Colloid Polym Sci (2004) 282: 1192–1197
DOI 10.1007/s00396-004-1057-8

ORIGINAL CONTRIBUTION

Masayoshi Okubo
Ryu Takekoh
Naohiko Saito

Formation mechanism of an "onionlike" multilayered structure by reconstruction of the morphology of micron-sized, monodisperse poly(methyl methacrylate)/polystyrene composite particles with the solvent-absorbing/solvent-releasing method

Received: 5 September 2003
Accepted: 12 December 2003

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

M. Okubo (✉) · R. Takekoh · N. Saito
Graduate School of Science and Technology, Kobe University,
657-8501 Kobe, Japan
E-mail: okubo@cx.kobe-u.ac.jp
Tel.: +81-78-803-6161
Fax: +81-78-803-6161

M. Okubo
Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University,
657-8501 Kobe, Japan

Abstract The formation mechanism of the "onionlike" multilayered morphology of micron-sized, monodisperse poly(methyl methacrylate) (PMMA)/polystyrene (PS) (1/1 w/w) composite particles by the solvent-absorbing/solvent-releasing method was discussed. It was concluded that the orientation of PMMA components at the outer interface of toluene-swollen particles with water is the trigger and that PMMA-*g*-PS operates to stabilize inner multilayer interfaces for the formation of the onionlike multilayered morphology.

Keywords Solvent-absorbing/solvent-releasing method · Multilayer · Poly(methyl methacrylate)-*g*-polystyrene · Morphology · Particle/medium interface

Introduction

Recently, micron-sized, monodisperse polymer particles have been used in biomedical, microelectronics and other fields. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized, monodisperse polymer particles. Corner [1] and Almog et al. [2] suggested that the dispersion polymerization technique is useful for the production of monodisperse polymer particles of less than 5 μm in diameter. Nevertheless, the technique seemed to be restricted for a variety of monomers for producing particles having functional groups at their surfaces, which would be required for use in the previously mentioned fields. Therefore, we have been producing monodisperse composite polymer particles having chloromethyl groups [3, 4] and vinyl groups [5, 6] by seeded dispersion copolymerization of styrene and chloromethylstyrene and of styrene and divinylbenzene in an ethanol/water medium, in the presence of 1.8 μm monodisperse polystyrene (PS) seed particles produced by dispersion polymerization.

In a previous study, poly(methyl methacrylate) (PMMA)/PS composite particles consisting of a PMMA core and a PS shell were produced by seeded dispersion polymerization of styrene with 1.91 μm monodisperse PMMA seed particles [7]. When toluene was absorbed into the composite particles and then released by evaporation, the reconstructed morphology was drastically changed. Especially, in the case of PMMA/PS (1/1 w/w) composite particles, an "onionlike" multilayered morphology was constructed [8]. We named this posttreatment the "solvent-absorbing/releasing method" (SARM). The viscosity within toluene-swollen composite particles, the release rate of toluene therefrom, the PMMA-to-PS ratio, and the kind of solvent had great influences on the reconstructed morphology of the PMMA/PS composite particles by the SARM. Simultaneously, the conditions for the preparation of the multilayered composite particles by the SARM were examined [9]. Moreover, it was clarified that PMMA-*g*-PS prepared in the process of the seeded dispersion polymerization was a key factor for the formation of the multilayered composite particles [10].

In this article, the formation mechanism of the multilayered composite particles is discussed in detail.

Experimental

Materials

Methyl methacrylate and styrene were purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-Azobis(isobutyronitrile) and 2,2′-azobis (2,4-dimethyl valeronitrile) (Wako Pure Chemical Industries, Japan) of reagent grade were purified by recrystallization. Deionized water with a specific resistance of 5×10^6 Ω cm was distilled. All other materials were used without further purification, including poly(vinylpyrrolidone) (PVP, weight-average molecular weight 3.6×10^5, Sigma Chemical Company), guaranteed reagent of methanol, toluene and sodium dodecyl sulfate (SDS).

PMMA seed particles and PMMA/PS (1/1 w/w) composite particles were produced by dispersion and seeded dispersion polymerizations according to the method in a previous article [9].

Reconstruction of the morphology by SARM

Swelling of composite particles with toluene was carried out under the conditions listed in Table 1. Toluene was emulsified in a SDS methanol/water (1/2 w/w) solution with an ultrasonic homogenizer (Nihonseiki US-300T, Japan) at 0 °C for 10 min. The toluene emulsion prepared was mixed with the composite emulsion and stirred with a magnetic stirrer at 140 rpm for 2 h at room temperature to prepare toluene-swollen particles. Toluene evaporated naturally at room temperature from 24.5 mL of the emulsion put in an uncovered glass cylindrical vessel whose evaporation area between the emulsion and air was 10 cm^2.

