Colloid Polym Sci 278:919–926 (2000)
© Springer-Verlag 2000

ORIGINAL CONTRIBUTION

M. Okubo
Y. Konishi
M. Takebe
H. Minami

Preparation of micron-sized, monodispersed, anomalous polymer particles by utilizing the solvent-absorbing/releasing method

Received: 3 August 1999
Accepted: 1 March 2000

Part CXCIX of the series "Studies on suspension and emulsion"

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

Abstract About 2-μm-sized polystyrene (PS) particles having uneven surfaces were prepared by a posttreatment in which toluene-swollen PS particles were thrown into a methanol bath to release toluene therefrom rapidly. The posttreatment was named the "solvent-absorbing/releasing method". The PS particle had large dents at the surface. The size of the dents was changed by the conditions of the posttreatment.

Key words Anomalous shape · Micron-sized, monodispersed particle · Solvent

Introduction

Polymer particles produced by emulsion polymerization are normally spherical because they minimize the interfacial free energy between the particle and the aqueous medium; however, in a series of our investigations on the production of sub-micron-sized composite polymer particles by seeded emulsion polymerization, various anomalous polymer particles have been produced [1–9].

On the other hand, recently, many researchers studying polymer colloids have been concentrating their attention on the production of micron-sized, monodispersed polymer particles [10–13] 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 (S) with chloromethyl styrene and divinylbenzene, respectively, in the presence of about 2-μm-sized, monodispersed polystyrene (PS) particles as seeds. However, it was difficult to produce monodispersed particles of more than 5-μm size even by dispersion polymerization and seeded dispersion polymerization. In order to produce monodispersed polymer particles having diameters above 5 μm, seeded polymerization utilizing a new type of swelling method of seed polymer particles with a large amount of monomer which was named "the dynamic swelling method" was suggested [17, 18]. In previous work [19, 20], this technique was developed to produce micron-sized, monodispersed polymer particles having one hollow in the inside, and the formation mechanism of the hollow structure was proposed [21]. Moreover, anomalous polymer particles having "rugby-ball-like" and "red-blood-corpuscle-like" shapes were observed at low conversions of the seeded polymerization for the production of hollow polymer particles [21, 22]. Control of the particle shape should be one of the functionalization of polymer particle [23].

In this study, the formation of micron-sized, monodispersed, anomalous polymer particles by a posttreatment is proposed.

Experimental

Materials

S was purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Poly(acrylic acid) used as a colloidal stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane [14]. The other ingredients were of reagent grade and were used as received.

Preparation of anomalous PS particles by posttreatment

Hydrophobic solvent was emulsified in an ethanol/water (2/3, v/v) medium dissolving sodium dodecyl sulfate by an ultrasonic homogenizer (US-300T, Nihonseiki) at 0 °C for 10 min. The prepared solvent emulsion was mixed with the ethanol aqueous dispersion of PS particles produced by dispersion polymerization of S under the conditions listed in Table 1. The mixture was stirred at room temperature with a magnetic stirrer at 200 rpm for 2.5 h. The mixture (about 10 g) was sprayed into an excess of methanol in a bath (200 ml) under stirring at 500 rpm with a nebulizer with a nozzle diameter of 0.39 mm equipped with an air pump (air pump: pressure, 0.12 kgf/cm^2; flow, 32 l/min) to release the solvent from the solvent-swollen PS particles rapidly. The PS particles and the swollen particles were observed with a Nikon MICROPHOT-FXA optical microscope, a Hitachi H-7100 TEM transmission electron microscope (TEM) and a Hitachi S-2500 scanning electron microscope (SEM).

Table 1 Production of micron-sized, monodispersed polystyrene (*PS*) particles by dispersion polymerization. N_2; 70 °C; 24 h; stirring rate, 60 rpm

Ingredients	
Styrene	30 g
2,2′-Azobis(isobutyronitrile)	540.5 mg
Poly(acrylic acid)	3.6 g
Ethanol	205.5 g
Water	60 g

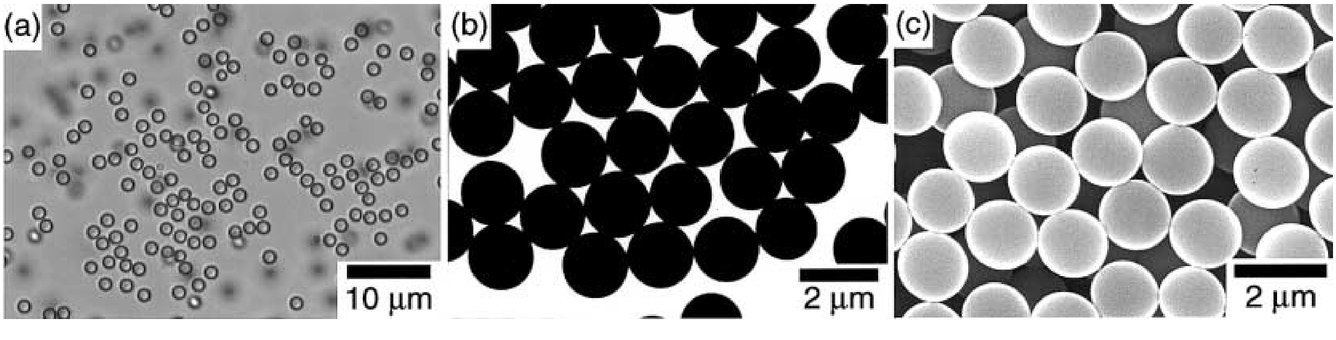


Fig. 1 **a** An optical micrograph, **b** a transmission electron microscope photograph and **c** a scanning electron microscope (*SEM*) photograph of polystyrene (*PS*) particles produced by dispersion polymerization under the conditions listed in Table 1

