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SHORT COMMUNICATION

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Production of micron-sized, monodispersed, multilayered composite polymer particles by multistep seeded dispersion polymerization

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Abstract Micron-sized, monodispersed, poly(methyl methacrylate) (PMMA)/polystyrene (PS)/PMMA/PS multilayered composite particles were successfully produced by three-step seeded dispersion polymerizations in methanol/water media. The first seeded dispersion polymerization was carried out with 2-μm-sized, monodispersed PMMA particles.

Key words Composite particle · Core/shell · Seeded dispersion polymerization · Multilayer · Monodisperse

Introduction

Recently, micron-sized, monodispersed polymer particles have been applied in the biomedical field, microelectronics, and other areas. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized, monodispersed polymer particles. Almog et al. [1] have suggested that the dispersion polymerization technique is required for their production. Ober et al. [2], Tseng et al. [3], and we [4] have also recognized the usefulness of this technique.

Nevertheless, this technique seemed to be restricted to a variety of monomers producing particles with functional groups thereon which would be required for use in the previously mentioned applications. Therefore, we have been producing about 2-μm-sized, monodispersed, composite polymer particles with 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 these composite particles, the functional groups are preferentially distributed at the surface layers. The results show the suitability of seeded dispersion polymerization (SDP) for the production of core/shell composite polymer particles.

In order to clarify this idea, in a previous article [8], SDP of *n*-butyl methacrylate (*n*-BMA) as an example of a general methacrylic monomer was carried out with 1.76-μm-sized, monodispersed PS seed particles. PS/poly(*n*-BMA) (P*n*-BMA) composite particles produced by SDP consisted of a PS core and a P*n*-BMA shell. Since, in a general SDP, almost all monomers exist in the medium, the viscosity of the seed particles is so high that polymer radicals are unable to diffuse into the inside from the particle surface. As a consequence, the polymers formed by the SDPs seem to accumulate on the PS seed particles, i.e., the morphology of the composite particles seems to be controlled kinetically.

Moreover, on the basis of this idea, poly(methyl methacrylate) (PMMA)/PS composite particles having a PMMA core and a PS shell were successfully produced by SDP of S with 1.91-μm-sized, monodispersed PMMA seed particles in a methanol/water (4/1, w/w) medium, though the morphology was thermodynamically unstable in the polar medium [9]. Composite particles having a complete core/shell structure over a wide range of seed particle/monomer ratios were produced by stepwise SDP in which the monomer concentration was maintained at a low level [10].

In this study, multilayered PMMA/PS/PMMA/PS composite particles were produced by alternate multistep SDPs of S and methyl methacrylate (MMA).

Experimental

Materials

MMA and S were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobis(isobutyronitrile) and 2,2′-azobis(2,4-dimethyl valeronitrile) Wako Pure Chemical Industries, Japan) were purified by recrystallization. Deionized water with a specific conductivity of $5 \times 10^6\ \Omega^{-1}\ \mathrm{cm}^{-1}$ was distilled. Poly(vinylpyrrolidone) (PVP, Sigma Chemical Company), tricaprylyl methylammonium chloride (Aldrich Chemical Company), reagent grade methanol, and acetic acid were used as received.

Preparation of PMMA seed particles

Monodispersed PMMA seed particles were produced by dispersion polymerization under the conditions listed in Table 1. The polymerization was carried out in a 300-ml three-necked round-bottom flask equipped with a Teflon paddle stirrer operating at 120 rpm.

Production of composite polymer particles

All SDPs were carried out with the corresponding seed particles under the conditions listed in Table 2. All the seed particles were washed repeatedly with methanol by centrifugation before use for the all the SDPs. The particles produced were observed with a JEOL JEM-2010 transmission electron microscope (TEM) and a Hitachi S-2500 scanning electron microscope (SEM). The number-average diameter (D_n) and the coefficient of variation (C_v) of each particle were measured from the TEM photographs with image analysis software for Macintosh computers. (Mac Scope, Mitani Corporation).