Table 1 Preparation of poly(methyl methacrylate) (*PMMA*)/polystyrene (*PS*)/toluene (1/1/20 weight ratio) particles by mixing a PMMA/PS composite emulsion and a toluene emulsion (prepared with an ultrasonic homogenizer)

Ingredients	Weight (g)
PMMA/PS emulsion	
PMMA/PS particles	0.1
Methanol	3.3
Water	6.6
Toluene emulsion	
Toluene	1.0
Sodium dodecyl sulfate	0.01
Methanol	3.3
Water	6.7

Observation of ultrathin cross-sections of the particles

The morphologies of the composite particles were estimated from the observation of their ultrathin cross-sections. Each cross-section was prepared as follows. The dried composite particles were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution, and then dispersed in an epoxy matrix, cured at room temperature for 24 h, and microtomed. The ultrathin cross-sections were observed with a JEOL JEM-200CX transmission electron microscope (TEM).

Observation of the surface of the particles

Dried PMMA/PS composite particles before and after the SARM were observed with a Hitachi S-2500 scanning electron microscope (SEM) and an atomic force microscope (AFM, Nanoscope IIIa, Digital Instruments) in the tapping mode using a SiN_4 cantilever in air.

X-ray photoelectron spectroscopy

Polymer compositions at the surfaces of the particles were estimated by X-ray photoelectron spectroscopy (XPS) (Kratos XSAM-800) using magnesium Kα radiation (1,253.6 eV) at a potential of 10 kV and an X-ray current of 20 mA. The pressure in the measurement chamber was around 2.7×10^{-6} Pa. The dried particles were spread on an indium plate with a spatula.

Preparation of the PMMA/PS dispersion

A toluene solution of PS and PMMA was mixed with an aqueous SDS solution under the conditions listed in Table 2 and was stirred by a Nissei ABM-2 homogenizer at 1,000 rpm for 2 min in a glass cylindrical vessel. The polymer dispersion was obtained by releasing toluene therefrom. The particles were classified into the size of the particles by centrifugal separation. Their ultrathin cross-sections were observed with the TEM after the particles had been stained with RuO_4 vapor for 30 min.

Results and discussion

SEM photographs of PMMA/PS (1/1 w/w) composite particles produced by seeded dispersion polymerization of styrene with PMMA particles in a methanol/water (7/3 w/w) medium and TEM photographs of their ultrathin cross-sections, before and after the SARM treatment with toluene in an uncovered glass cylindrical vessel, are shown in Fig. 1. In Fig. 1a, the surfaces of the com-

Table 2 Preparations of toluene droplets (the dispersion of toluene droplets was prepared with a homogenizer at 1,000 rpm for 2 min) dissolving PMMA/PS (produced by seeded dispersion polymerization)

Ingredients	Weight (g)
PMMA/PS	0.1
Toluene	1.0
Sodium dodecyl sulfate	0.01
Water	30.0

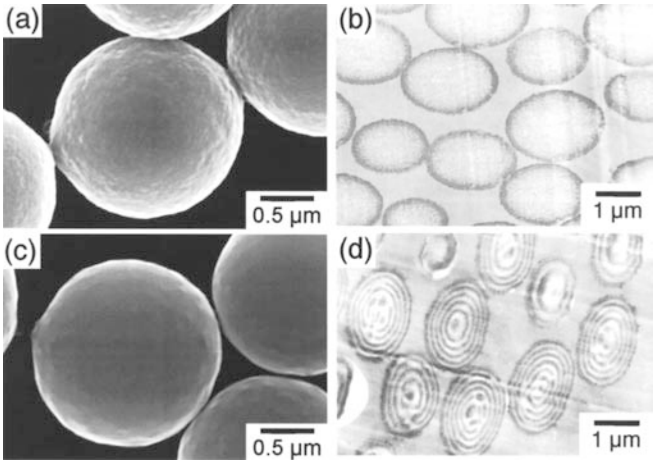

Fig. 1 **a, c** Scanning electron microscope photographs of poly (methyl methacrylate) (*PMMA*)/polystyrene (*PS*) composite particles and **b**, **d** transmission electron microscope (*TEM*) photographs of their ultrathin cross-sections, **a**, **b** before and **c**, **d** after the solvent-absorbing/solvent-releasing method (*SARM*) with toluene in an uncovered glass cylindrical vessel. Toluene-to-polymer ratio (w/w) Tp = 10

posite particles are not smooth, whereas those of the SARM-treated particles are smooth as shown in Fig. 1c. This difference was also confirmed in AFM images of the PMMA/PS composite particle before and after the SARM treatment as shown in Fig. 2. This seems to be the result of the formation of the PMMA core/PS shell morphology of the original particles by the seeded dispersion polymerization proceeded under kinetic control [7, 11], whereas the multilayered structure formed by the SARM was controlled thermodynamically.