Measurement of the solubility of the solvent in the bath

Toluene (1 g) or decalin (3 g) respectively, was, added to a methanol/water or a methanol bath (10 g) in glass cylindrical reactors and these reactors were left at 30 °C for several hours. The amounts of the solvents dissolving in the baths were measured by gas chromatography (Shimadzu, GC-18APFsc).

Measurement of the dissolving rate of toluene in the bath

Toluene (50 mg) dissolving small amount of oil blue dye was added into the bath (50 g) in a glass cylindrical reactor (diameter, 40 mm) without stirring. The time for the toluene droplets to disappear was measured at room temperature.

Turbidity measurement

A nonsolvent (methanol, ethanol or 2-propanol) for PS was slowly dropped into a 0.1 wt% PS toluene solution (8 g). The transmittance of the solution at various contents of the nonsolvent was measured at room temperature with a photoelectric photometer (Tokyo Koden, Co., model 7) at 470 nm.

Results and discussion

An optical micrograph, a TEM photograph and a SEM photograph of PS particles produced by the dispersion polymerization of S in an ethanol/water (7/3, w/w) medium with AIBN initiator at 70 °C for 24 h under the conditions listed in Table 1 according to the optimum conditions in a previous article [14] are shown in Fig. 1. The particles were spherical and homogeneous in the inside, and the size of particles was monodisperse: the number-average diameter and the coefficient of variation determined from the TEM photograph were 1.6 μm and 3.7%, respectively. The weight-average molecular weight of PS, which was measured by gel permeation chromatography with calibration obtained using PS standards with tetrahydrofuran as the eluent, was 2.0×10^5.

An optical micrograph of toluene-swollen PS particles (PS/toluene: 1/10, w/w) is shown in Fig. 2a. The swollen particles were prepared by mixing an ethanol aqueous dispersion of the toluene droplets and the PS particles under the conditions listed in Table 2. The

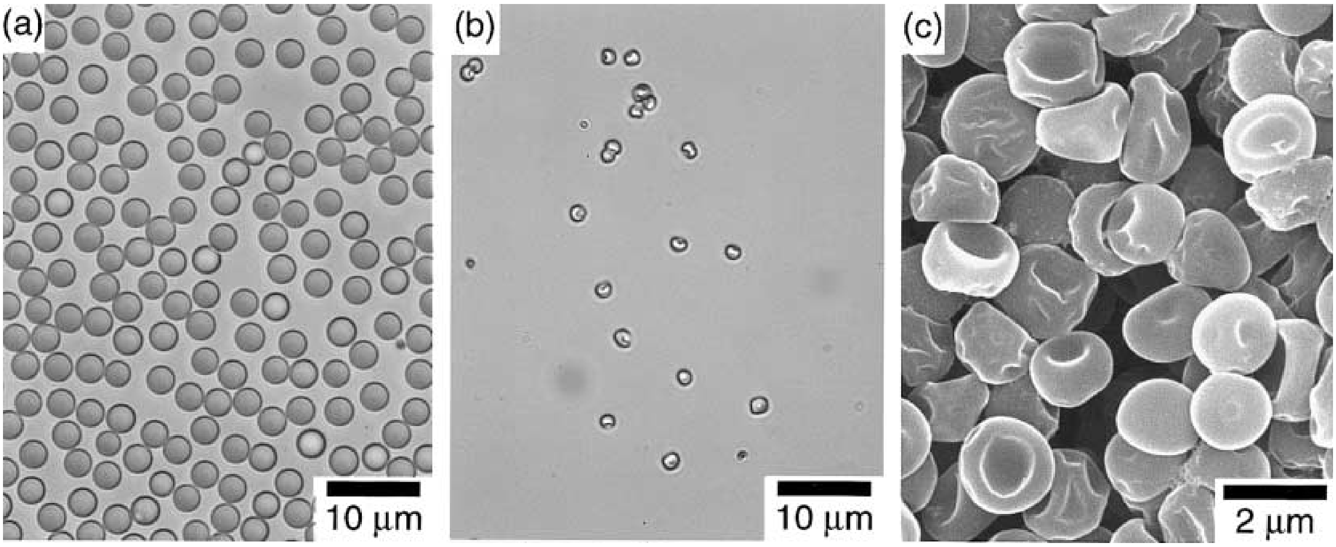


Fig. 2 **a** An optical micrograph of the toluene-swollen PS particles (PS/toluene: 1/10, w/w) prepared under the conditions listed in Table 2, and **b** an optical micrograph and **c** a SEM photograph of PS particles from which the toluene was released into a methanol bath by spraying the dispersion with a nebulizer

