Studies on Production of Micron-sized, Monodisperse, Hollow Polymer Particles and Its Application

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(Degree)
博士（工学）

(Date of Degree)
2002-04-26

(Date of Publication)
2007-08-09

(Resource Type)
doctoral thesis

(Report Number)
乙2624

(URL)
https://hdl.handle.net/20.500.14094/D2002624

神戸大学博士論文

Studies on Production of Micron-sized, Monodisperse, Hollow Polymer Particles and Its Application

ミクロンサイズの単分散な中空高分子微粒子の合成とその応用に関する研究

２００２年３月

南　秀人

Acknowledgment

This study presented in this thesis has been carried out under the guidance of Professor Dr. Masayoshi Okubo. I wish to express my sincere gratitude to Professor Dr. Masayoshi Okubo for his valuable discussion, fruitful suggestion and encouragement throughout this study.

I am thankful to Research Associate, Ms. Toyoko Suzuki for her constant help and useful suggestion and encouragement during the study.

I am also grateful to Dr. Tsuyoshi Yamashita, Dr. Hasan Ahmad, Dr. Yingjie Lu and Associate Professor Dr. Takashi Nishino for their fruitful suggestion and encouragement.

I am would like to acknowledge the considerable assistance of Mr. Yoshihiko Yamamoto, Ms. Yumei Jing, Mr. Keisuke Morikawa and Mr. Takanobu Komura, and thank to all members of the Laboratory of Colloid Polymer Chemistry, Department of Chemical Science & Engineering, Kobe University.

Finally, I wish to express my deepest gratitude to my wife, daughters and parents for their hearty help and dedication and support.

March, 2002

Hideto Minami

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General Introduction

Polymer emulsions prepared by emulsion polymerization have been used as films in many industrial fields, in painting, printing and manufacturing. Moreover, recently attention has been focused on using them directly as particles. For example, submicron-sized polymer particles having hollow space(s) inside have attracted much attention since thermoplastic styrene/ acrylic polymer particles with one hollow space at the center were produced by alkali swelling of carboxylated polymer particles having core-shell structures [1]. The hollow is filled with water in a polymer emulsion, but with air in a dried state. Such particles are commercially supplied as a hiding or opacifying agent in coating and molding compositions. Okubo et al. also found that submicron-sized, monodisperse styrene-butyl acrylate-methacrylic acid terpolymer emulsion particles were changed to those containing many hollows inside by stepwise treatment with alkali and acid [2-4].

Recently, micron-size monodisperse polymer particles also attract much attention to many researchers studying polymer colloids. Such polymer particles can be used as carriers for chromatography and immobilizers of biomolecules because they are easy to separate from media and simple to maintain. In addition, because of their monodispersity, these particles can be used as the spacer for the gap between two phases of a liquid crystal display and as a toner for xerography. However, micron-size monodisperse polymer particles had been difficult to produce because their size is between the diameter range of particles produced by emulsion polymerization (0.1~0.7 μm) and those produced by suspension polymerization (100~1000 μm).

Corner et al. [5] and Almog et al. [6] suggested that dispersion polymerization technique was useful for the production of monodisperse particle below 5 μm in diameter. Later, Ober et al. [7], Tseng et al. [8] and Okubo et al. [9] recognized the usefulness of this technique. Moreover, Okubo et al. have been producing micron-sized, monodisperse polystyrene (PS) particles having functional groups such as chloromethyl [9], vinyl [10, 11] and epoxy groups [12] by seeded dispersion copolymerization with corresponding functional monomers in the presence of about 2 μm-sized monodisperse PS particles as seed. Micron-sized monodisperse polymer particles having multihollow structures were also produced by extraction of PS with toluene under reflux from micron-sized monodisperse PS/ poly(styrene-divinylbenzene) composite particles produced by seeded dispersion copolymerization [13].

On the other hand, in order to produce monodisperse particles having the diameter above 5 μm, Vanderhoff et al. [14-17] succeeded in producing monodisperse particles up to ~ 30 μm in diameter under the gravity-free environment of space using successive seeded polymerization method. Ugelstad et al. [18-22] showed that seeded polymerization technique utilizing a two step swelling process with a swelling agent, which is characterized by a very low solubility in water and a low molecular weight, is useful for the production of micron-sized monodisperse polymer particles. Okubo et al. suggested a new type of swelling method of seed polymer particles with a large amount of monomer which was named “the dynamic swelling method

(DSM)" [23, 24]. In fact, about 13 μm-sized, monodisperse PS particles were produced by seeded polymerization utilizing DSM [25].

The aim of this doctoral dissertation is to develope the DSM technique to produce directly micron-sized, monodisperse, cross-linked polymer particles having hollow structure, and to functionalize the hollow polymer particles. The dissertation consists of following two parts which has been subdivided into ten Chapters in order to fulfil the above aim.

PART I is concerned with production of micron-sized, monodisperse, hollow polymer particles by seeded polymerization utilizing DSM and the formation mechanism of the hollow structure.

This PART contains six Chapters. In **Chapter 1**, the production of micron-sized, monodisperse, cross-linked hollow polymer particles by DSM is discussed. In **Chapter 2**, control of the size of the hollow is examined. In **Chapter 3**, the formation mechanism of hollow structure is discussed. In **Chapter 4**, in Chapter 3, nonsphrical polymer particles are observed at low conversions of the seeded polymerization. The conditions are clarified, under which such nonsphrical polymer particles are produced effectively at the completion of the seeded polymerization. In **Chapter 5**, the conditions to produce the nonsphrical polymer particles are examined more in detail. In addition, the transformable shape by absorbing and releasing of solvent is examined. In **Chapter 6**, the condition of transformation to the nonspherical particles is discussed in detail. In view of shell strength, I will try to apply to the system a theoretical pressure-buckling relation.

PART II is concerned with application of the micron-sized, monodisperse, hollow polymer particles.

This PART contains four Chapters. In **Chapter 7**, the penetration and release behaviors of various solvents into/from the hollow particles are examined to study the usefulness of hollow particles as carriers. In **Chapter 8**, the release behaviors of toluene from the hollow particles which have various cross-linking densities and shell thickness are studied in detail. In **Chapter 9**, micron-sized, monodisperse magnetic composite particles having vinyl grope at their surfaces are prepared by utilizing the micron-sized, monodisperse, hollow particles. In **Chapter 10**, the polymerization techniques in PART I is developed to produce composite particles encapsulating hinokitiol.

It was to be mentioned that the productions of micron-sized, monodisperse, functional, hollow polymer particles by seeded polymerization utilizing DSM were studied from the view point of polymer colloid chemistry. The author reports the work titled as "Studies on Production of Micron-sized, Monodisperse, Hollow Polymer Particles and Its Application".

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Part I

Production of micron-sized, monodisperse, hollow polymer particle

Chapter 1

Production of micron-sized, monodisperse, cross-linked polymer particles having hollow structure

1.1 Introduction

Submicron-sized polymer emulsions prepared by emulsion polymerization have been used as films in many industrial fields, for example, in painting, printing and manufacturing. Moreover, recently, attention is focused to apply it directly as particles. As one of them, polymer particles having hollow(s) in the inside have gotten much attention since thermoplastic styrene/acrylic polymer particles containing one hollow at the center were produced by alkali swelling of carboxylated polymer particles having core-shell structures [1]. The hollow is filled with water in polymer emulsion, but with air in a dried state. Such particles are commercially supplied as an hiding or opacifying agent in coating and molding compositions.

Okubo *et al* found that submicron-sized monodisperse styrene-butyl acrylate-methacrylic acid terpolymer emulsion particles were changed to those containing manyhollows in the inside by stepwise treatment with alkali and acid [2-4].

Recently, many researchers on polymer colloids are concentrating their attentions on the production of micron-sized monodisperse polymer particles [5-9]. Such particles had been difficult to produce because their size is between the diameter range of particles produced by emulsion polymerization and those produced by suspension polymerization.

Okubo *et al* have been producing micron-sized monodisperse polymer particles having functional groups by seeded dispersion copolymerization of functional monomer with about 2 μm-sized monodisperse polystyrene (PS) particles as seed [10, 11]. Moreover, in order to produce such particles having the diameter above 5 μm, they suggested a new type of swelling method of seed polymer particles with a large amount of monomer which was named "the dynamic swelling method (DSM)" [12, 13]. Actually, about 7 μm-sized monodisperse polymer particles were produced by seeded polymerization of such highly monomer-swollen particles.

In addition, micron-sized monodisperse polymer particles having multihollow structures were produced by extraction of PS with toluene under reflux from micron-sized monodisperse PS/poly(styrene-divinylbenzene) composite particles produced by seeded polymerization utilizing DSM [14, 15].

As the first chapter of the doctoral dissertation, seeded polymerization technique utilizing DSM will be developed to produce directly micron-sized monodisperse polymer particles having hollow structure.

1.2 Experimental

1.2.1 Materials

Divinylbenzene (DVB) was washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. The supplied DVB included ethylvinylbenzene and diethylbenzene, and the purity was 55%. Benzoyl peroxide (BPO) and 2, 2'-azobisisobutyronitrile (AIBN) of reagent grade were 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 stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane, according to a previous article [10]. Reagent grade of ethanol and toluene were used as received.

1.2.2 Preparation of seed particles

Micron-sized monodisperse PS seed particles were produced under the optimum dispersion polymerization conditions determined in the previous article (Ref.10). The dispersion polymerization of S was carried out at 70°C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask under the conditions listed in Table 1. The reaction mixture in the flask was stirred with an anchor-type stirrer at 60 rpm. The PS seed particles were observed with a JEOL JEM-200CX transmission electron microscope (TEM).

1.2.3 Swelling of seed particles with DVB and toluene utilizing DSM

Swelling of the PS particles with DVB and toluene was carried out using DSM as follows. Ethanol (7 g), water (3 g), DVB (0.3 g), toluene (0.15 g), BPO (0.006 g), and PVA (0.015 g) were charged into a glass cylindrical reactor. To this homogeneous solution, the PS particles (0.03 g) were dispersed.

Table 1 Preparation of micron-sized monodisperse PS seed particles by dispersion polymerization[a]

Ingredients		
Ethanol	(g)	959
Water	(g)	280
Styrene	(g)	140
AIBN	(g)	2.35
PAA	(g)	16.8

[a] N_2; 70°C; 24 h; stirring rate, 60 rpm

Finally, water (40 g) was added to the mixture at a speed of 2.88 ml/h with a micro feeder under stirring with a magnetic stirrer. For comparison, the same procedure was carried out without toluene.

Table 2 Recipes for the productions of two kinds of PS/PDVB (1/5.5, w/w) composite particles by seeded polymerizations[a] for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method at room temperature

Ingredient		No.1	No.2
Ethanol	(g)	7.0	7.0
Water	(g)	3.0 + 40.0[b]	3.0 + 40.0
DVB[c]	(g)	0.3	0.3
Toluene	(g)	0	0.15
PS particles[d]	(g)	0.03	0.03
PVA	(g)	0.015	0.015
BPO	(g)	0.006	0.006

[a] N_2, 70°C, 24 h.
[b] 40.0 g of water was post-added at the rate of 2.88 ml/h.
[c] Purity, 55 % (by catalog).
[d] 1.7 μm; Cv, 2.2 %
Abbreviations: DVB, divinylbenzene; PS, polystyrene; PVA, polyvinyl alcohol; BPO, benzoyl peroxide.

1.2.4 Seeded polymerization

Seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles were carried out in sealed glass tubes under a nitrogen atmosphere at 70°C for 24 h. The tubes were horizontally shaken at 120 cycles/min (2-cm strokes). The conversions measured by gas chromatography were about 98 %.

Each particle was observed with Nikon MICROPHOT-FXA optical microscope, TEM and a Hitachi S-2500 scanning electron microscope (SEM).

1.2.5 Observations of the ultrathin cross sections of particles

Dried PS and the two kinds of PS/PDVB composite particles were exposed to OsO_4 vapor at room temperature for 24 h in the presence of 1 % OsO_4 solution, and then dipped in epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross sections were observed with TEM.

1.3 Results and Discussion

Figure 1 shows a TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1. PS seed particles were spherical and monodisperse: the number-average diameter and the coefficient of variation measured with Personal Image Analysis System (PIAS Co. Ltd, LA-525, Osaka, Japan) were, respectively, 1.71 μm and 2.2%.

Figure 2 shows optical micrographs of PS seed particles (a), and swollen particles with DVB (b) and with toluene and DVB (c) prepared

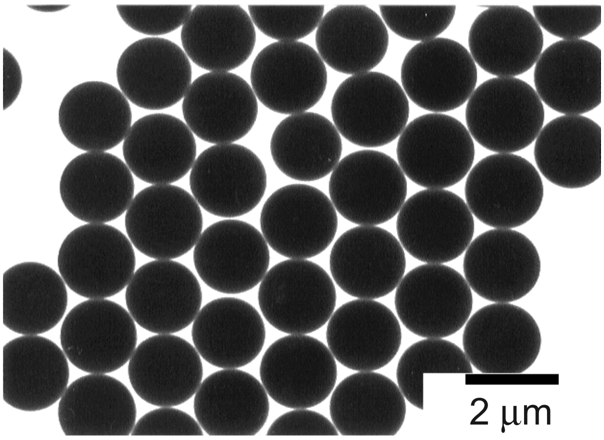


Fig. 1 TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1

utilizing DSM under the conditions of Nos. 1 and 2, respectively, listed in Table 2. Both swollen particles had high monodispersity and their insides were observed to be homogeneous. Seeded polymerizations of these swollen particles were carried out and resulted in the two kinds of PS/PDVB (1/5.5, w/w) composite particles. Hereafter, the composite particles produced under the conditions of Nos. 1 and 2 will be, respectively, expressed as N-particles

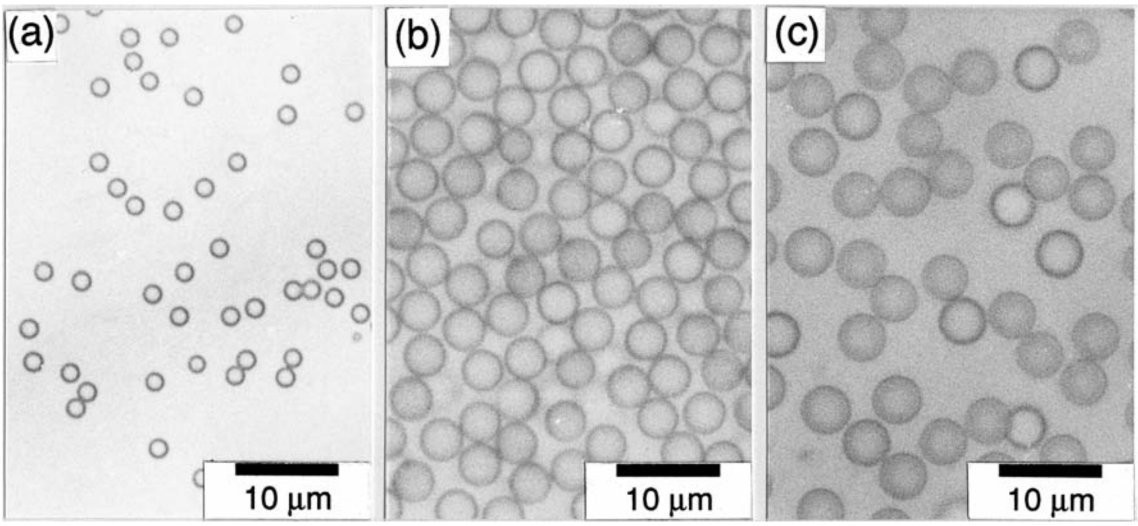


Fig. 2 Optical photographs of PS seed particles (a), and swollen particles with DVB (b) and with toluene and DVB (c) prepared utilizing the dynamic swelling method under the conditions of No. 1 and No. 2, respectively, listed in Table 2

and H-particles which originate, respectively, from normal and hollow particles.

As can be seen in optical micrographs shown in Fig. 3, both composite particles were highly monodisperse. The inside of N-particles produced by seeded polymerization for the dispersion of DVB-swollen PS particles was homogeneous. On the other hand, that of H-particles produced by seeded polymerization for the dispersion of (toluene/DVB) - swollen PS particles had a low contrast region in the center.

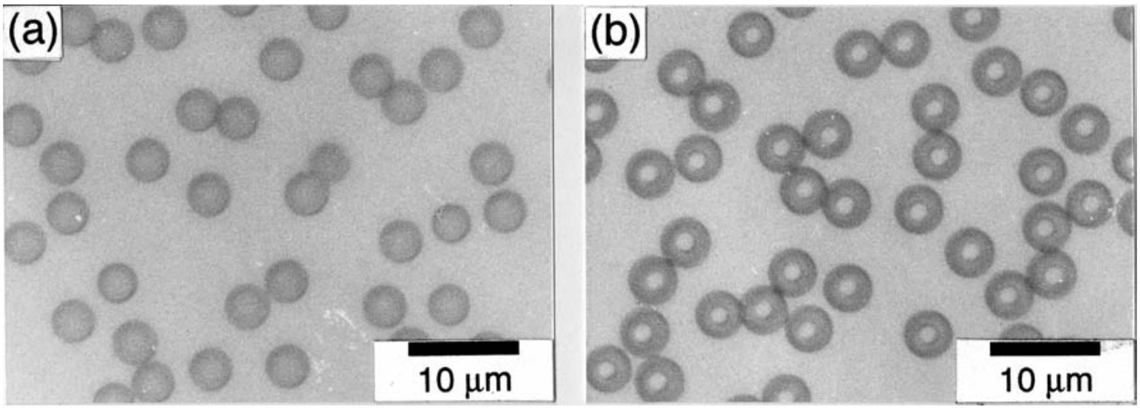


Fig. 3 Optical photographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 (a) and No. 2 (b), respectively, listed in Table 2

Figures 4 and 5 show, respectively, TEM and SEM photographs of N-particles (a) and H-particles (b). In the TEM photographs, the contrast of the inside of N-particles was homogeneous, whereas in H-particles there was a low contrast region in the inside. In the SEM photographs, both composite particles had smooth surfaces. Therefore, the reason why H-particles had the low contrast region in the TEM photograph shown in Fig. 4 seems to be based on not void but hollow.

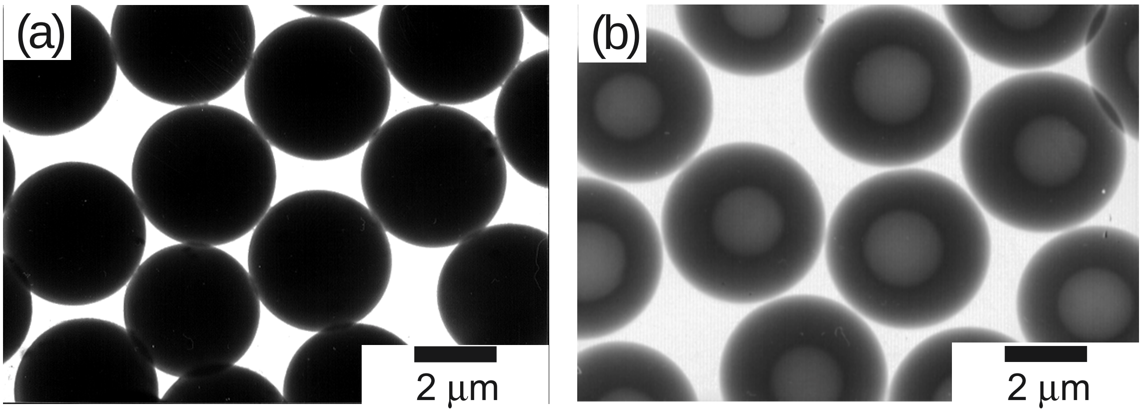


Fig. 4 TEM photographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 (a) and No. 2 (b), respectively, listed in Table 2

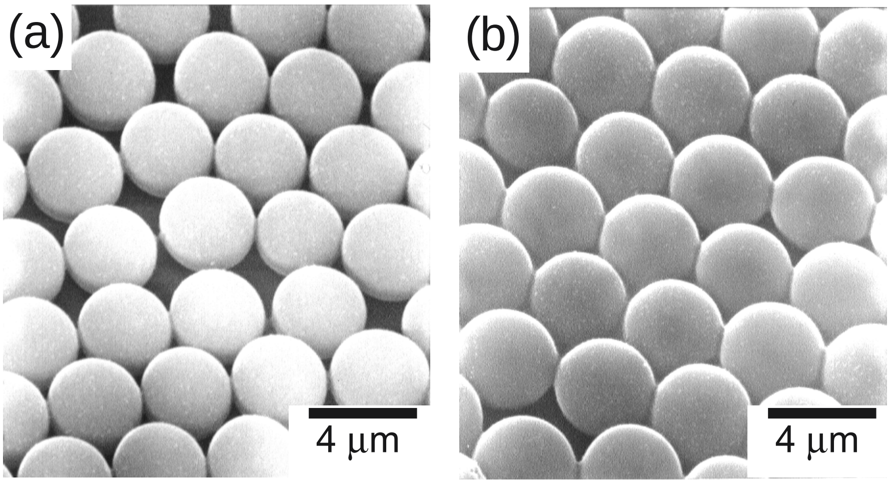


Fig. 5 SEM photographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 (a) and No. 2 (b), respectively, listed in Table 2

Figure 6 shows optical micrographs of both composite particles redispersed in water after drying. The observed states of both particles were similar to those before drying shown in Fig. 3. The hollows in the H-particles shown in Figs. 3 and 6 should be, respectively, filled with liquid (toluene and/or water) and air. As shown in Fig. 7, when both dried composite par-

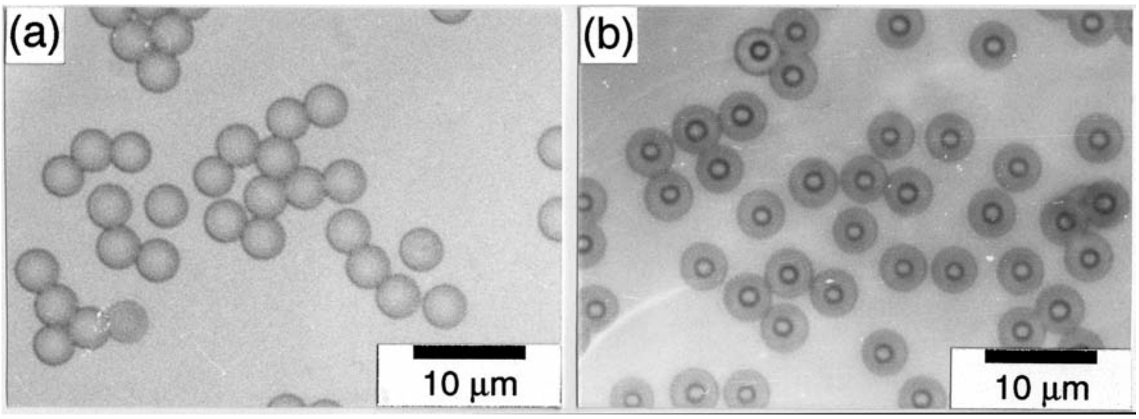


Fig. 6 Optical photographs of the PS/PDVB composite particles redispersed in the water after drying which had been produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 (a) and No. 2 (b), respectively, listed in Table 2

ticles were redispersed in phenylhydrazine whose refractive index is close to those of PS and PDVB (see Table 3), no N-particle was observed with the optical microscope. Whereas in the H-particles the particle-solvent interface similarly disappeared but the low contrast region of the inside was observed and it also gradually faded away with time as shown in Fig. 8. This seems to

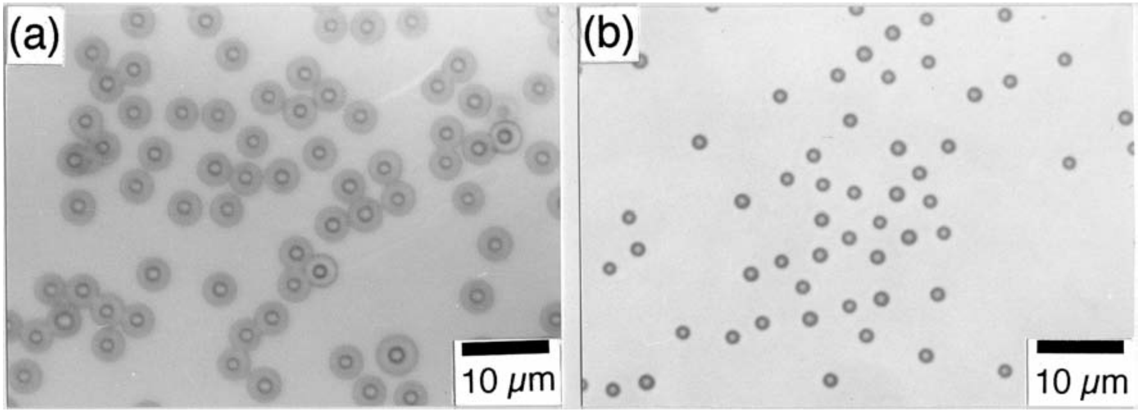


Fig. 7 Optical photographs of PS/PDVB composite particles redispersed in the water (a) and in the phenylhydrazine (b) after drying which had been produced by seeded polymerization for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling

Table 3 Refractive Index n_D (20°C)

	n_D
Polystyrene[a)]	1.59～1.592
Poly(*p*-divinylbenzene)[a)]	1.6150
Phenyl hydrazine[b)]	1.6081
Toluene[b)]	1.4969
Water[b)]	1.3330
Air[b)]	1.0003

[a)] *"Polymer Handbook" 3rd Ed.,* WILEY (1989).

[b)] *"Kagaku Binran" 4th Ed,* The Chemical Society of Japan (1993).

be based on that the hollow is filled with phenylhydrazine. That is, these results also suggest that H-particles have a hollow in the inside.

Figure 9 shows TEM photographs of ultrathin cross sections of both composite particles exposed to OsO_4 vapor for 2 h and a schematic model of sections sliced from different positions of particles. As shown in the

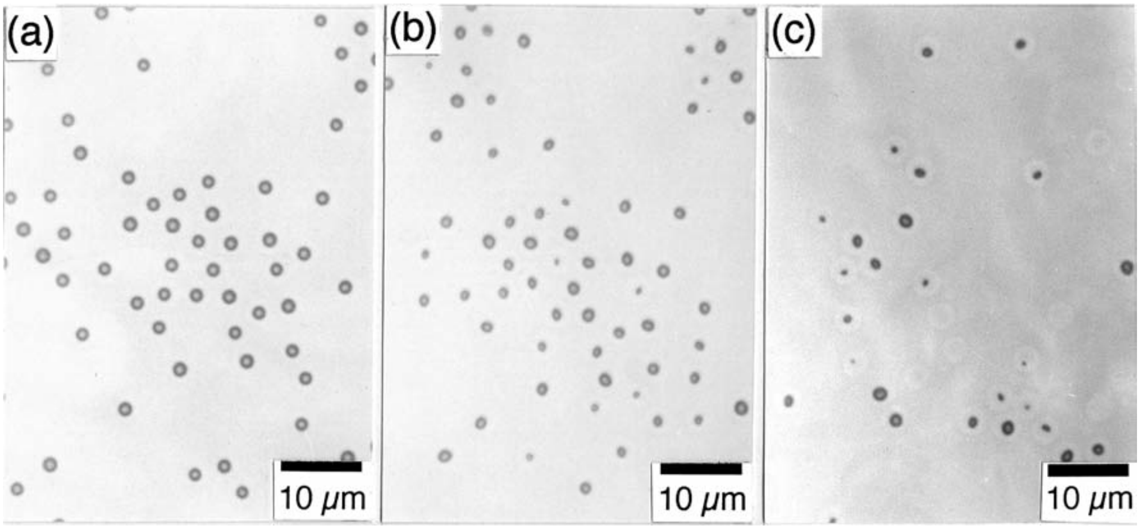
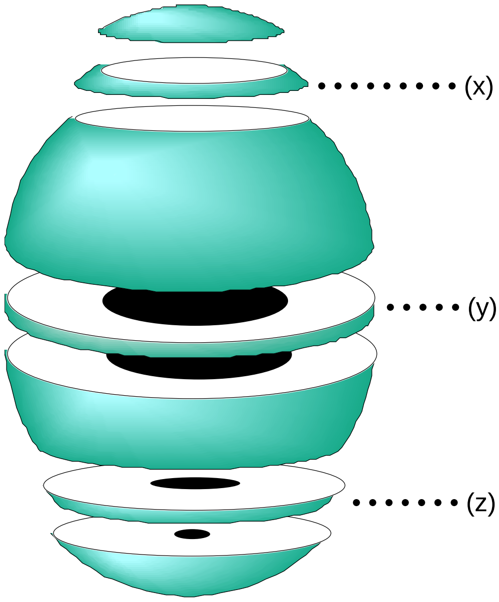


Fig. 8 Optical photographs of the PS/PDVB composite particles redispersed in the phenylhydrazine after 0 h (a), 4 h (b) and 8 h (c)



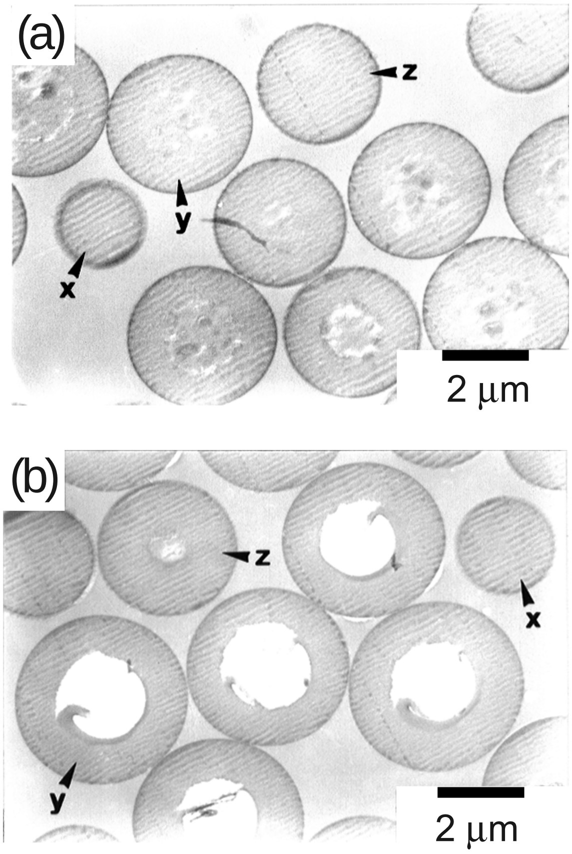


Fig. 9 TEM photographs of ultrathin cross sections of PS/PDVB composite particles exposed to OsO_4 vapor for 2 h which had been produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 (a) and No. 2 (b), respectively, listed in Table 2

shematic model, the sections having similar diameter to that of the composite particles (y-part) were sliced from the center particles and those having smaller diameter (x-, z-part) were sliced from the edges of particles. In the case of H-particles shown in Fig. 9 (b), the sections having small diameter didn't have a hollow, but those having similar diameter to that of the composite particles had a hollow and the hollow size increased with the diameter. These indicate that H-particles had a single hollow in the center. On the other hand, such a hollow structure was not observed in any sections of N-particles, although circular crack was observed in some sections. This may be based on a core-shell cross-linking structure and the existence of ethylbenzene as impurity in DVB used in this experiment. This will be clarified in a future article.

From these results, it is concluded that micron-sized monodisperse cross-linked polymer particles having hollow structure can be produced by seeded polymerization for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing DSM.

1.4 Conclusion

4 μm-sized, monodisperse, cross-linked polymer particles having a hollow structure were produced as follows. First, 1.7 μm-sized monodisperse polystyrene (PS) seed particles produced by dispersion polymerization were dispersed in ethanol/water (7/3, w/w) solution in which divinylbenzene (DVB), benzoyl peroxide (BPO), poly(vinyl alcohol), and toluene was dissolved. The PS seed particles were swollen with DVB, toluene and BPO maintaining high monodispersity throughout the dynamic swelling process where water was slowly added continuously. And then, the seeded polymerization of the (toluene/DVB)-swollen PS particles was carried out.

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Chapter 2

Control of hollow size of micron-sized, monodisperse polymer particles having a hollow structure

2.1 Introduction

Recently, micron-sized monodisperse polymer particles have been applied in the biomedical field, microelectronics, etc. Many researchers studying polymer colloids concentrate their attention on the production of micron-sized monodisperse polymer particles [1-4]. Corner [5] and Almog et al. [6] suggested a useful dispersion polymerization technique. We have been producing micron-sized monodisperse polystyrene (PS) particles having functional groups such as chloromethyl [7] and vinyl groups [8, 9] by seeded dispersion copolymerization with corresponding functional monomers in the presence of about 2 μm-sized monodisperse PS particles as seed. Micron-sized monodisperse polymer particles having multihollow structures were also produced by extraction of PS with toluene under reflux from micron-sized monodisperse PS/poly(styrene-divinylbenzene) composite particles produced by seeded dispersion copolymerization [10].

Moreover, in order to produce monodisperse particles having the diameter above 5 μm, Okubo *et al* suggested a new type of swelling method of seed polymer particles with a large amount of monomer which was named "the dynamic swelling method (DSM)" [11, 12]. In fact, about 7 μm-sized monodisperse PS particles were produced by seeded polymerization utilizing DSM. In Chapter 1, we [13] developed this technique to produce micron-sized monodisperse polymer particles having one hollow in the inside, as follows. About 2 μm-sized monodisperse PS seed particles produced by dispersion polymerization were dispersed in ethanol/water (7/3, w/w) solution in which divinylbenzene (DVB), benzoyl peroxide (BPO), poly(vinyl alcohol), and toluene were dissolved. Throughout the dynamic swelling process, water was slowly added continuously, the PS seed particles absorbed DVB, toluene and BPO. And then, the seeded polymerization of the monodisperse (toluene/DVB) - swollen PS particles was carried out.

In this chapter, the control of the hollow size of such particles will be tried by changing the kind and amount of solvent.

2.2 Experimental

2.2.1 Materials

Divinylbenzene (DVB) was washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. The supplied DVB included ethylvinylbenzene and diethylbenzene, and the purity was 55%. Benzoyl peroxide (BPO) and 2, 2'-azobisisobutyronitrile (AIBN) of reagent grade were 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 stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane [7]. Reagent grade of ethanol, toluene, xylene and benzene were used as received.

2.2.2 Preparation of seed particles

Micron-sized monodisperse PS seed particles were produced under the optimum dispersion polymerization conditions determined in the previous article [7]. The dispersion polymerization of styrene was carried out at 70°C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask under the conditions listed in Table 1. The reaction mixture in the flask was stirred with an anchor-type stirrer at 60 rpm. The PS seed particles were observed with a JEOL JEM-200CX transmission electron microscope (TEM).

2.2.3 Swelling of seed particles with DVB and toluene utilizing DSM

Swelling of the PS particles with DVB and toluene was carried out using DSM as follows. Ethanol (7 g), water (3 g), DVB (0.3 g), toluene (0~0.60 g),

Table 1 Preparation of micron-sized monodisperse PS seed particles by dispersion polymerization[a]

Ingredients		
Ethanol	(g)	959
Water	(g)	280
Styrene	(g)	140
AIBN	(g)	2.35
PAA	(g)	16.8

[a] N_2; 70°C; 24 h; stirring rate, 60 rpm

BPO (0.006 g), and PVA (0.015 g) were charged into a glass cylindrical reactor. To this homogeneous solution, the PS particles (0.03 g) were dispersed. Finally, water (40 g) was added to the mixture with a micro feeder under stirring with a magnetic stirrer at a rate of 2.88 ml/h or 1.44 ml/h. Instead of toluene, benzene or xylene was used by the same procedure.

2.2.4 Seeded polymerization

Seeded polymerizations for the dispersions of (solvent/DVB) - swollen PS particles were carried out in sealed glass tubes under a nitrogen atmosphere at 70°C for 24 h. The tubes were horizontally shaken at 120 cycles/min (2-cm strokes). After the polymerization, the emulsion was dropped onto slide glass, and then the droplet was covered with cover glass and observed with Nikon MICROPHOT-FXA optical microscope. Each particle was also observed with TEM. The conversion was measured by gas chromatography.

2.2.5 Observations of the ultrathin cross sections of particles

PS/PDVB composite particles were exposed to OsO_4 vapor at room temperature for 24 h in the presence of 1 % OsO_4 solution, and then dipped in epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross sections were observed with TEM.

2.2.6 Diameter measurements

The number-average diameter (Dn) and coefficient of variation (Cv) were determined by measuring on TEM negative films with a Personal Image Analysis System (PIAS Co. Ltd, LA-525, Osaka, Japan).

2.3 Results and discussion

Figure 1 shows a TEM photograph of PS particles produced by dispersion polymerization under the conditions listed in Table 1. PS particles were spherical and monodisperse: *Dn* and *Cv* were 1.71 μm and 2.2%, respectively.

