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SHORT COMMUNICATION

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Production of micron-sized monodispersed core/shell polymethyl methacrylate/polystyrene particles by seeded dispersion polymerization

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Abstract Micron-sized monodispersed polymethyl methacrylate (PMMA)/polystyrene (PS) (PMMA/PS = 2/1, wt ratio) composite particles consisting of PMMA-core and PS-shell were successfully produced by seeded dispersion polymerization of styrene in a methanol/water medium in the presence of about 2 μm-sized monodispersed PMMA particles. From the view point of thermodynamic equilibrium, such a morphology is difficult to form by usual seeded polymerization in a polar medium such as water. It is concluded that seeded dispersion polymerization in which almost all monomers and initiators exist in the medium has an advantage to produce core/shell polymer particles in which polymer layers accumulate in their order of the production regardless of the hydrophobicity of polymers, because of high viscosity in polymerizing particles.

Key words Composite polymer particles – core/shell – seeded dispersion polymerization – morphology – monodisperse

Introduction

Recently, micron-sized monodispersed 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 monodispersed polymer particles. Almog et al. [1] suggested that dispersion polymerization technique is useful for the production of them. Later, Ober et al. [2], Tseng et al. [3], and we [4] have recognized the usefulness of this technique.

Nevertheless, the technique seemed to be restricted for a variety of monomers for producing particles having functional groups thereon, which would be required for use in the above applications. Therefore, we have been producing about 2 μm-sized monodispersed polymer particles having chloromethyl groups [4, 5] and vinyl groups [6, 7] at the surfaces by the seeded dispersion copolymerizations of styrene (S) and chloromethylstyrene and of S and divinylbenzene in ethanol/water media, in the presence of 1.8 μm-sized monodispersed polystyrene (PS) seed particles produced by dispersion polymerization. In those produced composite particles, the functional groups preferentially distributed at the surface layers.

In a previous article [8], three types of seeded polymerization of *n*-butyl methacrylate as one of general methacrylic monomer were carried out with 1.76 μm-sized monodispersed PS seed particles. PS/poly(*n*-butyl methacrylate) (PBMA) composite particles produced by seeded dispersion polymerization consisted of PS-core and PBMA-shell.

Since, during a general seeded dispersion polymerization, almost all monomers exist in medium, viscosity in seed particles is so high that polymer radicals are unable to diffuse inside from the particle surface. As the consequence, each polymer formed by the seeded dispersion polymerizations described above seems to accumulate on the PS seed particle. That is, morphology of composite particles seemed to be controlled kinetically.

However, under the condition that polymers can move easily in particles, the morphology should be based on equilibrium surface thermodynamics in which the role of interfacial tensions was highlighted [9]. In fact, in the seeded emulsion polymerization of S with 90 nm-sized polyethylacrylate (PEA) particles [10], hydrophobic PS formed did not accumulate on the hydrophilic PEA seed particle, but diffused inside, resulting in PEA/PS composite particles consisting of PS-core and PEA-shell. Similar morphology was observed in polymethyl methacrylate (PMMA)/PS composite particles, in which PS is more hydrophobic than PMMA, produced by the seeded emulsion polymerization of S with about 200 nm-sized PMMA particles with monomer absorption method [11]. Where the viscosity in the particles is comparatively low, because almost all of S monomers were absorbed by PMMA seed particles prior to the polymerization. In this way, in PMMA/PS composite particles, if the morphology is thermodynamically controlled, it should consist of PS-core and PMMA-shell, whereas if it is kinetically controlled, it should consist of PMMA-core and PS-shell.

In this article, in order to clarify whether the particle morphology in the seeded dispersion polymerization is controlled kinetically, the morphology of micron-sized monodispersed PMMA/PS composite polymer particles produced by seeded dispersion polymerization of S with 1.91 μm-sized monodispersed PMMA particles will be examined.

Experimental

Materials

Methyl methacrylate (MMA) and S were purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-azobisisobutyronitrile (AIBN) and [2,2′-azobis-(2,4-dimethyl valeronitrile)] (VA-65, Wako Pure Chemical Industries, Ltd., Japan) of reagent grade were purified by recrystallization. Deionized water with a specific conductivity of $5 \times 10^6\ \Omega$cm was distilled. Polyvinylpyrrolidone (PVP, Sigma Chemical Company), tricaprylyl methylammonium chloride (Aliquat® 336, Aldrich Chemical Company, Inc.), reagent-grade methanol and cyclohexane were used as received.

Preparation of PMMA seed particles

Monodisperse PMMA seed particles were produced by dispersion polymerization under the conditions listed in Table 1, which was partially referred to the recipes used by Almog et al. [1] and El Aasser et al. [12]. The polymerization was carried out in a 300 ml three-neck round-bottom flask equipped with a Teflon paddle stirrer operating at 120 rpm.