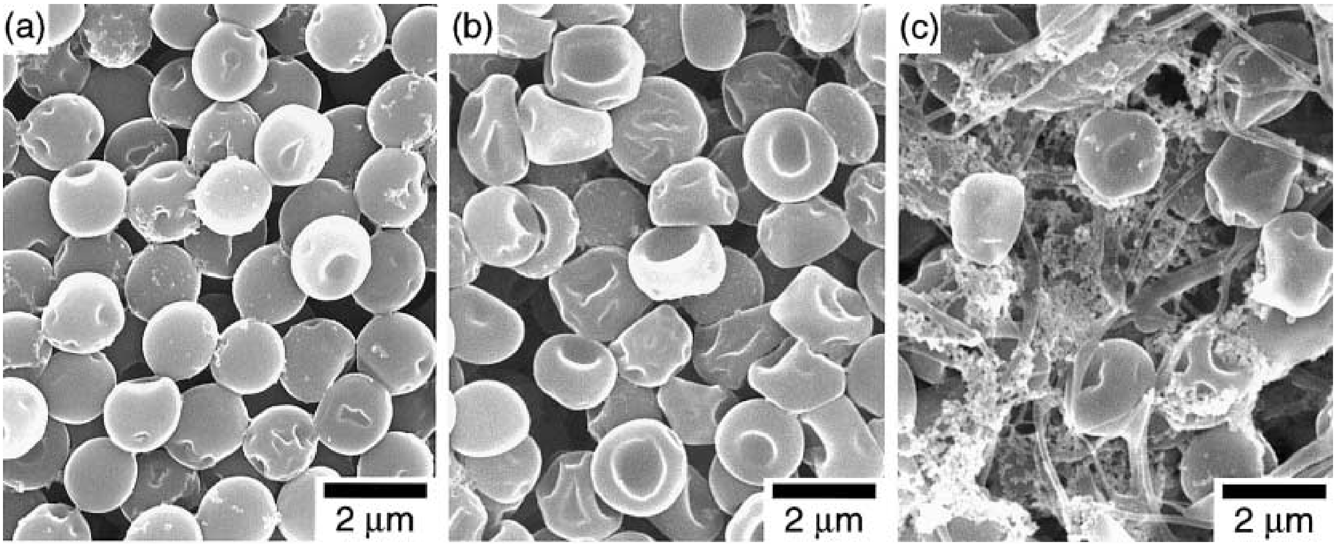
Table 2 Preparation of toluene-swollen PS particles by mixing a PS emulsion and a toluene emulsion

Ingredients	PS/toluene (w/w)		
	1/3	1/10	1/30
PS emulsion			
PS particles (g)	0.67	0.20	0.067
Ethanol (g)	23.6	18.8	17.5
Water (g)	47.1	37.7	35.0
Toluene emulsion[a]			
Toluene (g)	2.0	2.0	2.0
Sodium dodecyl sulfate (mg)	20	20	20
Ethanol (g)	3.3	3.3	3.3
Water (g)	6.7	6.7	6.7

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

mixture was stirred at room temperature with a magnetic stirrer at 200 rpm for 2.5 h to dissolve the PS particle in the swollen particle completely. The insides of the monodispersed swollen particles, of diameter 3.6 μm, were observed to be homogeneous. In all cases, the swollen particles were monodisperse and homo-

Fig. 3a–c SEM photographs of PS particles from which previously absorbed toluene was rapidly released into a methanol bath by spraying the dispersion with a nebulizer. PS/toluene (w/w): **a** 1/3; **b** 1/10; **c** 1/30



geneous. The swollen ratios were equal to the values calculated from the recipe. After the posttreatment described in the Experimental part, the PS particles dispersed in the bath had an anomalous shape as shown in an optical micrograph (Fig. 2b) and large dents at the surfaces were observed in a SEM photograph (Fig. 2c). Hereafter, this posttreatment will be called the ‘‘solvent-absorbing/releasing method’’ (SARM).

SEM photographs of PS particles after the absorbed toluene had been rapidly released into the methanol bath by spraying the emulsion with the nebulizer in which different swelling ratios of the toluene-swollen particles were dispersed are shown in Fig. 3. The concentration of the swollen particles in the ethanol/water media was constant. The size of the dents increased with an increase in the amount of toluene. At the PS/toluene ratio of 1/30, fiberlike PS particles were observed in addition to those having large dents. When the emulsion (20 μl) was dropped into methanol (10 ml) with a micropipet (about 6 mg per droplet), in which the shearing stress was not given to the swollen particles, fiberlike PS particles were not obtained. This indicates that the fiberlike PS particles might be prepared by high shearing stress to the swollen particles having low viscosity in the inside in the nebulizing process of the emulsion.

