produced by suspension polymerizations for DVB/EGDM/toluene droplets dissolving different amounts of PMMA. At PMMA concentrations of 1.0 and 2.4 wt % in the

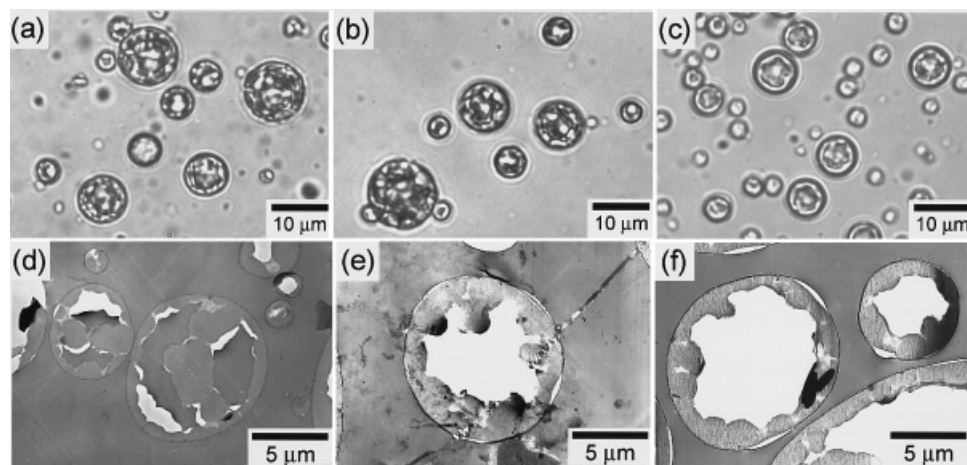


Figure 4 Optical micrographs (a, b, c) of PMMA/P(DVB-EGDM) composite particles produced by suspension polymerizations for DVB/EGDM/toluene droplets dissolving PMMA under the conditions of no. 4 listed in Table IV, and TEM micrographs (d, e, f) of ultrathin cross sections of the composite particles exposed to RuO_4 vapor for 30 min. DVB contents (mol %): (a, d) 50; (b, e) 30; (c, f) 10. BPO, 2 wt % based on (DVB + EGDM).

TABLE V
Relationship Between DVB/EGDM Ratio and the Structures of Composite Particles Produced by Suspension Polymerizations for DVB/EGDM/Toluene Droplets Dissolving Different Amounts of PMMA^a

DVB/EGDM (mol/mol)	PMMA content in droplets (wt %)			
	1.0	2.4	4.8	9.1
100/0	●	●	●	●
90/10	●	●	●	●
70/30	●	●	●	●
50/50	●	●	●	●
30/70	●	●	●	⊙
10/90	●	●	●	⊙
0/100	●	●	○	○

^a M_{zw} , 1.4×10^5 ; M_{zw}/M_n , 2.1; ○, hollow; ●, nonhollow; ⊙, incomplete hollow.

droplets, nonhollow particles were produced at any monomer compositions. At 9.1 wt %, the hollow particles were obtained at the DVB content of 10 mol % or less. The interfacial tension values of PEGDM, PMMA, and PDVB were 17.6, 18.4, and 29.5 mN/m, respectively. These values indicate that the strength of polymer adsorption at the interface of droplets is in the order PEGDM > PMMA > PDVB. Accordingly, in the production of PMMA/PDVB composite particles, the PMMA molecules adsorb more strongly than PDVB molecules at the interface of the droplets. In other words, because PDVB molecules do not adsorb at the interface, the PDVB shell is not formed. In the case of the copolymerization with EGDM monomer, the interfacial tension values of P(DVB-EGDM) would be varied in the range of 17.6 and 29.5 mN/m. At a certain monomer composition (DVB, about 10 mol %), given that P(DVB-EGDM) can adsorb more strongly than PMMA at the interface, exchange adsorption between PMMA and P(DVB-EGDM) should occur during the polymerization, and results in the P(DVB-EGDM) shell. These results suggest that the formation

of the hollow structure is based on the preferential adsorption of P(DVB-EGDM) molecules at the interface of the droplets over the PMMA previously dissolved there.

From these results, it is clearly confirmed that the preferential adsorption of polymer formed by the suspension polymerization for divinyl monomer/toluene droplets at the interface of the droplets over polymer previously dissolved is one of the key factors for the formation of the hollow structure. The reason that the polymer needs to be previously dissolved in the droplets for the formation of the hollow structure will be discussed in a future study.

This work is Part CCXX of the series "Studies on Suspension and Emulsion."

References

1. Corner, T. *Colloids Surf* 1981, 3, 119.
2. Almog, Y.; Reich, S.; Levy, M. *Br Polym J* 1982, 14, 131.
3. Ober, C. K.; Lok, K. P.; Hair, M. L. *J Polym Sci Polym Lett Ed* 1985, 23, 103.
4. Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Polym Chem Ed* 1986, 24, 2995.
5. Okubo, M.; Ikegami, K.; Yamamoto, Y. *Colloid Polym Sci* 1989, 267, 267.
6. Okubo, M.; Shiozaki, M.; Tsujihiro, M.; Tsukuda, Y. *Colloid Polym Sci* 1991, 269, 222.
7. Okubo, M.; Shiozaki, M. *Polym Int* 1993, 30, 469.
8. Okubo, M.; Yamashita, T.; Suzuki, T.; Shimizu, T. *Colloid Polym Sci* 1997, 275, 288.
9. Okubo, M.; Minami, H.; Yamashita, T. *Makromol Symp* 1996, 101, 509.
10. Okubo, M.; Minami, H. *Colloid Polym Sci* 1996, 274, 433.
11. Okubo, M.; Minami, H. *Colloid Polym Sci* 1997, 275, 992.
12. Okubo, M.; Konishi, Y.; Minami, H. *Colloid Polym Sci* 1998, 276, 638.
13. Okubo, M.; Konishi, Y.; Minami, H. *Colloid Polym Sci* 2000, 278, 659.
14. Okubo, M.; Konishi, Y.; Minami, H. *Colloid Polym Sci* 2001, 279, 519.
15. Okubo, M.; Konishi, Y.; Inohara, T.; Minami, H. *Macromol Symp* 2001, 175, 321.