Figure 2 shows optical micrographs of PS/polydivinylbenzene (PDVB) composite particles produced by seeded polymerization for the dispersions of swollen PS particles prepared utilizing DSM under the conditions of Nos. 1 (a), 2 (b), 3 (c), and 4 (d), respectively, listed in Table 2. Each conversion of DVB was more than 97 %, and all composite particles produced were highly monodisperse. The particle size increased with the increase in the toluene content. The insides of the No. 1-particles were observed to be homogeneous, whereas the Nos. 2-, 3-, and 4-particles had a hollow at their center. The hollow size increased with the increase in the toluene content. In the observation of No. 4-particles just after the polymerization with the

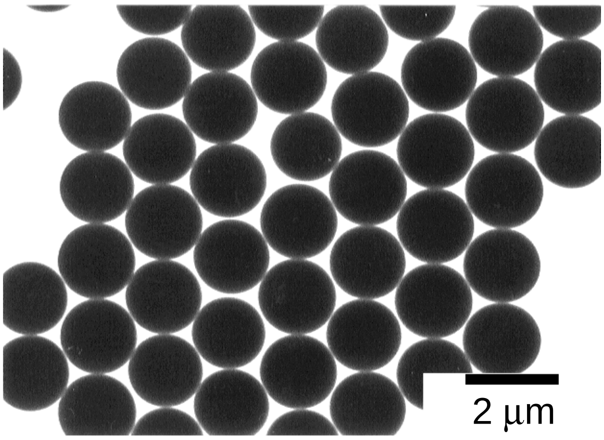

Fig. 1 TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1

optical microscope, the hollow structure was not observed in almost particles. However, the structure gradually appeared in the particles existing edge of cover glass and the hollow size increased to give rise to the structure as shown in Fig. 2d. Finally, the hollow structure was observed in all particles. This seems to be based on the fact that toluene in the hollow is replaced by ethanol/water mixture medium because of evaporation of toluene. The refractive index of toluene is close to those of PS and PDVB, but that of the medium is different from them. When Nos. 2~4-particles were completely dried under reduced pressure at room temperature and re-

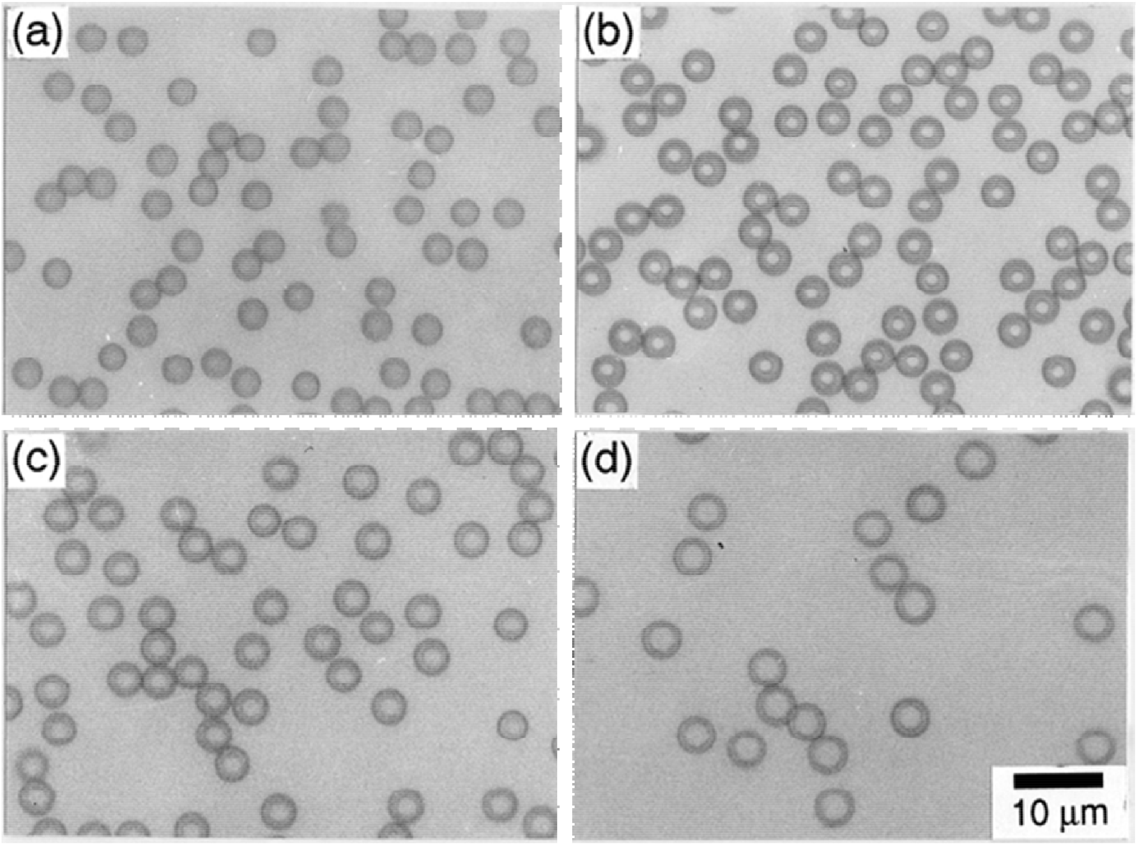

Fig. 2 Optical micrographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 (a), No. 2 (b), No. 3 (c) and No. 4 (d), respectively, listed in Table 2

dispersed in water, their hollow structures, which should be filled with air, were more distinct.

Figure 3 shows TEM photographs of Nos. 1- (a), 2- (b), 3- (c), and 4-particles (d). As will be seen, the contrast of the inside of No. 1-particles was homogeneous, whereas in the other Nos. 2~4-particles there was a less dark circular region due to the hollow structure. Both diameters of the composite particle and the less dark region increased with the increased in the toluene content. It was also observed that the hollow inside of No. 4-particles was rugged. This will be discussed in a future article.

Figure 4 shows a TEM photograph of ultrathin cross sections of No. 2-particles exposed to OsO_4 vapor for 2 h and a schematic model of sections

Table 2 Recipes for the productions of four kinds of PS/PDVB (1/5.5, w/w) composite particles by seeded polymerizations[a)] for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method at room temperature

Ingredients		No. 1	No. 2	No. 3	No. 4
PS particles[b)]	(g)	0.03	0.03	0.03	0.03
DVB[c)]	(g)	0.3	0.3	0.3	0.3
Toluene	(g)	0	0.15	0.3	0.6
PVA	(g)	0.015	0.015	0.015	0.015
BPO	(g)	0.006	0.006	0.006	0.006
Ethanol	(g)	7.0	7.0	7.0	7.0
Water	(g)	3.0 + 40.0[d)]	3.0 + 40.0[d)]	3.0 + 40.0[d)]	3.0 + 40.0[e)]

[a)] N_2, 70°C, 24 h.
[b)] 1.7 µm; Cv, 2.2 %
[c)] Purity, 55% (by catalog).
[d)] 40.0 g of water was post-added at the rate of 2.88 ml/h.
[e)] 40.0 g of water was post-added at the rate of 1.44 ml/h.
Abbreviations: DVB, divinylbenzene; PS, polystyrene; PVA, polyvinyl alcohol; BPO, benzoyl peroxide.

sliced from different positions of particles. As shown in the schematic model, the sections having similar diameter to that of the composite particles (y-part) were sliced from the center particles and those having smaller diameter (x-, z-part) were sliced from the edges of particles. The sections having a small diameter did not have a hollow structure, but those having similar diameters as the composite particles had the hollow whose size increased with an increase in the diameter of the section. These findings indicate that No. 2-particles have a single hollow at the center. The hollow size observed in the part sliced from the center of the particles was similar to

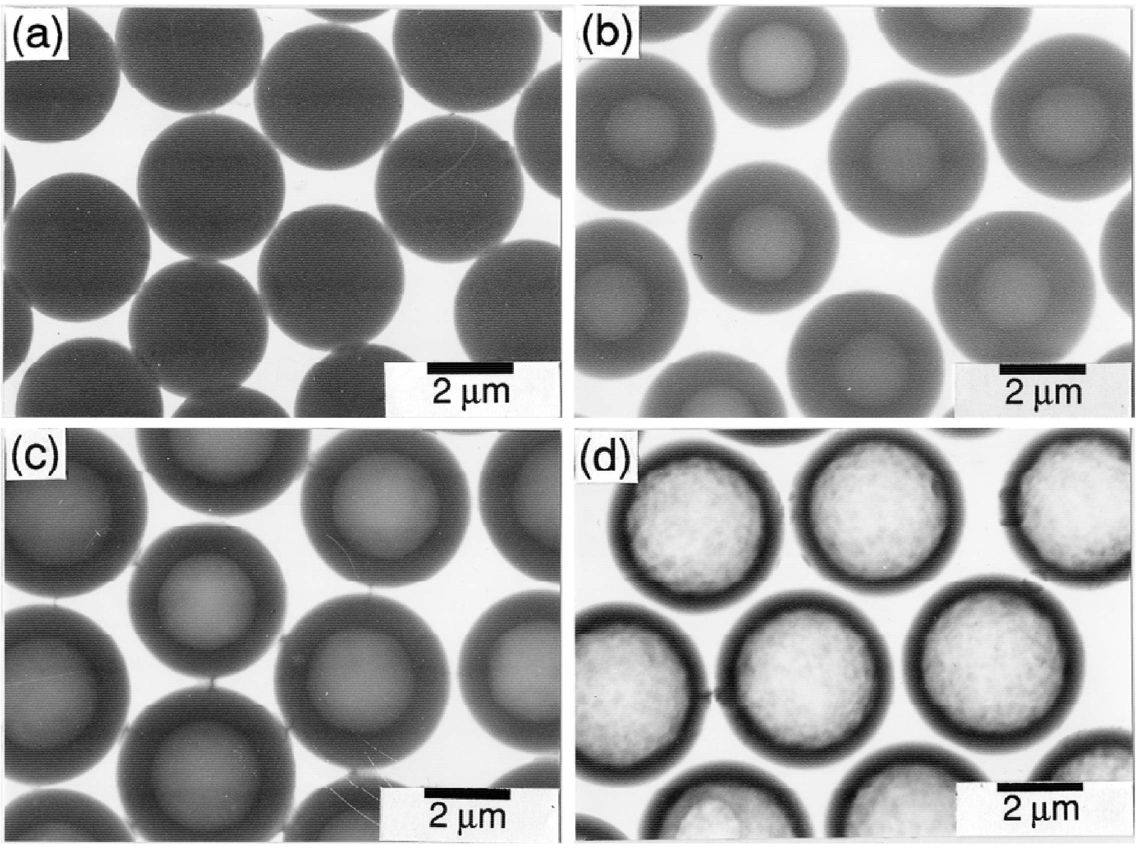

Fig. 3 TEM photographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 (a), No. 2 (b), No. 3 (c) and No. 4 (d), respectively, listed in Table 2

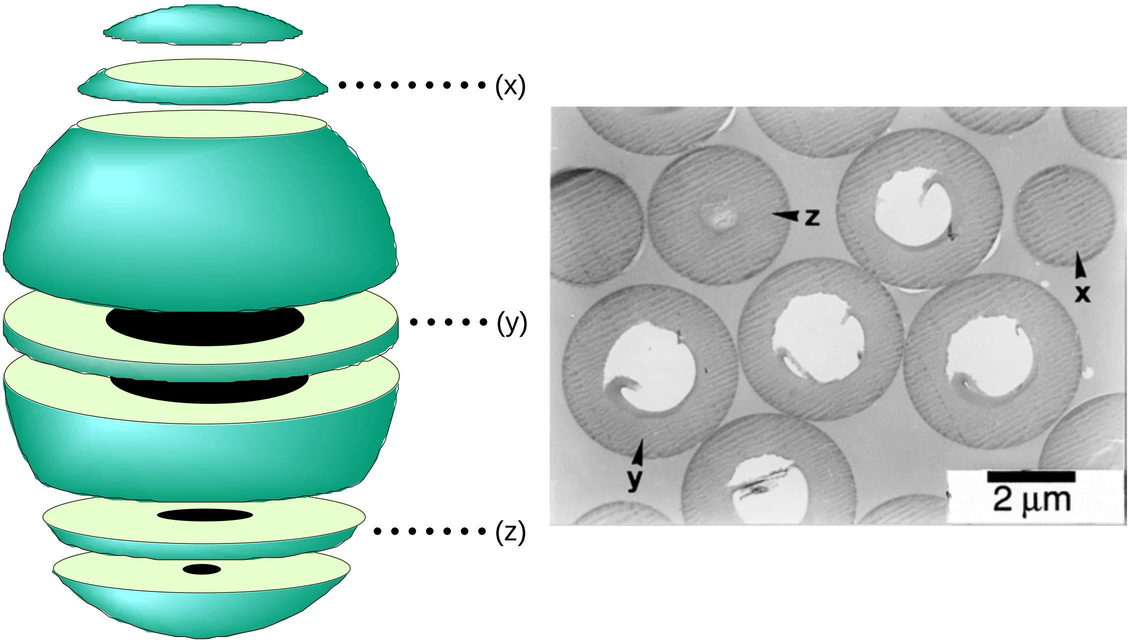

Fig. 4 TEM photographs of ultrathin cross sections of PS/PDVB composite particles exposed to OsO_4 vapor for 2 h which had been produced by seeded polymerizations for the dispersions of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 2 listed in Table 2

the diameter of the less dark region in the particles shown in Fig. 3b. Therefore, it is concluded that the diameter of the less dark regions in the TEM photographs corresponds to the hollow size.

Figure 5 shows relationships between the volume ratio of toluene to PS seed particle and the volume of PS/PDVB composite particles or the volume of hollow, which were, respectively, calculated from the diameters of composite particles or the less dark region. The particle and hollow volumes increased proportionately with the amount of toluene. This indicates that the increase in the particle volume is due to the increase in the hollow volume. In this way, the hollow size is controllable by the amount of toluene. However the hollow volume was much smaller than the hollow volume as calculated from the recipe. This is because a part of toluene added existed also in the

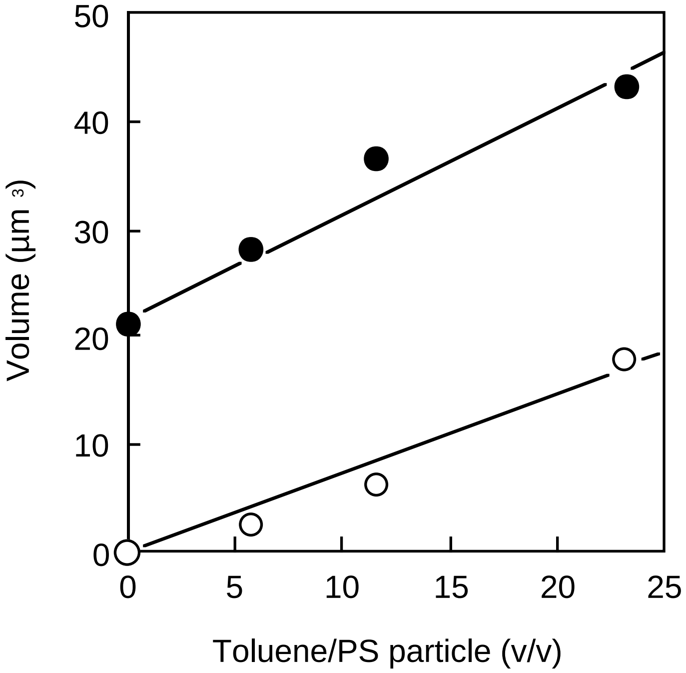

Fig. 5 Relationships between the volume ratio of toluene to PS seed particle and the volume of PS/PDVB composite particles (●) or the volume of hollow (○) produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles utilizing the dynamic swelling method under the conditions listed in Table 2

Table 3 Recipes for the productions of two kinds of PS/PDVB (1/5.5, w/w) composite particles by seeded polymerizations[a] for the dispersions of (solvent/DVB)-swollen PS particles prepared utilizing the dynamic swelling method at room temperature

Ingredients		
PS particles [b]	(g)	0.03
DVB[c]	(g)	0.3
Benzene or xylene	(g)	0.3
PVA	(g)	0.015
BPO	(g)	0.006
Ethanol	(g)	7.0
Water	(g)	3.0 + 40.0 [d]

[a] N_2, 70°C, 24 h.

[b] 1.7 µm; C_v 2.2 %

[c] Purity, 55% (by catalog).

[d] 40.0 g of water was post-added at the rate of 2.88 ml/h.

Abbreviations: DVB, divinylbenzene; PS, polystyrene; PVA, polyvinyl alcohol; BPO, benzoyl peroxide.

medium and gas phase in the sealed glass tube used in the polymerization.

Figure 6 shows TEM photographs of PS/PDVB composite particles produced by seeded polymerization for the dispersions of (benzene/DVB) - (a) and (xylene/DVB) - swollen PS particles (b) prepared utilizing DSM under the conditions listed in Table 3. Both composite particles had the hollow structure. Because the recipes of these systems were the same as that of No. 3 listed in Table 2 and the densities of the solvents are nearly equal as shown in Table 4, the volume ratios of solvents to PS seed particle can be considered to be same. However, as can be seen, the hollow size increased in order of the benzene- < the toluene- < the xylene-containing system. This seem to be affected by nature of solvents; solubility in medium, vaporization rate and vapor pressure. From the viewpoint of solubility, that order is in accord with the decreasing order of solubilities of the solvents in water as shown in Table 4. This suggests that a solvent having low solubility in the medium should be chosen to produce the hollow particles efficiently.

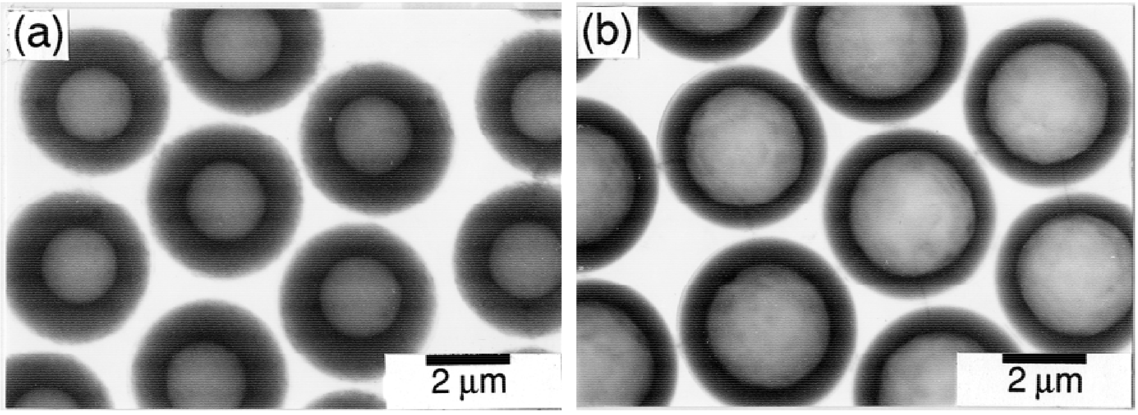

Fig. 6 TEM photographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of (solvent/DVB)-swollen PS particles prepared utilizing the dynamic swelling method using benzene (a) and xylene (b) respectively, under the conditions listed in Table 3

Table 4 Solubilities of solvents in water (25°C) and densities of solvents (25°C)

Solvent	Solubility (%)	Density (25°C)
DVB	0.005[a)]	0.9126[a)]
Toluene	0.052[b)]	0.8623[b)]
Benzene	0.178[b)]	0.8737[b)]
p-Xylene	0.019[b)]	0.8567[b)]

[a)] *"Tanryotai I" 1st Ed.*, Kyoritsu Syuppan Co. Ltd (1976).

[b)] *"Organic Solvents" 3rd Ed.*, The Chemical Society of Japan (1993).

From these results, it is concluded that the hollow size of micron-sized monodisperse cross-linked polymer particles produced by seeded polymerization utilizing the dynamic swelling method can be controlled by changing the amount and the nature of solvent.

2.4 Conclusion

Micron-sized, monodisperse, cross-linked polymer particles having one hollow in the inside were produced by the seeded polymerization for the dispersion of (toluene/divinylbenzene)-swollen PS particles prepared utilizing the dynamic swelling method which the authors proposed. In order to control the hollow size, the weight ratio of toluene/PS was changed in the range of 5~20. The hollow size increased with an increased in the weight ratio. Even if benzene and xylene were used in place of toluene, similar hollow particles were produced, though the hollow size was affected by their solubility in water.

2.5 Reference

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Chapter 3

Formation mechanism of micron-sized, monodisperse polymer particles having a hollow structure

3.1 Introduction

Micron-sized monodisperse 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 monodisperse polymer particles [1-5]. We have been producing micron-sized monodisperse polystyrene (PS) particles having functional groups such as chloromethyl [6] and vinyl groups [7, 8] by seeded dispersion copolymerization with corresponding functional monomers in the presence of about 2 μm-sized monodisperse PS particles as seed. Micron-sized monodisperse polymer particles having multihollow structures were also produced by extraction of PS with toluene under reflux from micron-sized monodisperse PS/ poly(styrene-divinylbenzene) composite particles produced by seeded dispersion copolymerization [9].

Moreover, in order to produce monodisperse particles having the diameter above 5 μm, Okubo *et al* suggested a new type of swelling method of seed polymer particles with a large amount of monomer which was named “the dynamic swelling method (DSM)” [10, 11]. In a previous paper [12], we developed this technique to produce micron-sized monodisperse polymer particles having one hollow in the inside. We also succeeded in controlling the hollow size [13].

In this chapter, the formation mechanism of hollow structure in the micron-sized monodisperse polymer particles will be discussed.

3.2 Experimental

3.2.1 Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) was washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. The supplied DVB included ethylvinylbenzene and diethylbenzene, and the purity was 55%. Benzoyl peroxide (BPO) and 2, 2'-azobisisobutyronitrile (AIBN) of reagent grade were 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 stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane [6]. Reagent grade ethanol and toluene were used as received.

3.2.2 Preparation of polystyrene (PS) seed particles

Micron-sized monodisperse PS seed particles were produced by dispersion polymerization of styrene in ethanol/water (7/3, w/w) medium with AIBN initiator at 70°C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask. The optimum conditions have been reported in the previous article [6]. The PS seed particles were spherical and monodisperse: the number-average diameter (*Dn*) and coefficient of variation (*Cv*) were 1.71 µm and 2.2%, respectively.

3.2.3 Swelling of seed particles with DVB and toluene utilizing DSM

Swelling of the PS seed particles with DVB (or styrene) and toluene was carried out under the recipes listed in Table 1 using DSM as follows. Ethanol, water, DVB (or styrene), toluene, BPO, and PVA were charged into a four-necked round-bottom flask or into a glass cylindrical reactor. To this homogeneous solution, the PS seed particles were dispersed. Finally, water was added to the mixture with a micro feeder at a rate of 18 ml/h or 2.88 ml/h under stirring.

3.2.4 Seeded polymerization

Seeded polymerizations for the dispersions of (toluene/DVB) and (toluene/styrene)-swollen PS particles were carried out in a four-necked round-bottom flask or in sealed glass tubes under a nitrogen atmosphere at 70°C for 24 h. The flask was stirred at 80 rpm and the tubes were horizontally shaken at 120 cycles/min (2-cm strokes). The emulsions pipetted out successively at chosen time intervals were dropped onto slide glasses, and then each droplet was covered with a cover glass and observed with Nikon MICROPHOT-FXA optical microscope. The conversion was measured by gas chromatography.

Table 1 Recipe for the productions of PS/PDVB (1/5.5, w/w) composite particles and PS particles by seeded polymerizations [a] for the dispersions of (toluene/DVB)- and (toluene/styrene)-swollen PS particles prepared utilizing dynamic swelling method at room temperature

Ingredients		No. 1 [b]	No. 2 [c]
PS particles [d]	(g)	0.3	0.03
DVB [e]	(g)	3.0	0
Styrene	(g)	0	0.3
Toluene	(g)	1.5	0.15
BPO	(g)	0.06	0.015
PVA	(g)	0.15	0.015
Ethanol	(g)	70	6
Water	(g)	30 + 400 [f]	4 + 40 [g]

[a] N_2, 70°C, 24 h

[b] polymerization was carried out in a four-necked round-bottom flask

[c] polymerization was carried out in sealed glass tubes

[d] 1.7 µm; Cv, 2.2 %

[e] Purity, 55 % (by catalog)

[f] 400 g of water was post-added at the rate of 18 ml/h.

[g] 40 g of water was post-added at the rate of 2.88 ml/h.

Abbreviations: PS, polystyrene; DVB, divinylbenzene; BPO, benzoyl peroxid PVA, polyvinyl alcohol

3.2.5 Observations of the ultrathin cross sections of particles

PS/PDVB composite particles were exposed to OsO_4 vapor at 50°C for 2 h in the presence of 1 % OsO_4 solution, and then dipped in epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross sections were put on copper grids and observed with TEM. To extract PS from the ultrathin cross sections of PS/PDVB composite particles, toluene was dropped onto the grid with the sections. When the grids was dried up, toluene was dropped onto the grid again. After several repetitions of this procedure, the ultrathin cross sections were observed with TEM.

3.3 Results and discussion

Figure 1 shows the time-conversion curve of DVB in seeded polymerization for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1. The polymerization proceeded smoothly and the conversion rose to more than 90 % after 6 h.

Figure 2 shows optical micrographs of PS/PDVB composite particles at various conversions of DVB, just after each polymer emulsion was pipetted out from the polymerization system. The contrasts in the insides of the produced composite particles at the all conversions were observed to be homogeneous and the shapes were spherical.

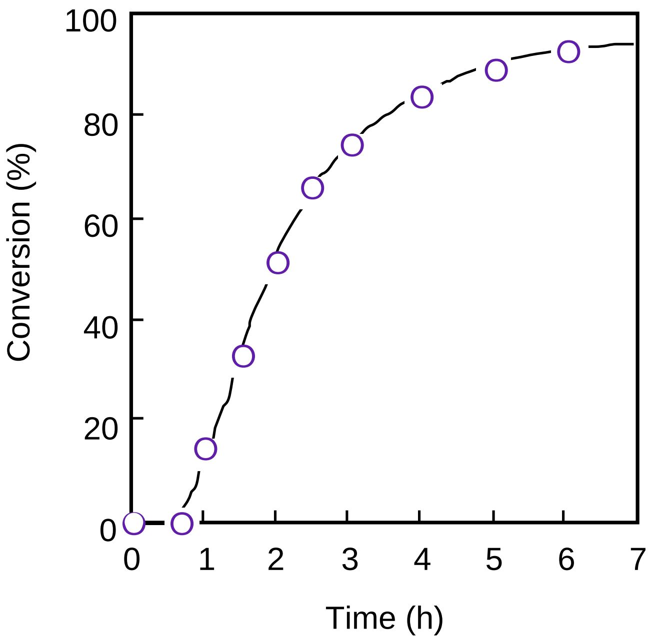

Fig. 1 Time-conversion curve of DVB in seeded polymerization at 70°C for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1

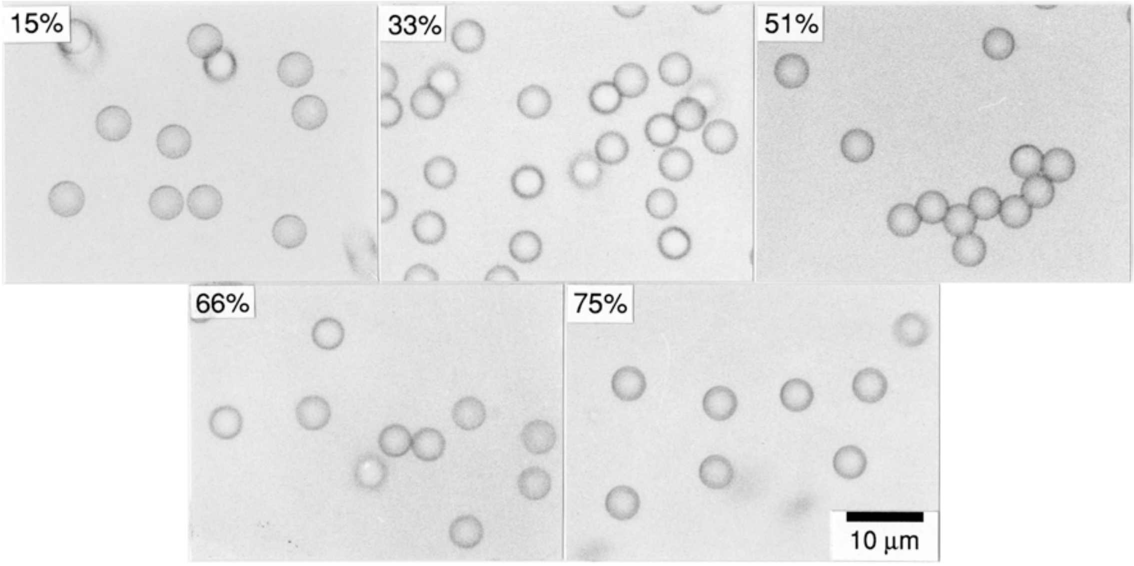

Fig. 2 Optical micrographs of PS/PDVB composite particles at the various conversions of seeded polymerization of DVB for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1, just after each polymer emulsion was pipetted out from the polymerization system

Figure 3 shows optical micrographs of the PS/PDVB composite particles at each conversion of DVB, whose emulsions were left at room temperature for 24 h in a capless small vessel after the polymerization was stopped. The composite particles at 15% conversion were spherical but clearly shrank compared to the composite particles observed just after pipetting out as observed in Fig. 2. Above 33%, such a shrinkage was not observed, but at 33~66% conversions flattened shapes of the particles were observed. Especially, the particles at 51% and 66% had such an anomalous shape as red blood corpuscle. This will be discussed in future. At 75% conversion a hollow structure was observed. These observations in Figs. 2 and 3 indicate that a cross-linked shell layer was formed, though at 15% conversion such a shell layer which depresses the shrinkage of particles with the

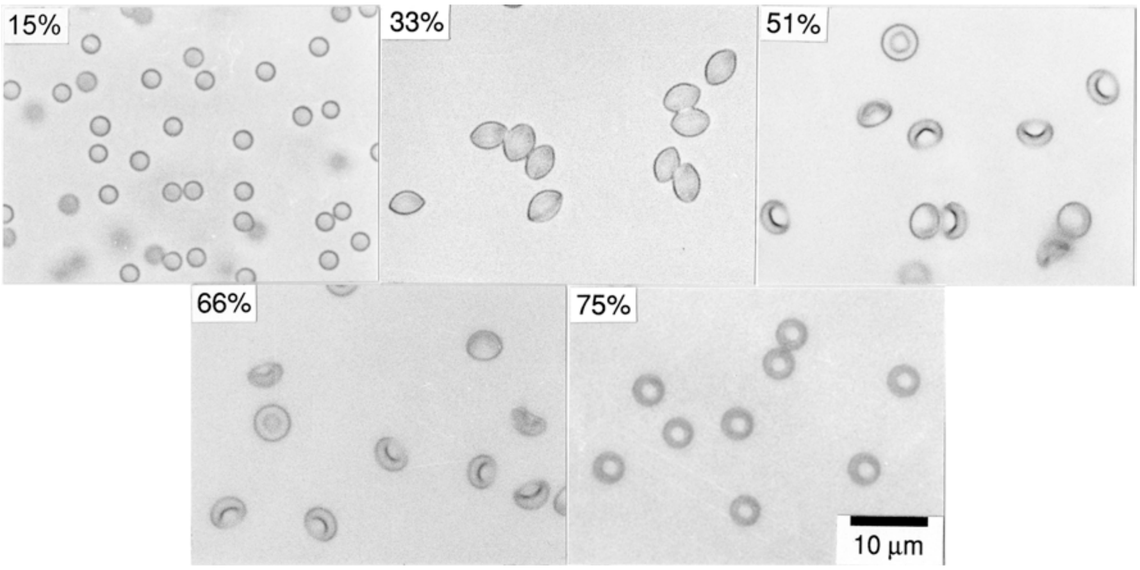

Fig. 3 Optical micrographs of PS/PDVB composite particles at the various conversions of the seeded polymerization of DVB for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1, after each polymer emulsion was kept for 24 h.

evaporation of toluene and unpolymerized DVB therefrom was not formed yet. The reason why the shell layer was not observed at the all conversions in Fig. 2 seems to be based on the similar refractive indexes of PDVB and mixture of DVB and toluene. On the other hand, the reason why the shell layer was observed in Fig. 3 seems to be based on the evaporations of toluene and unpolymerized DVB from the particles.

In order to clarify these points, just after pipetted out from the polymerization system at each conversion a small amount of emulsion was immediately dispersed in a large amount of tetrahydrofuran (THF) which is miscible with water, DVB and toluene, and a good solvent for PS. Its refractive index is relatively different from that of PDVB. As can be seen in Fig. 4, the particles at 33~75% conversions were observed to be spherical shape and having shell layer, though the particles at 33% conversion slightly shrank. It

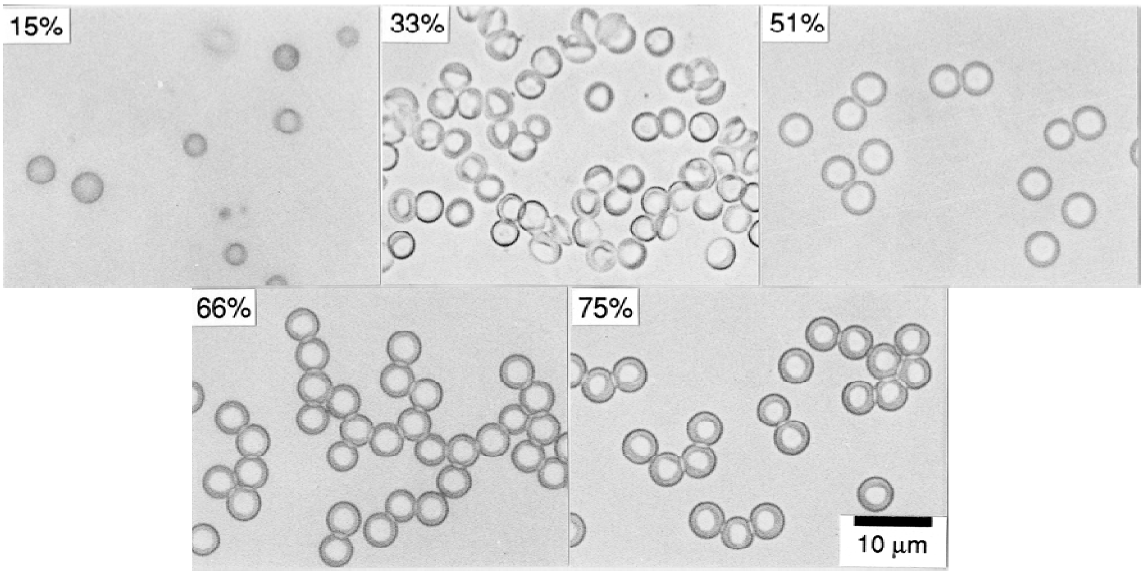

Fig. 4 Optical micrographs of PS/PDVB composite particles at various conversions of seeded polymerization of DVB for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1, after a small amount of each polymer emulsion was mixed with a large amount of tetrahydrofuran

is noted that the shell thickness increased with an increase in the conversion. At 15% conversion, some particles dissolved in THF, and the others maintained the spherical shape though they shrank. These also indicate that at 15% conversion the sufficient cross-linked shell layer was not formed and the cross-linking density was heterogeneous among particles.

Figure 5 shows TEM photographs of ultrathin cross sections of PS/PDVB composite particles at 100% conversion exposed to OsO_4 vapor for 2 h, before (a) and after (b) the extraction of PS with toluene. In Fig. 5a, the phase separation of PS and PDVB was observed around the inner wall of the hollow in the PS/PDVB composite particles. By extraction of PS with toluene from the ultrathin cross section (Fig. 5b), a layer adhering inner wall of the hollow was removed. This indicates that the removed inner layer

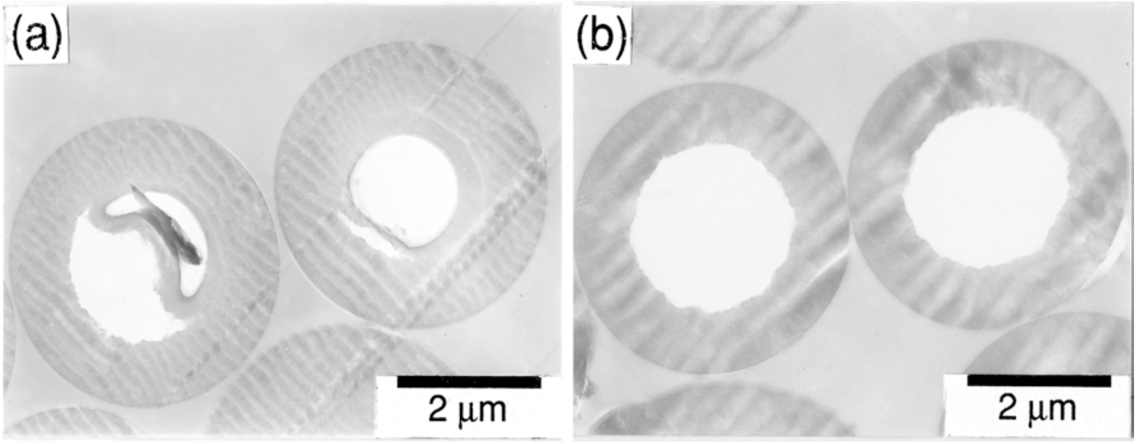

Fig. 5 TEM photographs of ultrathin cross sections of PS/PDVB composite particles at 100% conversion exposed to OsO_4 vapor for 2 h, which had been produced by seeded polymerization for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method, before (a) and after (b) the extraction of PS with toluene from the sections

consisted of PS seed polymer. The PS/PDVB ratio calculated from the thicknesses of the layer agreed well with that calculated according to the polymerization recipe.