Figure 4 shows SEM photographs of PS particles after the absorbed toluene (PS/toluene: 1/10, w/w) had been released into the methanol bath with the nebulizer and with the micropipet. The particles formed with the

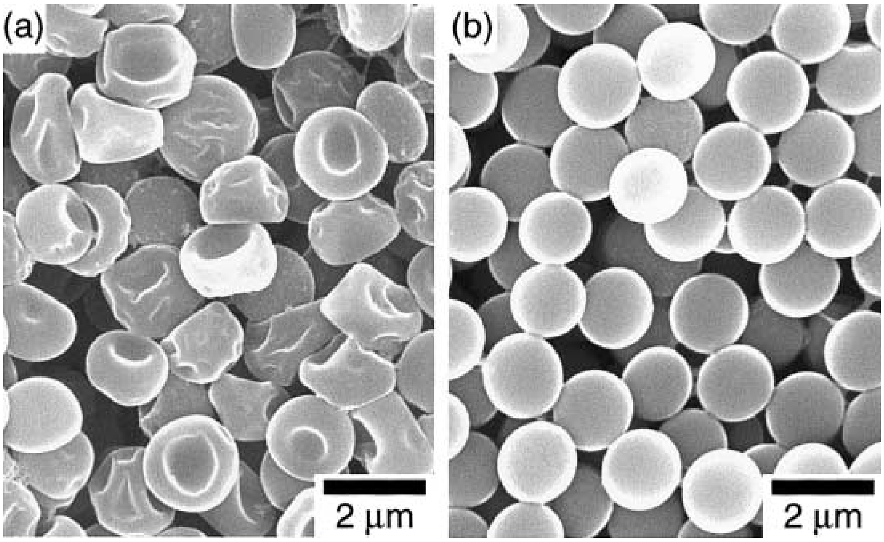


Fig. 4 SEM photographs of PS particles from which previously absorbed toluene (PS/toluene: 1/10, w/w) was rapidly released into a methanol bath by spraying the dispersion with **a** a nebulizer and **b** a micropipet

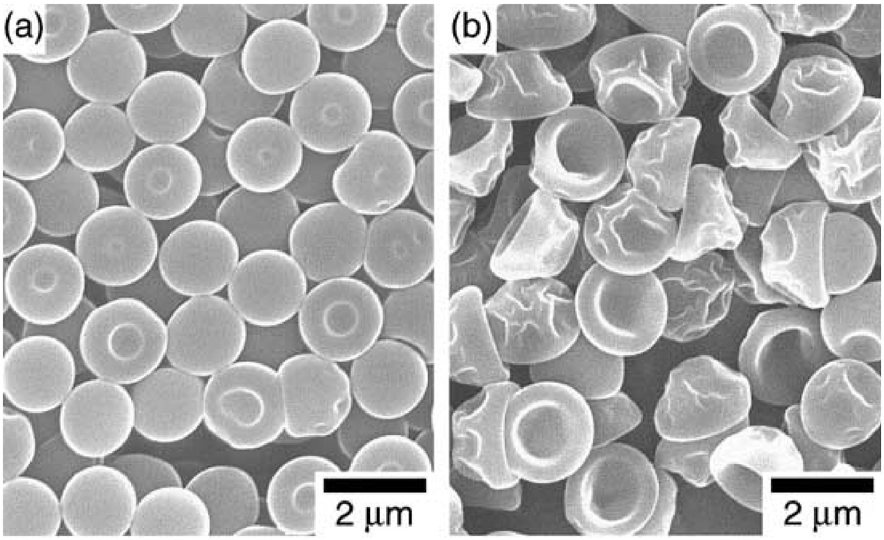


Fig. 5a, b SEM photographs of PS particles from which previously absorbed decalin was released into a methanol bath by dropwise addition of the dispersion with a micropipet. PS/decalin (w/w): **a** 1/3; **b** 1/10 nebulizer had large dents; on the other hand, those formed with the micropipet were spherical. Since the size (about 2.4 mm) of the droplets dropped with the micropipet was much bigger than that (less than 20 μm) with the nebulizer, the total interfacial area between the emulsion droplets containing swollen particles and the methanol bath was much smaller in the micropipet than that in the nebulizer. As a result, the release rate of toluene from the swollen particles to the bath should be slower in the micropipet than that in the nebulizer. In the former case, the shearing stress was not important as shown in Fig. 5.