Preparation of PMMA/PS composite particles

Seeded dispersion polymerization of S was carried out in the presence of the PMMA seed particles in a sealed glass tube under a nitrogen atmosphere at 60 °C for 24 h under the conditions listed in Table 2. The tube was horizontally shaken at 120 cycles/min (2 cm strokes). Diameter and distribution of each particle were observed with a JEOL JEM-2010 transmission electron microscope (TEM). The number-average diameter (D_n) and the coefficient of variation (C_v) were measured with a Personal Image Analysis System (PIAS Co., Ltd., LA-525, Japan).

Table 1 Preparation of micron-sized monodispersed PMMA seed particles by dispersion polymerization[a)]

Ingredient		
MMA	(g)	24
V-65	(g)	0.36
PVP	(g)	5.6
Aliquat® 336	(g)	1.6
Methanol	(g)	179.2
Water	(g)	44.8

[a)] N_2; 46 °C; 24 h; stirring rate, 120 rpm.
Abbreviations: PMMA, polymethyl methacrylate; V-65, [2,2′-Azobis-(2,4-dimethyl valeronitrile)]; PVP, poly(vinyl pyrrolidone); Aliquat® 336, tricaprylylmethylammonium chloride.

Table 2 Recipe for the production of PMMA/PS (2/1, w/w) composite particles by seeded dispersion polymerization[a)]

Ingredient		
PMMA seed particles[b)]	(g)	0.6
S	(g)	0.3
AIBN	(mg)	4.71
PVP	(g)	0.03
Methanol	(g)	9.6
Water	(g)	2.4

[a)] N_2; 60 °C; 24 h.
[b)] D_n, 1.91 μm; C_v, 3.1%.
Abbreviations: PMMA, polymethyl methacrylate; PS polystyrene; S, styrene; AIBN, 2,2′-azobisisobutyronitrile; PVP, poly(vinyl pyrrolidone).

Determination of the amount of S monomer in the medium

The amount of S dissolved in the methanol/water medium from which PMMA seed particles was separated by centrifugation prior to the seeded dispersion polymerization was determined by gas chromatography.

Determination of the weight ratio of PMMA/PS in the composite particles

The weight ratio of PMMA/PS in the composite particles was determined with ^{1}H-NMR. ^{1}H-NMR measurement was carried out with a BRUKER DPX250 MHz spectrometer at rt in $CDCl_3$.

X-ray photoelectron spectroscopy (XPS)

XPS data were obtained with a Kratos XSAM-800 apparatus using magnesium Kα radiation (1253.6 eV) at a potential of 12.5 kV and an X-ray current of 12 mA. The pressure in the measurement chamber was ca. 4×10^{-7} Torr. A Digital Equipment Corporation DS-800 computer system was used for spectrometer control and data handling. Dried particles were stored under reduced pressure by continuous operation of a diffusion pump just before XPS measurement. The dried particles were spread on an indium plate with a spatula.

Extraction of PS from PMMA/PS composite particles

The medium of PMMA/PS dispersion was changed from methanol/water to cyclohexane by repeated centrifugation. Cyclohexane dissolves PS but not PMMA above 35 °C. The extraction was carried out under stirring at 40 °C for 48 h.

Observation of ultrathin cross sections of PMMA/PS composite particles

Dried PMMA seed particles and PMMA/PS composite particles before and after the extraction treatment of PS with cyclohexane were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution, and then dispersed in epoxy matrix, cured at room temperature for 24 h, and at 40 °C for 1 h, and microtomed. The ultrathin cross sections were observed with TEM.

Extraction of PMMA from the ultrathin cross sections of PMMA/PS composite particles

In order to extract PMMA from the ultrathin cross sections of original PMMA/PS composite particles, acetic acid was dropped onto the grid with the cross sections, and the grid was dried up at room temperature. After several repetitions of this procedure, the ultrathin cross sections were observed with TEM.

Results and discussion

Figure 1 shows a TEM photograph of PMMA seed particles by dispersion polymerization under the conditions listed in Table 1. D_n and C_v were 1.91 μm and 3.1%, respectively.

Figure 2 shows TEM photographs of PMMA/PS composite particles produced by the seeded dispersion polymerization under the conditions listed in Table 2, before (a) and after (b) centrifugal washing to remove PVP. It was confirmed experimentally with gas chromatography that almost all S monomers dissolved in the methanol/water medium before the polymerization. In the seeded dispersion polymerization for 24 h, the conversion of S was 96%, and no by-produced PS particle was observed as shown in Fig. 2a. Moreover, the result of ^{1}H-NMR measurement also indicates that the weight ratio of PMMA/PS in the produced composite particles was 2/1, which agreed well with that calculated from the polymerization recipe.