Figure 6 shows an optical micrograph of the PS/PDVB composite particles at 100% conversion of DVB, a small amount of which was dispersed in a large amount of ethanol immediately after polymerization. In all composite particles, high contrast regions were observed at center as well as at shell layer. The similar observation is more clearly shown in TEM photographs of ultrathin cross sections of the PS/PDVB composite particles exposed to OsO_4 vapor for 2 h (Fig. 7a). As can be seen, high contrast regions which correspond to the high contrast regions in Fig. 6 were observed in the inside of hollow. The regions were removed by extraction of PS with toluene from the sections shown in Fig. 7b. This is because PS dissolved in the hollow was precipitated due to rapid exchange of the medium

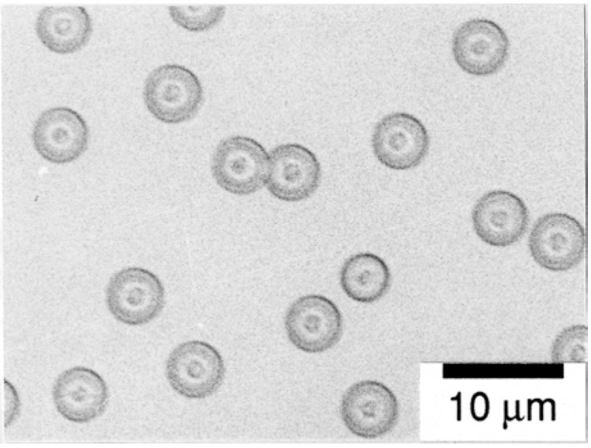

Fig. 6 Optical micrograph of PS particles produced by seeded polymerization of DVB for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1, a small amount of which was dispersed in a large amount of ethanol immediately after polymerization

from toluene to ethanol. Ethanol is non-solvent for PS. In other word, these results suggest that PS seed polymer dissolved in toluene inside the PDVB shell before evaporation of toluene.

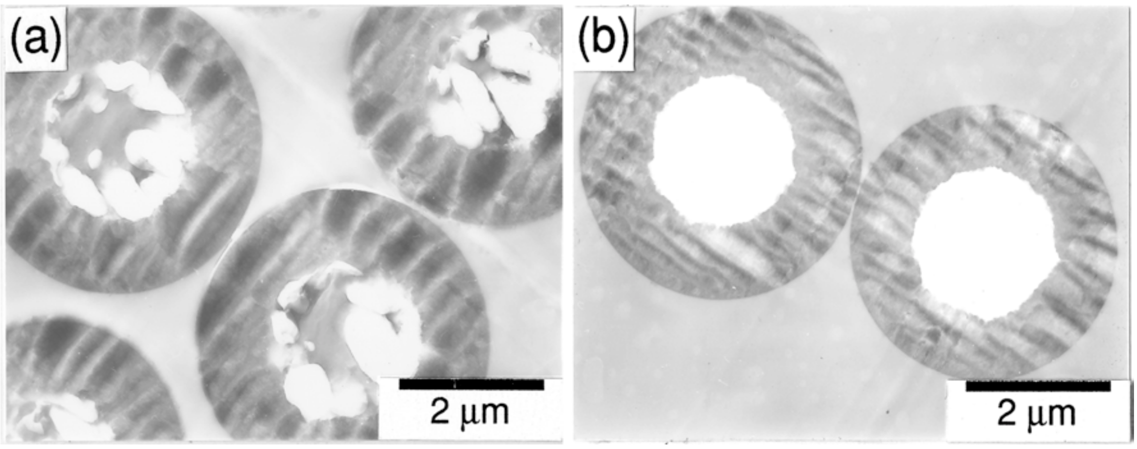

Fig. 7 TEM photographs of ultrathin cross sections of the PS/PDVB composite particles, a small amount of which was dispersed in a large amount of ethanol immediately after polymerization, exposed to OsO_4 vapor for 2 h, before (a) and after (b) the extraction of PS with toluene from the sections

Figure 8 shows optical micrographs of PS particles produced by seeded polymerization for the dispersions of (toluene/styrene)-swollen PS particles prepared utilizing DSM under the conditions of No. 2 listed in Table 1. The produced PS dispersion was left at room temperature for 24 h in a capless small vessel before the observation. The obtained particles had no hollow structure. This suggests that cross-linking is needed to form hollow structure.

From these results, we propose the formation mechanism of hollow polymer particles as schematically shown in Fig. 9. Initially, PS particles absorb toluene and DVB by the dynamic swelling method, and PS dissolved therein homogeneously. As the seeded polymerization proceeds, PDVB molecules in the swollen particles precipitate in (toluene/DVB)-swollen PS particle because of cross-link. They are trapped near the interface based on surface coagulation[14)] and gradually piled at the inner surface, which results in cross-linked PDVB shell. PS which dissolve in toluene and DVB are repelled gradually to the inside. After the completion of the polymerization,

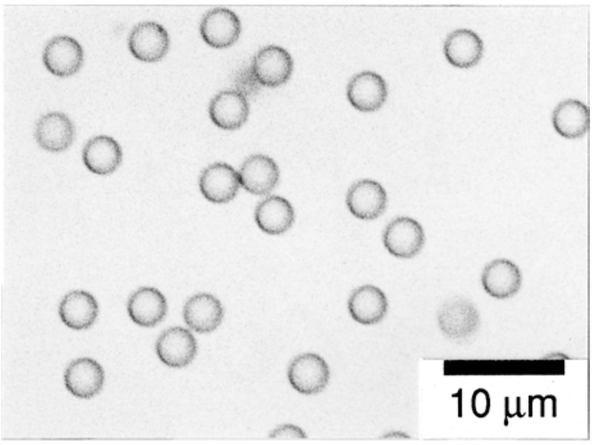

Fig. 8 Optical micrograph of PS particles produced by seeded polymerization for the dispersion of (toluene/styrene)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 2 listed in Table 1

toluene and dissolving PS are entrapped by PDVB shell, then toluene in the hollow evaporates by drying, and PS clings to the inner wall of the shell uniformly.

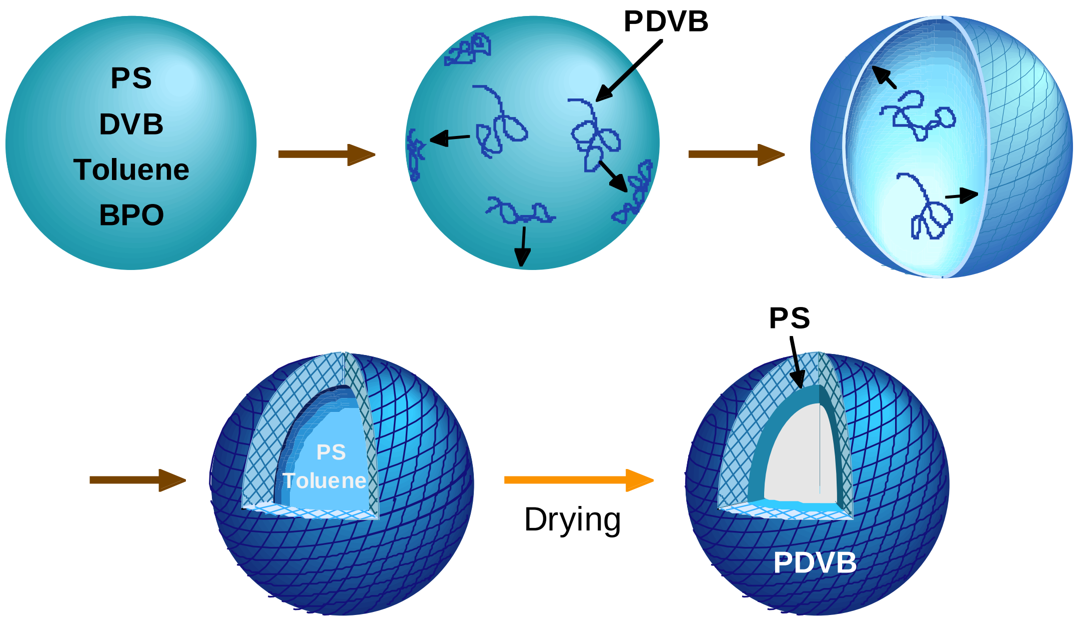

Fig. 9 The formation mechanism of micron-sized monodispersed hollow polymer particles by seeded polymerization for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method

3.4 Conclusion

Micron-sized, monodisperse, cross-linked polymer particles having single hollow in the inside were produced by the seeded polymerization for the dispersion of (toluene/divinylbenzene)-swollen polystyrene (PS) particles prepared utilizing the dynamic swelling method which Okubo et al. had proposed. In this chapter, the particles at various conversions of the seeded polymerization were observed with an optical microscope in detail. From the obtained results, the formation mechanism of the hollow structure was suggested as follows. As the seeded polymerization proceeds, polydivinylbenzene (PDVB) molecules precipitated in the swollen particle are trapped near the interface and gradually piled at the inner surface, which results in cross-linked PDVB shell. PS which dissolve in the swollen particles are repelled gradually to the inside. After the completion of the polymerization, toluene in the hollow evaporates by drying, and PS clings to the inner wall of the shell uniformly.

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Chapter 4

Production of micron-sized, monodisperse, nonspherical polymer particles having red blood corpuscle shape

4.1 Introduction

In general, emulsion polymerization produces spherical particles within the limits of resolution of electron microscope, of which shape is arisen from the surface tension force. However, in a series of investigations on the production of submicron-sized composite polymer particles by seeded emulsion polymerization technique, Okubo et al. have found the preparation of various nonspherical polymer particles: “confetti-like” [1], “raspberry-like” [2, 3], “void-containing” [4], “snowman-like” [5], “octopus ocellatus-like” [6] and “golf ball-like” [7, 8].

On the other hand, recently, many researchers studying polymer colloids are concentrating their attention on the production of micron-sized monodispersed polymer particles [9-13] which have been applied in the biomedical field, microelectronics, etc. We have been producing micron-sized monodispersed polymer particles having functional groups such as chloromethyl [14] and vinyl groups [15, 16] by seeded dispersion copolymerizations of styrene with chlorometyl styrene and divinylbenzene, respectively, in the presence of about 2 μm-sized monodispersed PS particles as seed. Moreover, in order to produce monodispersed particles having the diameter above 5 μm, Okubo et al.suggested seeded polymerization utilizing a novel swelling method of seed polymer particles with a large amount of monomer, which was named “the dynamic swelling method (DSM)” [17, 18]. In previous articles [19, 20], this technique was developed to produce micron-sized monodispersed polymer particles having one hollow in the inside, and the formation mechanism of hollow structure was proposed [21]. Moreover, in the production process of the hollow polymer particles, nonspherical polymer particles having “rugby ball-like” and “red blood corpuscle-like” shapes were observed at low conversions of the seeded polymerization.

Similar nonspherical polymer particles were prepared by Hoshino et al. [22] and Rudin et al. [23], but their formation mechanisms should be quite different from that of our produced polymer particles.

In this chapter, it will be clarified the conditions under which such nonspherical polymer particles are produced effectively at the completion of the seeded polymerization.

4.2 Experimental

4.2.1 Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Purity 96 and 55% divinylbenzenes (96-DVB and 55-DVB, supplied by Nippon Steel Chemical. Co. Ltd) and vinyltoluene (VT) were washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. Benzoyl peroxide (BPO) and 2, 2'-azobisisobutyronitrile (AIBN) of reagent grade were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Poly(vinyl 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 stabilizer was prepared by solution polymerization of acrylic acid in 1,4-dioxane [14]. Reagent grade ethanol and analytical grade xylene, toluene, tetrahydrofuran, 1,4-dioxane and N, N-dimethylformamide were used as received.

4.2.2 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 in the previous article [14]. The PS seed particles were spherical and monodispersed: the number-average diameter (*Dn*) and coefficient of variation (*Cv*) were 1.71 μm and 2.2%, respectively.

4.2.3 Swelling of seed particles with DVB and solvent utilizing DSM

Swelling of the PS seed particles with DVB (and VT) and toluene or xylene was carried out using DSM as follows. Ethanol, water, DVB (and VT), toluene or xylene, BPO, and PVA were charged into a four-necked round-bottom flask or into a glass cylindrical reactor. The homogeneous solution was mixed with the PS seed dispersion. Finally, water was added to the mixture with a micro feeder at a rate of 18 ml/h or 2.88 ml/h under stirring.

4.2.4 Seeded polymerization

Seeded polymerizations for the dispersions of (monomer/solvent)-swollen PS particles were carried out in a four-necked round-bottom flask or in sealed glass tubes under a nitrogen atmosphere at 70°C for 24 h. The flask was stirred at 80 rpm and the tubes were horizontally shaken at 120 cycles/min (2-cm strokes).

The conversion was measured by gas chromatography (Yanaco, G-2800, Japan) with nitrogen as a carrier gas. Dimethylformamide was used as solvent and *p*-xylene used as standard reagent. The dispersions were dropped onto slide glasses, and then each droplet was covered with a cover glass and observed with Nikon MICROPHOT-FXA optical microscope, a JEOL JEM-200CX transmission electron microscope (TEM) and a Hitachi S-2500 scanning electron microscope (SEM).

4.3 Results and discussion

Figures 1 and 2 show, respectively, TEM and SEM photographs of PS/PDVB composite particles at various conversions produced by seeded polymerization for the dispersion of (55-DVB/toluene)-swollen PS particles prepared utilizing DSM, under the conditions listed in Table 1. The composite polymer particles at 15% conversion were bigger than the PS seed particles and spherical. They had a “rugby ball-like” shape at 33% conversion and “red blood corpuscle” shapes at 51 and 66% conversions. At 75% conversion, they were spherical ones having a hollow structure.

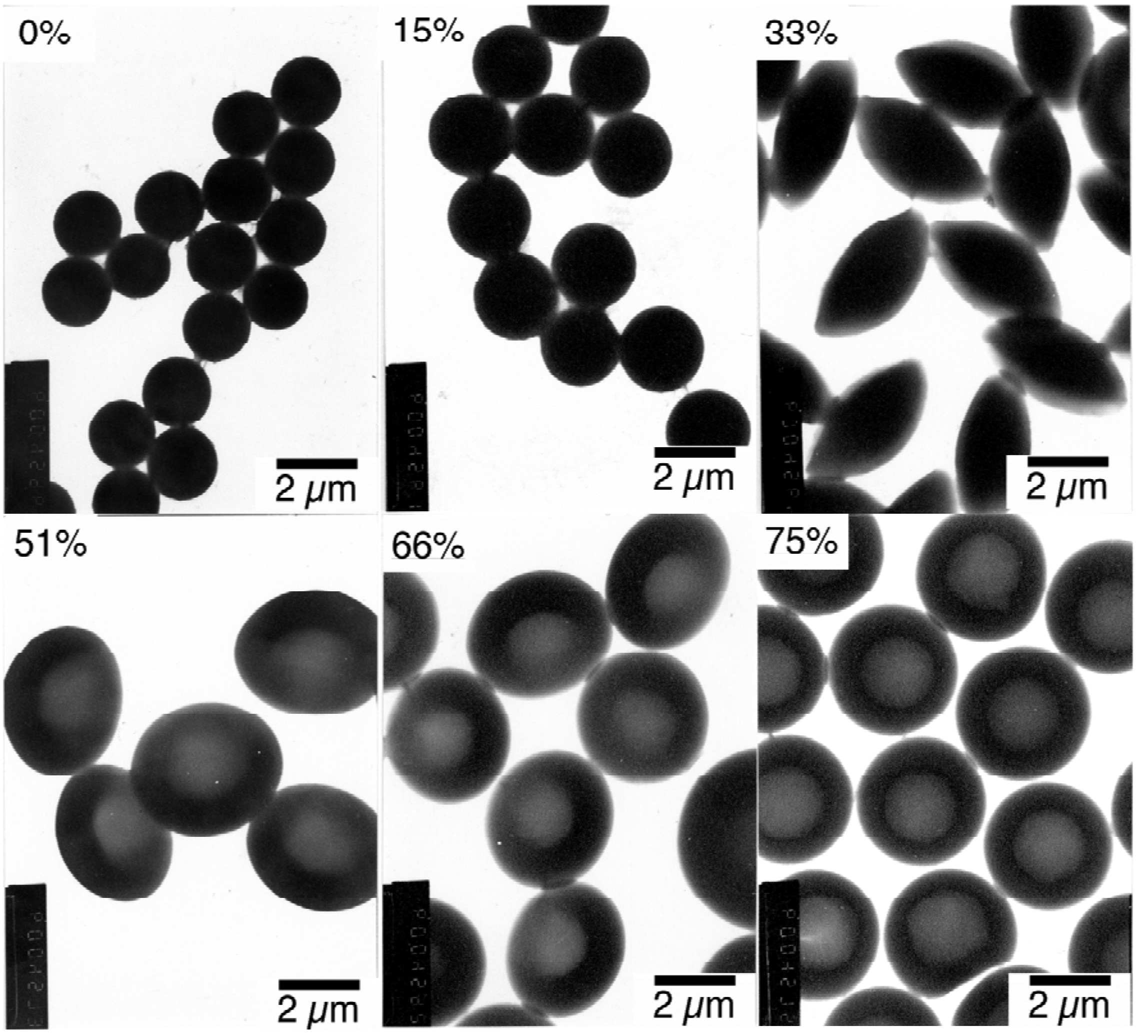


Fig. 1 TEM photographs of PS/PDVB composite particles at various conversions of the seeded polymerization for the dispersion of (55-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swilling method under the conditions listed in Table 1

Figure 3 shows optical micrographs of the PS/PDVB composite particles at 66% conversion of 55-DVB, whose dispersion was left at room temperature in a capless small vessel for 0 h (a), 12 h (b) and 24 h (c) after it was pipetted off. The particles transformed from spherical shape to nonspherical one with the time. Such a transformation was not observed when the sample dispersion was kept in a sealed small vessel to prevent the evaporations of unpolymerized DVB and toluene. These results suggest that the shapes of

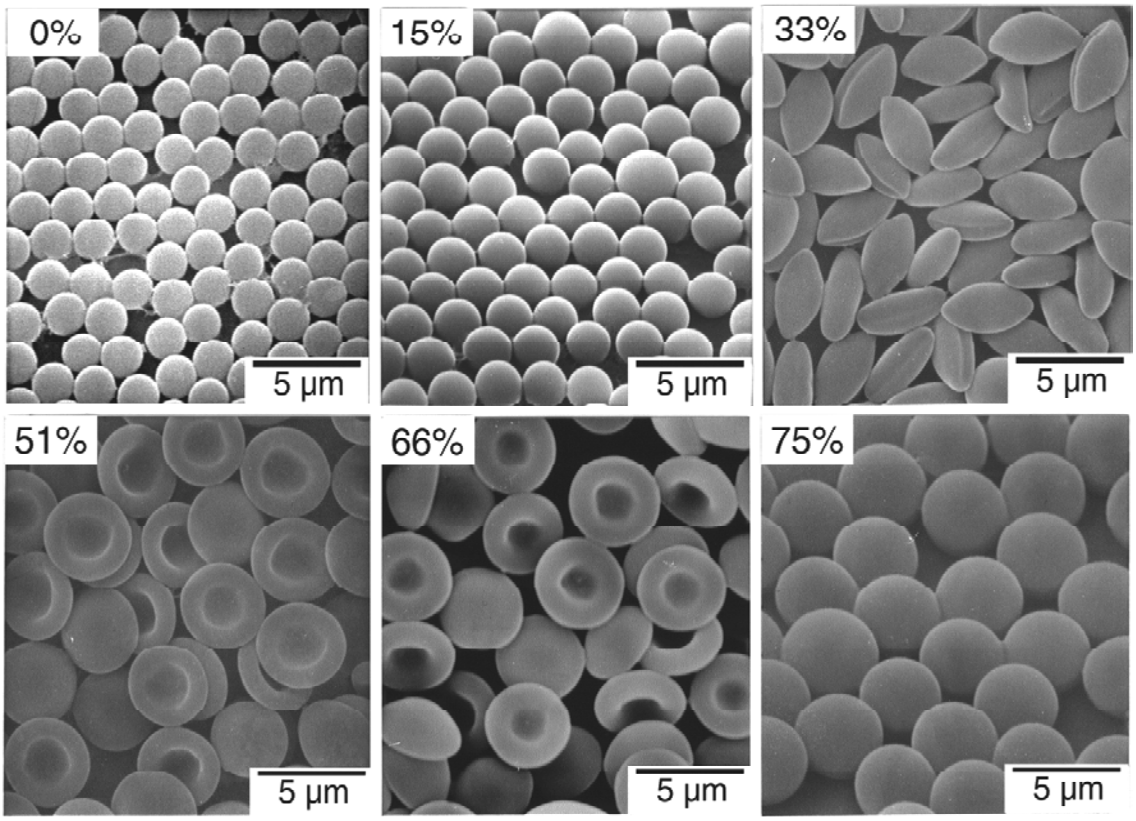


Fig. 2 SEM photographs of PS/PDVB composite particles at various conversions of the seeded polymerization for the dispersion of (55-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swilling method under the conditions listed in Table 1

the dried composite particles at the various conversions shown in Figs. 1 and 2 are formed as follows.

At the low conversion of 15%, since the shell is not formed yet, the composite particles shrink homogeneously to spherical ones by evaporations of unpolymerized DVB and toluene. At the middle conversions (33~66%), the composite particles have cross-linked shells. When unpolymerized DVB and toluene are evaporated from the composite particles having cross-linked shell, water (and ethanol) should penetrate into the hollow from the medium (ethanol/water: 14/86, w/w) because the hollow space is evacuated. However, since the shell is hydrophobic, the penetration rate of water into the

Table 1 A recipe for the production of PS/PDVB (1/5.5, w/w) composite particles by the seeded polymerization[a)] for the dispersion of (DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method at room temperature

Ingredients		
PS particles[b)]	(g)	0.3
55-DVB[c)]	(g)	3.0
Toluene	(g)	1.5
BPO	(g)	0.06
PVA	(g)	0.15
Ethanol	(g)	70
Water	(g)	30 + 400[d)]

a) N_2, 70°C, 24 h.

b) Dn, 1.7 μm; Cv, 2.2%

c) Purity, 55 % (by catalog).

d) 400 g of water was post-added at the rate of 18 ml/h.

Abbreviations: PS, polystyrene; DVB, divinylbenzene; BPO, benzoyl peroxide; PVA, poly(vinyl alcohol).

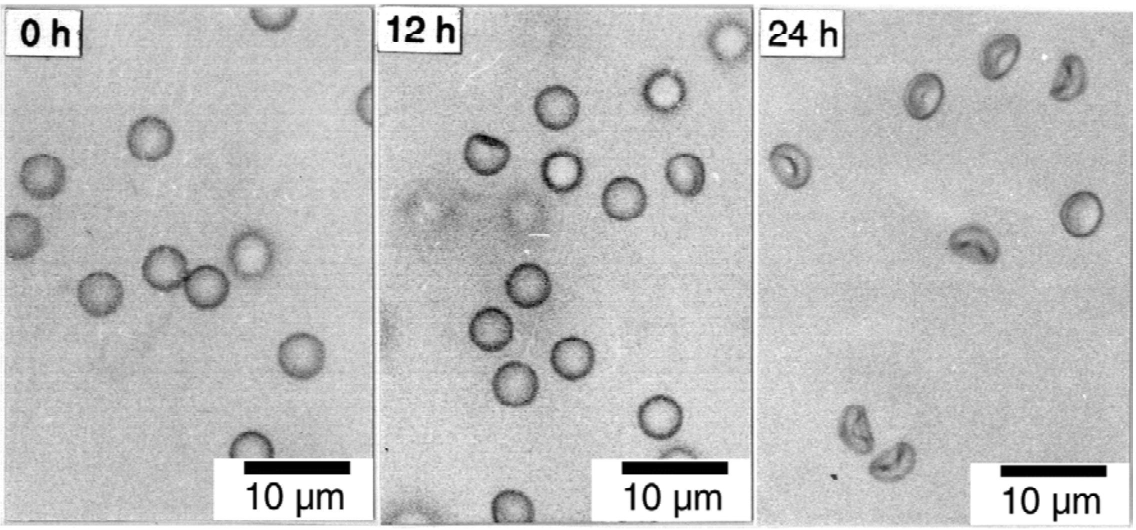
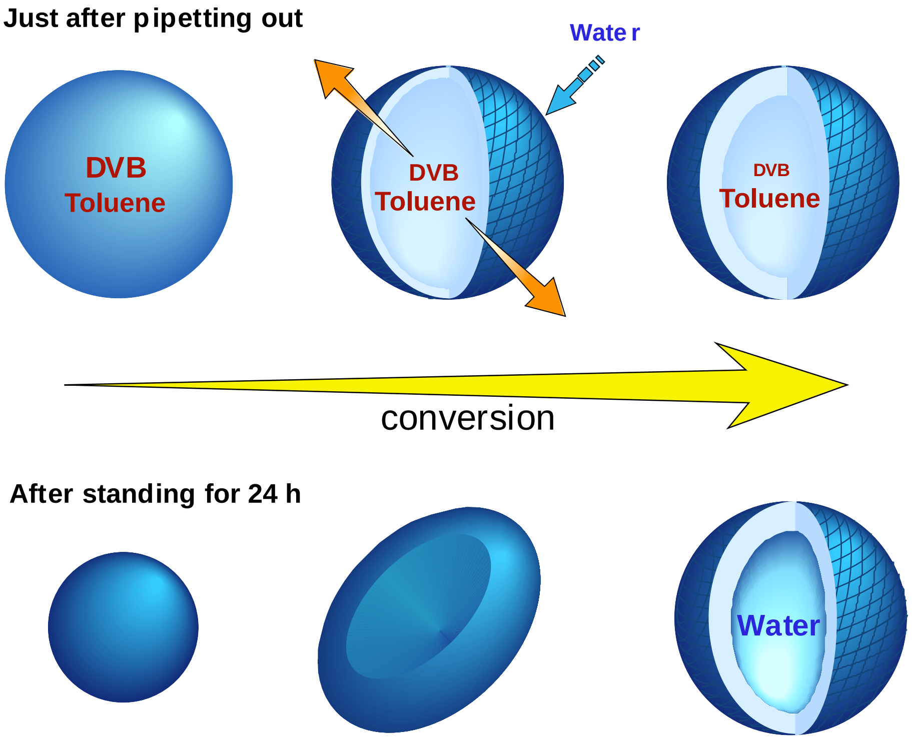


Fig. 3 Optical micrographs of PS/PDVB composite particles at 66% conversion of the seeded polymerization for the dispersion of (55-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions listed in Table 1, after the polymer dispersion was kept in a capless vessel for different times (h): (a) 0, (b) 12, (c) 24.

hollow is much slower than the evaporation rates of DVB and toluene from the hollow [24]. As the result, a part of the shell caves in because the thicknesses are not enough to withstand the pressure. At the high conversion (75%), the composite particles have an enough tough cross-linked shell to maintain spherical shape and the space from which unpolymerized DVB and toluene evaporate is occupied by the medium after some time lag.

Figure 4 shows optical micrographs of PS/ PDVB composite particles at various conversions of seeded polymerization for the dispersion of (96-DVB/ toluene)-swollen PS particles prepared by utilizing DSM, under the conditions of No. 1 listed in Table 2. They were left in capless vessels for 24 h after pipetted off. In comparison with the result obtained using 55-DVB shown in Fig. 2, a similar result was obtained, but there was a clear difference around conversion of 60%. That is, the composite particles prepared with 96-DVB



at 60% conversion had a spherical shape, but those with 55-DVB at 66% conversion had the red blood corpuscle-like shape. This difference seems to be based on the difference in cross-linking densities between their shells.

In order to change the penetration rate of the medium into the hollow of the composite particle, a small amount of dispersion at 25% conversion of 96-DVB, just after pipetted off from the polymerization system, was immediately dispersed in a large amount of various solvents which have different solubility parameters as shown in Table 3 and are miscible with water, DVB and toluene.

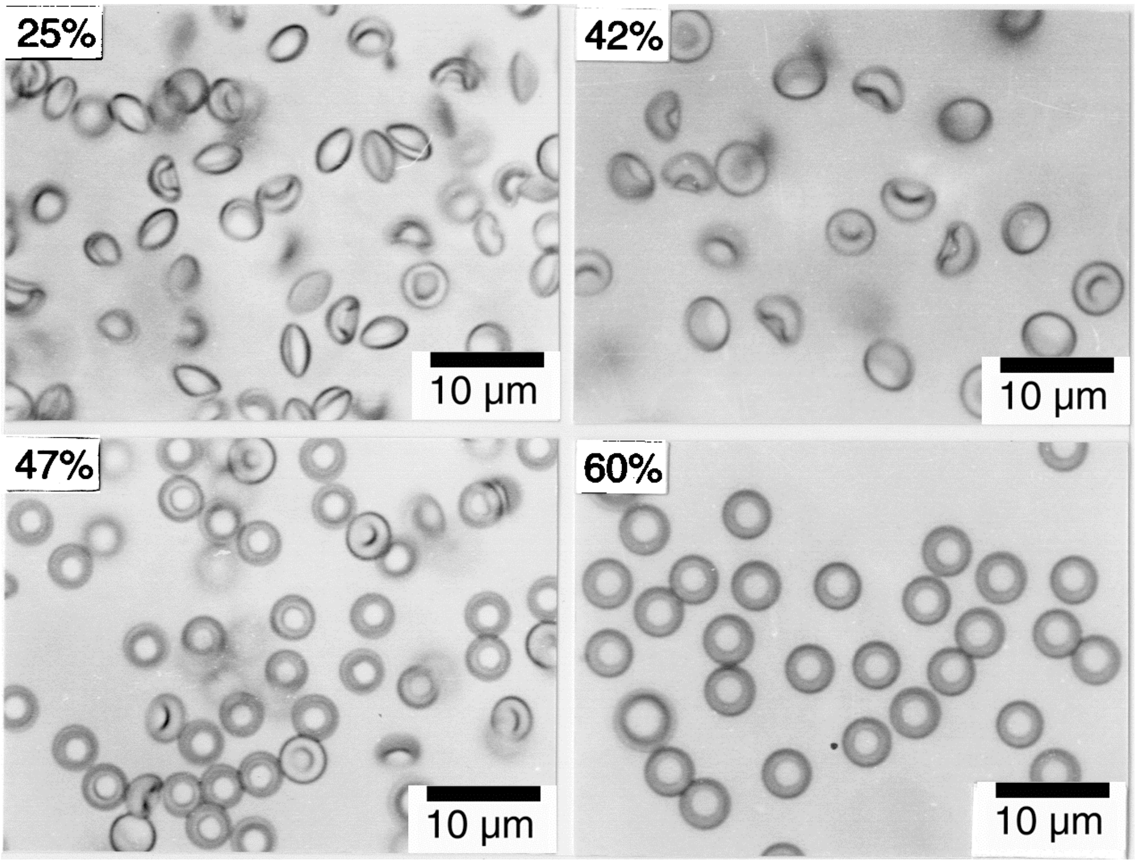


Fig. 4 Optical micrographs of PS/PDVB composite particles at the various conversions of the seeded polymerization for the dispersion of (96-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 2, after each polymer dispersion was kept in a capless vessel for 24 h.

Table 2 Recipes for the productions of PS/PDVB and PS/P(DVB-VT) composite particles by seeded polymerizations[a] for the dispersions of (DVB/xylene)- and (DVB/VT/xylene)-swollen PS particles, respectively, prepared by utilizing the dynamic swelling method at room temperature

Ingredients		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
PS particles[b]	(mg)	30	30	30	30	30	30
96-DVB[c]	(mg)	300	120	60	60	30	15
VT	(mg)	-	-	-	60	90	105
Xylene	(mg)	150	330	390	330	330	330
PVA	(mg)	15	15	15	15	15	15
BPO	(mg)	6.0	2.4	1.2	2.4	2.4	2.4
Ethanol	(g)	7	7	7	7	7	7
Water	(g)	43[d]	43[d]	43[d]	43[d]	43[d]	43[d]

[a] N_2, 70°C, 24 h.

[b] Dn, 1.7 µm; Cv, 2.2%

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

[d] 40 g of water was post-added at the rate of 2.88 ml/h.

Abbreviations: PS, polystyrene; DVB, divinylbenzene; VT, vinyltoluene; PVA, poly(vinyl alcohol); BPO, benzoyl peroxide.

Table 3 Solubilitiy parameters[a] (δ) of polystyrene and solvents

	δ [(MPa)$^{1/2}$]
Polystyrene	17.5
Tetrahydrofuran	18.6
1, 4-Dioxane	20.5
N, N-Dimethylformamide	24.8
Ethanol	26.0

[a] *"POLYMER HANDBOOK" 3rd Ed.*, JOHN WILLY & SONS (1989).

Figure 5 shows optical micrographs of the dispersed particles. In the tetrahydrofuran system (a), they were spherical hollow particles. In 1,4-dioxane (b) and N,N-dimethylfolmamide (c) systems, the hollow structure was observed in the composite particles, and the shape of some particles was not spherical and the shell lightly caved in. In the ethanol system (d), all the particles completely caved in. As the solubility parameter of the solvents deviates from that of PS, the degree of dent of the composite particles became remarkable. This suggests that the transformation is based on the dif-

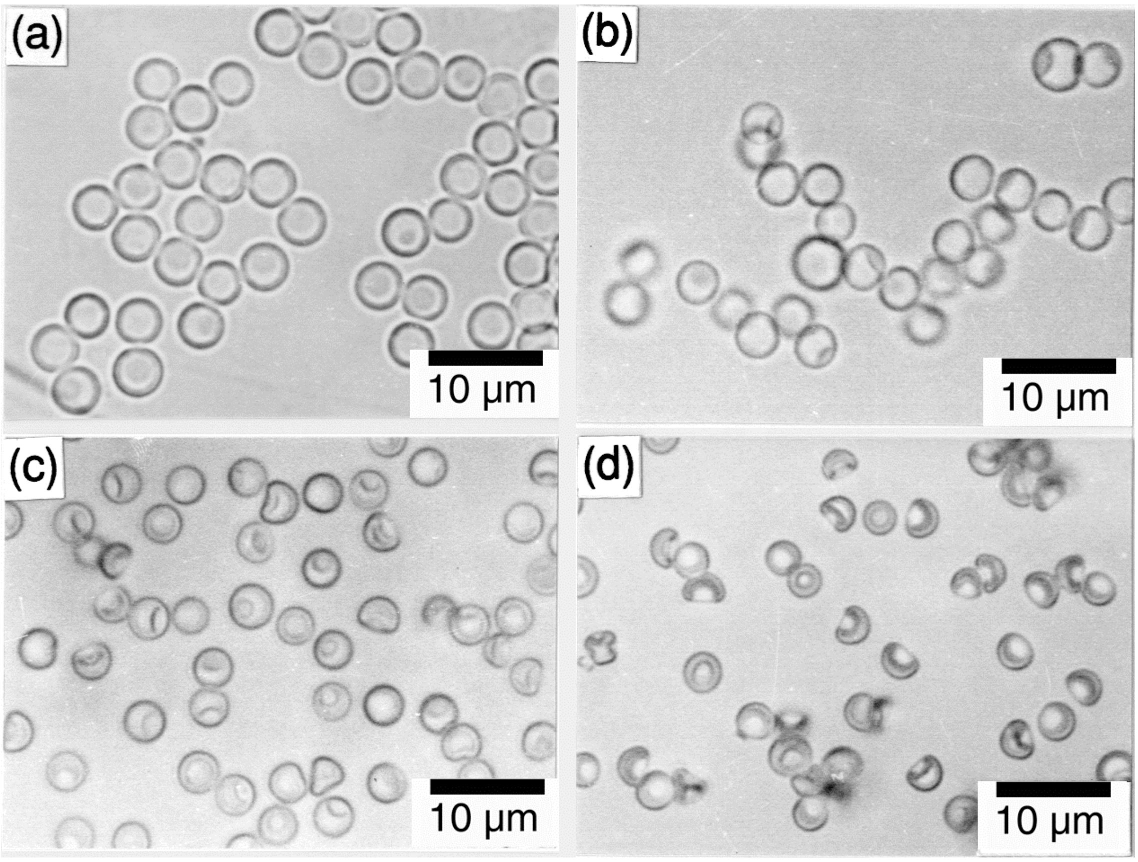


Fig. 5 Optical micrographs of PS/PDVB composite particles at 25% conversion of the seeded polymerization for the dispersion of (96-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions listed in Table 2, of which a small amount of pippetted dispersion was mixed with a large amount of tetrahydrofuran (a), 1,4-dioxane (b), N, N-dimethylformamide (c) and ethanol (d)

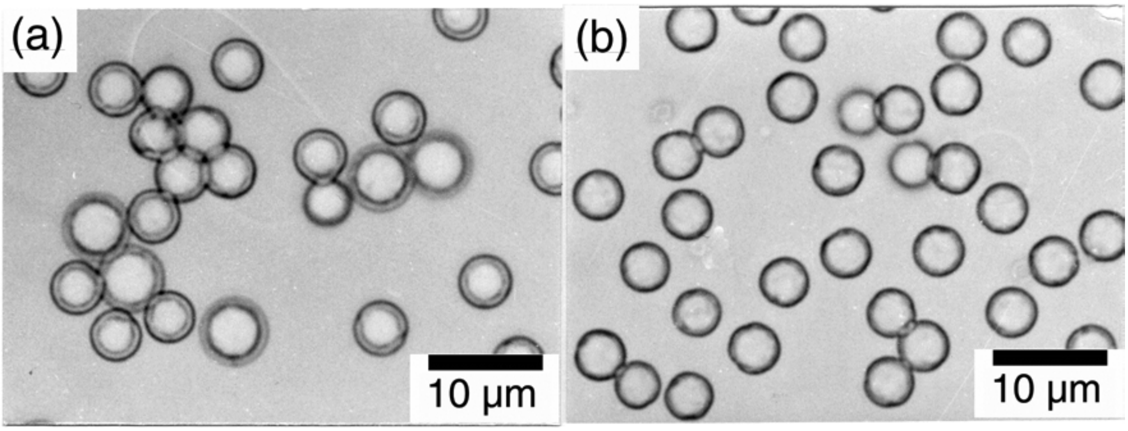


Fig. 6 Optical micrographs of PS/PDVB composite particles at 100% conversion of the seeded polymerizations for the dispersions of (96-DVB/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions of Nos. 2 (a) and 3 (b) listed in Table 2: PS/96-DVB/xylene (weight ratio): (a) 1/4/11; (b) 1/2/13

ference between the release rates of DVB and toluene and the penetration rates of the media.