Table 1 Preparation of micron-sized, monodispersed poly(methyl methacrylate) (*PMMA*) seed particles by dispersion polymerization (N_2; 60 °C; 24 h; stirring rate, 120 rpm)

Ingredients	
Methyl methacrylate (g)	24
V-65[a] (g)	0.36
Poly(vinyl pyrrolidone) (g)	5.6
Aliquat 336[b] (g)	1.6
Methanol (g)	179.2
Water (g)	44.8

[a] 2,2′-Azobis(2,4-dimethyl valeronitrile)
[b] Tricaprylyl methylammonium chloride

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) data were obtained with a Kratos XSAM-800 apparatus using Mg 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 about 2.0×10^{-7} torr. A Digital Equipment Corporation DS-800 computer system was used for the spectrometer control and data handling. Dried particles were stored under reduced pressure by continuous operation of a diffusion pump just before the XPS measurement. The dried particles were spread on an indium plate with a spatula.

Observation of ultrathin cross sections of composite particles

Dried PMMA seed particles, composite particles, and those after the extraction treatment with acetic acid were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution and were 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 using the TEM.

Results and discussion

A TEM photograph of PMMA seed particles produced by dispersion polymerization under the conditions listed

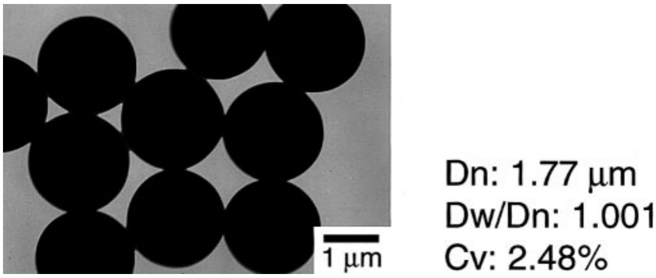


Fig. 1 Transmission electron microscope (*TEM*) photograph of poly(methyl methacrylate) (*PMMA*) seed particles produced by dispersion polymerization under the conditions listed in Table 1

Table 2 Recipes for the production of multilayered composite particles by stepwise seeded dispersion polymerizations of PMMA and polystyrene (PS)

Ingredients	PMMA/PS[a]	PMMA/PS/PMMA[b]	PMMA/PS/PMMA/PS[c]
Seed particles (g)	6.0	1.0	0.6
Styrene (g)	3.0	–	0.3
Methyl methacrylate (g)	–	0.5	–
2,2′-Azobis(isobutyronitrile) (mg)	47	–	4.7
V-65[d] (mg)	–	12.4	–
Poly(vinyl pyrrolidone) (g)	0.3	0.05	0.03
Methanol (g)	96	7.0	9.6
Water (g)	24	3.0	2.4

[a] N_2; 60 °C; 24 h; stirring rate, 60 rpm; PMMA seed (D_n, 1.77 μm; C_v, 2.48%)
[b] N_2; 50 °C; 24 h; PMMA/PS seed (D_n, 1.89 μm; C_v, 2.54%)
[c] N_2; 60 °C; 24 h; PMMA/PS/PMMA seed (D_n, 2.28 μm; C_v, 2.82%)
[d] 2,2′-Azobis(2,4-dimethyl valeronitorile)

Fig. 2 TEM photographs of **a** PMMA seed, **b** PMMA polystyrene (*PS*), **c** PMMA/PSPMMA, and **d** PMMA/PS/PMMA/PS composite particles produced by stepwise seeded dispersion polymerizations under the conditions listed in Table 2