Figure 3 shows a TEM photograph of PMMA/PS composite particles after exposed to strong electron beam: Accelerating voltage, 200 kV; current density, 40 pA/cm^2. In Fig. 2b, the contrast of the inside of the particles was homogeneous, whereas in Fig. 3 each particle had a less dark circular region inside the particle. As it is known that

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

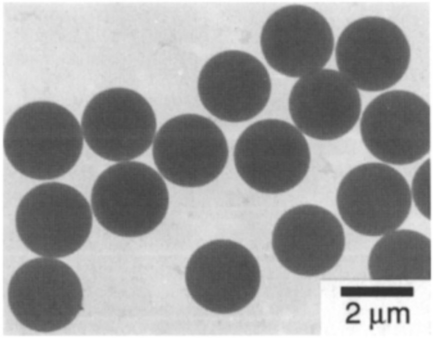
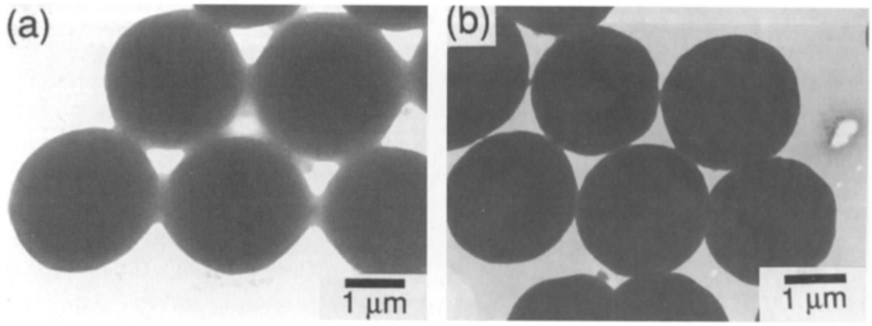


Fig. 2 TEM photographs of PMMA/PS composite particles produced by seeded dispersion polymerization under the conditions listed in Table 2, before (a) and after (b) centrifugal washing



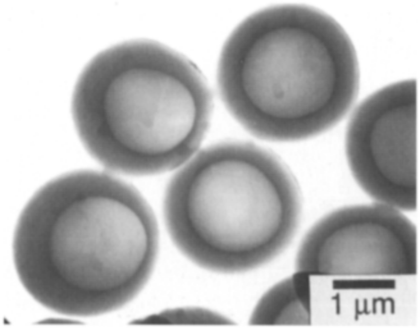


Fig. 3 TEM photograph of PMMA/PS (2/1, w/w) composite particles after exposed to strong electron beam

electron beam resolutes PMMA, this result indicates that the composite particle had PMMA-core.

Figure 4 shows the results of C1s peak shape analysis of XPS spectra of PMMA (a), PS (b), and PMMA/PS composite particles (c). In Fig. 4a, a peak due to carbonyl groups was observed at 289 eV, whereas in Fig. 4c no such peak and a strong peak due to PS at 285 eV as shown in Fig. 4b were observed although there were some small peaks due to PVP. These results indicate that the surface layer of the composite particle, of thickness about 50 Å, consisted of PS.

Figure 5 shows TEM photographs of ultrathin cross sections of PMMA seed particles (a) and PMMA/PS

Fig. 4 C1s peak shape analysis of XPS spectra for PMMA (a), PS (b), and PMMA/PS (2/1, w/w) composite particles (c)

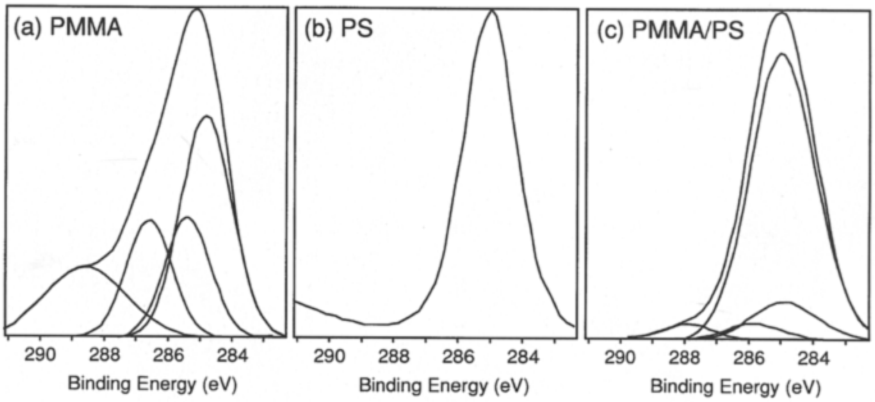
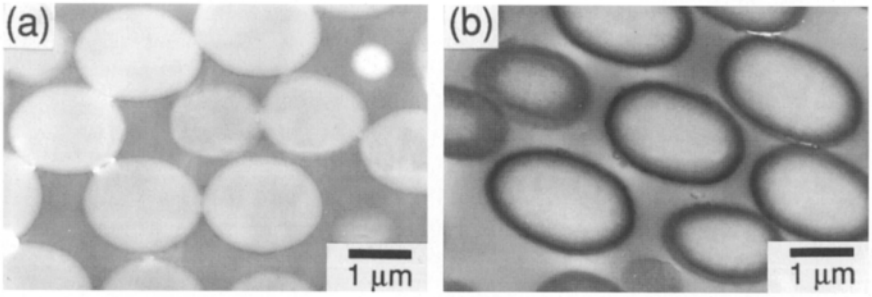