Figure 6 shows optical micrographs of PS/PDVB composite particles at 100% conversion of the seeded polymerizations for the dispersions of (96-DVB/xylene)-swollen PS particles prepared by utilizing DSM, under the conditions of Nos. 2 (a) and 3 (b) listed in Table 2. These composite particles produced at the two xylene/96-DVB ratios should have the same diameter as No. 1-particle at 100% conversion and different shell thicknesses, if the produced composite particles have the hollow structure. All the composite particles had the hollow structure. Nos. 2 and 3-particles were spherical. No. 3-particles didn’t cave in, although their shell thickness was thinner than that (Fig. 4) of the dented No. 1-particles at 25% conversion. This seems to be based on that the cross-linking density in the shell of No.3-particles is higher than that of No. 1-particles at 25% conversion, because the possibility of reaction of the dangling vinyl groups, which gives cross-linking, must be higher in the former than in the latter.

Figure 7 shows optical micrographs of PS/P(DVB-VT) composite particles at 100% conversion of the seeded polymerizations for the dispersions of (96-DVB/VT/xylene)-swollen PS particles prepared utilizing DSM, under the conditions of Nos. 4 (a), 5 (b) and 6 (c) listed in Table 2: 96-DVB/VT (w/w): (a) 1/1; (b) 1/3; (c) 1/7. The three kinds of composite particles should have different cross-linking densities and the same shell thickness as No. 1-particles at 40% conversion at which the dented composite particles were observed. The percentage of dented composite particles increased with a

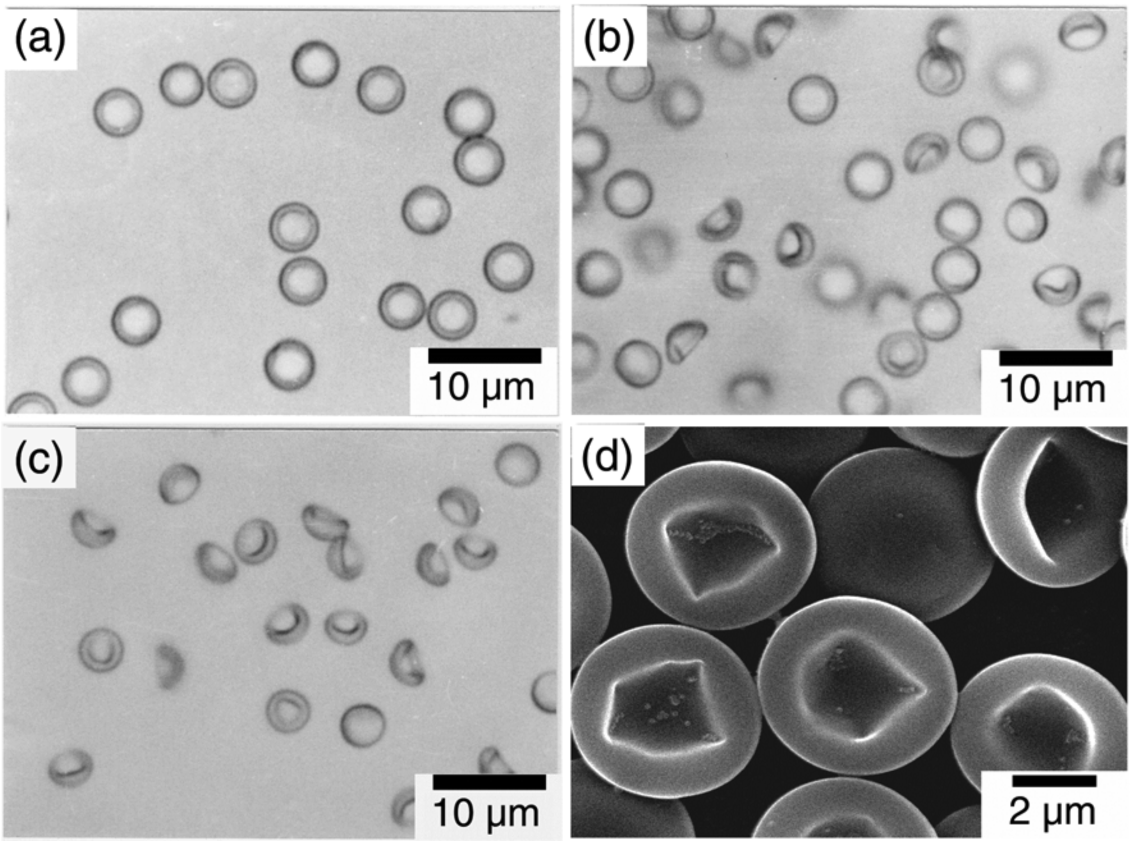


Fig. 7 Optical (a, b, c) and SEM (d) micrographs of PS/P(DVB-VT) composite particles at 100% conversion of the seeded copolymerizations for the dispersions of (96-DVB/VT/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions of Nos. 4 (a), 5 (b) and 6 (c, d) listed in Table 2: PS/96-DVB/VT/xylene (weight ratio): (a) 1/2/2/11; (b) 1/1/3/11; (c, d) 1/0.5/3.5/11

decrease in the cross-linking density, and all No. 6-particles had the red blood corpuscle-shape. This was more clearly shown in SEM observation (d).

From the above results, it is concluded that micron-sized monodispersed nonspherical polymer particles having the red blood corpuscle shape can be prepared by evaporation of xylene from the hollow in the composite particles having an optimum cross-linking density and shell thickness, produced by the seeded polymerization for (DVB and/or VT/xylene)-swollen PS particles prepared by utilizing DSM.

4.4 Conclusion

Micron-sized monodispersed polymer particles having a "red blood corpuscle-shape" were produced effectively at the completion of the seeded polymerization for the dispersion of highly (divinylbenzene/toluene)-swollen polystyrene particles prepared in an ethanol/water medium by utilizing the dynamic swelling method under optimum ratios of xylene/divinylbenzene and vinyltoluene/divinylbenzene

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Chapter 5

Production of micron-sized, monodisperse, transformable rugby-ball-like-shaped polymer particles

5.1 Introduction

Recently, many researchers studying polymer colloids are concentrating their attention on the production of micron-sized, monodisperse polymer particles [1-5] which have been applied in the biomedical field, microelectronics, etc. We have also been producing micron-sized, monodisperse polymer particles having functional groups such as chloromethyl [6] and vinyl groups [7, 8] by seeded dispersion copolymerizations of styrene with chloromethyl styrene and divinylbenzene, respectively, in the presence of about 2 μm-sized, monodisperse PS particles as seed. In order to produce monodisperse particles having a diameter above 5 μm, we suggested seeded polymerization utilizing a novel swelling method to make seed polymer particles absorb with a large amount of monomer, which was named “the dynamic swelling method (DSM)” [9, 10]. Moreover, we produced micron-sized, monodisperse, cross-linked polymer particles having one hollow in the inside by utilizing the seeded polymerization with DSM, in which hydrophobic solvent such a toluene and xylene was used for the formation mechanism of hollow structure [11-13].

In general, emulsion, suspension, and dispersion polymerizations produce spherical particles within the limits of the resolution of electron microscopy. We have already been producing various nonspherical composite polymer particles by utilizing seeded emulsion polymerization [14-21] and seeded dispersion polymerization [22-24]. Moreover, in the process of the seeded polymerization for the production of hollow polymer particles described above, nonspherical polymer particles having “rugby ball-like” and “red blood corpuscle-like” shapes, from which solvent was removed by spontaneous evaporation, were observed at low conversions [13]. Afterward, the conditions to produce the “red blood corpuscle-like” polymer particles at the completion of the seeded polymerization were clarified [25].

In this chapter, the conditions to produce the “rugby ball-like” polymer particles at the completion of the seeded polymerization will be clarified. In addition, it will be reported that the particle shape is reversibly transformable by absorbing and releasing of solvent.

5.2 Experimental

5.2.1 Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) and vinylbiphenyl (VBP) were supplied by Nippon Steel Chemical Co., Ltd., Tokyo, Japan. The purity of DVB, which included ethylvinylbenzene, was 96%. The purity of VBP, which included ethylbiphenyl, methylbiphenyl and biphenyl, was 75%. DVB, VBP and vinyl toluene (VT) were washed with 1 N NaOH and deionized water to remove polymerization inhibitors before use. Reagent grade benzoyl peroxide

(BPO) and 2,2'-azobisisobutyronitrile (AIBN) were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Poly(vinyl alcohol) (PVA) used as a colloidal stabilizer was supplied by Nippon Synthetic Chemical Ind. Co., Ltd., Osaka, Japan (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 [6]. Reagent grade ethanol and analytical grade xylene, toluene, 1,4-dioxane, dodecyl alcohol and chlorobenzene were used as received.

5.2.2 Preparation of PS seed particles

Micron-sized, monodisperse PS seed particles were produced by dispersion polymerization of styrene in an ethanol/water (7/3, w/w) medium in the presence of PAA 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 given in the previous article [6].

5.2.3 Measurement of solubilities of DVB, VT and VBP in ethanol/water medium

A large amount of DVB, VT or VBP was added to an ethanol/water (7/43, w/w) medium (50 g) in 100 mL-glass cylindrical reactors, and these reactors were left at 25°C for 4 h. The amount of DVB, VT or VBP dissolved in the ethanol/water medium was measured by gas chromatography (GC-18APFsc, SHIMADZU, Kyoto, Japan) with helium as a carrier gas.

5.2.4 Swelling of seed particles with monomers and xylene utilizing DSM

Swelling of the PS seed particles with DVB, VBP (or VT) and xylene was carried out utilizing DSM under the conditions described in Table 4 (or 2). The PS seed particles were dispersed in the homogeneous ethanol/water (7/3, w/w) solution dissolving DVB, VBP (or VT), BPO and PVA. Water (40 g) was added to the dispersion with a micro feeder at a rate of 2.66 ml/h under stirring with a magnetic stirrer for 15 h at room temperature.

5.2.5 Seeded polymerization

Seeded polymerization for the dispersions of (monomers/solvent)-swollen PS particles was carried out in sealed glass tubes under a nitrogen atmosphere at 70°C for 24 h. The tubes were horizontally shaken at 60 cycles/min (3-cm strokes). The conversion was measured by gas chromatography with helium as a carrier gas. Dodecyl alcohol (or chlorobenzene) and 1,4-dioxane were used as standard reagent and solvent, respectively. Droplets in the dispersion were observed on a slide glass, which was covered with a cover glass, with a Nikon MICROPHOT-FXA optical microscope.

5.2.6 Electron microscopy

A Hitachi H7100-TE electron microscope and a Hitachi S-2500 electron microscope were used for transmission electron microscopic (TEM) and scanning electron microscopic (SEM) observations, respectively. For the TEM samples, each emulsion was diluted down and a drop was placed onto a carbon-coated grid. For the SEM samples, each emulsion was dropped onto an aluminum plate. The samples were allowed to dry at room temperature in a desiccator.

5.3 Results and discussion

Figure 1 shows a TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1. PS particles were spherical and monodisperse: the number-average diameter (*Dn*) and coefficient of variation (*Cv*) were 1.71 µm and 2.2%, respectively, which were determined from the particle observation on TEM photographs with a Personal Image Analysis System (PIAS Co., Ltd., LA-525, Osaka, Japan).

Figure 2 shows TEM photographs of PS/P(DVB-VT) composite particles produced by seeded polymerizations for the dispersions of (DVB/VT/xylene)-swollen PS particles prepared by utilizing DSM under the conditions listed in Table 2. Ratios on the photographs indicate the weight ratios of

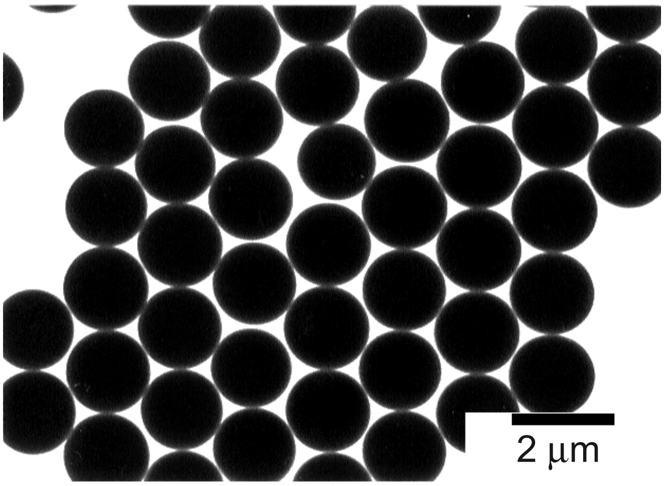


Fig. 1 A TEM photograph of PS seed particles produced by dispersion polymerization under the condition listed in Table 1

Table 1 A recipe for the preparation of micron-sized monodisperse PS seed particles by dispersion polymerization[a)]

Ingredient		
Styrene	(g)	140
AIBN	(g)	2.35
PAA	(g)	16.8
Ethanol	(g)	959
Water	(g)	280

[a)] 70℃; 24 h; N_2; stirring rate, 60 rpm

Abbreviations: PS, polystyrene; AIBN, 2,2'-azobisisobutyronitrile; PAA, poly(acrylic acid)

DVB/VT. These particles should have different cross-linking densities and the same shell thickness as the particles having "rugby ball-like" shape prepared at 33% conversion in the previous article [13]. At the DVB/VT weight rations of 1/6 and 1/12, the dried composite particles had nonspherical shapes,

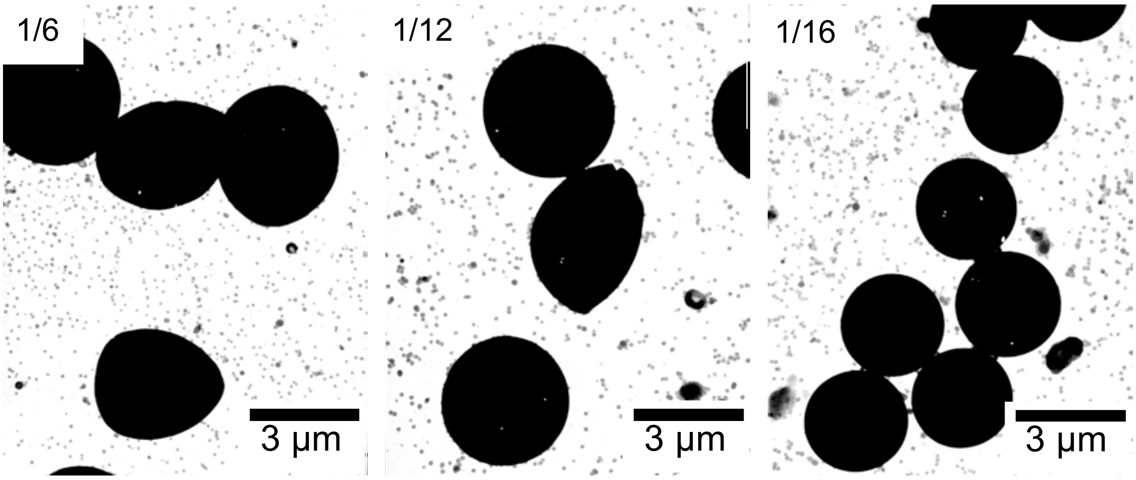


Fig. 2 TEM photographs of PS/P(DVB-VT) composite particles produced by seeded copolymerizaitions for the dispersions of (DVB/VT/xylene)-swollen PS particles prepared by utilizing DSM under the conditions listed in Table 2. Ratios on the photographs indicate the weight ratios of DVB/VT.

Table 2 Recipes for the productions of PS/P(DVB-VT) composite particles by seeded copolymerizations[a)] for the dispersions of (DVB/VT/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method

DVB/VT	(w/w)	1/6	1/12	1/16
PS particles[b)]	(mg)	30	30	30
96-DVB[c)]	(mg)	12.9	6.9	5.3
VT	(mg)	77.1	83.1	84.7
Xylene	(mg)	360	360	360
BPO	(mg)	1.8	1.8	1.8
PVA	(mg)	15	15	15
Ethanol	(g)	7	7	7
Water[d)]	(g)	43	43	43

[a)] In sealed tube: 70℃; 48 h; N_2; shaking rate, 60 cycles/min (3-cm strokes)

[b)] D_n, 1.7 μm; C_v, 2.2%

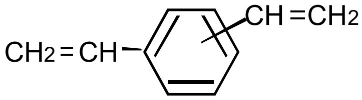
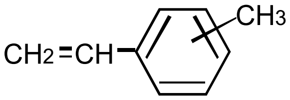
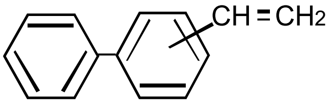
[c)] Purity, 96% (by catalog)

[d)] Water (40 g) was post-added at the rate of 2.66 ml/h using a microfeeder

Abbreviations: PS, polystyrene; DVB, divinylbenzene; VT, vinyltoluene; BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

which were produced at completion of the seeded polymerization. At the DVB/VT weight ratio of 1/16, the dried composite particles had a spherical shape because the cross-linked shell was not formed. In each system, a lot of 150 nm-sized by-product particles were observed with TEM as shown in Fig 2, though they were not observed with optical microscope. The amounts of the by-product particles were determined to be above 30% of the total monomers (DVB and VT) by gravimetric analysis. These indicate that the polymerization did not always proceed in the swollen particles, which gave difficulty to control the cross-linking density and shell thickness of the composite polymer particles. This seems to be based on high solubility of VT in the polymerization medium compared with DVB as shown in Table 3. In order to depress

Table 3 Solubilities of monomers in ethanol/water medium (14/86, w/w) at 25°C

Monomer		Solubility (%)
DVB		0.005
VT		0.016
VBP		~0

Abbreviations: DVB, divinylbenzene; VT, vinyltoluene; VBP, vinylbiphenyl

the formation of by-product particles, VBP, which has low solubility in the medium as shown in Table 3, was used in place of VT.

Figures 3 and 4 show, respectively, TEM and SEM photographs of PS/P(DVB-VBP) composite particles produced by seeded polymerization for the dispersion of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing DSM, under the conditions listed in Table 4. Ratios on the photographs indicate the weight ratios of DVB/VBP. As shown in Fig. 3, by-produced particles were hardly observed in all systems. These suggest that the polymerization proceeded effectively in the swollen particles, and the cross-linking density and shell thickness of the composite polymer particles were controlled. As shown in Fig. 4, all the composite particles were nonspherical ones at the completion of seeded polymerization. The cave became bigger with a decrease in the cross-linking density. This suggests that the shell strength

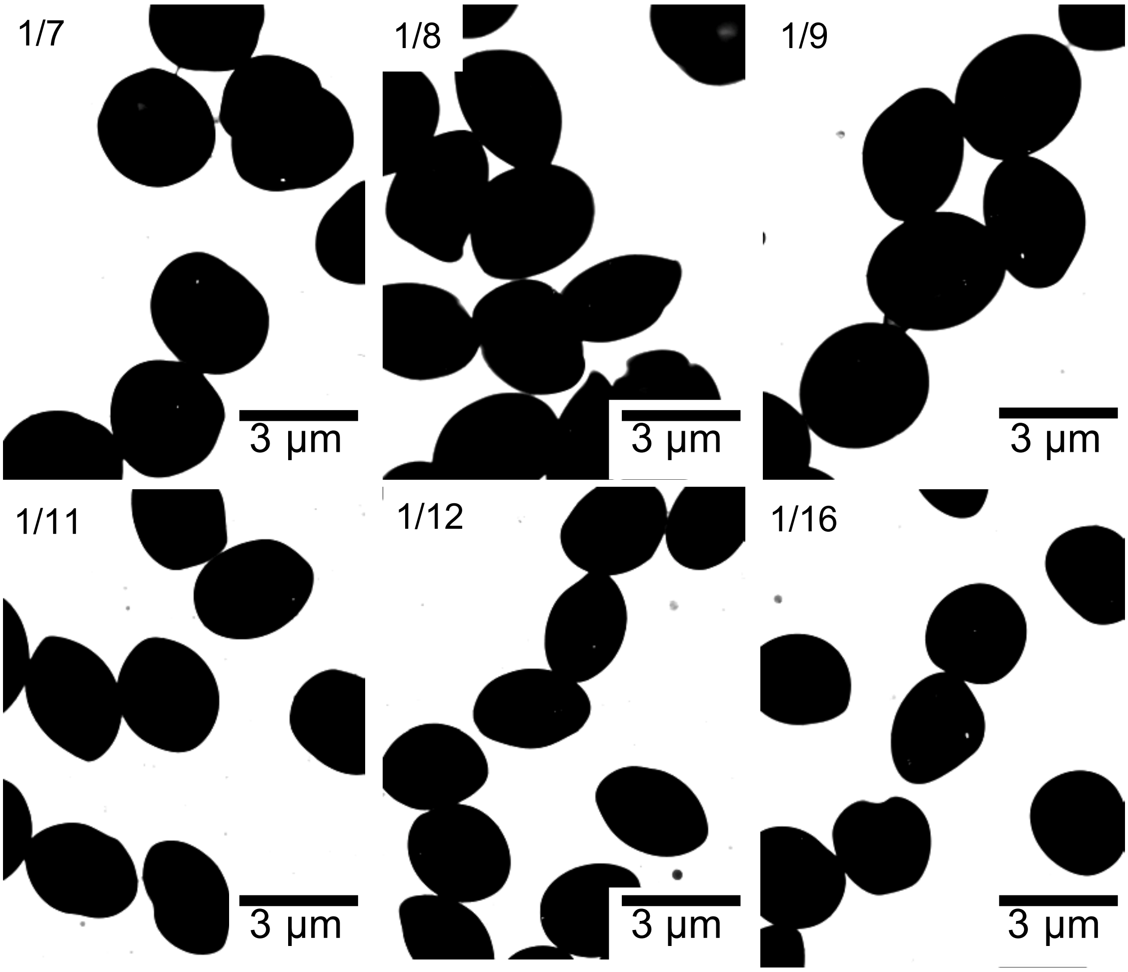


Fig. 3 TEM photographs of PS/P(DVBVBP) composite particles produced by seeded copolymerizations for the dispersions of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing DSM under the conditions listed in Table 4. Ratios on the photographs indicate the weight ratios of DVB/VBP.

of the composite polymer particle decreased with the decrease in the crosslinking density. When the ratios of DVB/VBP were 1/11 ~ 1/16 (w/w), PS/P(DVB-VBP) composite particles having a “rugby ball-like” shape were successfully produced. There were also observed some particles having a red blood corpuscle-like or spherical shape rather than the rugby ball-like shape at the ratios of 1/11 and 1/16, respectively. This indicates that the crosslinking density had a distribution among the composite particles, which had

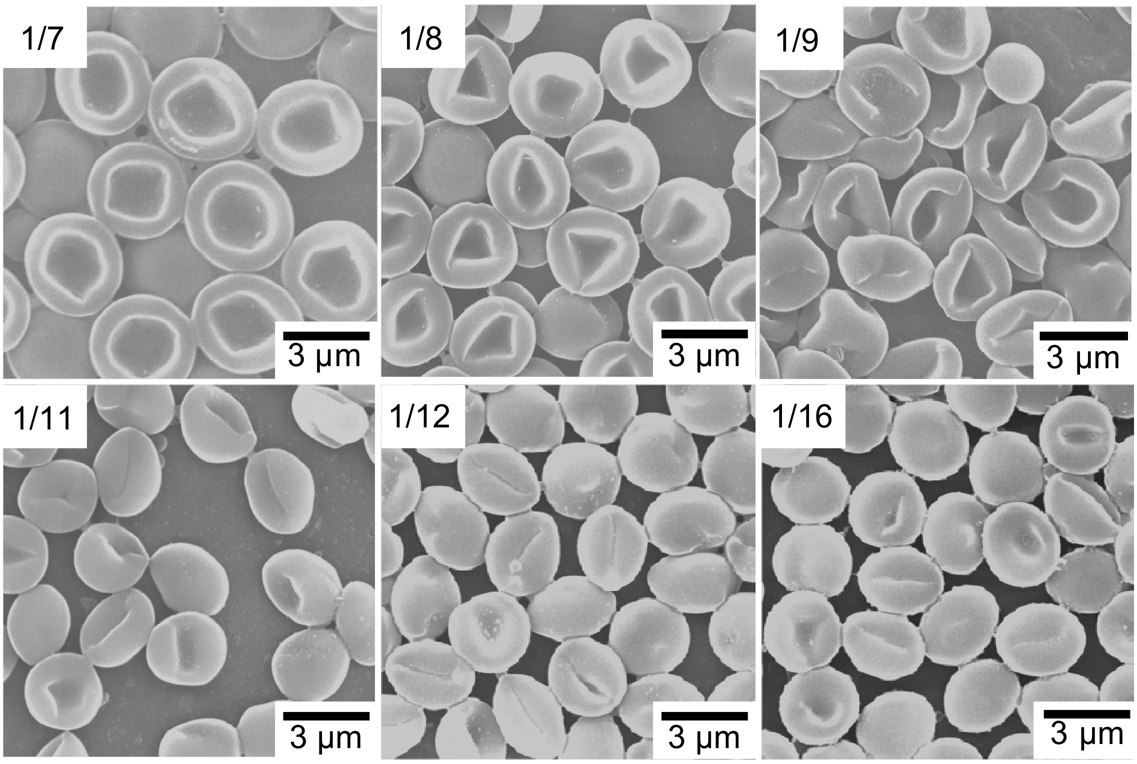


Fig. 4 SEM photographs of PS/P(DVBVBP) composite particles produced by seeded copolymerizations for the dispersions of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing DSM under the conditions listed in Table 4. Ratios on the photographs indicate the weight ratios of DVB/VBP.

been already discussed in the previous articles [13, 26]. The schematic diagram of the relation between the cross-linking density and particle shape is shown in Fig. 5. Under the same shell thickness (the shell thickness also affect the particle shape), as the cross-linking density decreases, the shape changes in order of the hollow spherical (I), red blood corpuscle-like (II), rugby ball-like (III), and spherical (IV) shapes though the boundaries are not clear. The cross-linking densities of the composite particles produced at the DVB/VBP weight ratios of 1/7 and 1/12 are contained in single regions II and III, respectively. On the other hand the cross-linking at 1/11 and 1/16 systems, respectively, ranges from regions II to III and regions III to IV, which

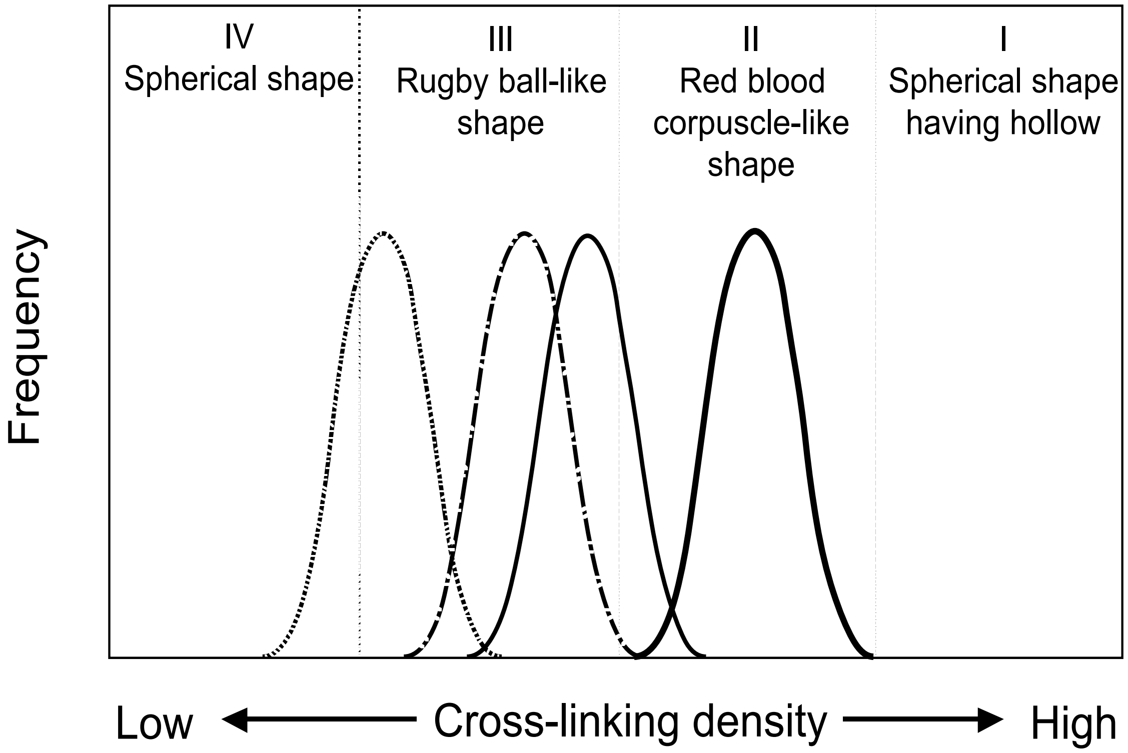


Fig. 5 Schematic diagram showing the relationship between the cross-linking density and the shape for the PS/P(DVB-VBP) composite particles having the same shell thickness. Curves indicate distribution of cross-linking density among the composite particles: DVB/VBP (w/w): 1/7, ▬ ; 1/11, — ; 1/12, - - - ; 1/16, ····· .

result in a mixture of particles having different shapes in the each system.

In drying process, xylene in the hollow evaporated faster than the medium. The medium should penetrate into the hollow through the hydrophobic shell because the hollow space is evacuated. However, the penetration rate of the medium into the hollow through the shell is much slower than the evaporation rate of xylene from the hollow. As a result, when they had low cross-linking density or thin shell thickness, which are not enough to withstand the water pressure, a part of the shell caved in during drying as discussed in the previous article [25].

These rugby ball-like PS/P(DVB-VBP) (DVB/VBP=1/12, weight ratio) composite particles transformed from spherical shape after the polymer dispersion was kept in a capless vessel for 24 h as shown in Fig 6a. To absorb toluene, which is good solvent for the polymer, 200 μL of toluene was added to 10 mL of the dispersion of the nonspherical composite particles, and the dispersion was left for 3 h under stirring with a magnetic stirrer at room temperature. Interestingly, the composite particles at the original state were changed from the rugby ball-like shape (Fig. 6a) to spherical one (Fig. 6b). Moreover, the spherical shape was changed to the rugby ball-like shape by releasing of toluene again (Fig 6c).

From above results, we clarified that the micron-sized, monodisperse, “rugby ball-like” polymer particles could be produced by the seeded polymerization for (DVB/VBP/xylene)-swollen PS particles prepared by utilizing DSM at the optimum conditions: monomers/xylene=1/4 and DVB/VBP=1/11 ~ 1/16 (weight ratios). Moreover, the unique shape was reversibly transformable to/from by absorbing/ releasing of toluene.

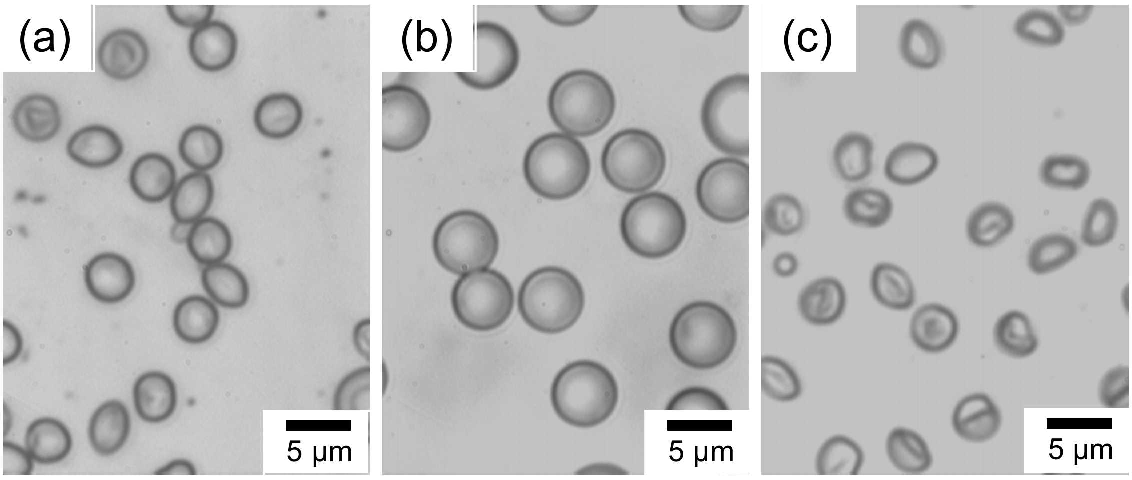


Fig. 6 Optical micrographs of PS/P(DVB-VBP) (DVB/VBP=1/12) composite particles at various conditions: (a) original state; (b) toluene absorbed-state; (c) toluene released-state

5.4 Conclusion

Micron-sized, monodisperse, "rugby ball-like" polymer particles were produced by seeded polymerization for the dispersion of (divinylbenzene/vinylbiphenyl/xylene)-swollen polystyrene particles prepared by utilizing the dynamic swelling method which Okubo et al. proposed in 1991. The shape of the composite polymer particle was reversibly transformed between rugby ball-like shape and spherical one by absorbing/releasing of toluene.

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Chapter 6

Influence of shell strength on shape transformation of micron-sized, monodisperse, hollow polymer particles

6.1 Introduction

Recently, many researchers studying polymer colloids are concentrating their attenRecently, many researchers studying polymer colloids are concentrating their attention on the production of micron-sized, monodisperse polymer particles [1-5], which have been applied in the biomedical field and microelectronics. We have also been producing micron-sized, monodisperse polymer particles having functional groups such as chloromethyl [6] and vinyl groups [7, 8] by seeded dispersion copolymerizations of styrene with chloromethyl styrene and divinylbenzene, respectively, in the presence of about 2 μm-sized, monodisperse PS particles as seed. In order to produce monodisperse polymer particles having a diameter above 5 μm, we suggested seeded polymerization utilizing a novel swelling method to make seed polymer particles absorb with a large amount of monomer, which was named “the dynamic swelling method (DSM)” [9, 10]. Moreover, we produced micron-sized, monodisperse, cross-linked polymer particles having one hollow in the center by utilizing the seeded polymerization with DSM, in which hydrophobic solvent such as toluene and xylene was used for the formation of hollow structure [11-13]. In the process of the seeded polymerization for the production of hollow polymer particles described above, nonspherical polymer particles having “rugby ball-like” and “red blood corpuscle-like” shapes, from which solvent was removed by spontaneous evaporation, were observed at low conversions [13]. Afterward, the conditions to produce the “red blood corpuscle-like”[14] and “rugby ball-like”[15] polymer particles at the completion of the seeded polymerization were clarified. It was also reported that the nonspherical polymer particles had transformable shapes between spherical and nonspherical ones by absorbing/releasing toluene [15].