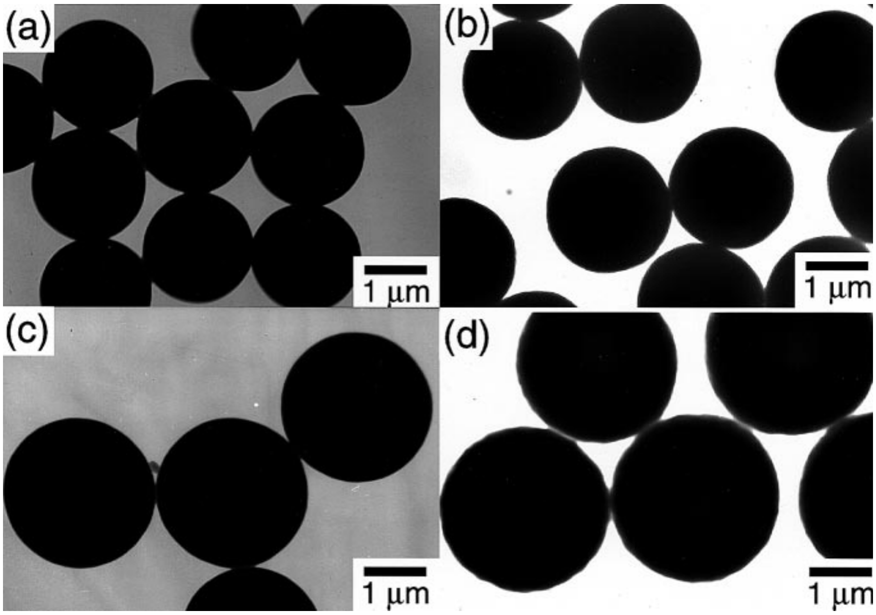
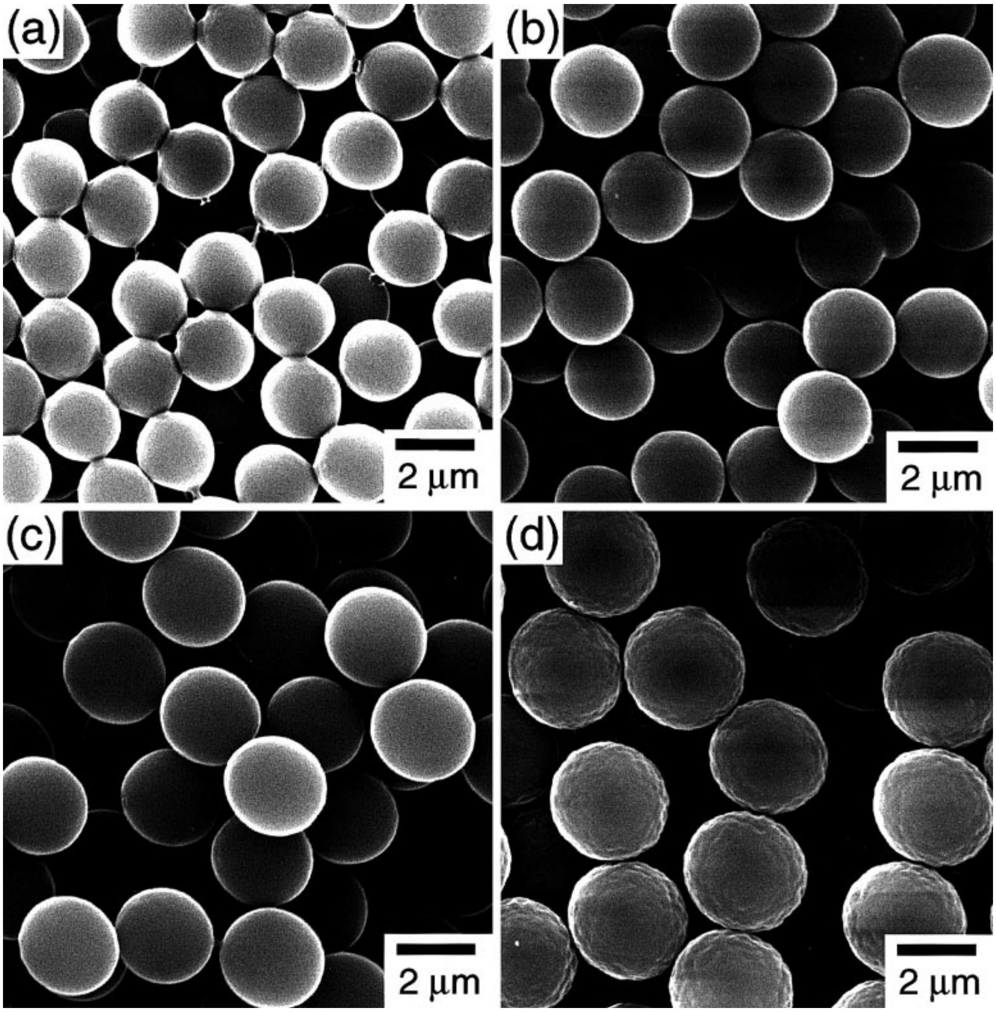