SEM photographs of PS particles after the absorbed toluene (PS/toluene: 1/10, w/w) had been released into different compositions of the methanol/water bath with the nebulizer are shown in Fig. 6. The size of dents was the biggest in the case of methanol (Fig. 6a) and decreased with the decrease in the methanol content (Fig. 6b, c). When the ratio of methanol/water was less than 60/40, the particles were almost spherical (Fig. 6d, e, f). The size of the dents decreased with a decrease in the ratio of methanol/water. The influence of the composition of the methanol/water bath on the time to dissolve toluene is shown in Table 3. The release rate of toluene decreased with a decrease in the ratio of methanol/water, which seems to relate to the solubility of toluene in the bath as shown in Fig. 7. When the release rate of toluene decreases, the penetration rate of nonsolvent for PS from the bath should decrease. As a result, the precipitation rate of PS at the interface of the swollen particle should decrease with a decrease in

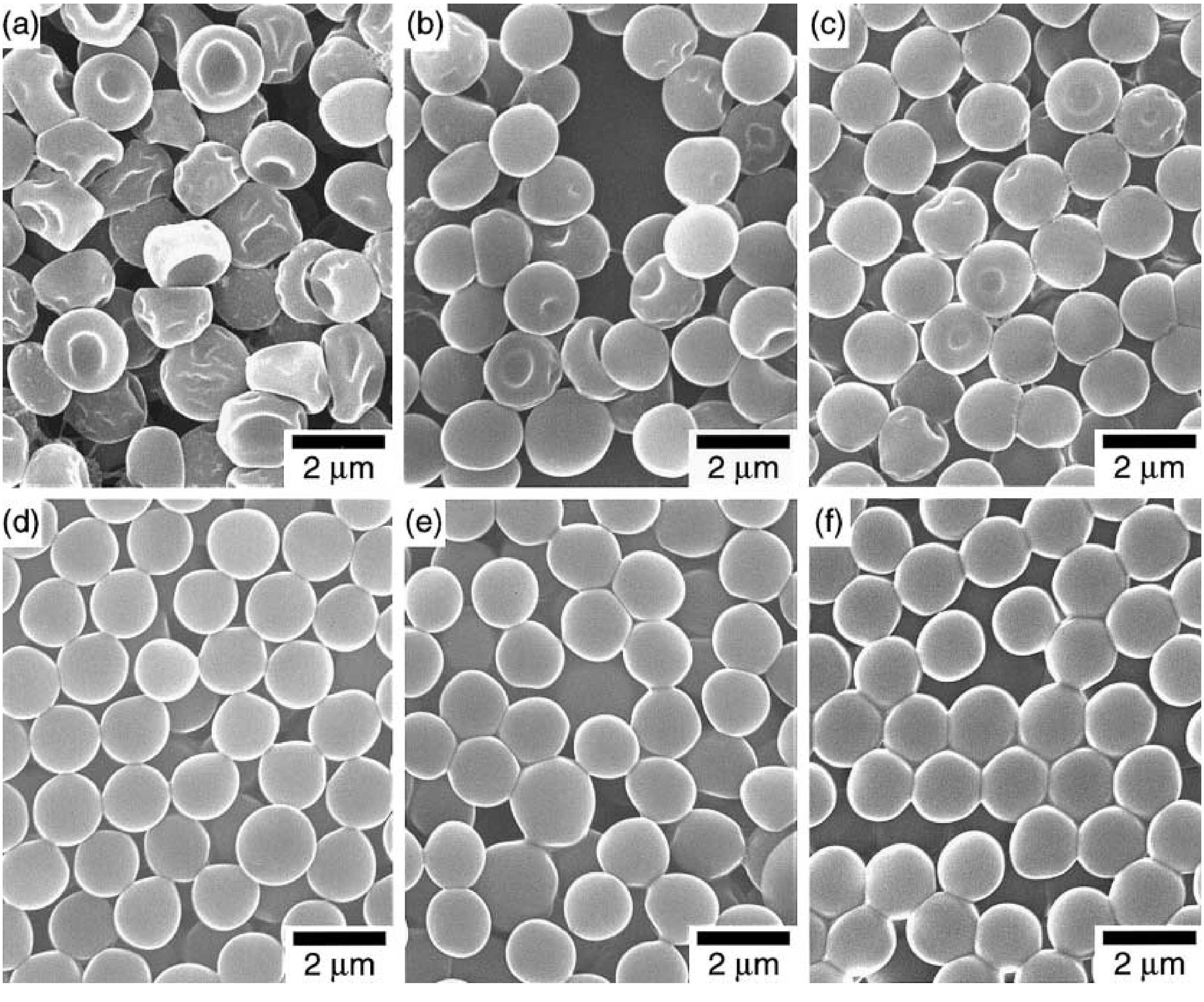


Fig. 6 SEM photographs of PS particles from which previously absorbed toluene (PS/toluene: 1/10, w/w) was released by spraying the dispersion with a nebulizer into a methanol/water bath (w/w): **a** 100/0; **b** 90/10; **c** 80/20; **d** 60/40; **e** 30/70; **f** 0/100

the release rate of toluene. This suggests that the release rate of toluene from the swollen particle is an important factor for the preparation of anomalous PS particles by the SARM.