In this article, the shell strength to occur the shape transformation between them will be discussed experimentally in comparison with a theoretical pressure-buckling relation.

6.2 Experimental

6.2.1 Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) and vinylbiphenyl (VBP) were supplied by Nippon Steel Chemical Co., Ltd., Tokyo, Japan. The purity of DVB, which included ethylvinylbenzene, was 96%. The purity of VBP, which included ethylbiphenyl, methylbiphenyl and biphenyl, was 75%. DVB and VBP were washed with 1 N NaOH and deionized water to remove polymerization inhibitors before use. Reagent grade 2,2'-azobisisobutyronitrile (AIBN) benzoyl peroxide (BPO) and 2,2’-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Poly(vinyl alcohol) (PVA) used as a colloidal stabilizer was supplied by Nippon Synthetic Chemical Ind. Co., Ltd., Osaka, Japan (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 [6]. The other materials were used as received.

6.2.2 *Preparation of PS seed particles*

Micron-sized, monodisperse PS seed particles were produced by dispersion polymerization of styrene in an ethanol/water (7/3, w/w) medium in the presence of PAA 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 given in the previous article [6].

6.2.3 *Swelling of seed particles with monomers and xylene utilizing DSM*

Swellings of the PS seed particles with DVB, VBP and xylene were carried out utilizing DSM under the conditions described in Table 1. The PS seed particles were dispersed in the homogeneous ethanol/water (7/3, w/w) solution dissolving DVB, VBP, BPO and PVA. Water (40 g) was added to the dispersion with a micro feeder at a rate of 2.66 ml/h under stirring with a magnetic stirrer for 15 h at room temperature.

6.2.4 *Seeded polymerization*

Seeded polymerizations for the dispersions of (monomers/solvent)-swollen PS particles were carried out in sealed glass tubes under a nitrogen atmo-

Table 1 Recipes for the productions of PS/P(DVB-VBP) composite particles by seeded copolymerizations[a)] for the dispersions of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method

DVB/VBP	(w/w)	1/0	1/1	1/8	1/16
PS particles[b)]	(mg)	30	30	30	30
DVB[c)]	(mg)	90.0	45.0	10.0	5.3
VBP[d)]	(mg)	−	45.0	80.0	84.7
Xylene	(mg)	360	360	360	360
BPO	(mg)	1.8	1.8	1.8	1.8
PVA	(mg)	15	15	15	15
Ethanol	(g)	7	7	7	7
Water[e)]	(g)	43	43	43	43

[a)] In sealed tube: 70°C; 48 h; N_2; shaking rate, 60 cycles/min (3-cm strokes)

[b)] D_n, 1.7 μm; C_v, 2.2%

[c)] Purity, 96% (by catalog)

[d)] Purity, 75% (by catalog)

[e)] Water (40 g) was post-added at the rate of 2.66 mL/h using a microfeeder

Abbreviations: PS, polystyrene; DVB, divinylbenzene; VBP, vinylbiphenyl; BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

sphere at 70°C for 48 h. The tubes were horizontally shaken at 60 cycles/min (3-cm strokes). The conversion was measured by gas chromatography with helium as a carrier gas. Dodecyl alcohol and 1,4-dioxane were used as standard reagent and solvent, respectively. Droplets in the dispersion were observed on a slide glass, which was covered with a cover glass, with a Nikon MICROPHOT-FXA optical microscope.

6.2.5 *Electron microscopy*

A JEOL JEM-2010 electron microscope and a Hitachi S-2500 electron microscope were used for transmission electron microscopic (TEM) and scanning electron microscopic (SEM) observations, respectively. For the TEM samples, each emulsion was placed onto a carbon-coated grid. For the SEM samples, each emulsion was dropped onto an aluminum plate.

6.2.6 Preparations of PDVB and P(DVB-VBP) films

Preparations of PDVB and P(DVB-VBP) films were carried out by bulk polymerizations under the conditions listed in Table 2. The thickness of films were about 500 μm.

Table 2 Recipes for the preparations of PDVB and PDVB-VBP films by bulk polymerizations[a)]

DVB/VBP	(w/w)	1/0	1/1	1/8	1/16
DVB	(g)	4.0	2.0	0.44	0.24
VBP	(g)	−	2.0	3.56	3.76
V-70	(g)	0.08	0.08	0.08	0.08

[a)] 30˚C; 24 h

Abbreviations: DVB, divinylbenzene; VBP, vinylbiphenyl; V-70, 2,2’-azobis(4-methoxy-2,4-dimethyl valeronitrile)

6.2.7 Tensile test

Tensile test was carried out by a tensile tester (Shimadzu, AUTOGRAPH AGS-1kND, SHIMADZU, Kyoto, Japan) at room temperature to measure the tensile moduli of PDVB and P(DVB-VBP) films. The original length of the specimen was 10 mm and the elongation rate was 1 mm/min. The films at wet state were measured just after immersing in xylene for 24 h at room temperature.

6.3 Results and discussion

Figure 1 shows a TEM photograph of PS seed particles produced by dispersion polymerization. PS particles were spherical and monodisperse: the number-average diameter and the coefficient of variation (*Cv*) were 1.71 μm and 2.2%, respectively, which were determined from the particle observation on TEM photographs with a Personal Image Analysis System (PIAS Co., Ltd., LA-525, Osaka, Japan).

Figure 2 shows SEM photographs of PS/P(DVB-VBP) (1/3, w/w) composite particles produced by seeded polymerizations for the dispersion of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing DSM under the conditions listed in Table 1. Ratios on the photographs indicate the weight ratios of DVB/VBP in P(DVB-VBP). All polymerizations were completed and all the produced particles were observed to spherical shape with an optical microscope before releasing xylene. At the DVB/VBP ratios of 1/0 and 1/1, the composite polymer particles after releasing xylene were still spherical

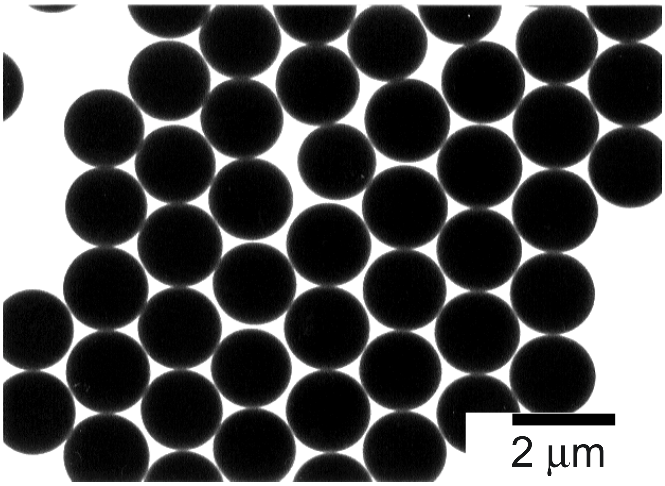

Fig. 1 A TEM photograph of PS seed particles produced by dispersion polymerization

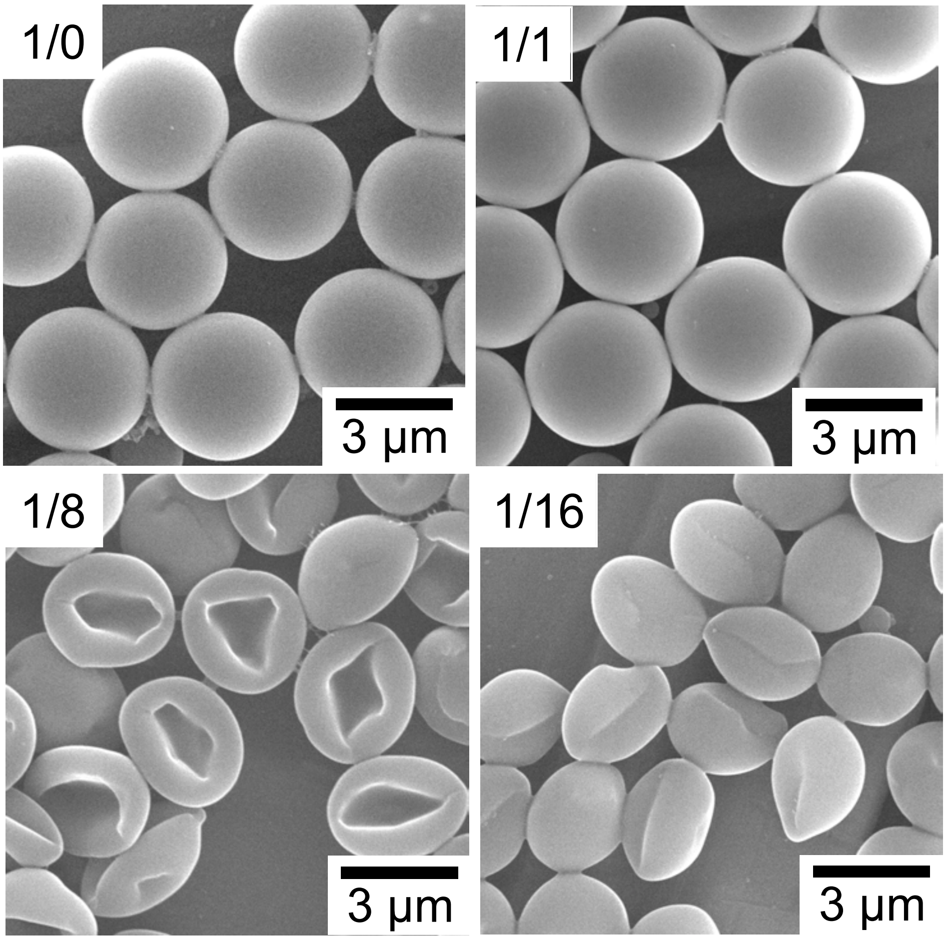

Fig. 2 SEM photographs of PS/P(DVB-VBP) (1/3, w/w) composite particles produced by seeded copolymerizations for the dispersions of (DVB/VBP/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method. Ratios on the photographs indicate the weight ratios of DVB/VBP in P(DVB-VBP).

and had single hollow structure which was observed with TEM. On the other hand, at the DVB/VBP ratios of 1/8 and 1/16, the composite polymer particles after the releasing xylene were nonspherical. In drying process, xylene in the hollow evaporated faster than ethanol/water (7/43, w/w) mixture solution as the medium. The alcoholic water should penetrate into the hollow through the hydrophobic shell because the hollow space is evacuated. However, the penetration rate into the hollow through the shell is much slower than the evaporation rate of xylene from the hollow. Accordingly, when they had low cross-linking density, which was not enough to withstand the external pressure due to the evaporation of xylene, a part of the shell buckled during the drying process as discussed in the previous article [14, 15].

Tsien [16] and Uemura and Yoshimura [17] investigated a theoretical pressure-buckling relation of a thin spherical shell segment under external pressure (ΔP) as shown in Fig. 3 for material design of airplane and rocket and so on. Uemura proposed the following equation about a lower critical buckling load (x) of thin spherical shell [18].

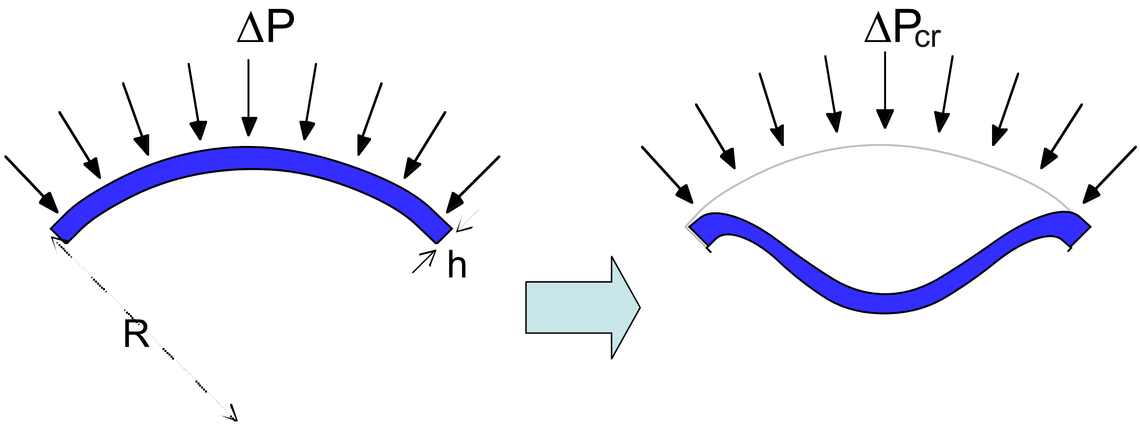

Fig. 3 A schematic diagram of buckling of a sherical shell under external pressure

$$x = \frac{\Delta P_{cr} R^2}{2Eh^2} = \frac{2}{3}\sqrt{\frac{7-\nu}{5\ (23-9\nu)(1-\nu^2)}} \tag{1}$$

where ΔP_{cr} is the lower critical buckling pressure, R is the radius of spherical shell, E is the tensile modulus, h is the thickness of shell, ν is the poisson’s ratio. The equation can be rewritten as follows.

$$E_{cr} = \frac{3\Delta P_{cr} R^2}{4h^2}\sqrt{\frac{5\ (23-9\nu)(1-\nu^2)}{7-\nu}} \tag{2}$$

where E_{cr} is defined as the critical buckling tensile modulus.

The relation was applied to understand buckling of the above hollow particles. When the tensile modulus of the shell of the hollow particles is more than E_{cr}, the shell should not buckle and the particles keep the spherical shape after releasing xylene. On the contrary, when the tensile modulus is lower than E_{cr}, the shell should buckle and the spherical particles transform to nonspherical ones after releasing xylene. In this case, the E_{cr} calculated from Eq. 2 was 0.035 GPa using following values: R and h are 1.92 μm and 0.17 μm, respectively, which were determined from the TEM observation of the hollow particles (DVB/VBP: 1/0, w/w) with image analysis software for Macintosh (Mac Scope, Mitani Co., Fukui, Japan), ν is 0.33 which is PS value, and ΔP is $1\text{x}10^5$ Pa which is atmospheric pressure.

Instead of measuring the tensile modulus of the shell, tensile moduli of P(DVB-VBP) films prepared by bulk polymerization under the conditions listed in Table 2 were measured, of which the compositions were the same as those of the shells. As shown in Table 3, the tensile moduli of all the films at dry state were much higher than the E_{cr} value (0.035 GPa). Even at DVB/VBP ratios (w/w) of 1/8 and 1/16, at which the PS/P(DVB-VBP) composite particles buckled as indicated above, the tensile moduli were, respectively, 0.4 and 0.11 GPa. However, since the shell of the composite polymer particle before releasing was slightly swollen with xylene, which is good solvent for the shell polymer, the tensile moduli must be lowered. In order to estimate the tensile moduli corresponding to the swollen shell, the tensile moduli at the wet state of the films just after immersing in xylene for 24 h were measured at room temperature. At the DVB/VBP ratios of 1/0 and 1/1, at which the PS/P(DVB-VBP) composite particles did not buckle as shown in Fig. 2, the tensile moduli were, respectively, 1.03 and 0.13 GPa. That is, they were still more than the E_{cr} value (0.035 GPa). On the other hand, at the DVB/VBP ratios of 1/8 and 1/16, at which the PS/P(DVB-VBP) composite particles buckled as shown in Fig. 2, the tensile moduli at the wet state were, respectively, 0.01 and 0.004 GPa. That is, they were below the E_{cr} value. These results indicate that there is a threshold of the tensile moduli of the shell to occur the buckling of the spherical shell and the plasticization of the shell is important for the shape transformation of the hollow polymer particles.

Table 3 Tensile moduli[a)] measured at dry and wet[b)] states of PDVB and P(DVB-VBP) films prepared by bulk polymerizations

DVB/VBP (w/w)	Tensile modulus (GPa)		
	Dry	Wet[b)]	
		Xylene	*n*-Octane
1/0	1.14	1.03	-
1/1	0.77	0.13	-
1/8	0.40	0.01	0.37
1/16	0.11	0.004	-

[a)] Measured at room temperature; elongation rate: 1 mm/min
[b)] Just after immersing in solvents for 24 h at room temperature

Abbreviations: DVB, divinylbenzene; VBP, vinylbiphenyl

In order to confirm a relationship between the shell plasticization and the formation of nonspherical polymer particle more in detail, the releasing solvent in drying process was changed from xylene to *n*-octane which is non-solvent for the shell polymer. However, *n*-octane can not be absorbed easily because of non-solvent for the polymers. Accordingly, the following procedure was carried out. First, toluene (180 mg), which is a good solvent for the polymers and the evaporation rate is faster than that of *n*-octane because of high solubility in water as compared with *n*-octane, was added to the dispersion of PS/P(DVB-VBP) (DVB/VBP: 1/8, w/w) composite polymer particles (18 mg) having nonspherical shape under stirring with a magnetic stirrer. The composite particles were changed from nonspherical shape (Fig. 4a) to spherical one (Fig. 4b) by absorbing toluene into the hollow. Second, *n*-octane emulsion, which consisted of *n*-octane (400 mg), SDS (4 mg), ethanol (534

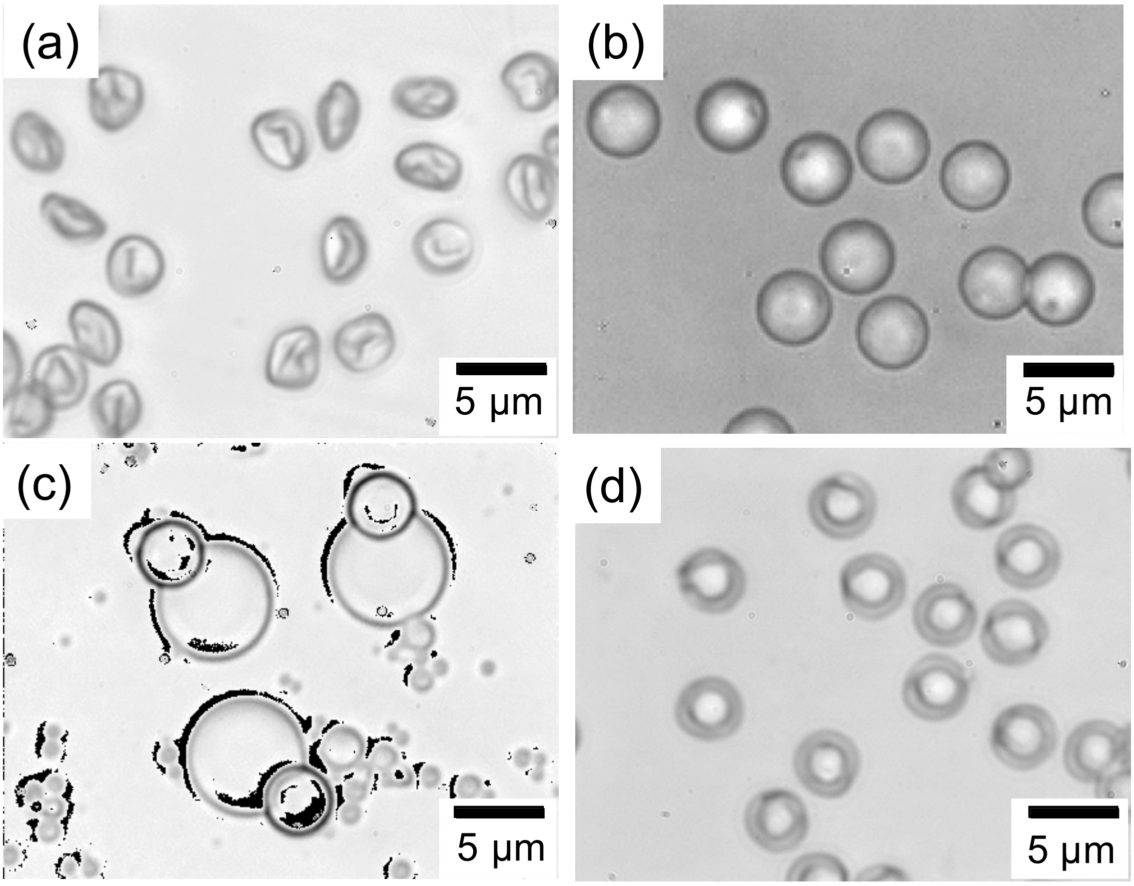

Fig. 4 Optical micrographs of PS/P(DVB-VBP) {3/(1-8), weight ratio} composite particles at various states: (a) xylene-free original state; (b) toluene-absorbed state; (c) n-octane-adsorbed state on the toluene-absorbed particles; (d) released state of n-octane from the hollow

mg) and water (1 g), was prepared with an ultrasonic homogenizer (NIHONSEIKI KAISHA LTD., US-300T, Tokyo, Japan) at 0˚C for 10 min, and the emulsion (2 g) was mixed with the dispersion (10 g) of toluene-swollen PS/P(DVB-VBP) composite particles by a similar way as a pervious paper [19]. Snowman-like *n*-octane adsorbed toluene-swollen composite particles were prepared as shown in Fig. 4c. In previous papers [20-23], monomer-adsorbed polymer particles having a similar shape have been already observed. The mixture was stirred with a magnetic stirrer for about 3 h in a sealed vessel. Since *n*-octane is miscible with toluene, *n*-octane should penetrate into the hollow. Finally, toluene and *n*-octane in the emulsion were released with stirring in the capless vessel, in which toluene evaporate faster than *n*-octane. As a result, only *n*-octane was remained in the hollow of the composite polymer particles. After further releasing *n*-octane from the hollow, the spherical shape of the composite particles was kept as seen in the

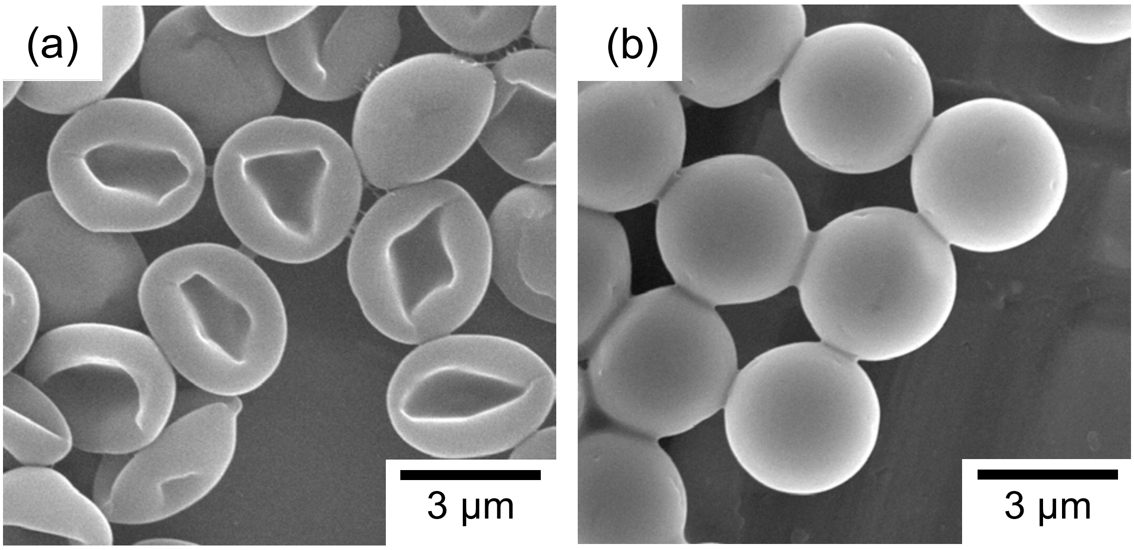

Fig. 5 SEM photographs of PS/P(DVB-VBP) {3/(1-8), weight ratio} composite particles after releasing xylene (a) and *n*-octane (b) from the hollow

optical micrograph (Fig. 4d) and SEM photograph (Fig. 5). Since the shell of the composite polymer particle should not swell with *n*-octane, the tensile modulus of the shell hardly decreased. The shell was enough to withstand the external pressure. In fact, the tensile modulus of the P(DVB-VBP) film (DVB/VBP: 1/8, w/w) at wet state with n-octane was 0.37 GPa as shown in Table 3, which was about ten times of the E_{cr} value. As seen in Fig. 6, the composite particles having spherical shape was changed to nonspherical ones again by absorbing/releasing toluene.

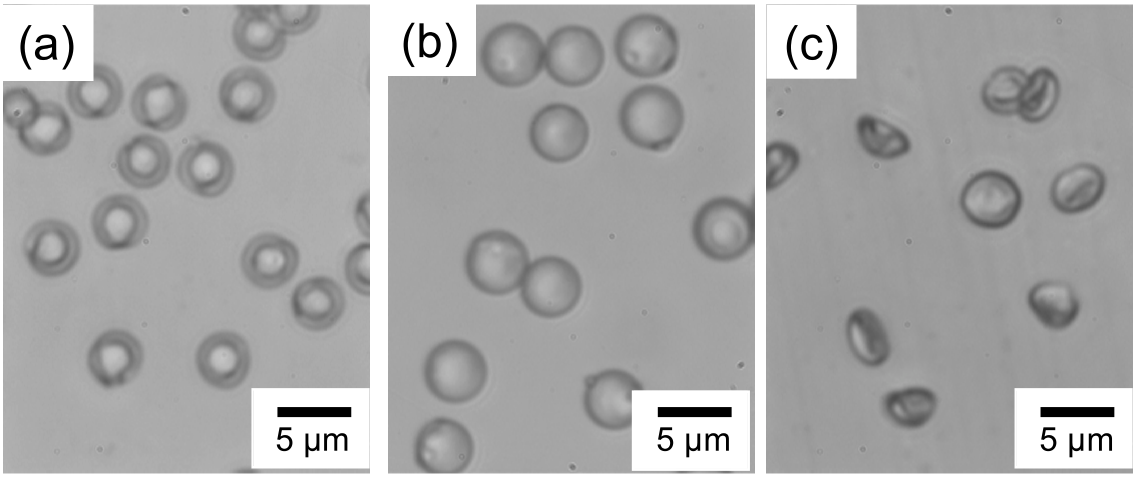

Fig. 6 Optical micrographs of PS/P(DVB-VBP) {3/(1-8), weight ratio} composite particles at various states: (a) *n*-octane-released state; (b) toluene-absorbed state; (c) toluene-released state

From the above results, it is concluded that the shell strength was an important key for the shape transformation of the micron-sized, monodisperse, hollow polymer particles.

6.4 Conclusion

Micron-sized, monodisperse, nonspherical polymer particles having “rugby ball” and “red blood corpuscle”-like shapes were produced by seeded polymerization for the dispersion of (divinylbenzene/vinylbiphenyl/xylene)-swollen polystyrene particles prepared by utilizing the dynamic swelling method which the authors proposed in 1991. Their nonspherical shapes were based on buckling of the shell of the produced hollow particles. In this article, the reversible shape transformation of the hollow composite polymer particle between spherical and such nonspherical shapes was studied in detail by controlling the shell strength. A part of the shell was buckled by external pressure which was caused by evaporation of xylene from the hollow when the shell had the tensile modulus below the critical value calculated from the pressure-buckling relation of a spherical shell proposed by Uemura. The plasticization of the shell by a good solvent was one of key factors for the shape transformation.

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Part II

Application of micron-sized, monodisperse hollow polymer particle

Chapter 7

Penetration/release behaviors of various solvents into/from micron-sized, monodisperse, hollow polymer particles

7.1 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 is focused to apply it directly as particles. As one of them, polymer particles having hollow in the inside have gotten much attention as an hiding or opacifying agent in coating and molding compositions [1-4].

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

In order to produce such particles, we suggested a new type of swelling method of seed polymer particles using a large amount of monomer, which was named "the dynamic swelling method (DSM)" [10, 11]. In a previous study [12], this technique was developed to produce micron-sized monodisperse cross-linked PS/PDVB composite polymer particles having one hollow in the inside. We succeeded in controlling the size of the hollow [13] and proposed the formation mechanism of the hollow particles [14].

In this chapter, the penetration and release behaviors of various solvents into/from the hollow particles will be examined to study the usefulness of hollow particles as carriers.

7.2 Experimental

7.2.1 Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) was washed with 1 N NaOH and deionized water to remove polymerization inhibitors before use. The DVB supplied included ethylvinylbenzene and diethylbenzene, and the purity was 55%. Benzoyl peroxide (BPO) and 2, 2'-azobisisobutyronitrile (AIBN) of reagent grade were 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 stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane. Reagent-grade methanol, ethanol, 1-propanol, 1-butanol, methyl propyl ketone, 1,4-dioxane, tetrahydrofuran (THF), benzene, toluene, xylene, and 5(and 6)-carboxyfluorescein were used as received.

7.2.2 Production of hollow PS/PDVB composite particle

Swelling of the 1.7 μm monodisperse PS seed particles produced by dispersion polymerization with DVB and toluene was carried out utilizing DSM as reported in the previous article [12]. 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-200CX transmission electron microscope (TEM).

7.2.3 Measurement of diameters of the particle and the hollow

The number-average diameters (*Dn*) and coefficient of variations (*Cv*) of the particle and the hollow were determined from the particle observation on TEM negative films with a Personal Image Analysis System (PIAS Co. Ltd. , LA-525, Osaka, Japan). The percentage of hollow volume (*Vh*) was calculated from those diameters.

7.2.4 Penetration of solvent into the hollow

Penetration of various solvents into the hollows of the dried PS/PDVB composite particles which were redispersed in each solvent was observed with an optical microscope (Nikon MICROPHOT-FXA optical microscope). They were evaluated by measuring the time to fill whole of the hollow with the solvent. Penetration of water, in which 5(and 6)-carboxyfluorescein was dissolved as fluorescent reagent, into the hollows was observed by confocal laser scanning spectroscopy (OLYMPUS LSM-GB200). Scanning was carried out at the plane of center of the particles.

7.2.5 Release of the solvent from the particles

Release of various solvents from the PS/PDVB composite particles was observed with the optical microscope and evaluated by measuring weight loss of solvent with thermogravimetry (Seiko Instrument TG/DTA 220U) at 20°C under flow of nitrogen gas. Dried hollow PS/PDVB composite particles were placed on an aluminium pan and immersed in enough amount of solvent. The measurement of weight loss was started after the hollow was filled with the solvent.

7.3 Results and discussion

Figure 1 shows a TEM photograph of PS/PDVB composite particles produced by seeded polymerization for the dispersion of (DVB/toluene)-swollen PS particles prepared utilizing DSM under the conditions listed in Table 1. The particles were monodisperse and had a single hollow: *Dn*, *Cv*

Table 1 Recipe for the production of PS/PDVB (1/5.5, w/w) composite particles by seeded polymerization[a)] for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method

Ingredient		
PS particles[b)]	(g)	0.03
DVB[c)]	(g)	0.3
Toluene	(g)	0.15
BPO	(g)	0.006
PVA	(g)	0.015
Ethanol	(g)	7.0
Water	(g)	3.0 + 40.0[d)]

[a)] N_2, 70°C, 24 h

[b)] 1.64 µm; Cv, 2.8%

[c)] Purity, 55% (by catalog)

[d)] 40.0 g of water was post-added at the rate of 2.88 ml/h at room temperature

Abbreviations: PS, polystyrene; DVB, divinylbenzene; BPO, benzoyl peroxide; PVA, polyvinyl alcohol

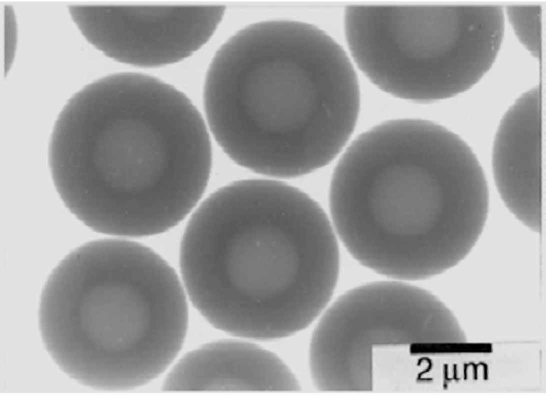

Fig. 1 TEM photograph of PS/PDVB (1/5.5, w/w) composite particles produced by seeded polymerization for the dispersion of (toluene/DVB (1/1.1, w/w))-swollen PS particles prepared utilizing the dynamic swelling method under the conditions listed in Table 1

and *Vh* were 3.82 µm, 3.2% and 10.6 vol%, respectively.

Figure 2 shows optical micrographs of the hollow PS/PDVB composite particles redispersed in water (a) and toluene (b) after they were dried. The interface of the hollow was clearly observed in Fig. 2 (a), whereas it was not in Fig. 2 (b). This seems to be based on closeness of the refractive indexes of the polymer and toluene. In other word, it indicates that toluene is absorbed

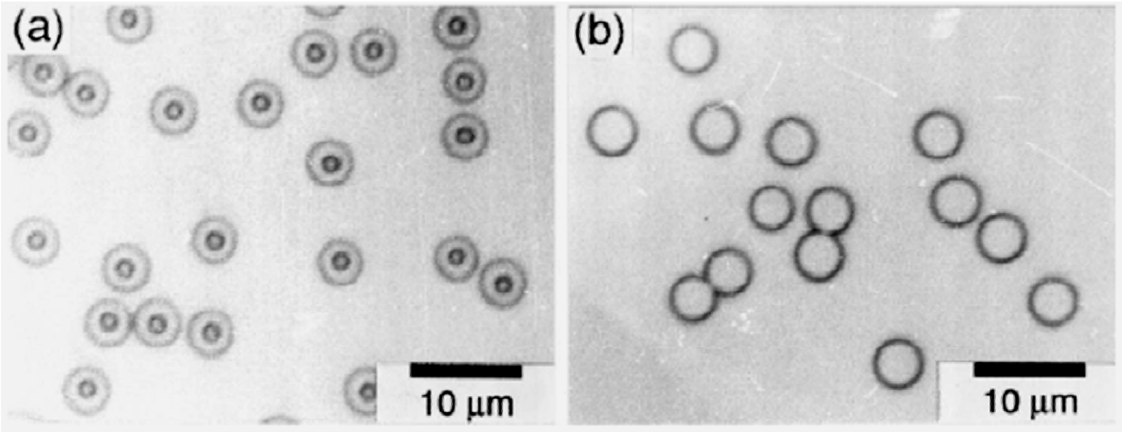

Fig. 2 Optical micrographs of hollow PS/PDVB (1/5.5, w/w) composite particles redispersed in water (a) and in toluene (b)

Table 2 Solubility parameters (δ) of solvents and viscosities of solvents (20 °C) and times needed to fill the hollows of PS/PDVB (1/5.5, w/w) composite particles with various solvents at room temperature[a]

	δ[b] $(\mathrm{MPa})^{1/2}$	Viscosity[c] at 20°C (mPa•s)	Time (min)
Toluene	18.2	0.586	~0
1-Butanol	23.3	2.95	520
1-Propanol	24.3	2.20	410
Ethanol	26.0	1.19	150
Methanol	29.7	0.611	55
Water	47.9	1.00	∞

[a] Determined from optical microscopic observation

[b] Solubility parameter: polystyrene, 17.5 $(\mathrm{MPa})^{1/2}$; "Polymer Handbook" 3rd Ed., JOHN WILEY & SONS (1989)

[c] "Kagaku Binran" 4th Ed., The Chemical Society of Japan (1993)

in the hollow. As shown in Table 2, toluene with a solubility parameter close to that of PS penetrated through the polymers layer into the hollow immediately, whereas alcohols which have solubility parameters different from that of PS penetrated slowly. In addition, the higher the viscosity of the alcohol, the more slowly it penetrated. Water with a solubility parameter quite different from that of PS was not absorbed into the hollow in which air remained.