Fig. 3 Scanning electron microscope photographs of **a** PMMA seed, **b** PMMA/PS, **c** PMMA/PSPMMA, and **d** PMMA/PS/PMMA/PS composite particles produced by stepwise seeded dispersion polymerizations under the conditions listed in Table 2



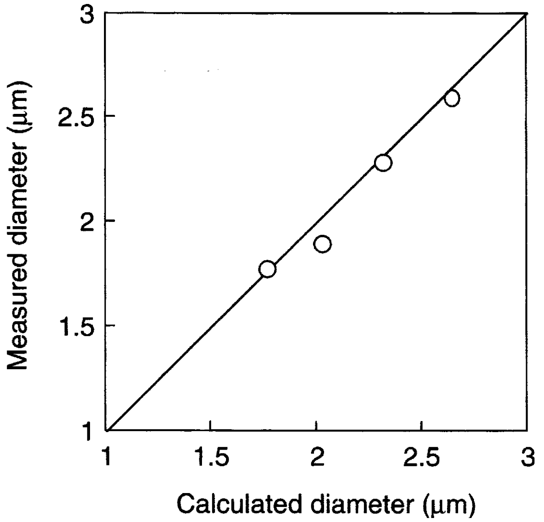


Fig. 4 The increase in the particle size with the stepwise seeded dispersion polymerizations

in Table 1 is shown in Fig. 1. D_n and C_v were 1.77 μm and 2.48% respectively.

Figures 2 and 3, respectively, show TEM and SEM photographs of PMMA/PS, PMMA/PS/PMMA, and PMMA/PS/PMMA/PS composite particles produced by continuous stepwise SDPs under the conditions listed in Table 2, after centrifugal washing. The final conversions of all the SDPs measured by gas chromatography were above 90%. The photographs indicate that all the SDPs gave monodispersed composite particles.

The increase in the particle size with the stepwise SDPs is shown in Fig. 4. The measured diameter of the composite particles almost agreed with the calculated one based on the polymerization recipes. This indicates that the three-step SDPs proceeded in the corresponding seed particles.

The results of the C_{1s} peak shape analysis of the XPS spectra for PMMA, PMMA/PS, PMMA/PS/PMMA, and PMMA/PS/PMMA/PS composite particles are shown in Fig. 5. In Fig. 5a and c, peaks due to carbonyl groups of PMMA were observed at 289 eV, whereas in Fig. 5b and d no such peaks seen but strong peaks due