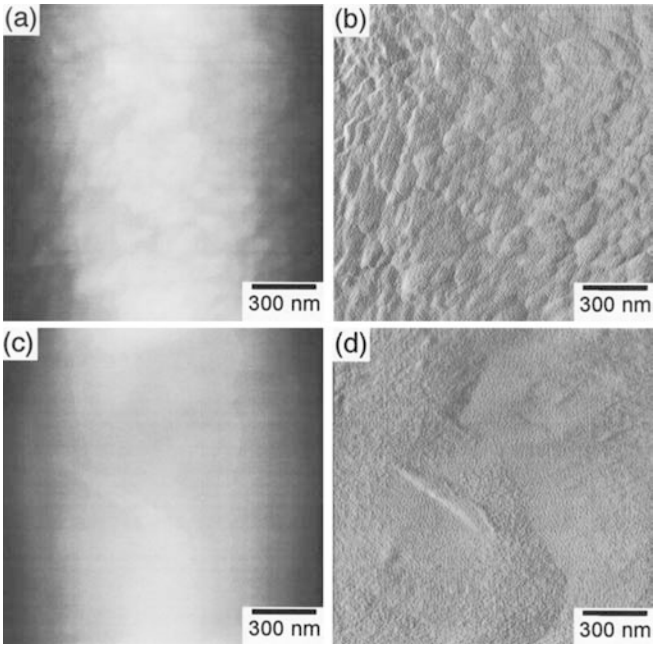

Fig. 2 Atomic force microscope **a**, **c** height and **b**, **d** amplitude images in the tapping-mode for the PMMA/PS (1/1 w/w) composite particle **a**, **d** before and **c**, **d** after the SARM with toluene

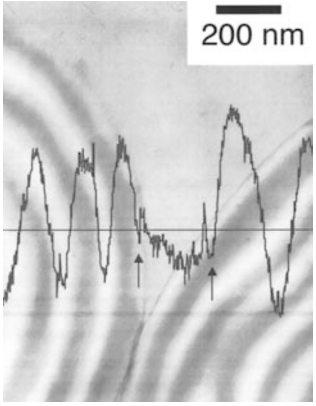

Fig. 3 A TEM photograph of an ultrathin cross-section of RuO_4-stained PMMA/PS composite particles after the SARM with toluene at Tp = 10 in an uncovered glass cylindrical vessel

A TEM photograph of the ultrathin cross-section indicating the outer surface of the SARM-treated RuO_4-stained PMMA/PS (1/1 w/w) composite particles is shown in Fig. 3. The wavy line indicates the variation of the transmittance on the scanning straight line across the cross-section around the particle surface. Light and shaded layers, which were, respectively, due to PMMA and PS, were observed alternately and the particle surface had a light, thin layer. This suggests that the SARM-treated structure and the particle surface consisted of PMMA.

C_{1s} X-ray photoelectron spectra of the PMMA/PS (1/1 w/w) composite particles before and after the SARM treatment are shown in Fig. 4. In Fig. 4b, a peak due to carbonyl groups of PMMA is observed at around 289 eV, whereas in Fig. 4a, no such peak is observed but a strong peak due to PS is observed at 285 eV in addition to two small broad peaks due to PVP at 287 and

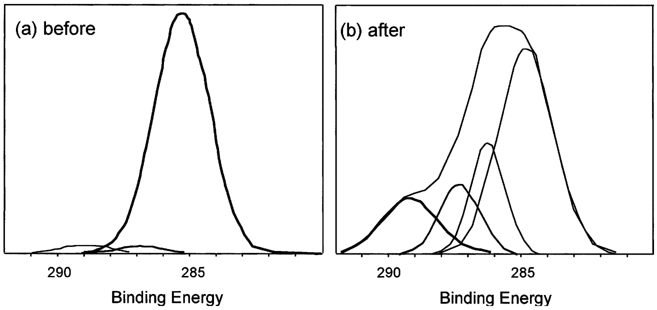

Fig. 4 X-ray photoelectron spectroscopy C_{1s} peak shape analyses of the PMMA/PS (1/1 w/w) composite particles **a** before and **b** after the SARM with toluene