Figure 3 shows optical micrographs of the hollow PS/PDVB composite particles redispersed in THF (a) and in water (b) just after they were dipped in THF. THF penetrated into the hollow as rapidly as toluene. The interface of the hollow shown in Fig. 3 (a) was unclear because of the closeness of the refractive indexes of the polymers and THF. Refractive indexes at 20°C of air, water, THF, PS and PDVB are 1.00, 1.33, 1.40, 1.59 and 1.62, respectively. The interface of the hollows of the particles redispersed in water just after the THF treatment was observed Fig. 3 (b), though it was

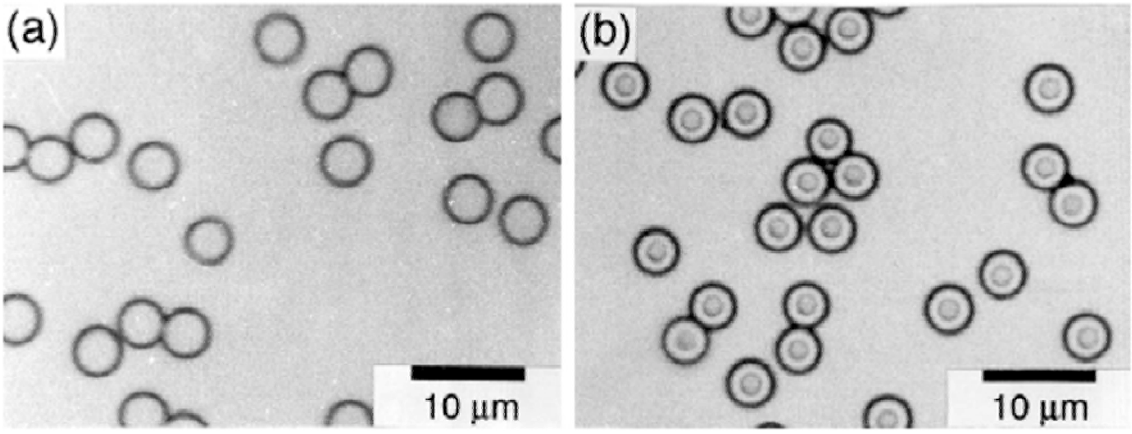

Fig. 3 Optical micrographs of hollow PS/PDVB composite particles redispersed in THF (a) and in water just after they were dipped in THF (b)

indistinct as compared to Fig. 2 (a). This suggests the penetration of water into the hollow. This was confirmed more clearly in a following experiment.

Figure 4 shows confocal laser scanning micrographs of the hollow PS/PDVB composite particles redispersed in aqueous solution of 5-(and 6)-carboxy fluorescein mixed isomers without (a) / with (b) preliminary immersion in THF. In the micrographs, bright regions indicate water phase and circular dark regions indicate the hollow PS/PDVB composite particles.

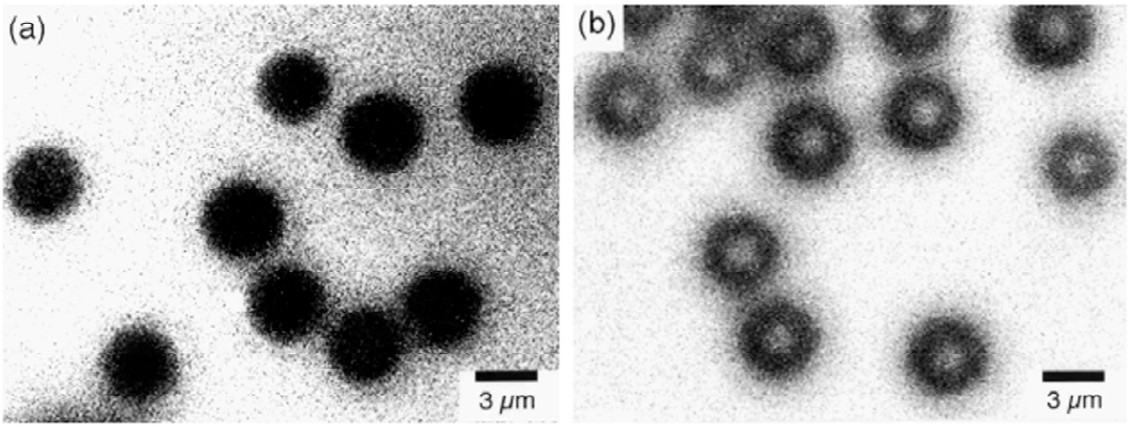

Fig. 4 Confocal laser scanning micrographs of hollow PS/PDVB (1/5.5, w/w) composite particles redispersed in aqueous solution of 5-(and 6)-carboxyfluorescein without (a) / with (b) preliminarily dipping in THF

In Fig. 4 (b), a domain indicating fluorescence was observed having the same size as the hollow at the center of the particles though it was not observed in the particles in Fig. 4 (a). This indicates that water containing fluorescent reagent penetrated into the hollow by the preliminary THF treatment.

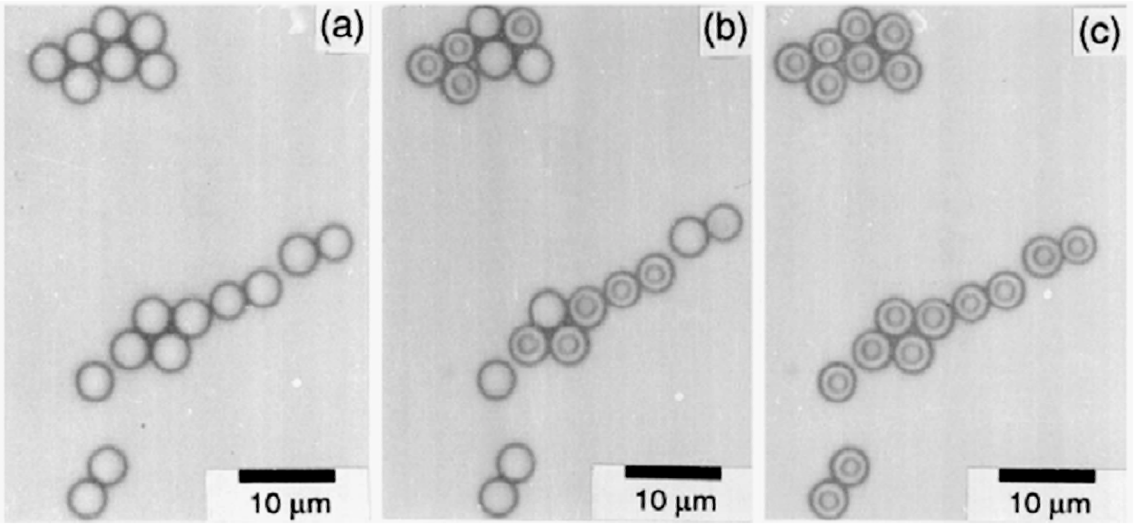

Fig. 5 Optical micrographs of hollow PS/PDVB (1/5.5, w/w) composite particles from which toluene reserved escapes in the drying process: standing time (sec): (a) 0; (b) 40; (c) 60

Figure 5 shows consecutive optical micrographs indicating the escape of reserved toluene from the hollow to air in the drying process. The percentage of the particles in which the hollow can be clearly observed increases with the drying time and finally attained 100%.

Figure 6 shows the weight loss curves due to the evaporations of toluene from the dispersions in which hollow-present or hollow-free PS/PDVB composite particles were dispersed and from pure toluene. The weight of pure toluene decreased at a constant rate at all times. On the other hand, the weight of toluene in which the hollow-present or hollow-free particles were

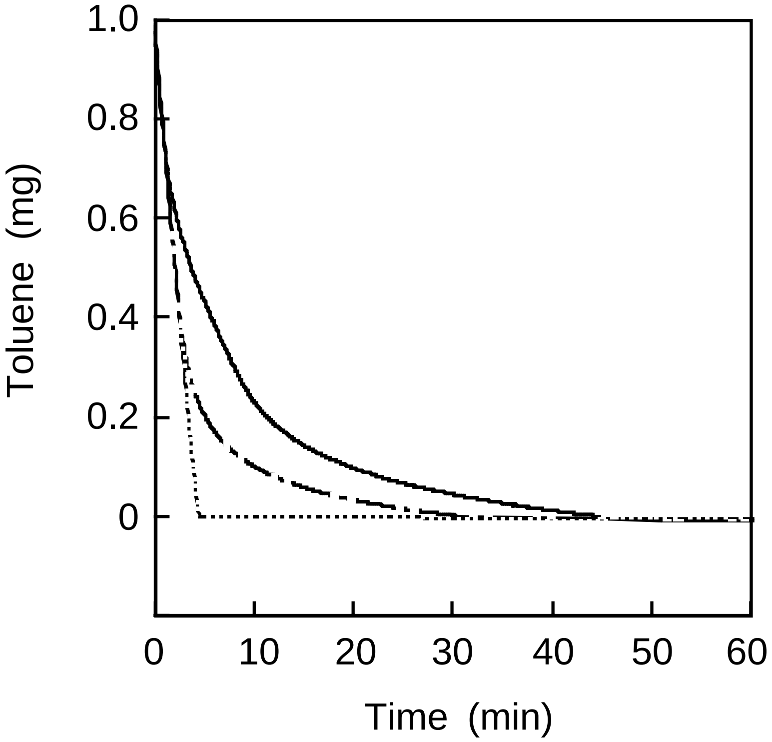

Fig. 6 Weight loss curves due to the evaporation of toluene at 20°C from the dispersions in which hollow (——) or hollow-free (— - —) PS/PDVB (1/5.5, w/w) composite particles were dispersed. (- - - - -); pure toluene.

dispersed initially decreased at a constant rate and slowed down after certain times. The constant rate of the initial weight loss agreed with that of the evaporation from the pure toluene. This indicates that in the initial stage toluene existing outside the particles evaporates. The later weight loss is due to the evaporation of the toluene existing inside the particles, that is, in the polymer layer and in the hollow. The weight loss from the hollow-present particles was larger than that from the hollow-free particles.

Figure 7 shows typical curves of weight loss and its rate due to the evaporation of toluene in which hollow PS/PDVB composite particles had been dispersed. It seems that the weight loss of toluene after the time of point A corresponds to the weight of the toluene reserved in the particles.

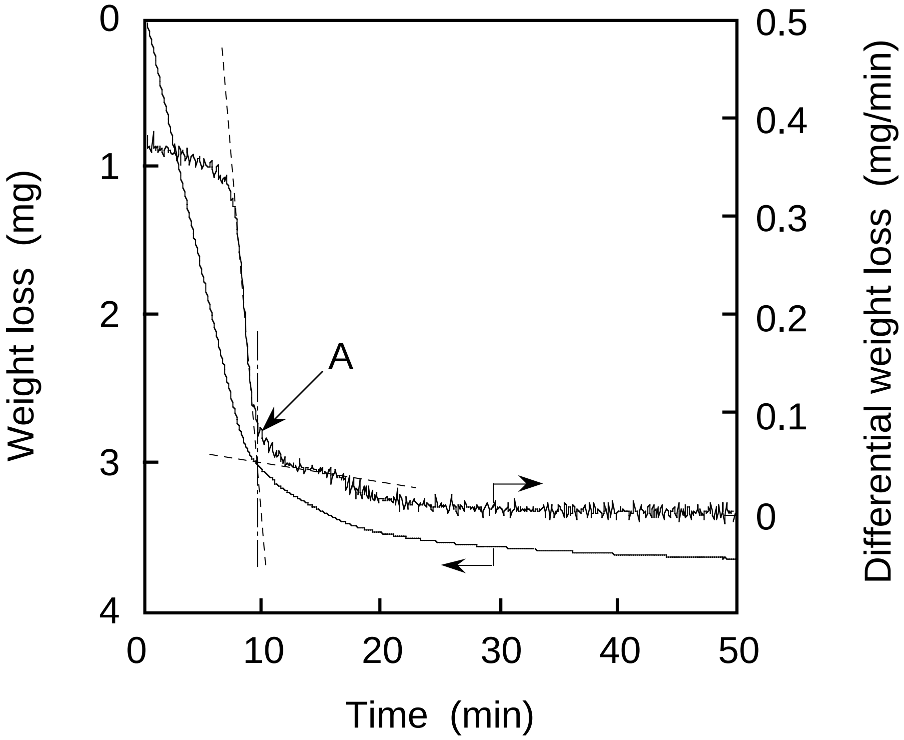

Fig. 7 Weight loss and its differential curves due to the evaporation of toluene at 20°C from the dispersions in which hollow PS/PDVB (1/5.5, w/w) composite particles were dispersed

Figure 8 shows the relationships between the weights of toluene reserved in hollow-free and hollow-present particles and their dried weights. The weight of toluene reserved in each particle increased in proportion to the weights of the dried particles. The weight of toluene reserved in hollow particles is calculated by the subtraction the weights of toluene reserved in hollow-free particles from that of the hollow-present particles. The obtained value approximately agreed with the weight of toluene calculated assuming that all of the hollows are completely filled with toluene. These results suggest that toluene was reserved in the hollows.

Figure 9 shows the relationship between the evaporation rates of point A per weight of the hollow particles and the reciprocal numbers of the layers

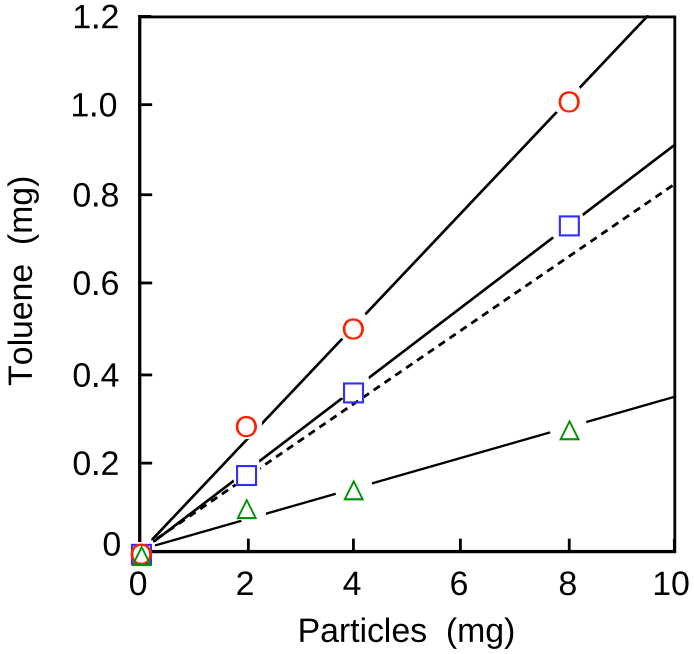

Fig. 8 Relationships between the weights of toluene evaporated from hollow-free (△) and hollow-present (○) PS/PDVB (1/5.5, w/w) composite particles which had been at maximum absorbing states and their dried weights. Symbol (□) indicates [(○) - (△)]. (-----) indicates the calculated amounts of toluene which fills the hollows.

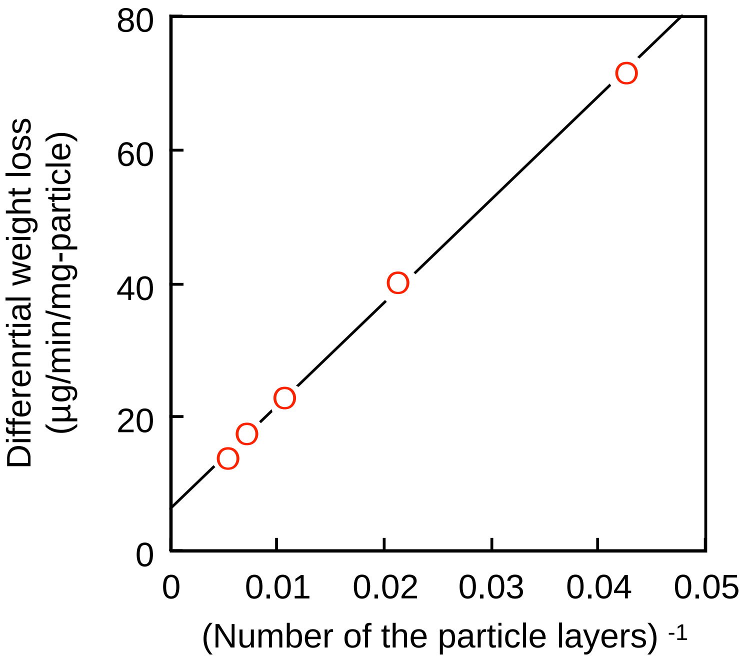

Fig. 9 Relationship between the evaporation rates per weight of the hollow PS/PDVB (1/5.5, w/w) composite particles and the reciprocal numbers of the layers of the hollow particles

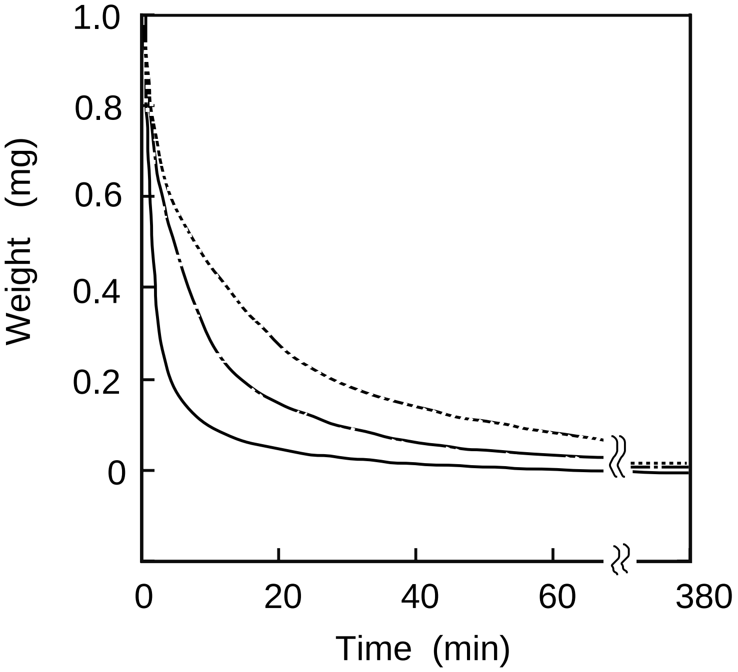

Fig. 10 Weight loss curves due to the evaporations of three kinds of solvents from the dispersions in which 4 mg of the dried hollow PS/PDVB (1/5.5, w/w) composite particles were dispersed at 20˚C: ———, benzene; —·—, toluene; - - - - -, xylene

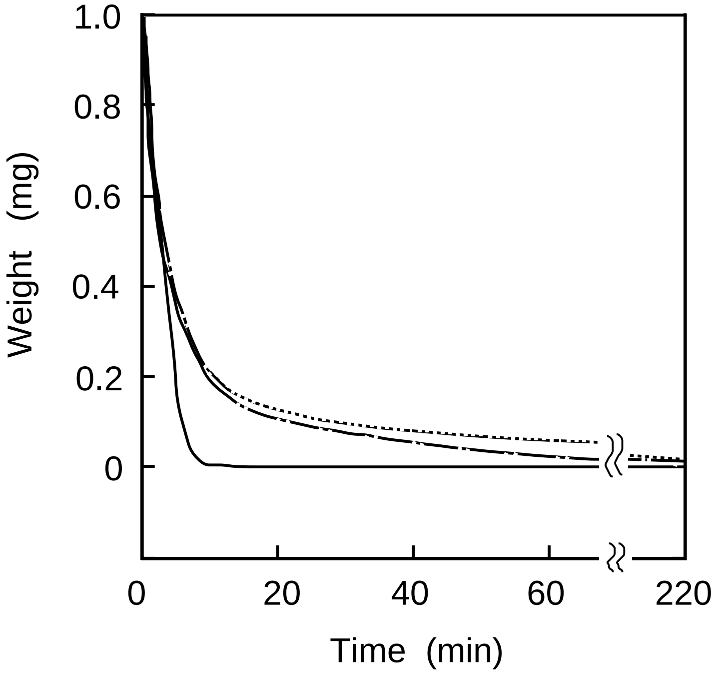

Fig. 11 Weight loss curves due to the evaporation of three kinds of solvents from the dispersions in which 4 mg of the dried hollow PS/PDVB (1/5.5, w/w) composite particles were dispersed at 20˚C: ———, ethanol; —·—, 1,4-dioxane; - - - - -, methyl propyl ketone.

of the hollow particles in the aluminium pan. An inversely proportional relationship was obtained. It seems that evaporation of toluene from the lower particle layer is prevented by the upper particle layer.

Figures 10 and 11 show the weight loss curves due to the evaporations of various solvents from the dispersions in which 4 mg of the dried hollow particles were dispersed. As can be seen in Fig. 10, the evaporations of the three kinds of solvents having similar solubility parameter (δ) became slower in order of decrease of evaporation rates (RE). On the other hand, in Fig. 11, the three kinds of solvents having similar RE evaporated slowly as δ of solvent approaches that of PS. Each RE, δ, and the release time to complete evaporation of solvent after point A were shown in Table 3. The release time was affected by RE of solvent and its affinity for the base polymers.

From these results, it is clear that the hollow of the PS/PDVB composite

Table 3 Solubility parameters (δ) of solvents and evaporation rates (RE) of solvents (20°C) and times needed to release solvents from hollow PS/PDVB (1/5.5, w/w) composite particles[a)]

	δ[b)] (MPa)$^{1/2}$	RE[c)]	Time (min)
Xylene	18.0	63	370
Toluene	18.2	240	205
Benzene	18.8	630	55
Methyl propyl ketone	17.8	320	180
1,4-Dioxane	20.5	311	75
Ethanol	26.0	340	10

[a)] Determined from thermogravimetric measurements at 20°C using 4 mg hollow PS/PDVB (1/5.5 w/w) composite particles

[b)] Solubility parameter: polystyrene, 17.5 (MPa)$^{1/2}$; “Polymer Handbook” 3rd Ed., JOHN WILEY & SONS (1989)

[c)] Evaporation rate at 20°C: Butyl acetate, 100; “Youzai Binran”, Makishoten (1967) particles could reserve various solvents, which indicates the possibility to use them as reservoir and release material.

7.4 Conclusion

The penetration/release behavior of various solvents into/from the hollow of micron-sized monodisperse cross-linked polystyrene (PS)/ polydivinylbenzene (PDVB) (1/5.5, w/w) composite particle was examined. The hollow particles were produced by seeded polymerization utilizing the dynamic swelling method which the authors proposed earlier. The penetration into the hollow was affected by viscosity of the solvents and its affinity for the base polymers. Toluene saved in the hollow was released slowly. These results suggest that there is a possibility to apply such hollow particles as a controlled release material.

7.5 References

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Chapter 8

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

8.1 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 is focused to apply it directly as particles. As one of them, polymer particles having hollow(s) in the inside have gotten much attention as an hiding or opacifying agent in coating and molding compositions [1-4].

On the other hand , recently, many researchers in polymer colloids are concentrating their attentions on the production of micron-sized, monodisperse polymer particles [5-9] because they have been 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 of 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, monodisperse, cross-linked, polystyrene(PS)/polydivinylbenzen(PDVB) composite polymer particles having one hollow at the center. The size of the hollow was controllable [13] and the formation mechanism 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 chapter, the release behaviors of toluene from the hollow particles which have various cross-linking densities and shell thickness were studied in detail.

8.2 Expermental

8.2.1 Materials

Vinyl toluene (VT) and divinylbenzene (DVB) which was supplied by Nippon Steel Chemical. Co. Ltd. (DVB-960, purity was 96%) were washed with 1N 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 received.

8.2.2 Preparation of PS seed particles

Micron-sized monodisperse 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 monodisperse: the number-average diameter (D_n) and coefficient of variation (C_v) were 1.7 µm and 2.2%, respectively.

8.2.3 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).

Table 1 Recipes for the productions 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% (by catalog).

[d)] 40.0 g of water was 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, vinyl toluene; DVB, divinylbenzene; BPO, benzoyl peroxide; PVA, polyvinyl alcohol

8.2.4 Release of the toluene from the hollow particles

Release rate of toluene from the hollow particles was evaluated by measurement of weight loss of toluene as a time. The same number (about 1 X 10^8) of dried hollow particles, which were calculated from volume of a particle, were 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 with thermogravimetry (Seiko Instrument TG/DTA 220U) at 20˚C under a nitrogen atmosphere.

8.3 Results and Discussion

Figure 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 condition 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 TEM photograph with a Personal Image Analysis System (PIAS Co. Ltd. , LA-525, Osaka, Japan). The particles had low C_v, which means high monodispersity, and each particle had single hollow structure: D_n, C_v and D_h were 4.27 µm, 3.1% and 1.99 µm, respectively. The other monodisperse, 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 were shown in Table 1. When each hollow particle absorbed by toluene, there were little changes of the diameter and

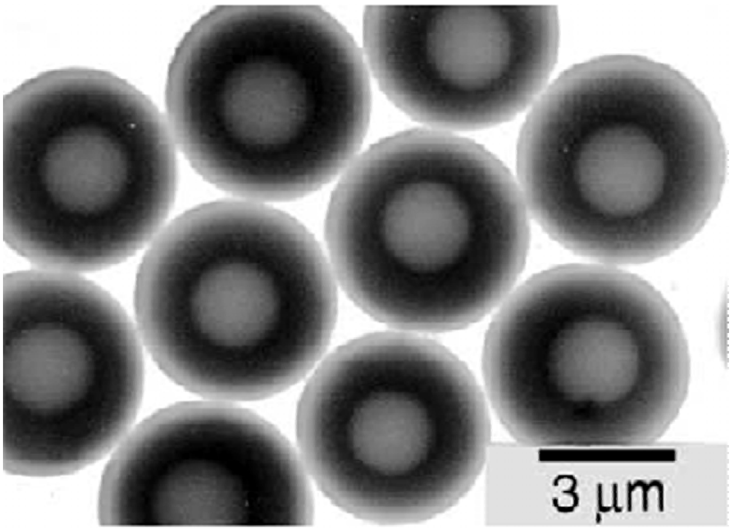

Figure 1 A TEM photograph of PS/PDVB (1/9.6 w/w) composite particles produced by seeded polymerization for the dispersion of (DVB/xylene)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 3 listed in Table 1

shell thickness of these hollow particles because of high cross-linking.

Figure 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 initially toluene 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 in comparison with both 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 released gradually in 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

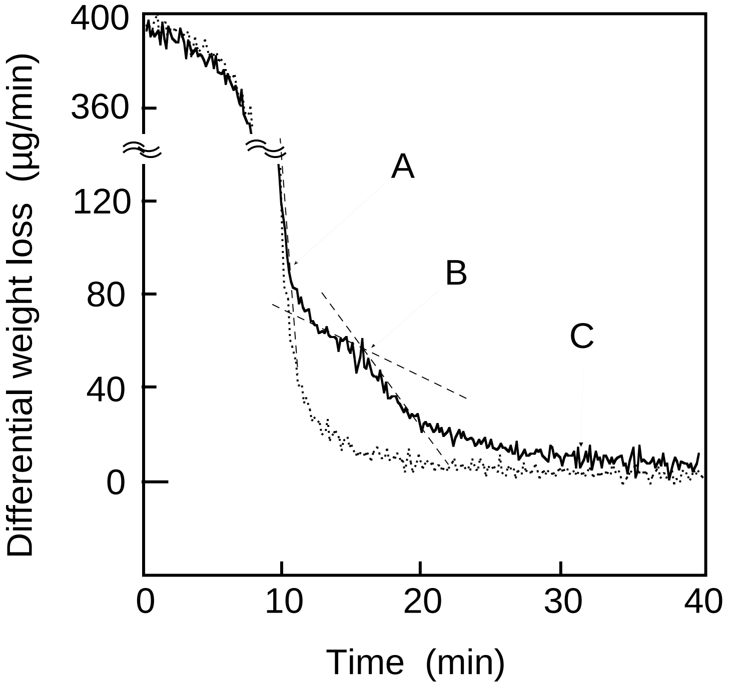

Figure 2 Differential weight loss curves due to the evaporation of toluene at 20°C from the dispersions in which hollow-present (No. 3, ———) and hollow-free (No. 6, - - - - - -) PS/PDVB composite particles were dispersed

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.

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

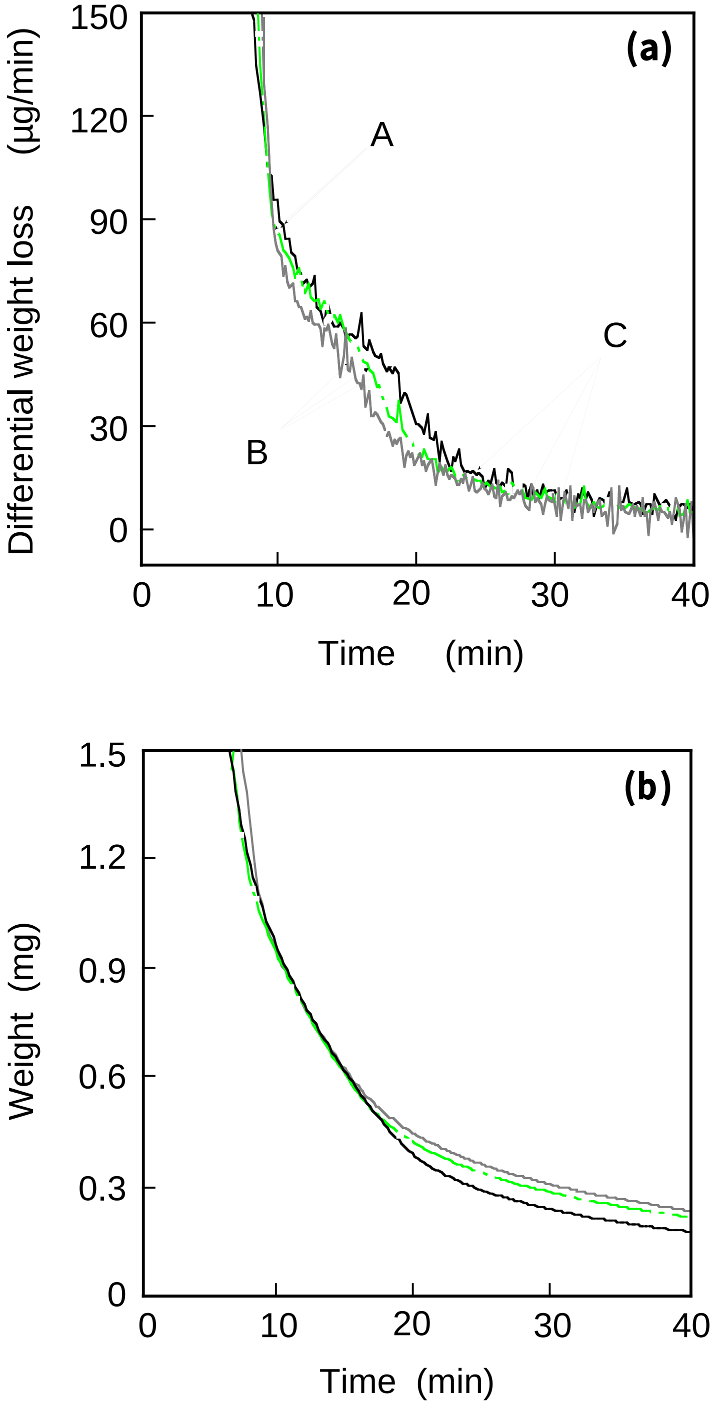

Figure 3 Differential weight loss curves (a) and weight loss curves (b) due to the evaporation of toluene at 20°C from the dispersions in which hollow PS/P(DVB-VT) or PS/PDVB composite particles having different compositions were dispersed. (———), No. 1; (—·—), No. 2; (- - - - - .), No. 3 listed in Table 1. Numbers in figure show DVB contents in the shell [DVB/(DVB+VT)x100, wt%].

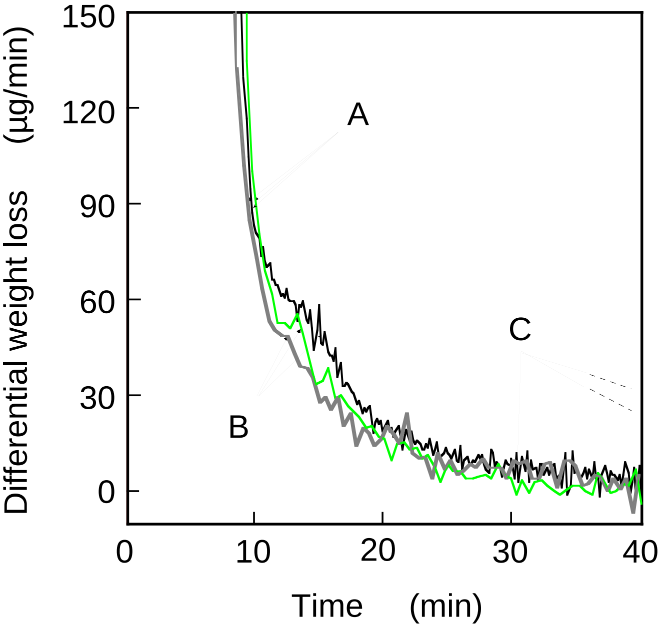

Figure 4 Differential weight loss curves due to the evaporation of toluene at 20°C from the dispersions in which hollow PS/PDVB composite particles having different shell thicknesses were dispersed. (———), No. 3; (— - —), No. 4; (- - - - - -), No. 5 listed in Table 1. Numbers in figure show number-average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

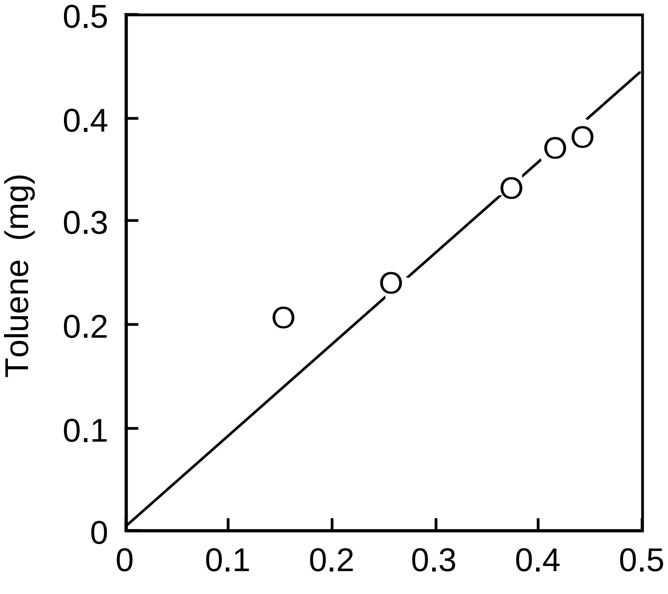

Figure 5 Relationship between total hollow volume (○) of the PS/P(DVB-VT) and PS/PDVB composite particles and the amounts of toluene released between points A and B on the weight loss curves. Full line indicates the calculated amounts of toluene to fill the hollows.

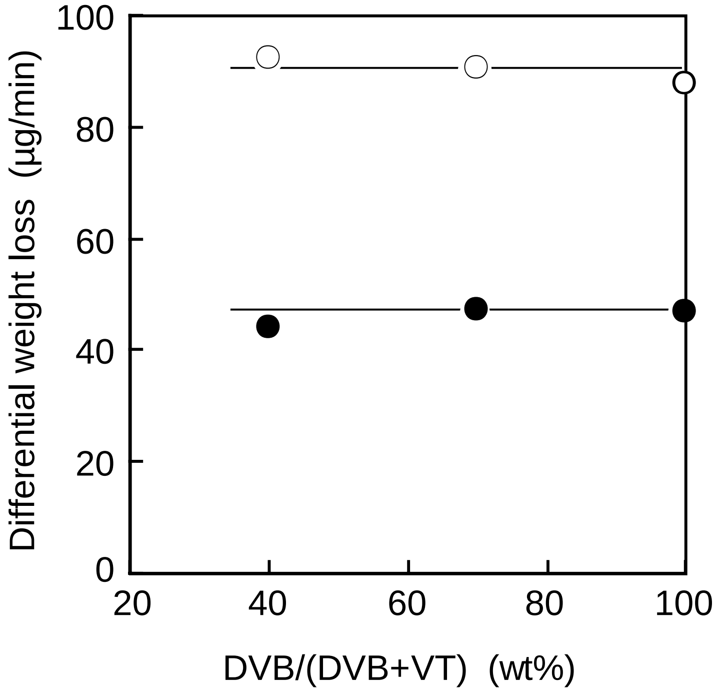

Figure 6 Relationships between DVB content in the shell of the hollow PS/P(DVB-VT) or PS/PDVB composite particles and the release rates of toluene due to their evaporation at the points A (○) and B (●) on the curve in shown in Fig. 2

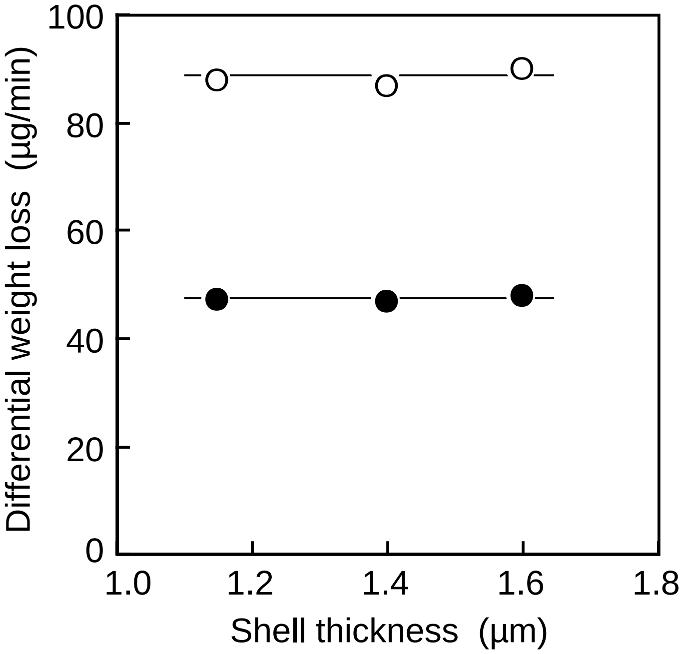

Figure 7 Relationships between the shell thickness of the hollow PS/PDVB composite particles and the release rates of toluene due to their evaporation at the points A (○) and B (●) on the curve shown in Fig. 3

Figure 4 shows release rate curves due to the evaporations of toluene at 20˚C from the dispersions in which hollow polystyrene/polydivinylbenzen (PS/PDVB) having different shell thicknesses were dispersed. In Fig. 4, the release rate decreased with increases in the PDVB shell thickness, and toluene was reserved for a long time as shell thickness increased.