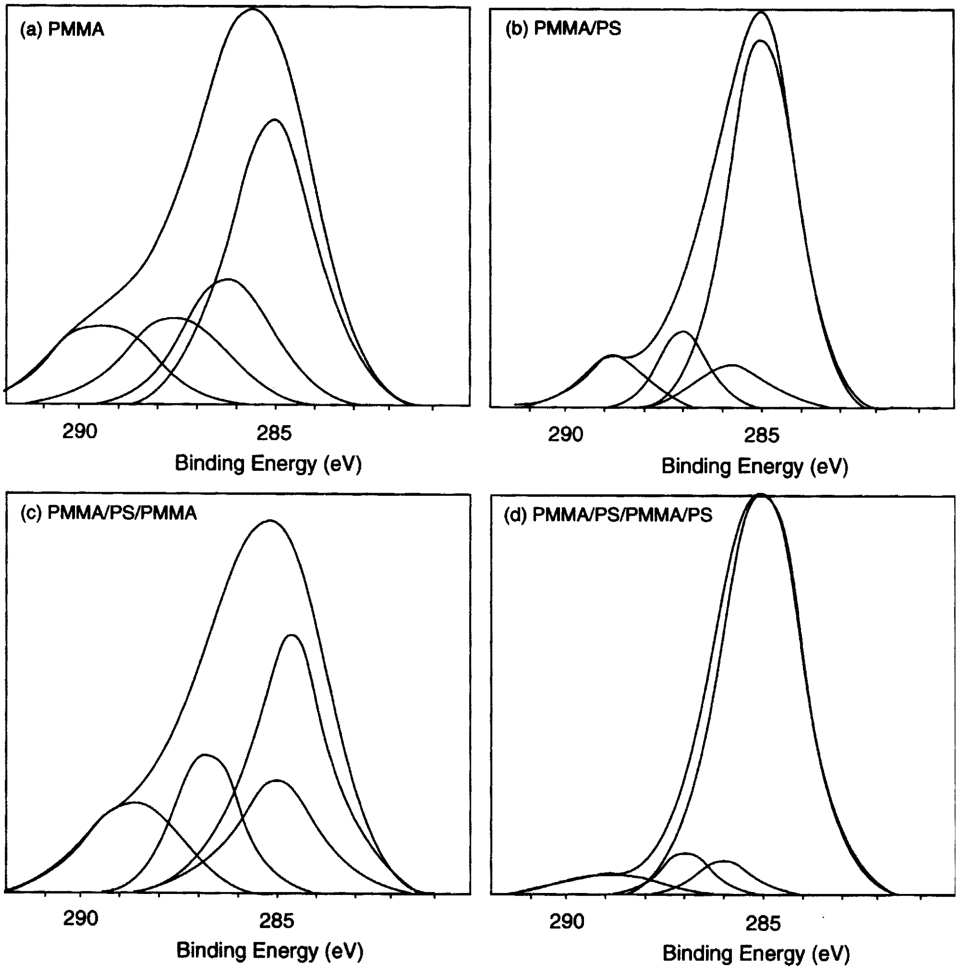


Fig. 5 C_{1s} peak shape analyses of X-ray photoelectron spectroscopy spectra for **a** PMMA seed, **b** PMMA/PS, **c** PMMA/PSPMMA, and **d** PMMA/PS/PMMA/PS composite particles produced by stepwise seeded dispersion polymerizations

to PS were observed at 285 eV in addition to some small peaks due to PVP. These indicate that the surface layer of the PMMA/PS/PMMA composite particles consisted of PMMA, whereas those of the PMMA/PS and PMMA/PS/PMMA/PS composite particles consisted of PS. However, it is insufficient to conclude that the PMMA/PS/PMMA/PS composite particles have a completely multilayered structure. Therefore, ultrathin cross sections of the PMMA seed and the three composite particles which were stained with RuO_4 vapor for 30 min were observed. It is known that RuO_4 stains PS, but not PMMA [11].

TEM photographs of ultrathin cross sections of the PMMA seed, PMMA/PS, PMMA/PS/PMMA, and PMMA/PS/PMMA/PS composite particles are shown in Fig. 6. In Fig. 6a, the contrast inside the PMMA seed particles is homogeneous, whereas in Fig. 6b–d all the composite particles have heterogeneous contrasts. As already reported [9], the PMMA/PS composite particles in Fig. 6b consist of a PMMA core and a PS shell. In Fig. 6c and d, three- and four-layered structures, respectively, are observed. The first core and third layer are not stained, but the second and fourth layers are stained; their boundaries are clearly observed. These observations suggest that the first and third layers consist of PMMA, whereas the second and fourth layers consist of PS. In orded to confirm the multilayered structure in more detail, PMMA was extracted from the PMMA/PS/PMMA/PS composite particles with acetid acid, which dissolves PMMA but not PS. Before the extraction, the medium of the composite dispersion was changed from methnol/water to acetic acid by repeated centrifugation. The extraction was carried out under stirring at 40 °C for 72 h.