Table 3 Dissolving rate of a toluene layer (50 mg) (dissolving oil blue dye) into methanol/water media (50 g) in a glass cylindrical reactor of 40-mm diameter without stirring at room temperature

Methanol/water (w/w)	100/0	90/10	70/30	60/40	50/50	40/60	30/70
Dissolving time	< 1 s	< 1 s	1 min	5 min	10 min	18 min	> 1 h

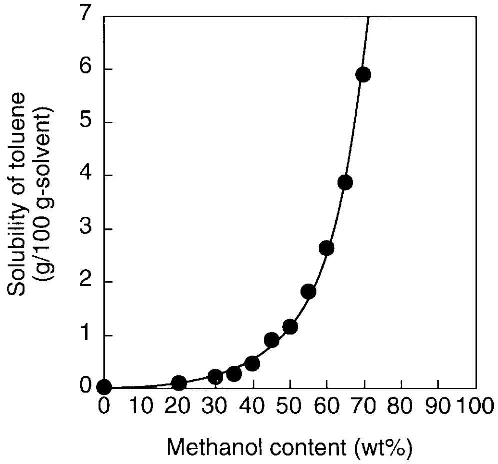


Fig. 7 A solubility curve of toluene in methanol/water media at 30 °C

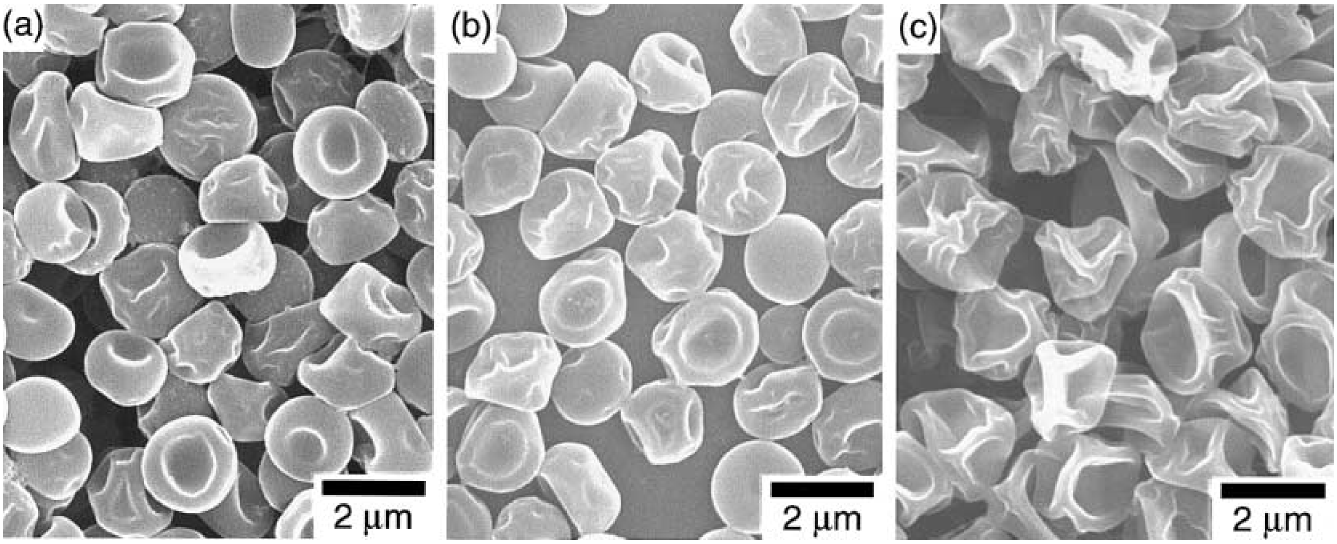


Fig. 8a–c SEM photographs of PS particles from which previously absorbed toluene (PS/solvent: 1/10, w/w) was released into a methanol bath by spraying the dispersion with a nebulizer. Solvent: **a** toluene; **b** ethylbenzene; **c** decalin

Table 4 Solubility of solvents in methanol at 30 °C

Solvent	Solubility (g/100 g methanol)
Toluene	∞
Ethylbenzene	∞
Decalin	14.5

SEM photographs of PS particles after the three kinds of absorbed solvents (PS/solvent: 1/10, w/w) had been released into the methanol bath with the nebulizer are shown in Fig. 8. Toluene, ethylbenzene and decalin were used as solvents. In all cases, the particles had anomalous shapes. In the case of decalin, the particle had the largest dents, although the release rate of the decalin should be slower than those of toluene and ethylbenzene because of its lower solubility in methanol (Table 4). Since decalin consisting of 60% *cis*-decalin and 40% *trans*-decalin has a θ temperature at 15 °C [2], it should be a poor solvent for PS at room temperature in comparison with toluene and ethylbenzene which are good solvents for PS. That is, the state of PS dissolved in the decalin must be compact in comparison with the states in toluene and ethylbenzene. These results indicate that the solubility power of a solvent for PS in the swollen particles is also an important factor for the preparation of anomalous polymer particles by the SARM.

As seen in Fig. 5, in the case of the decalin, the PS particles prepared by the SARM with the micropipet were also anomalous, while in the case of toluene they were spherical. These results indicate that the shearing stress is not important for the preparation of anomalous polymer particles by the SARM.