Figure 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 assuming that all of the hollow are completely filled with toluene.

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

Figures 8 and 9 show, respectively, relationships between the DVB contents and the shell thickness and the release rate of toluene reserved 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 property. The higher the cross-linking density or the thicker the shell thickness of the hollow particles, the more slowly toluene released. These suggest 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

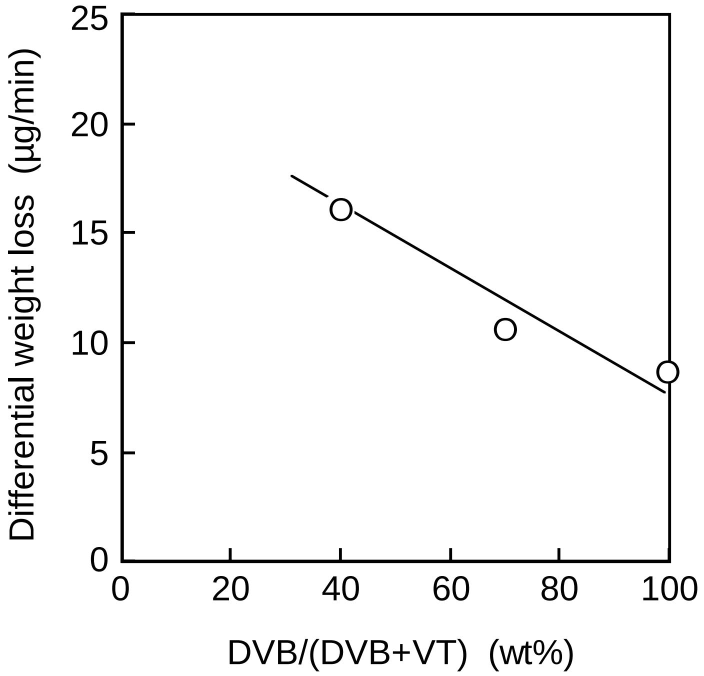

Figure 8 Relationship between DVB content in the shell of the hollow PS/P(DVB-VT) or PS/PDVB composite particles and the release rates of toluene due to their evaporation at the point C on the curve shown in Fig. 2

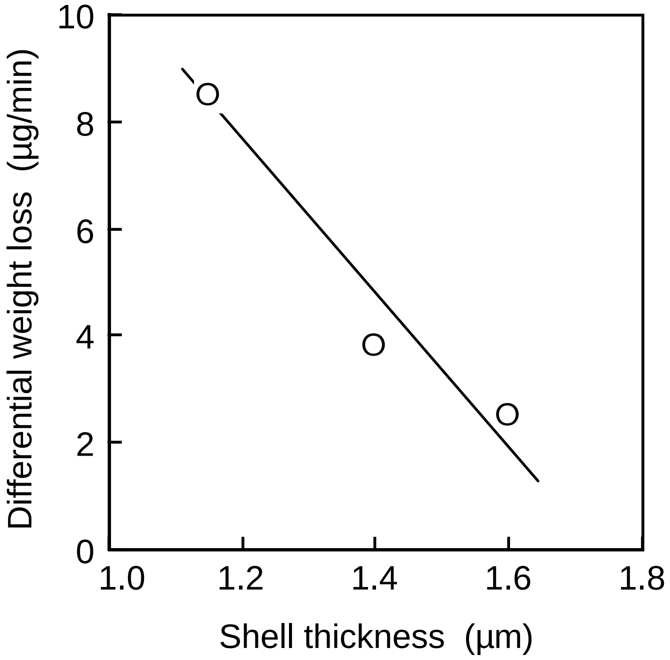

Figure 9 Relationship between the shell thickness of the hollow PS/PDVB composite particles and the release rates of toluene due to evaporation at the point C on the curves shown in Fig. 3.

composite particles seems to proceed as a schematic diagram shown 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 its evaporation 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 inner shell surface. After toluene disappears 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.

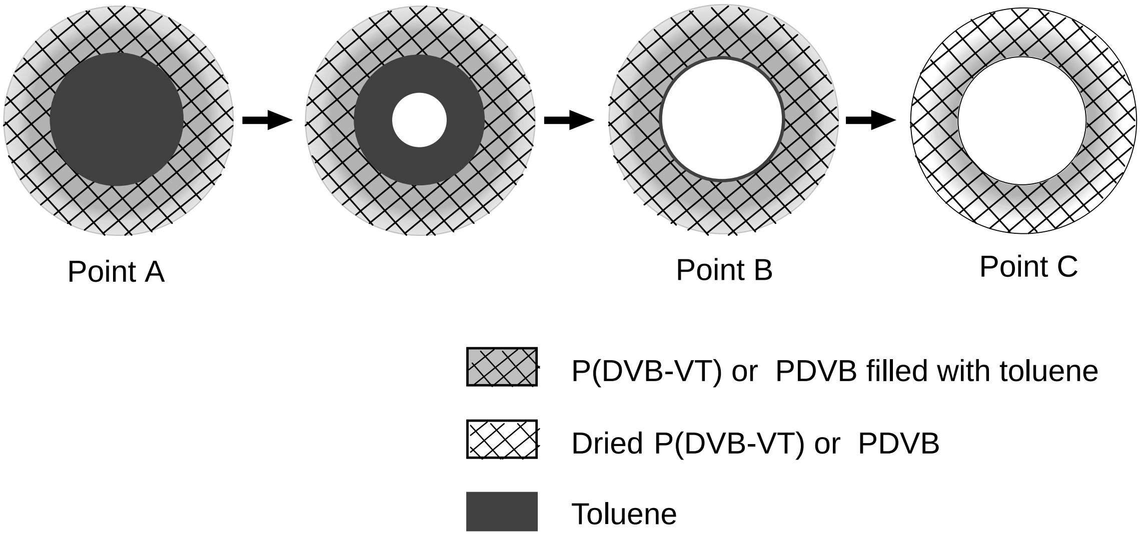

Figure 10 Schematic diagram for release of toluene reserved in the hollow PS/P(DVB-VT) and PS/PDVB composite particles

8.4 Conclusion

The release behavior of toluene from the hollow inside micron-sized, monodisperse, 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.

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Chapter 9

Preparation of micron-sized, monodisperse, magnetic polymer particles

9.1 Introduction

Polymer particles having hollow structure have gotten much attention in many industrial fields. Such particles are used as weight saving, thermal insulation, hiding and opacifying agents, and a microcapsule. For example, submicron-sized thermoplastic styrene/acrylic polymer particles containing one hollow at the center were produced by alkali swelling of carboxylated polymer particles having core-shell structures [1]. We have also prepared submicron-sized, monodisperse styrene-butyl acrylate-mathacrylic acid terpolymer and styrene-methacrylic acid copolymer emulsion particles having many hollows in the insides, respectively, by the stepwise treatment with alkali and acid [2-4] and by alkali treatment at higher temperature than glass transition temperature of the base polymer, following cooling to room temperature [5-7]. Moreover, micron-sized, monodisperse, cross-linked polymer particles having a single hollow at the center have been produced [8-10] by seeded polymerization for highly (divinyl monomer/solvent)-swollen particles prepared utilizing the “dynamic swelling method” (DSM) which was proposed for production of micron-sized, monodisperse polymer particles having more than 5-μm-size diameter by authors [11, 12].

Magnetic particle is attractive for waste water treatment [13] and the area of biotechnology [14] to separate and purify enzymes and cells. The particles should be desirable to have a suitable size and narrow size distribution and functionalized surface.

In this chapter, micron-sized, monodisperse magnetic composite particles having vinyl group at their surfaces will be prepared by utilizing the micron-sized, monodisperse, hollow particles described above.

9.2 Expermental

9.2.1 Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) (Nippon Steel Chemical. Co. Ltd., DVB-960; purity, 96%) was washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. Regent grade benzoyl peroxide (BPO) and 2,2’-azobis(isobutyronitrile) (AIBN) were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Polyvinyl alcohol (PVA) (Nippon Synthetic Chemical Ind. Co., Ltd., Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%) and poly(acrylic acid) (PAA) were used as a colloidal stabilizer. The PAA was prepared by solution polymerization of acrylic acid in 1,4-dioxane. Analytical grade p-xylene, reagent grade ethanol and hydrochloric acid, and pentacarbonyliron (Aldrich, purity was 99.999%) were used as received.

9.2.2 Preparation of PS seed particles

Micron-sized, monodisperse PS seed particles were produced by dispersion polymerization of styrene in an ethanol/water (7/3, w/w) medium in the presence of PAA colloidal stabilizer with AIBN initiator at 70˚C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask according to the optimum conditions in a previous articles [15] listed in Table 1.

Table 1 A recipe for the preparation of micron-sized monodisperse PS seed particles by dispersion polymerization[a)]

Ingredient		
Styrene	(g)	140
AIBN	(g)	2.35
PAA	(g)	16.8
Ethanol	(g)	959
Water	(g)	280

[a)] 70°C; 24 h; N_2; stirring rate, 60 rpm

Abbreviations: PS, polystyrene; AIBN, 2,2’-azobisisobutyronitrile; PAA, poly(acrylic acid)

9.2.3 Production of composite particles having single hollow at the center

Swelling of the PS seed particles produced by dispersion polymerization with DVB and xylene was carried out utilizing DSM under the conditions listed in Table 2 according to the previous articles [8-10]. Seeded polymerization for the (DVB/xylene)- 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).

Table 2 A recipe for the production of PS/PDVB composite particles by seeded polymerization[a)] for the dispersion of (DVB/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method

Ingredients		
PS particles[b)]	(g)	0.3
DVB[c)]	(g)	1.5
Xylene	(g)	4.5
BPO	(g)	0.03
PVA	(g)	0.15
Ethanol	(g)	70.0
Water	(g)	30.0 + 400[d)]

[a)] 70˚C; 24 h; N_2; stirring rate, 60 rpm

[b)] D_n, 1.74 μm; C_v, 3.4%

[c)] Purity, 96%

[d)] 400 g of water was post-added at the rate of 18 mL/h.

Abbreviations: PS, polystyrene; DVB, divinylbenzene; BPO, benzoylperoxide; PVA, poly (vinyl alcohol)

9.2.4 Production of magnetic polymer particles

TThe dried hollow particles were dipped in pentacarbonyliron at room temperature for 20 h to make it penetrate into the hollow. This dispersion was placed in a 50 ml-capacity stainless steel pressure-resistant vessel having a polytetrafluoroethylene inner container and the vessel was dipped in oil bath at 200˚C for 4 h. After the treatment, the composite particles were washed with 12N HCl aqueous solution and water. Hereafter, these treatments will be called "inclusion treatment".

9.2.5 Observation of particles by optical microscopes

Each particle was observed with a Nikon MICROPHOT-FXA optical microscope, TEM and a Hitachi S-2500 scanning electron microscope.

9.2.6 Observations of the ultrathin cross sections of particles

Each dried particle was dipped in epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross sections were put on copper grids and observed with TEM. They were also observed with X-ray electron probe microanalyzer (JEOL, JXA-8900) to analyze distribution states of iron and oxygen atoms.

9.2.7 X-ray diffraction (XRD)

XRD of the magnetic polymer particles were measured with a Rigaku RINT 2100 diffractometer, using Cu $K\alpha$ (40 kV, 20 mA).

9.2.8 Measurement of magnetite content in particle

The content of magnetite in the magnetic polymer particles was evaluated by measuring weight loss with thermogravimetry (Seiko Instrument TG/DTA 220U). The dried particles were placed on platinum pan (ϕ5 mm) and temperature was raised until 750˚C at 10˚C/min under N_2 flow.

9.2.9 Introducion of sulfate group at the surface of the composite particle

Chemical modification of the vinyl groups at the surface of the composite particle was carried out with concentrated sulfuric acid for 2 h at 0˚C to introduce sulfate group. The particle was washed repeatedly by centrifugation with water after the modification.

9.2.10 X-ray photoelectron spectoroccopy (XPS)

XPS data were obtained with a Shimadzu ESCA-3400 using Mg $K\alpha$ (12 kV, 20 mA). The pressure in the measurement chamber was ~5x10^{-7} Pa. Dried particles were spread on an indium plate with a spatula.

9.2.11 Determination of the amount of sulfate groups at the particle surface

The amount of sulfate group was determined by measuring the heat of the The amount of sulfate group at the particles surface was determined by measuring the heat of the neutralization reaction between sulfate group and KOH with isothermal titration calorimetry (CSC Co., 4200 ITC) according to the optimum conditions given in a previous article [16]

9.3 Results and Discussion

Figure 1 shows a TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1. The PS particles were spherical and monodisperse: the number-average diameter (D_n) and coefficient of variation (C_v) were 1.74 μm and 3.4%, respectively, which were determined from the particle observation on TEM photographs with a Personal Image Analysis System (PIAS Co., Ltd., LA-525, Osaka, Japan).

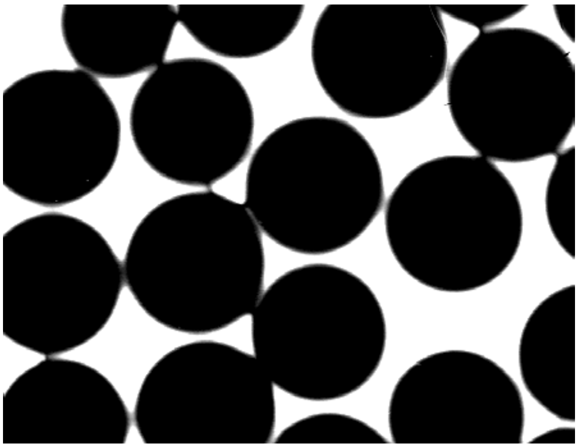


Fig. 1 A TEM photograph of PS seed particles produced by dispersion polymerization

Figure 2 shows an optical micrograph of hollow PS/PDVB

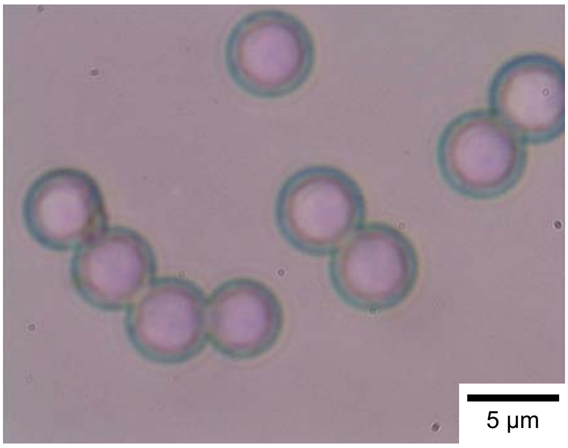


Fig. 2 An optical micrograph of PS/PDVB composite particles produced by seeded polymerization for the dispersion of (DVB/xylene)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions listed in Table 2

composite particles produced by seeded polymerization for the dispersion of (DVB/xylene)-swollen PS particles prepared utilizing DSM under the condition in Table 2. The D_n, C_v, and number-average hollow diameter (D_h) were 4.8 μm, 6.1%, and 4.2 μm, respectively. The low C_v means high monodispersity. All particles had single hollow at the center.

Figure 3 shows a schematic diagram of the inclusion treatment of magnetic substance in the hollow of the PS/PDVB composite particle. Since pentacarbonyliron existed both inside and outside of the hollow polymer particle, the decomposition products of pentacarbonyliron also existed both surfaces after the treatment at 200˚C for 4 h. In order to remove selectively the decomposition products at the outside surface, the particles were washed with 12 N HCl aqueous solution. In this time, HCl aqueous solution was hard to penetrate into the composite particle because of the hydrophobic shell [17].

Figure 4 shows optical micrographs photographs of the hollow PS/PDVB composite particles before (a) and after (b) the inclusion treatment. The size and monodispersity after the treatment were, respectively, the same

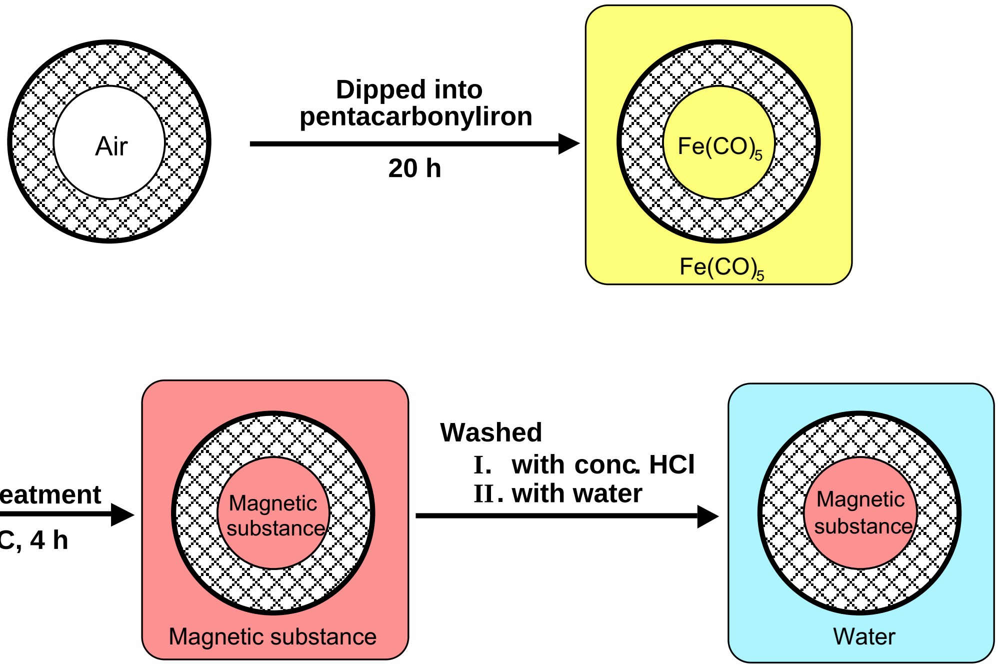


Fig. 3 Schematic diagram for the inclusion of magnetic substance in the hollow of PS/ PDVB composite particle

as those before the treatment. The contrast of the particles after the treatment was more dark than that of ones before the treatment. This seems to be based on a decomposition product of pentacarbonyliron. In other words, it suggests that a magnetic substance was introduced into the hollow particles.

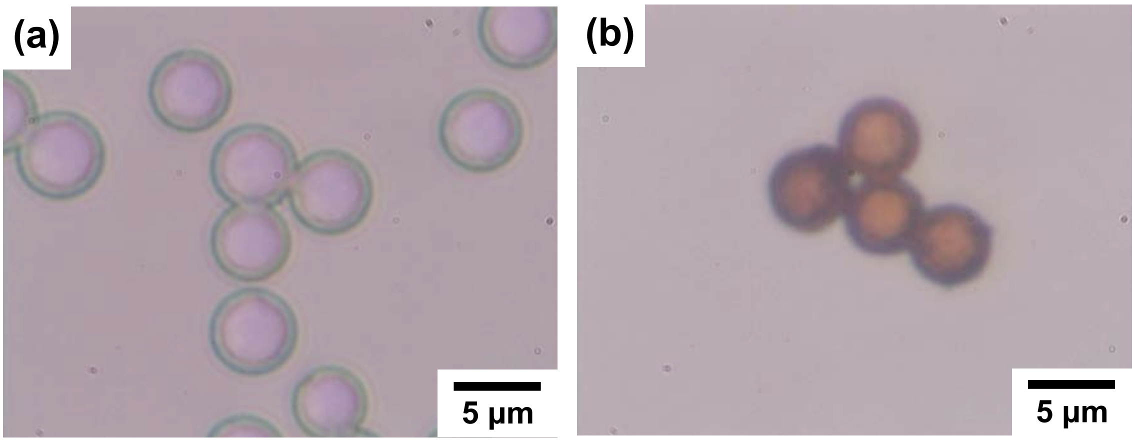
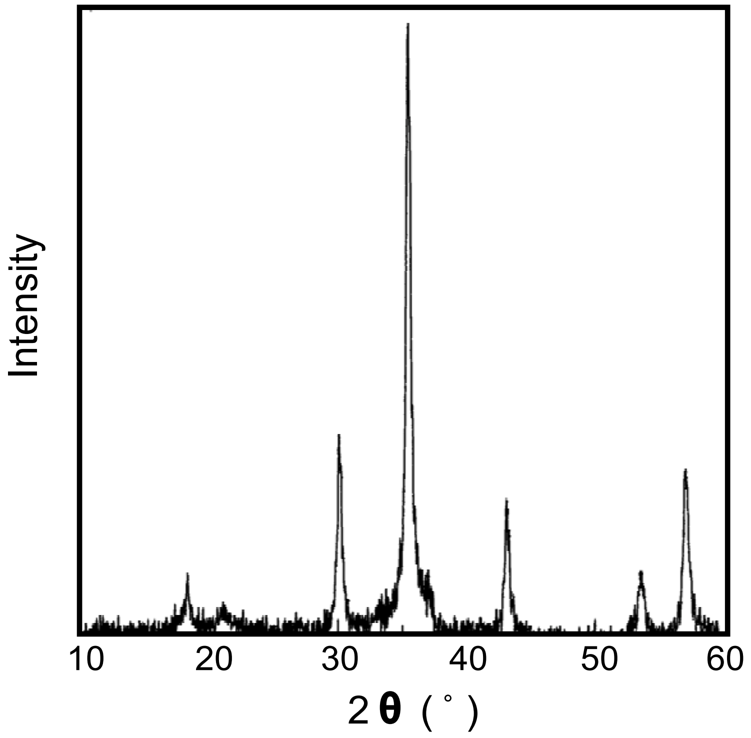


Fig. 4 Optical micrographs of PS/PDVB composite particles before (a) and after (b) the inclusion treatment



Sample

d-Value/nm	Intensity
0.48361	9
0.29617	30
0.25266	100
0.24219	6
0.20952	20
0.17093	9
0.16122	27

Fe_3O_4 (Magnetite)

d-Value/nm	Intensity
0.4852	8
0.2967	30
0.2532	100
0.24243	8
0.20993	20
0.17146	10
0.16158	30

Fig. 5 A X-ray diffraction pattern of the PS/PDVB/Fe_3O_4 composite particles after the inclusion treatment of the magnetic substance

Figure 5 shows a X-ray diffraction pattern of the hollow PS/PDVB composite particles after the inclusion treatment. All of the peak positions and intensity ratios, which were observed in 2θ range between 10 and 60°, respectively, agreed well with those of the Fe_3O_4 crystalline [18]. This indicates that Fe_3O_4 was included in the composite particle as the decomposition product of pentacarbonyliron.

Figure 6 shows a thermogravimetric analysis (TGA) curve of the PS/PDVB/Fe_3O_4 composite particles. PS and PDVB in the composite particles were markedly decomposed around 400 and 600°C, respectively. The content of Fe_3O_4 in the composite particle determined from the TGA curve was 49 wt%.

Figure 7 shows consecutive photographs indicating the attraction of

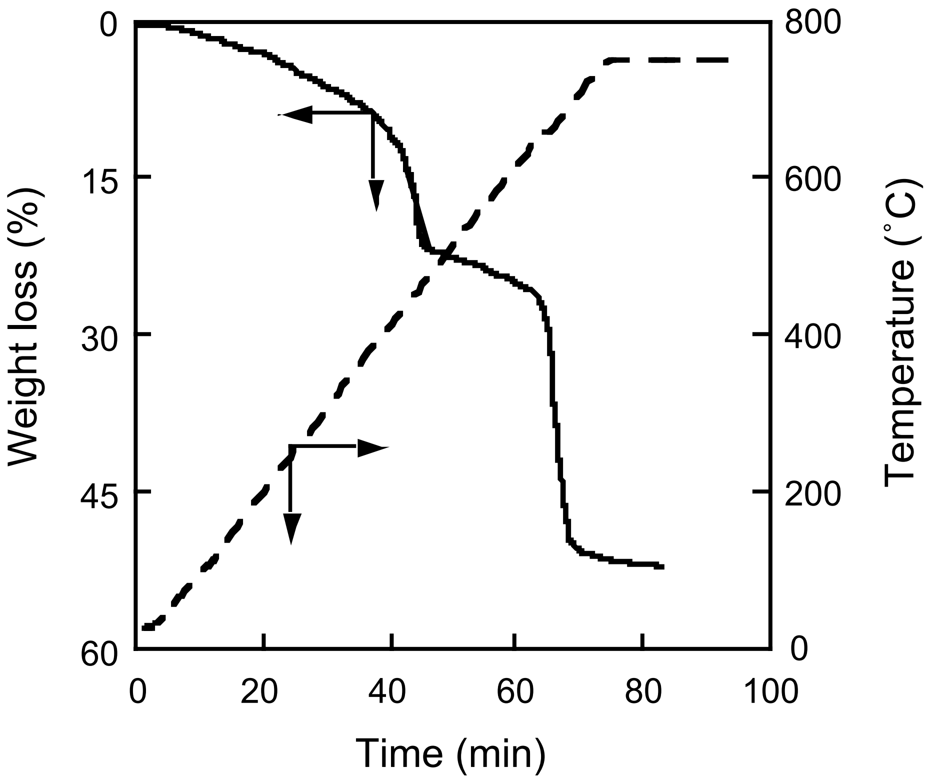


Fig. 6 A TGA curve of PS/PDVB/Fe_3O_4 composite particles

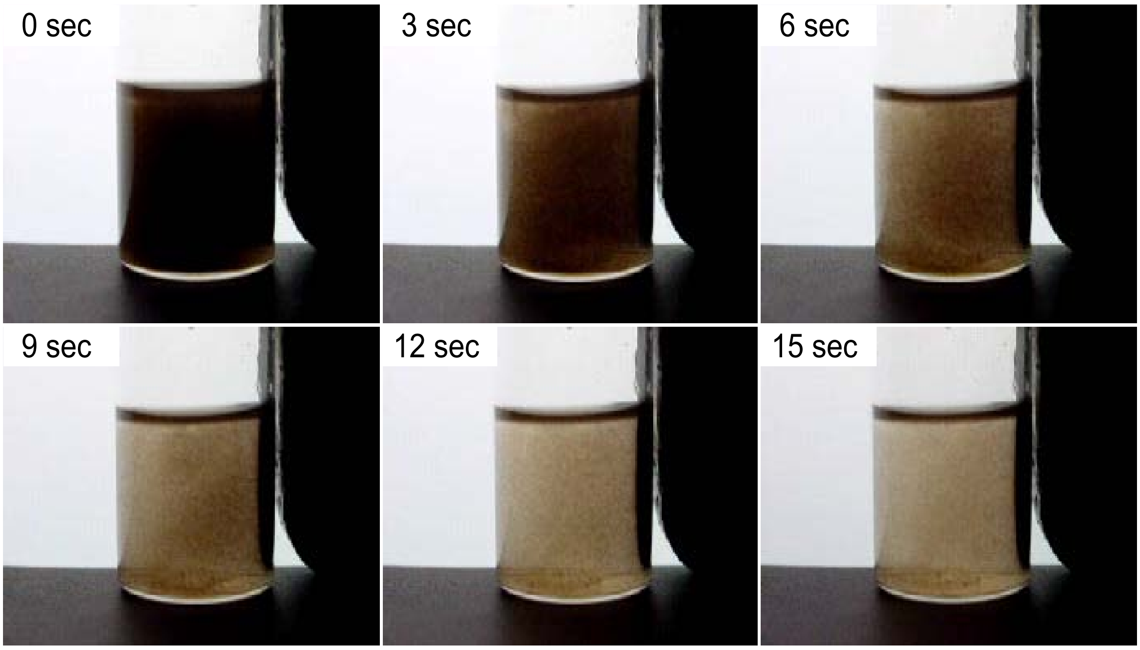


Fig. 7 Consecutive photographs indicating the attraction of PS/PDVB/Fe_3O_4 composite particles by a magnet (1650 G)

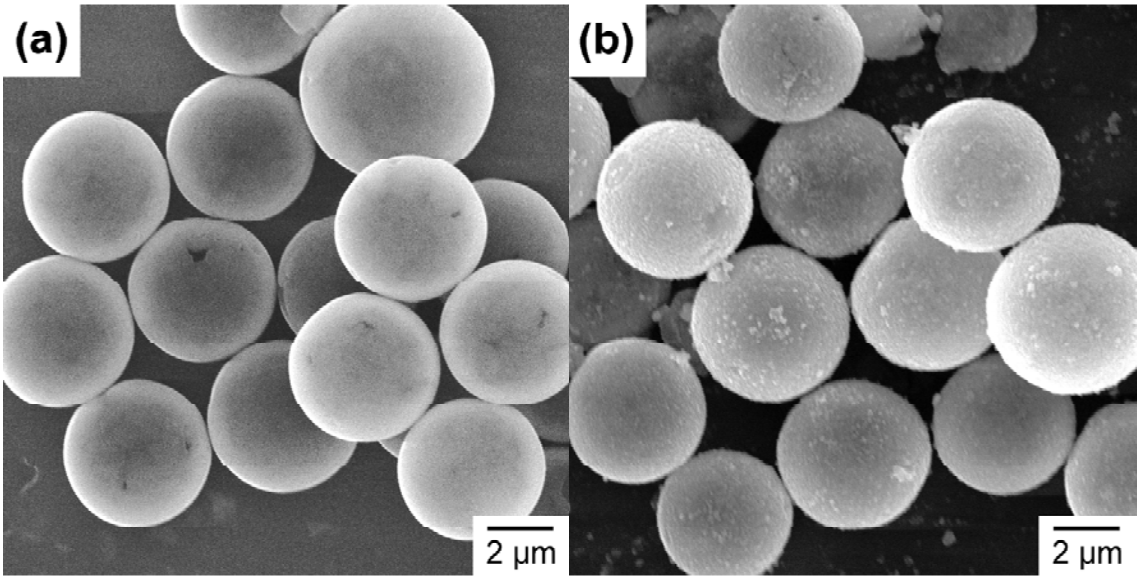


Fig. 8 SEM photographs of PS/PDVB composite particles before (a) and after (b) the inclusion treatment

the PS/PDVB/Fe_3O_4 composite particles dispersing in water by a magnet (1650 G). As can be seen, the composite particles were swiftly attracted by the magnet within 15 sec.

Figures 8 shows SEM photographs of the hollow PS/PDVB (a) and PS/PDVB/Fe_3O_4 (b) composite particles. Almost all decomposition product (Fe_3O_4) was removed by washing with 12 N HCl aqueous solution for a few minute, though a small amount of the decomposition product was observed at the surfaces.

Figure 9 shows TEM photographs of the hollow PS/PDVB composite particles (a, b) and of ultrathin cross sections of the particles (c, d) before (a, c) and after (b, d) the inclusion treatment. In the TEM photographs of the composite particles after the treatment, high contrast region was observed at the inner wall of the hollow, which was not observed before the treatment. In TEM photographs of ultrathin cross sections of the composite particles, the

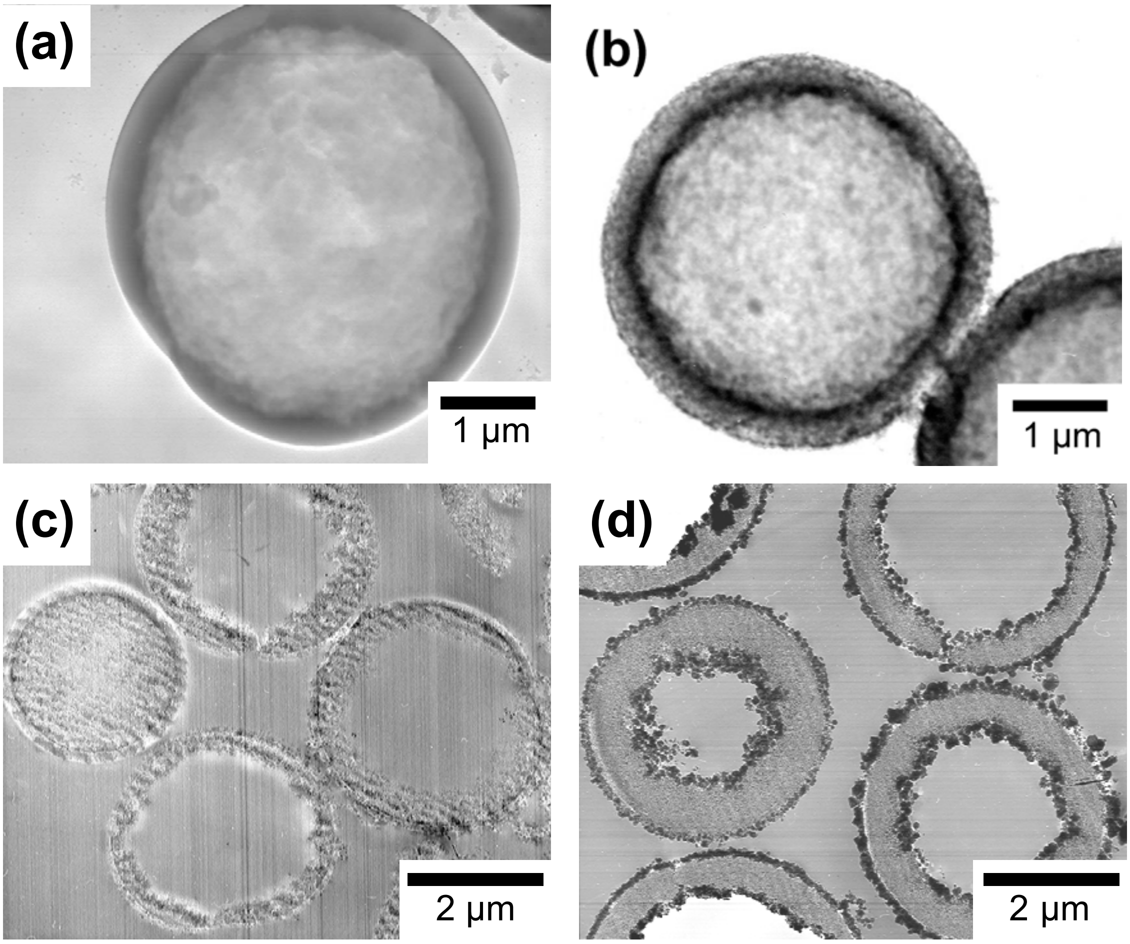


Fig. 9 TEM photographs of the PS/PDVB composite particles (a, b) and of ultrathin cross sections of the particles (c, d), before (a, c) and after (b, d) the inclusion treatment of the magnetic substance

high contrast region, which was due to Fe_3O_4, was observed along the inner wall of the hollow of the composite particle after the treatment. It was observed at the outer surfaces of the composite particles.

Figure 10 shows a SEM photograph (a) and distribution images of iron (b) and oxygen (c) atoms in ultrathin cross sections of the hollow PS/PDVB/Fe_3O_4 composite particles after the inclusion treatment measured with X-ray electron probe microanalyzer. The iron and oxygen atoms existed at the inner wall of the hollow structure and in the shell of the composite particles. This indicates that Fe_3O_4 could be encapsulated in the hollow. It was also observed at the outer surfaces of the composite particles, but it was removed by the longer washing time as shown in Fig. 11. It is confirmed that the composite particles after removing Fe_3O_4 at the outer surfaces were attracted by the magnet.