TEM photographs of the particles after extraction and of their ultrathin cross sections, stained with RuO_4 vapor for 30 min are shown in Fig. 7. The first core and third layer have disappeared, whereas the second and fourth layers remain, i.e., the first and third PMMA regions were selectively extracted through the second and fourth PS layers with acetic acid. The morphologies of the PMMA/PS and PMMA/PS/PMMA/PS composite particles dispersing in the polar methanol/water mixture medium,

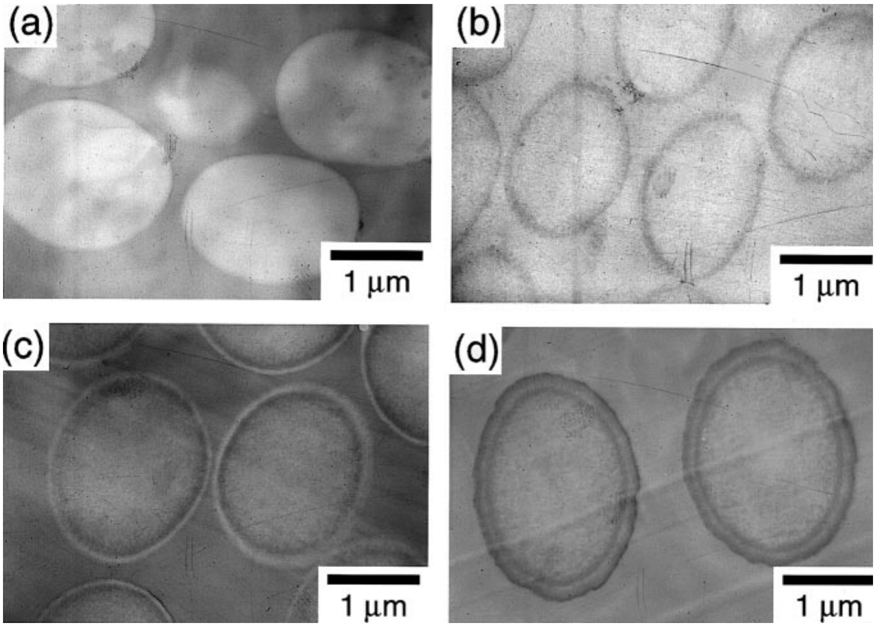


Fig. 6 TEM photographs of ultrathin cross sections of **a** PMMA seed, **b** PMMA/PS, **c** PMMA/PSPMMA, and **d** PMMA/PS/PMMA/PS composite particles stained with RuO_4 vapor for 30 min

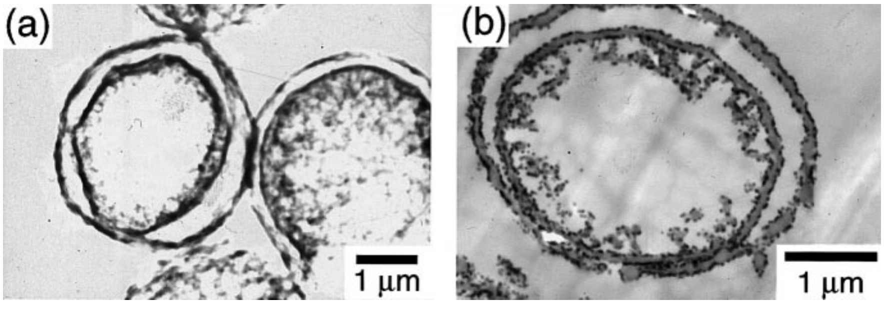


Fig. 7 TEM photographs of the particles **a** after the extraction of PMMA from PMMA/PS/PMMA/PS composite particles with acetic acid under stirring at 40 °C for 72 h and **b** of the ultrathin cross section

which were prepared by the SDPs, are thermodynamically unstable, because PS is more hydrophobic than PMMA.

For the results presented here, it should be emphasized that multistep SDP has the advantage that the polymer layers accumulate in the order of their formation and result in multilayered composite particles even if the morphology is thermodynamically unstable.

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