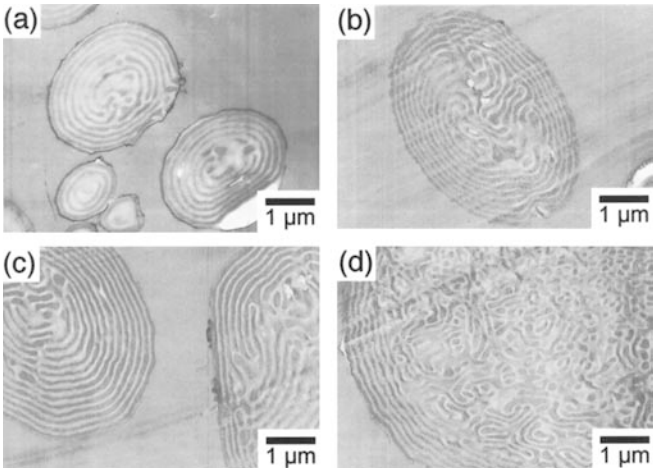

Fig. 5 TEM photographs of ultrathin cross-sections of RuO_4-stained PMMA/PS (1/1 w/w) composite particles by releasing toluene from toluene droplets dissolving PMMA/PS particles, which were produced by seeded dispersion polymerization, at Tp = 10 in aqueous medium: Number-average diameters (μm)/coefficient of variation (%): **a** 3.3/37.5; **b** 6.6/26.6; **c** 9.3/17.4; **d** 13.3/19.2

289 eV. This clearly shows that the surfaces of the composite particles before and after the SARM treatment consisted of PS and PMMA, respectively. The replacement of PS by the PMMA homopolymers and/or the part of PMMA chains belonging to PMMA-*g*-PS at the particle surface during the SARM should decrease the interfacial tension with water. That is, the replacement proceeds under a thermodynamically stable state.

In the SARM treatment, when the SDS concentration was high or a nonionic emulsifier was used, it was found that the particle surface was occupied partially or completely by a PS layer. This will be discussed elsewhere.

TEM photographs of ultrathin cross-sections of RuO_4-stained PMMA/PS (1/1 w/w) composite particles with different diameters prepared by releasing toluene from toluene droplets dissolving the composite particles are shown in Fig. 5. As the particle diameter was increased, the formation of an onionlike multilayered structure was limited only near the surface of the particles and the layered structure fell into disorder in the inside. This result suggests that the particle/medium interface had a great influence on the reconstruction of the onionlike multilayered morphology of the composite particle.

TEM photographs of ultrathin cross-sections of RuO_4-stained PMMA/PS (1/1 w/w) composite particles, which were prepared by releasing toluene rapidly from the toluene-swollen composite particles by dropping the aqueous dispersion into methanol, are shown in Fig. 6. The release rate of toluene is so fast that a phase-separated structure in the swelling state seems to be closely related to the reconstructed morphology of the composite particles. The toluene solution dissolving the original PMMA/PS composite particles was kept homogeneous at a toluene-to-polymers weight ratio of 9.7/1, but took place in phase separation below a ratio of 8/1. In Fig. 6a, the particles prepared from a swelling state at the ratio of 9.7/1 had a different morphology from the multilayered one. In the other cases below the ratio of 6.5/1, the morphologies of the composite particles were the multilayered structures though the structure was incomplete at a high ratio. This result suggests that the multilayered structure was already constructed in the swelling state.

TEM photographs of ultrathin cross-sections of RuO_4-stained PMMA/PS (1/1 w/w) composite particles, which were prepared by releasing toluene from toluene-swollen particles in a petri dish after the dispersion had been kept in a covered glass cylindrical vessel for 12 h, are shown in Fig. 7. The release rate of toluene in the dispersion (toluene-to-polymer ratio of 10/1 w/w) kept in the petri dish was so fast for the composite particles that the multilayered structure could not be formed as