Figure 12 shows a part of XPS spectra for the PS/PDVB/Fe_3O_4 composite particles (a) and its modified ones (b) with sulfuric acid. After the modification, the peak due to S_{2p} was observed at ca 169 eV of binding energy. This indicates that sulfate group was introduced by the reaction of vinyl

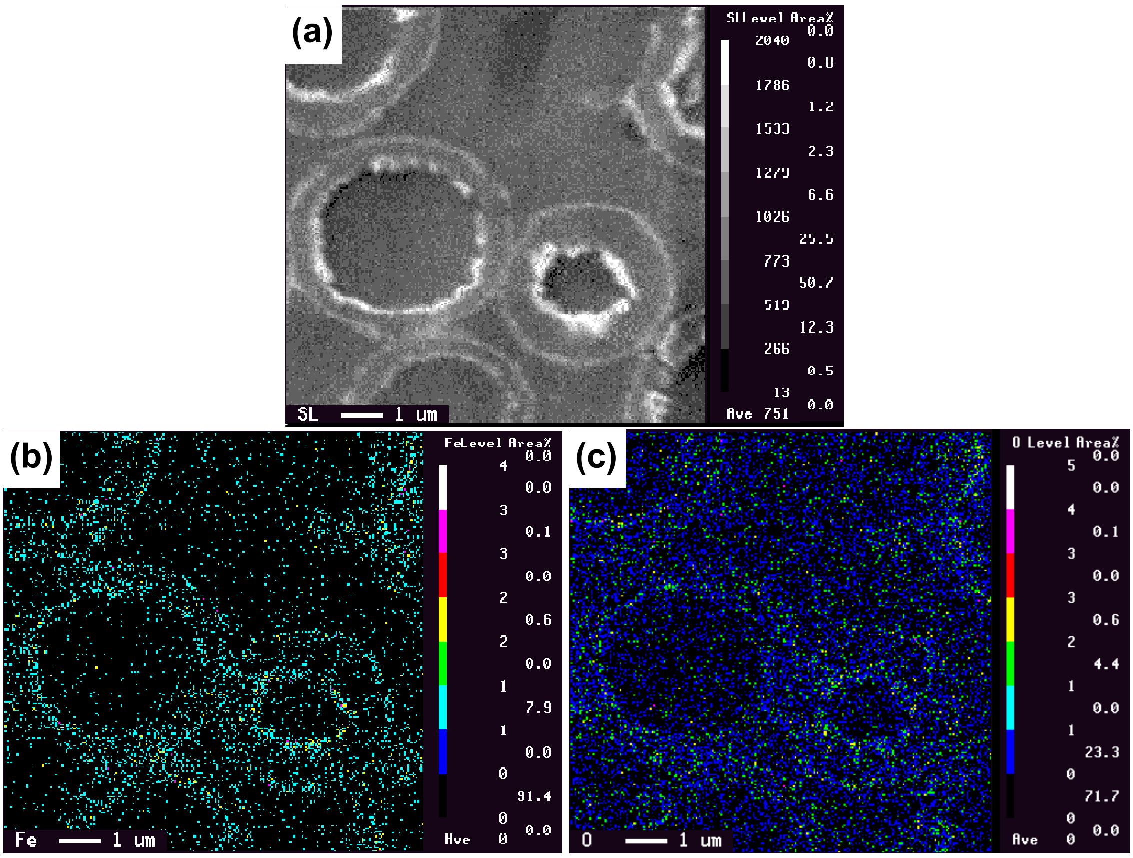


Fig. 10 A SEM photograph (a), and distribution images of iron (b) and oxygen (c) in ultrathin cross sections of PS/PDVB/Fe_3O_4 composite particles after the inclusion treatment, by electlon probe microanalyzer

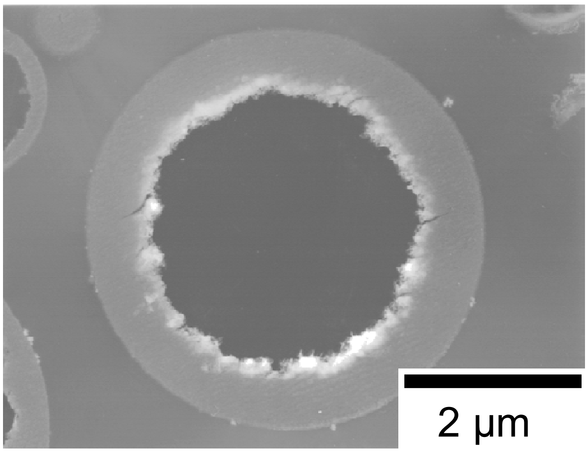


Fig. 11 A TEM photograph of ultrathin cross sections of the PS/PDVB/Fe_3O_4 composite particles after removing Fe_3O_4 at the outer surfaces

groups at the surface of the composite particle with concentrated sulfuric acid. The amount of sulfate group at the surface was determined to be 0.7 μmol/m^2 by measurement with isothermal titration calorimetry. The occupied area of one sulfate group calculated from the value was 2.5 Å^2, though

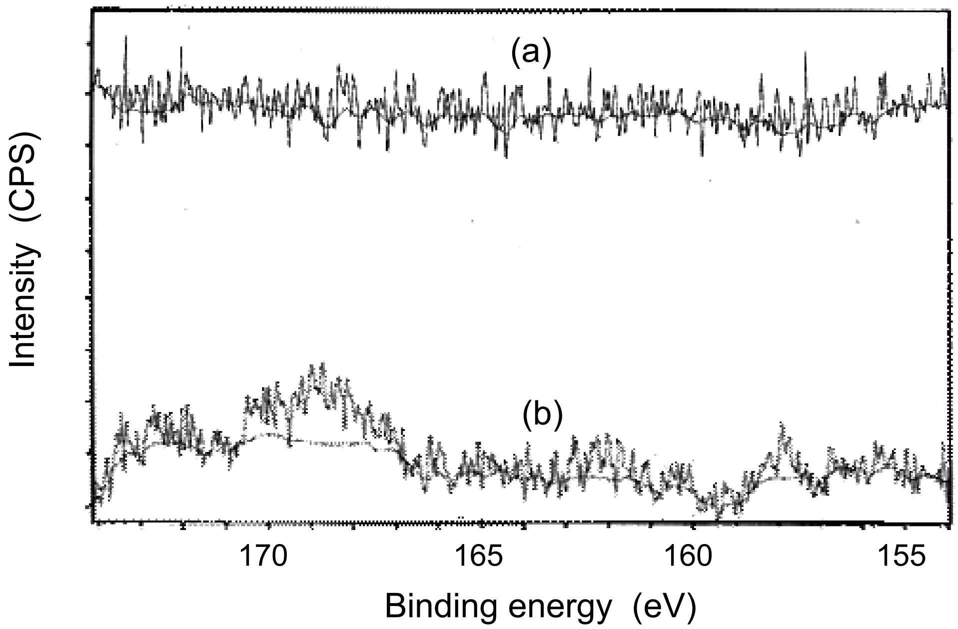


Fig.12 X-ray photoelectron spectroscopy spectra of S_{2p} for magnetic PS/PDVB/Fe_3O_4 composite particles before (a) and after (b) sulfuric acid treatment

the value might include sulfate groups existing inside the shell of which thickness is less than 10 nm. This occupied area was comparable to that (4 Å^2) of vinyl group at the surface of the PS/PDVB composite particles produced by DSM [19].

From above results, it is concluded that about 5-μm-sized, monodisperse, magnetic polymer particle having reactive vinyl group at their surface could be prepared.

9.4 Conclusion

Micron-sized, monodisperse, magnetic composite particles were prepared by heating the micron-sized, monodisperse, hollow polystyrene/polydivinylbenzene composite polymer particles at 200°C for 4 h, which had been dipped in pentacarbonyliron, following washing 12 N HCl and water. The hollow polymer particles were produced by seeded polymerization utilizing the dynamic swelling method which was proposed by authors. The magnetic composite particles contained Fe_3O_4 of which content was 49% based on total weight and were attracted easily in water by a 1650 G magnet.

9.5 Refference

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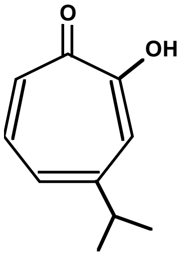
Chapter 10

Production of polystyrene/poly(ethylene glycol dimethacrylate) composite particles encapsulating hinokitiol

10.1 Introduction

Polymer particles having hollow structure have gotten much attention in many industrial fields. Such particles are used as a microcapsule, weight saving or thermal insulation agents, and applied to a hiding or opacifying agents in coating and molding compositions because of the high light-scattering ability. For example, submicron-sized thermoplastic styrene/acrylic polymer particles containing one hollow at the center were produced by alkali swelling of carboxylated polymer particles having core-shell structures [1]. We have also prepared submicron-sized, monodisperse styrene-butyl acrylate-mathacrylic acid terpolymer emulsion particles having many hollows in the inside by the stepwise treatments with alkali and acid [2-4], which was named the stepwise alkali/acid method. Moreover, we succeeded in producing micron-sized, monodisperse, crosslinking polymer particles having a single hollow at the center [5, 6] by seeded polymerization for highly (divinyl monomer/solvent)-swollen particles prepared utilizing the “dynamic swelling method” (DSM), which was proposed for the production of micron-sized, monodisperse polymer particles having more than 5-μm diameter [7, 8]. The formation mechanism of the hollow structure was discussed [9]. In a previous work, similar hollow polymer particles were produced by suspension polymerization for divinylbenzene (DVB)/toluene droplets dissolving polystyrene (PS) though they were polydisperse [10]. Suspension polymerization is one of polymerization techniques widely applying in industrial manufacturing. In the polymerization, PS dissolving in the droplets seemed to be one of the key factors for the formation of the hollow structure, because such a hollow polymer particle was not obtained without PS. Effect of the PS on the formation of the hollow structure was clarified in detail [11-13].

In this chapter, the suspension polymerization techniques will be developed to produce composite particles encapsulating hinokitiol (HT) which is sublimate and has melting point of 50~52˚C.



Hinokitiol

HT is abstracted from natural coniferous woods, and has attractive properties such as aromaticity, antibacterial activity and mildew resistance.

10.2 Expermental

10.2.1 Materials

Styrene (S) was purified by distillation under reduced pressure in nitrogen atmosphere. Ethylene glycol dimethacrylate (EGDM) and DVB (Nippon Steel Chemical. Co. Ltd., DVB96; purity 96%) were washed with 1N NaOH and deionized water to remove polymerization inhibitors. HT (Osaka Organic Chemical Industry Ltd., HT-SF; purity 99.9%) was directly used as received. Reagent grade benzoyl peroxide (BPO), 2,2’-azobis(isobutyronitrile) (AIBN), and 2,2’-azobis(4-methoxy-2, 4-dimethylvaleronitrile) (V-70) were purified by recrystallization. Polyvinyl alcohol (PVA) (Nippon Synthetic Chemical Ind. Co. Ltd., Gohsenol GH-17: Degree of polymerization, 1700; Degree of saponification, 88%) was used as colloidal stabilizer. Deionized water was distilled with a Pyrex distillator.

10.2.2 Preparation of PS

PS, which was dissolved in EGDM droplets, was prepared by solution polymerization of S (18 g) in toluene (54 g) with AIBN initiator (12 mg) in a sealed glass tube at 60˚C for 24 h. The PS was purified by reprecipitation into methanol and dried under reduced pressure. Weight- and number-average molecular weights (Mw; Mn) were, respectively, 1.6 x10^5 and 3.4 x10^5, which were measured by gel permeation chromatography with calibration obtained using PS standard with tetrahydrofuran as the eluant.

10.2.3 Suspension polymerization

A typical suspension polymerization is as follows: EGDM (250 mg) dissolving PS (50 mg), HT (25~250 mg) and AIBN (15 mg) were mixed with 3.80 wt% PVA aqueous solution (7.5 g) and stirred by NISSEI ABM-2 homogenizer at 1500 rpm for 2 min at room temperature in a glass cylindrical reactor. The suspension polymerization was carried out in a sealed glass at 40 or 70˚C for 48 h under nitrogen atmosphere listed in Table 1. The glass tubes were horizontally shaken at 80 cycles/min (3-cm strokes). The conversion was determined by gravimetry method with 100˚C oven.

10.2.4 Observation of composite particles

The composite particles were observed with a Nikon MICROPHOT-FXA optical microscope and a Hitachi S-2500 scanning electron microscope.

10.2.5 ^{1}H NMR measurement of HT

The ^{1}H NMR spectra were obtained with a BRUKER DPX250 NMR spectrometer operating at 250 MHz for protons. Dried PS/poly(ethylene glycol dimethacrylate) (PEGDM)/HT composite particles and pure HT were dispersed in $CDCl_3$, which does not dissolve the polymer particle but HT, dissolving tetramethylsilane as a standard reagent in a 5-mm NMR tube.

10.2.6 Measurement of the weight loss

Release rate of HT from the composite particles, which were placed on ϕ5-mm-aluminum pan, was evaluated by continuously measuring weight loss due to the evaporation of HT with thermogravimetry (Seiko Instrument TG/DTA 220U) at 150˚C under the N_2 flow.

10.2.7 Observation of ultrathin cross sections of the composite particles

The dried composite particles were dipped in epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross sections were observed with TEM.

10.3 Results and Discussion

In the previous paper [10], polymer particles having single hollow at the center had been successfully produced by suspension polymerization for DVB/toluene droplets dissolving PS and BPO initiator. In this article, HT was used in place of toluene.

Table 1 shows the polymerization recipes. In the system of 250 mg of HT (No. 3), the polymerization of DVB did not proceed for 48 h at 70˚C. The conversion increased with a decrease in HT content, but even in the system of 25 mg of HT (No. 1), it was 75% after 48 h. These results seem to be based on high chain transfer ability of HT which is a derivative of tropolone. In order

Table 1 Suspension polymerizations for PS/DVB droplets containing HT[a)]

Ingredients		No. 1[b)]	No. 2[b)]	No. 3[b)]	No. 4[c)]
PS[d)]	(mg)	50	50	50	50
DVB	(mg)	250	250	250	250
HT	(mg)	25	100	250	100
BPO	(mg)	15	15	15	-
V-70	(mg)	-	-	-	15
PVA	(mg)	24	24	24	24
Water	(g)	7.48	7.48	7.48	7.48
Conversion[e)]	(%)	75	40	0	41

a) Purity, 99.9% (by catalog)
b) N_2; 70˚C; 48 h
c) N_2; 40˚C; 48 h
d) M_w, 3.4×10^5; M_n, 1.6×10^5: Dissolved in DVB
e) Determined by gravimetry

Abbreviations: PS, polystyrene; DVB, divinylbenzene; HT, hinokitiol; BPO, benzoyl peroxide; V-70, 2, 2'-azobis(4-methoxy-2, 4-dimethylvaleronitrile); PVA, poly(vinyl alcohol)

Table 2 Transfer constants[a)] to additives in radical polymerization of styrene (S) or methyl methacrylate (MMA)

	S	MMA
Phenol	8.1×10^{-4} (50˚C)	2.5×10^{-4} (50˚C)
Hydroquinone	3.6×10^{-4} (60˚C)	7.0×10^{-4} (45˚C)
p- benzoquinone	227 (60˚C)	4.5 (60˚C)

[a)] *"Polymer Handbook" 4th Ed.*, WILEY (1999)

to depress a chain transfer reaction, V-70 was used as a initiator, of which half-life period at 30˚C is 10 h. However, the polymerization of DVB did not complete for 48 h at 40˚C. As shown in Table 2, transfer constants of S which is similar to DVB in radical polymerization to *p*-benzoquinone which have a similar chemical structure to HT has a large transfer constant in comparison with those of phenol and hydroquinone. On the other hand, in radical polymerizaiton of methylmethacrylate, the transfer constant to *p*-benzoquinone is much smaller than that in styrene system. Accordingly, EGDM, which is a kind of methacrylate monomer, was used as crosslinking monomer in place of DVB.

Table 3 shows the conditions and results. According to expectation, even at the system of 250 mg of HT (No. 3), the polymerization almost completed for 48 hours at 40˚C.

Figure 1 shows optical micrographs of PS/PEGDM/HT and PEGDM/HT composite particles produced by suspension polymerization under the conditions of Nos. 2 and 4 listed in Table 3. The composite particles pro-

Table 3 Suspension polymerizations[a)] for PS/EGDM droplets containing HT[b)]

Ingredients		No. 1	No. 2	No. 3	No. 4
PS[c)]	(mg)	50	50	50	-
EGDM	(mg)	250	250	250	250
HT	(mg)	25	100	250	100
V-70	(mg)	15	15	15	15
PVA	(mg)	24	24	24	24
Water	(g)	7.48	7.48	7.48	7.48
Conversion[d)]	(%)	100	100	94	93

[a)] N_2; 40˚C; 48 h

[b)] Purity, 99.9% (by catalog)

[c)] M_w, 3.4 x 10^5; M_n, 1.6 x 10^5: Dissolved in EGDM

[d)] Determined by gravimetry method

Abbreviation: EGDM, ethyleneglycol dimethacrylate

duced by the suspension polymerization of EGDM/HT droplets dissolving PS (Fig. 1a) seem to have heterogeneous structure in the inside. The other composite particles produced in presence of PS had similar heterogeneous structures. On the other hand, for comparison, the PEGDM/HT composite particles produced by the same procedure without PS (Fig. 1b) had a homo-

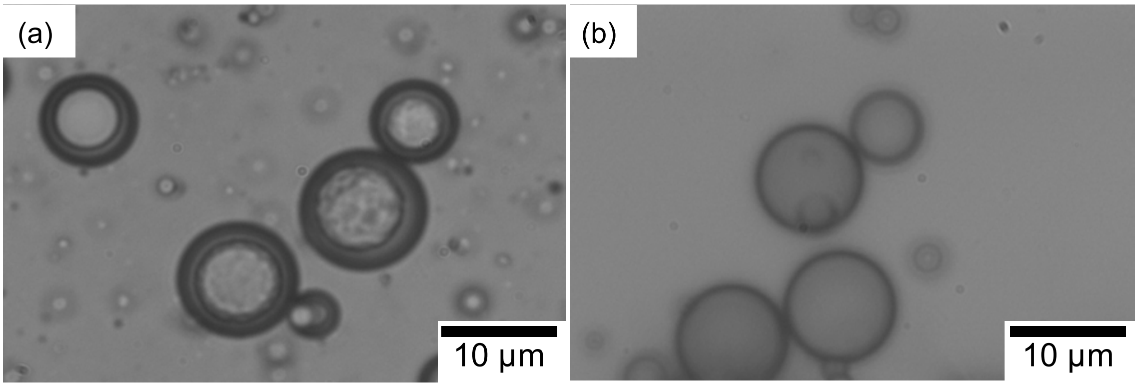


Fig. 1 Optical micrographs of PS/PEGDM/HT (a) and PEGDM/HT (b) composite particles produced by suspension polymerizations under the conditions of Nos. 2 and 4 listed in Table 3

geneous structure.

Figure 2 shows a SEM photograph of the PS/PEGDM/HT composite particles. The composite particles had smooth surfaces. Therefore, it is clear that the reason why the PS/PEGDM/HT composite particles had the heterogeneous structure on the optical micrograph shown in Fig. 1 was based on the heterogeneous structure in the inside.

Figure 3 shows TEM photographs of ultrathin cross sections of the PS/PEGDM/HT (a) and the PEGDM/HT (b) composite particles, which were, respectively, produced by suspension polymerizations under the conditions of Nos. 2 and 4 listed in Table 3. As can be seen in Fig. 3a, the shell and hollow structure were observed. The less dark regions indicate hollow region after evaporation of HT. The darker regions indicate remaining HT, which was removed by extraction with ethanol as shown in Fig. 4. The region of a similar contrast as the shell was also observed in the core. This is based on the polymers (PEGDM and PS), which was trapped in crystallized HT during the polymerization. At 40˚C, as EGDM monomer was consumed during the po-

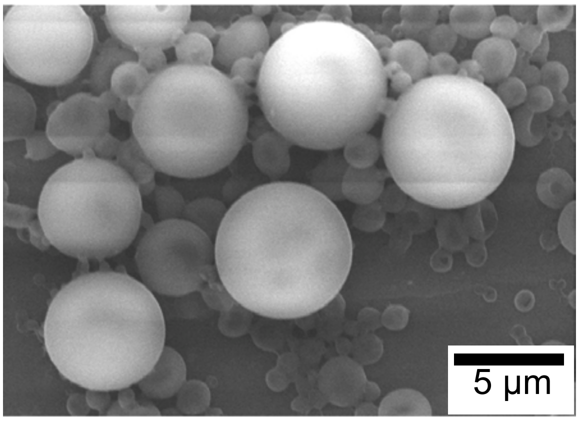


Fig. 2 SEM photograph of PS/PEGDM/HT composite particles produced by suspension polymerization for PS/EGDM droplets containing hinokitiol under the conditions of No. 2 listed in Table 3

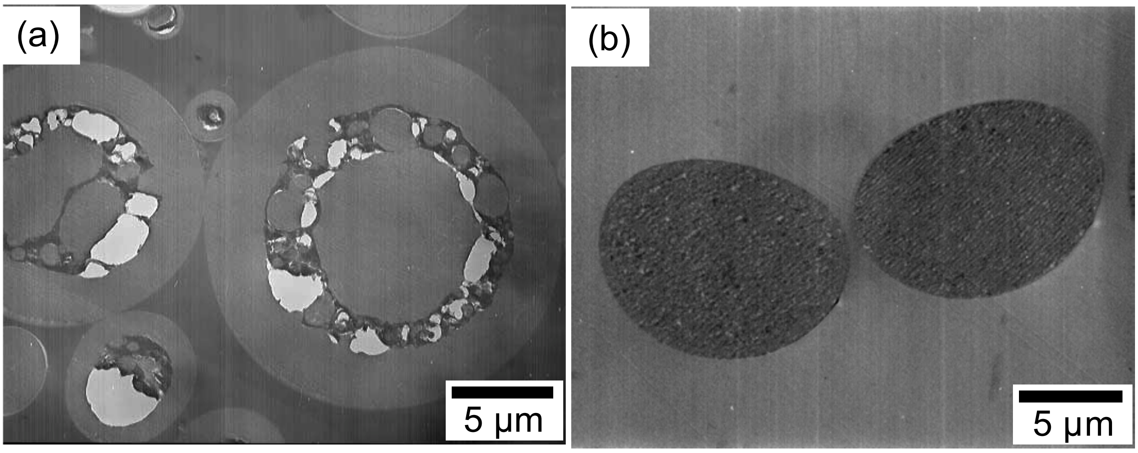


Fig. 3 TEM photographs of ultrathin cross sections of PS/PEGDM/HT (a) and PEGDM/HT (b) composite particles produced by suspension polymerization under the conditions of Nos. 2 and 4 listed in Table 3

lymerization, HT precipitated in the droplet because the polymerization temperature was below the melting point of the HT. Since the viscosity inside the polymerizing droplet became high, the polymers were trapped in the core region. On the other hand, such a core/shell structure was not observed in any sections of the PEGDM/HT composite particles and the inside of the sections was observed to be almost homogeneous. This suggests that the HT was dispersed homogeneously in the particles. In this way, the existence of

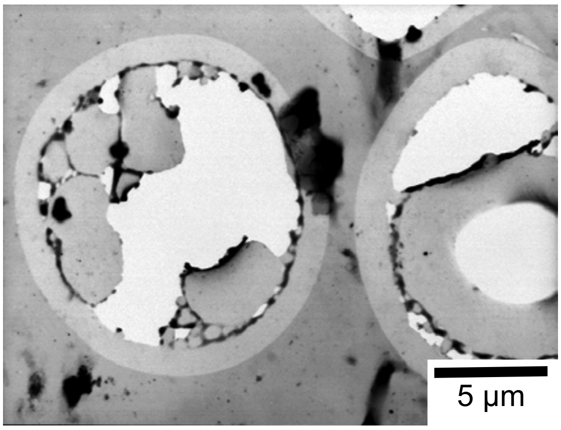


Fig. 4 A TEM photograph of ultrathin cross sections of PS/PEGDM/HT composite particles (Nos. 2 listed in Table 3) after extraction of HT with ethanol on the TEM grid

the PS dissolving in the droplets is important for the encapsulation of the HT by the PEGDM shell.

Figure 5 shows ^{1}H NMR spectra of the pure HT and the PS/PEGDM/HT composite particles. Most of peaks of the HT encapsulated in the hollow PS/PEGDM composite particle were in agreement with those of the pure HT, except for the broad peaks at 1~2, 5 and 6.2~7.2 ppm, which were assigned to PS and PVA. This indicates that the HT was not denaturalized during the suspension polymerization. This was also supported by the fact that the dried composite particle had the same smell as the pure HT.

Figure 6 shows weight loss curves due to the evaporation of the HT at 150˚C from the pure HT, the PS/PEGDM/HT and PEGDM/HT composite particles. Both composite particles were obtained by drying at room temperature in a desiccator with silica gel for few days to prevent depress the evaporation of the HT. Since PS and PEGDM are not decomposed at 150˚C, the

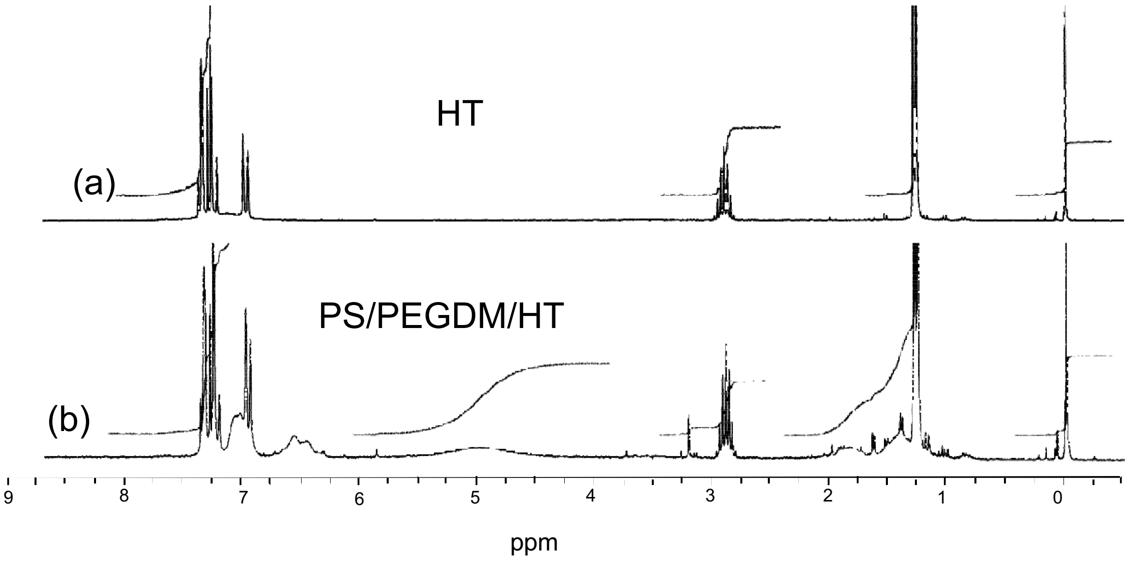


Fig. 5 ^{1}H NMR spectra of pure HT (a) and PS/PEGDM/HT composite particles (No. 2 listed in Table 3) (b) in $CDCl_3$ including 0.1 wt% TMS weight loss is due to only evaporation of HT. The weight of the pure HT decreased to zero within several minutes at 150˚C. On the other hand, the rate of weight loss from both composite particles was much slower than that of the pure HT. The rate of weight loss of the HT from the PS/PEGDM/HT composite particles was slower than that from the PEGDM/HT composite particles. The time needed to evaporate all the HT from the PS/PEGDM/HT and the PEGDM/HT composite particles were about 220 and 100 min, respectively. This indicates that the shell of the PS/PEGDM composite particle depresses the evaporation of the HT. The amounts of the HT in the composite particles calculated from the weight losses were about 80% based on the polymerization recipe. It seem that about 20% of the HT was lost by dissolving in the medium during the polymerization.

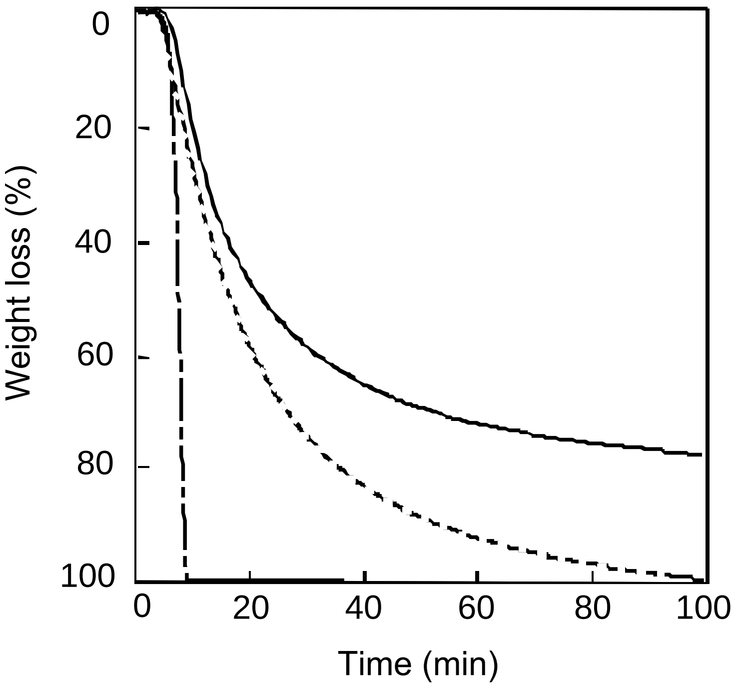


Fig. 6 Weight loss curves due to the evaporation of hinokitiol at 150˚C under the N2 flow from PS/PEGDM/HT (———) and PEGDM/HT (-------) composite particles which are produced by suspension polymerization under the conditions of Nos. 2 and 4 listed in Table 3, and pure HT (—— - ——)

Figure 7 shows optical micrographs of the PS/PEGDM/HT composite particles (a), and those (b) after drying at 100˚C for 6 days. In the latter composite particles from which the HT was completely released, less dark regions were observed in the inside, because of the evaporation of HT from the inside of the particle. The space was filled with air. This suggests that the PS/PEGDM/HT composite particles had an enough tough cross-linked shell to keep spherical shape even if the HT was released at 100˚C.

From the above results, it is concluded that the PS/PEGDM composite particle encapsulating the HT in the hollow was successfully produced by suspension polymerization for EGDM droplet dissolving PS and HT.

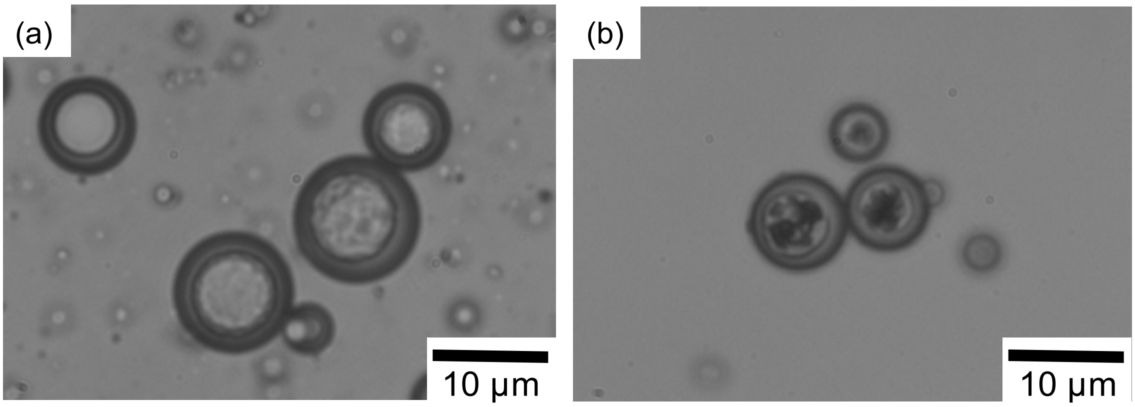


Fig. 7 Optical micrographs of PS/PEGDM/HT composite particles (a) produced by suspension polymerization for PS/EGDM droplets containing HT under the conditions of Nos. 2 listed in Table 3, and (b) redispersed in water after drying at 100˚C for 6 days.

10.4 Conclusion

Polystyrene/poly(ethylene glycol dimethacrylate) composite polymer particles containing hinokitiol (HT) were produced by suspension polymerization for ethylene glycol dimethacrylate droplets dissolving HT and polystyrene (PS) in poly(vinyl alcohol) aqueous solution. The composite particle had a hollow structure in which HT was included. Evaporation rate of HT from the composite particles became slower than that of pure HT.

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Conclusions

In the doctoral dissertation, production of micron-sized, monodisperse, functional polymer particles having single hollow structure were studied. The results have been summarized here.

PART I concerns the production of micron-sized, monodisperse polymer particles having single hollow structure by seeded polymerization utilizing the dynamic swelling method (DSM).

In **Chapter 1**, the polymer particles having single hollow structure were successfully produced by seeded polymerization for divinylbenzene (DVB)/ toluene-swollen polystyrene (PS) particles produced by DSM. First, 1.7 μm-sized monodispersed PS seed particles produced by dispersion polymerization were dispersed in ethanol/water (7/3, w/w) solution in which DVB, BPO, poly(vinyl alcohol), and toluene was dissolved. The PS seed particles were swollen with DVB, toluene and BPO maintaining high monodispersity throughout the DSM process where water was slowly added continuously. And then, the seeded polymerization of the (toluene/DVB)-swollen PS particles was carried out.

In **Chapter 2**, the control of hollow size of the hollow polymer particles was discussed. The hollow size was controllable by changing the amount of toluene or the kind of solvent. The hollow size increased with an increased in the weight ratio. Even if benzene and xylene were used in place of toluene, similar hollow particles were produced, though the hollow size was affected by their solubility in water.

In **Chapter 3**, the formation mechanism of the hollow structure was discussed. As the seeded polymerization proceeds, polydivinylbenzene (PDVB) molecules precipitated in the swollen particle are trapped near the interface and gradually piled at the inner surface, which results in cross-linked PDVB shell. PS which dissolve in the swollen particles are repelled gradually to the inside. After the completion of the polymerization, toluene in the hollow evaporates by drying, and PS clings to the inner wall of the shell uniformly.

In **Chapter 4**, the productions of micron-sized monodispersed polymer particles having a "red blood corpuscle-shape" were examined. In Chapter 3, nonspherical polymer particles having “rugby ball-like” and “red blood corpuscle-like” shapes were observed at low conversions of the seeded polymerization. It was clarified the conditions under which such nonspherical polymer particles were produced effectively at the completion of the seeded polymerization.

In **Chapter 5**, the conditions to produce the “rugby ball-like” polymer particles at the completion of the seeded polymerization were clarified. The optimum conditions were as follows: monomers/xylene=1/4 and DVB/VBP=1/11 ~ 1/16 (weight ratios). Moreover, the unique shape was reversibly transformable to/from by absorbing/ releasing of toluene.

In **Chapter 6**, the reversible shape transformation of the hollow composite polymer particle between spherical and such nonspherical shapes was studied in detail by controlling the shell strength. The nonspherical shapes were based on buckling of the shell of the produced hollow particles. A part of the shell was buckled by external pressure which was caused by evaporation of xylene from the hollow when the shell had the tensile modulus below the critical value calculated from the pressure-buckling relation of a spherical shell proposed by Uemura. The plasticization of the shell by a good solvent was one of key factors for the shape transformation.

In **Chapter 7**, the penetration and release behaviors of various solvents into/from the hollow particles were examined to study the usefulness of hollow particles as carriers. The penetration into the hollow was affected by viscosity of the solvents and its affinity for the base polymers. Toluene saved in the hollow was released slowly. These results suggest that there is a possibility to apply such hollow particles as a controlled release material.

In **Chapter 8**, the release behaviors of toluene from the hollow particles which have various cross-linking densities and shell thickness were studied in detail. The release of toluene from the hollow PS/PDVB composite particles seems to proceed as follows. During the release of toluene from the particles in which toluene exists in the polymer shell and the hollow, toluene is delivered to the shell from the hollow as soon as its evaporation from the particle, where the hollow is working as a reservoir. In the stage, a steady state was attained between evaporation from the outer shell surface and supply of toluene from the hollow to inner shell surface. After toluene disappears in the hollow, 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.

In **Chapter 9**, micron-sized, monodisperse magnetic composite particles having vinyl grope at their surfaces were prepared. The magnetic composite particles were prepared by heat treatment (200˚C; 4 h) of the micron-sized, monodisperse, hollow PS/PDVD composite polymer particles dipping pentacarbonyliron, following washing 12 N HCl and water. The hollow polymer particles were produced by seeded polymerization utilizing DSM

In **Chapter 10**, the production technique of hollow polymer particle was developed to produce composite particles encapsulating hinokitiol (HT). The PS/PEGDM composite particle encapsulating the HT in the hollow was successfully produced by suspension polymerization for EGDM droplet dissolving PS and HT. The composite particle had a hollow structure in which HT was included. Evaporation rate of HT from the composite particles became slower than that of pure HT.

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Chapter 1

Production of micron-sized monodispersed cross-linked polymer particles having hollow structure

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Chapter 2

Control of hollow size of micron-sized monodispersed polymer particles having a hollow structure

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Chapter 3

Formation mechanism of micron-sized monodispersed polymer particles having a hollow structure

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Chapter 4

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Chapter 5

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Chapter 7

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Chapter 10

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