Figure 9 shows SEM photographs of PS particles after the absorbed toluene (PS/toluene: 1/10, w/w) had been released with the nebulizer into the three kinds of

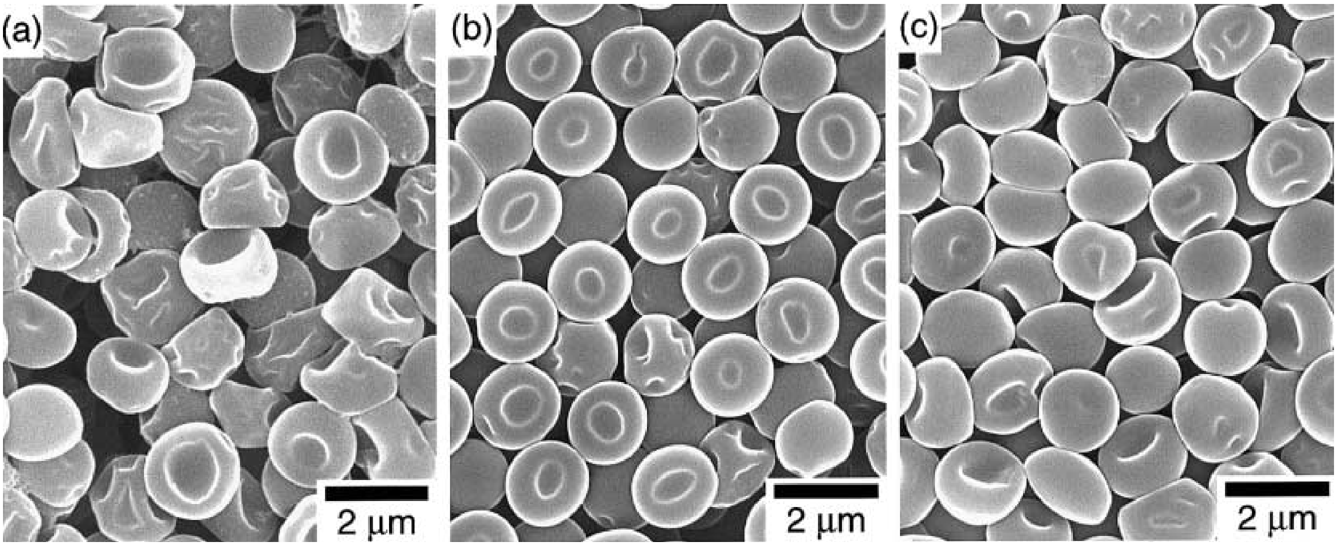


Fig. 9 SEM photographs of PS particles from which previously absorbed toluene (PS/toluene: 1/10, w/w) was released by spraying the dispersion with a nebulizer into **a** methanol, **b** ethanol and **c** 2-propanol baths

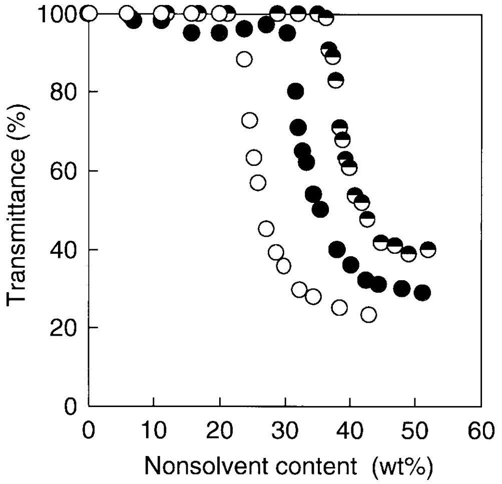
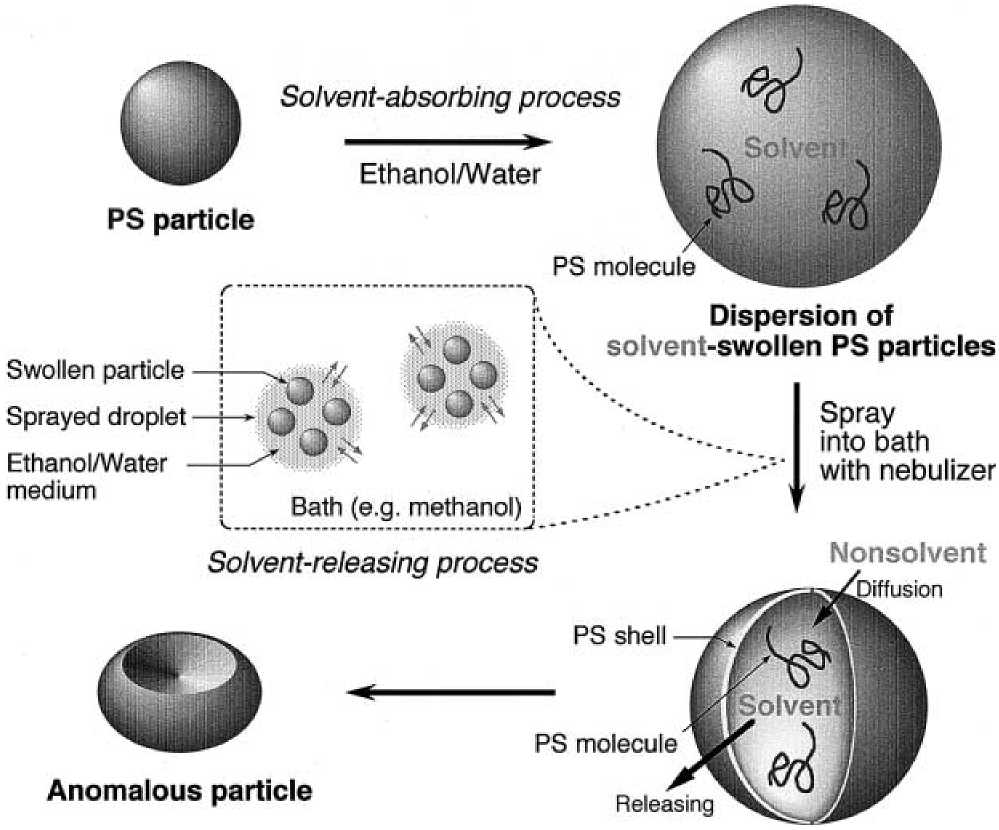