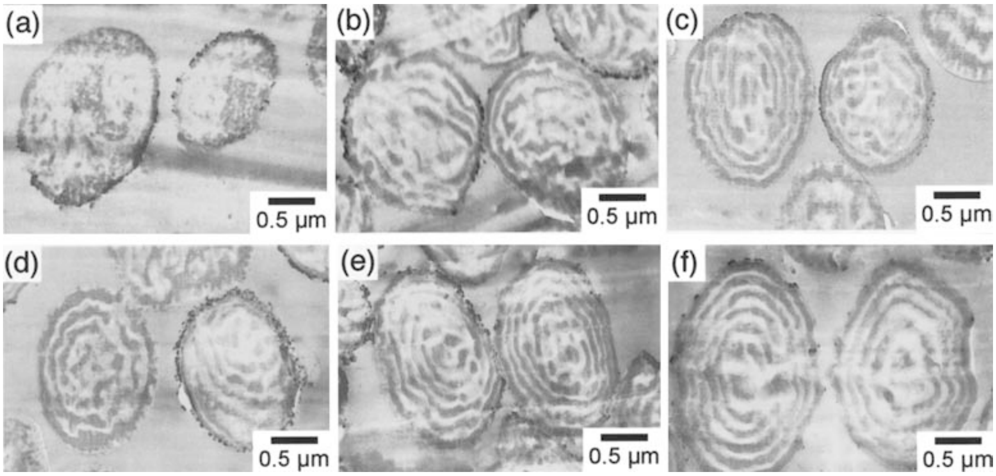

Fig. 6 TEM photographs of ultrathin cross-sections of RuO_4-stained PMMA/PS (1/1 w/w) composite particles prepared by dropping toluene-swollen composite particles, which were dispersed in water and released toluene slowly by evaporation, into methanol: Toluene-to-polymer ratio (v/v) just before the dropping: **a** 9.7/1; **b** 6.5/1; **c** 4.0/1; **d** 2.8/1; **e** 1.4/1; **f** 0.3/1

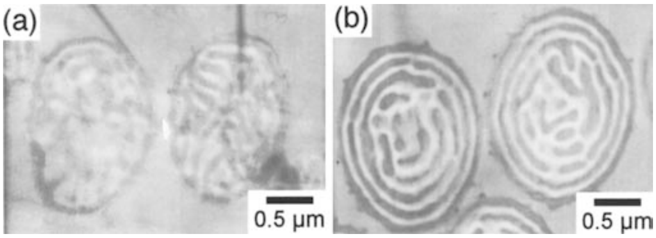

Fig. 7 TEM photographs of ultrathin cross-sections of RuO_4-stained PMMA/PS (1/1 w/w) composite particles after placing toluene-swollen composite particles at **a** Tp = 10 and **b** Tp = 6 in water for 12 h in a covered glass cylindrical vessel and the toluene was evaporated quickly therefrom in a petri dish

reported in a previous article [9]. In fact, in Fig. 7a, the morphology of the composite particles is not a multilayered structure. On the other hand, a multilayered structure is observed in Fig. 7b. The formation of the multilayered structure seems to be due to the equilibrium swelling state that was formed by keeping the droplets for 12 h. In the case of a toluene-to-polymer weight ratio of 10/1, the inside of the droplets was homogeneous even after being left for 12 h because phase separation does not occur. On the other hand, in the case of the ratio of 6/1, phase separation must proceed in the droplet within 12 h. Therefore, the multilayered particles seem to be obtained in spite of the high release rate of toluene. That is, the multilayered structure may be reconstructed before the toluene release.

In a previous study [12], it was clarified that the morphology of the SARM-treated PMMA/PS composite particles depended markedly on the nature of the solvent in the SARM. When the solubility parameter (Table 3) of the solvent is close to that of PS or PMMA, respectively, the sea-islands structure in which PMMA-domains were dispersed in a PS-matrix or the inverse sea-islands structure was obtained. When toluene with an intermediate solubility parameter was used, composite particles with a multilayered structure were prepared. That is, the morphology of the SARM-treated PMMA/PS composite particles depended on the nature of the solvent in the swelling state. These results are similar to those in previous articles [13] in that the final morphology of the cast films depended on the nature of the solvent. In a previous article [9], it was also clarified that the morphology of the SARM-treated composite particles depended on the polymer composition. At PMMA-to-PS weight ratios of 2/1, 1/1, and 2/3, the morphologies of the SARM-treated composite particles had a sea-islands structure consisting of a PMMA-matrix and PS-domains, a multilayered structure, and an inverse sea-islands structure consisting of a PS-matrix and PMMA-domains, respectively. These tendencies are similar to the results that polymer compositions and the kind of solvent changed the morphologies of block copolymer films [13] and block copolymer/homopolymer blend films [14], respectively, to lamellae, cylinders and spheres. According to Sadronand Gallot [13] the morphology of an A–B diblock copolymer in a given solvent mainly depends on the volume ratio $(V_A + V_{SA})/(V_B + V_{SB})$, where V_A (or V_B) is the volume of sequence A (or B) in the A–B diblock copolymer and V_{SA} (or V_{SB}) is the volume of the solvent contained in sequence A (or B) in the phase-separation state. Inoue et al. [14] pointed out that the morphology depended on the volume ratio $(V_A + V_{HA})/(V_B + V_{HB})$, where V_{HA} (or V_{HB}) is the volume of the homopolymer contained in sequence A (or B) in the phase-separation state [14]. As already described, the morphology of the SARM-treated PMMA/PS composite particles also changed to sea-islands, multilayered and inverse sea-islands structures on changing the polymer compositions and the kind of solvent (Fig. 8).