Fig. 5 TEM photographs of ultrathin cross sections of PMMA seed particles (a) and PMMA/PS (2/1, w/w) composite particles (b), stained with RuO_4 vapor for 30 min



composite particles (b), stained with RuO_4 vapor. It is known that RuO_4 predominantly stains PS [13]. In Fig. 5a, the contrast inside the PMMA seed particles was homogeneous, whereas in Fig. 5b the surface layer which was more dark than the inside was observed in the composite particles. Moreover, the thickness of the surface layer was in accord with that of PS shell which was calculated from the polymerization recipe assuming that all polymerized PS accumulate on the PMMA seed particles. These results indicate that the composite particles had a core/shell structure consisting of a PMMA-core and a PS-shell.

Figure 6 shows TEM photograph after the extraction of PMMA from the original ultrathin cross sections of the PMMA/PS composite particles on the TEM grid with acetic acid. In comparison with Figs. 5b and 6, it seems that less contrast region disappeared by the extraction of PMMA. This result supports the morphology described above.

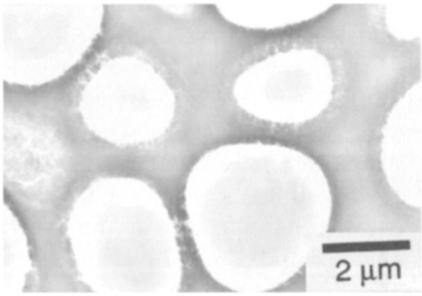


Fig. 6 TEM photograph after the extraction of PMMA from ultrathin cross sections of the PMMA/PS composite particles on the TEM grid with acetic acid

Figure 7 shows TEM photographs of the PMMA/PS composite particles (a) and ultrathin cross sections (b) after the extraction of PS with cyclohexane. In comparison with Figs. 2b and 7a, the shape of the composite particles was not changed by extraction. In Fig. 7b the dark shell layer shown in Fig. 5b disappeared by the extraction of PS. This result also supports the morphology described above, which will be shown experimentally to be unstable thermodynamically in a following article.

From these results, it is clear that the particle morphology in this seeded dispersion polymerization system was controlled kinetically. In other words, it is concluded that seeded dispersion polymerization technique has an advantage to produce core/shell polymer particles in which polymer layers accumulate in their order of production, regardless of the hydrophobicity of polymers forming core and shell, namely, even if produced morphology is unstable thermodynamically.

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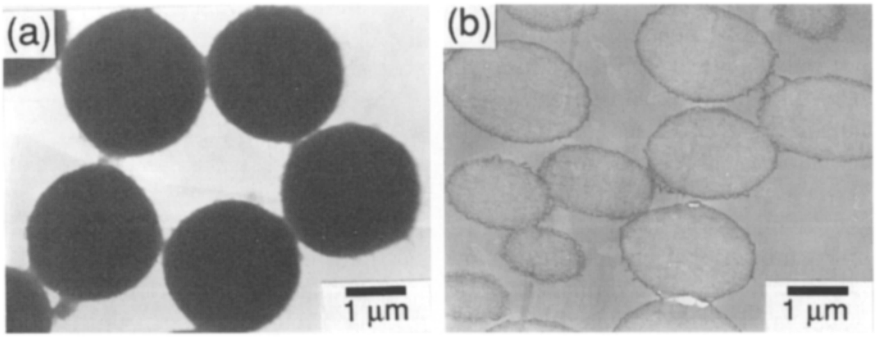
Fig. 7 TEM photographs of the PMMA/PS (2/1, w/w) composite particles (a) and the ultrathin cross sections (b) after the extraction with cyclohexane under stirring at 40 °C for 48 h



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