Fig. 10 Variations of optical transmittance of 0.1 wt% toluene solution of PS at 470 nm with the addition of nonsolvent: methanol (○); ethanol (●); 2-propanol (◓)

baths: methanol, ethanol and 2-propanol. As shown in Fig. 10, the precipitation power for PS increased in the order methanol > ethanol > 2-propanol. The stronger the precipitation power of the bath for PS, the larger the dents formed. These results indicate that the precipitation power of the bath for PS, in which toluene is released from the swollen particles, is also an important factor for the preparation of anomalous polymer particles by the SARM.

From these results, it is concluded that the SARM proposed here is a useful technique for the formation of the anomalous polymer particle having large dents at the surface. The formation mechanism of the anomalous particles by the SARM is proposed as shown in Fig. 11. The PS particle dissolves completely in the swollen particle prepared by the solvent-absorbing process. In the solvent-releasing process, the dispersion is sprayed into the bath. Since the medium of the dispersion is mixable with the bath solvent, the swollen particles disperse in the bath solvent in a short time. Since the swelling solvent in the swollen particles is mixable with the bath solvent, the swelling solvent is released from the particle into the bath and the bath solvent, which is nonsolvent for PS, penetrates into the particle and PS starts to precipitate at the interface, which results in a PS shell. The penetration rate of the bath solvent is slower than the release rate of the swelling solvent because of the hydrophobicity of the PS shell. As a result, a part of the shell dents because the shell strength is not enough to withstand the outer pressure.

Fig. 11 The formation mechanism of an anomalous particle by the solvent-absorbing/releasing method



References

1. Matsumoto T, Okubo M, Shibao S (1976) Kobunshi Ronbunshu 33:575
2. Okubo M, Katsuta Y, Yamada A, Matsumoto T (1979) Kobunshi Ronbunshu 36:459
3. Okubo M, Katsuta Y, Matsumoto T (1980) J Polym Sci Polym Lett Ed 18:481
4. Okubo M, Ando M, Yamada A, Katsuta Y, Matsumoto T (1981) J Polym Sci Polym Lett Ed 19:143
5. Okubo M, Katsuta Y, Matsumoto T (1982) J Polym Sci Polym Lett Ed 20:45
6. Okubo M, Kanaida K, Matsumoto T (1987) Colloid Polym Sci 265:876
7. Okubo M, Murakami Y, Tsukuda Y (1993) Chem Express 8:253
8. Okubo M, Murakami Y, Fujiwara T (1996) Colloid Polym Sci 274:520
9. Okubo M, Fujiwara T, Yamaguchi A (1998) Colloid Polym Sci 276:186
10. Corner T (1981) Colloids Surf 3:119
11. Almog Y, Reich S, Levy M (1982) Br Polym J 14:131
12. Ober CK, Lok KP, Hair ML (1985) J Polym Sci Polym Lett Ed 23:103
13. Tseng CM, Lu YY, EL-Aasser, Vanderhoff JW (1986) J Polym Sci Polym Chem Ed 24:2995
14. Okubo M, Ikegami K, Yamamoto Y (1989) Colloid Polym Sci 267:193
15. Okubo M, Katayama Y, Yamamoto Y (1991) Colloid Polym Sci 269:217
16. Yamamoto Y, Okubo M, Iwasaki Y (1991) Colloid Polym Sci 269:1126
17. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) Colloid Polym Sci 269:222
18. Okubo M, Shiozaki M (1993) Polym Int 30:469
19. Okubo M, Minami H, Yamashita T (1996) Makromol Chem Macromol Symp 101:509
20. Okubo M, Minami H (1996) Colloid Polym Sci 274:433
21. Okubo M, Minami H (1997) Colloid Polym Sci 275:992
22. Okubo M, Minami H Makromol Chem Macromol Symp (in press)
23. Chou C-S, Kowalski A, Rokowski JM, Schaller EJ (1987) J Coat Technol 59:93
24. Brandrup J, Immergut EH, Grulke EA (1999) Polymer handbook, 4th edn. Wiley, New York