From these results, it is concluded that the formation mechanism of the multilayered composite particles is as follows. The PMMA/PS composite particles produced by seeded dispersion polymerization consist of PMMA, PS and PMMA-*g*-PS [10]. The inside of the toluene-swollen particles was homogeneous before toluene evaporation in the SARM treatment. When phase separation occurs in the toluene-swollen particles with toluene evaporation, PMMA molecules and/or some of the PMMA chains belonging to PMMA-*g*-PS adsorb at the particle/medium interface to decrease the interfacial

Table 3 Solubility parameters of PMMA, PS and various solvents

	Solubility parameter ($MPa^{1/2}$) [15]
PS	17.5–18.5
p-Xylene	18.0
Ethylbenzene	18.0
Toluene	18.2
Benzene	18.8
Chloroform	19.0
PMMA	18.5–19.5

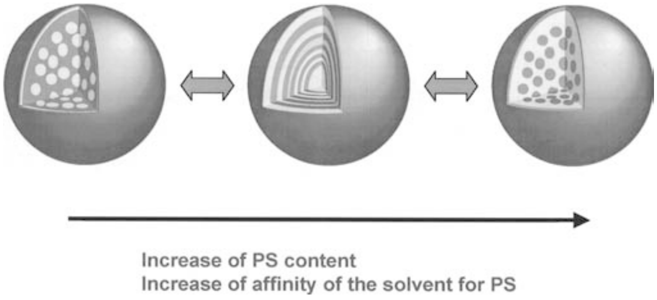

Fig. 8 Schematic model of the reconstruction of the morphology of a PMMA/PS composite particle by the SARM

tension and PS chains belonging to PMMA-*g*-PS orient to the center of the swollen particles. PS homopolymers and/or some of the PS chains belonging to PMMA-*g*-PS migrate to some of the PS chains belonging to the PMMA-*g*-PS at the outer surface layer and this results in a second layer consisting of PS, and some of the PMMA chains belonging to PMMA-*g*-PS orient to the center of the toluene-swollen particles. When the volume of the PS phase is almost the same as that of the PMMA phase, the multilayered structure of the toluene-swollen particles is reconstructed. This multilayered structure is kept until the end of the toluene evaporation, and finally the multilayered composite particles are prepared.

References

1. Corner T (1981) Colloids Surf 3:119
2. Almog Y, Reich S, Levy M (1982) Br Polym J 14:131
3. Okubo M, Ikegami K, Yamamoto Y (1989) Colloid Polym Sci 267:193
4. Okubo M, Yamamoto Y, Iwasaki Y (1991) Colloid Polym Sci 269:1126
5. Okubo M, Katayama Y, Yamamoto Y (1991) Colloid Polym Sci 269:217
6. Okubo M, Nakagawa T (1994) Colloid Polym Sci 272:530
7. Okubo M, J Izumi, T Hosotani, T Yamashita (1997) Colloid Polym Sci 275:797
8. Okubo M, Izumi J, Takekoh R (1999) Colloid Polym Sci 277:875
9. Okubo M, Takekoh R Izumi J (2001) Colloid Polym Sci 279:513
10. Okubo M, Takekoh R, Saito N Colloid Polym Sci (in press)
11. Okubo M, Yamada A, Matsumoto T (1980) J Polym Sci Polym Chem Ed 16 3219
12. Okubo M, Takekoh R, Saito N Prog Colloid Polym Sci (in press)
13. Sadron C, Gallot B (1973) Makromol Chem 164:301
14. Inoue T, Soen T, Hashimoto T, Kawai H (1970) Macromolecules 3:87
15. (1999) Polymer handbook, 4th edn. Wiley, New York